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## S1. General experimental procedures

All syntheses and manipulations were conducted under argon with rigorous exclusion of oxygen and water using Schlenk line and glove box techniques. Toluene, benzene and hexane were dried by refluxing over potassium and were stored over potassium mirrors. Dichloromethane (DCM) and 1,2-difluorobenzene were dried over  $\text{CaH}_2$  and stored over or 4 Å molecular sieves. All solvents were degassed before use. For NMR spectroscopy  $\text{C}_6\text{D}_6$  was dried by refluxing over K and  $\text{CD}_2\text{Cl}_2$  was dried by refluxing over  $\text{CaH}_2$ . Both NMR solvents were vacuum transferred and degassed by three freeze-pump-thaw cycles before use. Anhydrous  $\text{LnCl}_3$  ( $\text{Ln} = \text{Y}$  or  $\text{Dy}$ ) were purchased from Alfa Aesar and were used as received.  $\text{KCp}^{\text{III}}$  <sup>1</sup> and  $[\text{H}(\text{SiEt}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]^{2,3}$  were prepared according to literature methods.  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz and 125 MHz),  $^{13}\text{C}\{^{19}\text{F}\}$  (126 MHz),  $^{11}\text{B}\{^1\text{H}\}$  (128 MHz) and  $^{19}\text{F}\{^1\text{H}\}$  (376 MHz) NMR spectra were obtained on an Avance III 400 MHz or 500 MHz spectrometer at 298 K. These were referenced to the solvent used, or to external TMS ( $^1\text{H}$ ,  $^{13}\text{C}$ ),  $\text{H}_3\text{BO}_3/\text{D}_2\text{O}$  ( $^{11}\text{B}$ ) or  $\text{C}_7\text{H}_5\text{F}_3/\text{CDCl}_3$  ( $^{19}\text{F}$ ). UV-Vis-NIR spectroscopy was performed on samples in Youngs tap appended 10 mm pathlength quartz cuvettes on an Agilent Technologies Cary Series UV-Vis-NIR Spectrophotometer from 175–3300 nm. Fourier transform infrared spectra were recorded as Nujol mulls in KBr discs using a Shimadzu IRAffinity-1S spectrometer. Raman spectra were recorded on crystalline samples pressed between two quartz slides sealed with vacuum grease using a XploRATM PLUS Horiba Scientific spectrometer. Elemental analyses were performed by Mrs Anne Davies and Mr Martin Jennings at The University of Manchester, UK.

## S2. Experimental synthesis

$[Dy(Cp^{III})_2][B(C_6F_5)_4]$  (**1**). A solution of  $[H(SiEt_3)_2][B(C_6F_5)_4]$  (0.745 g, 0.82 mmol) in benzene (10 mL) was added dropwise to a stirred solution of  $[Dy(Cp^{III})_2(Cl)]$  (0.544 g, 0.82 mmol) in benzene (10 mL) at room temperature to immediately give a bright yellow reaction mixture. The mixture was stirred for 48 hours, forming a small amount of bright yellow precipitate. The volatiles were removed *in vacuo* to give a bright yellow powder, which was washed with hexane (2 x 10 mL) and benzene (20 mL). The crude material was dissolved in DCM (2 mL) at 4 °C, and layered with hexane (2 mL). Storage at –25 °C afforded **1** as bright yellow crystals (0.645 g, 60%). Anal calcd (%) for  $C_{58}H_{58}BF_{20}Dy \cdot 0.5CH_2Cl_2$ : C, 52.01; H, 4.40; Found: C, 52.08; H, 4.19. The paramagnetism of **1** precluded assignment of its  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra.  $^{11}B\{^1H\}$  NMR ( $CD_2Cl_2$ , 128 MHz, 298 K):  $\delta = -29.04$  (s).  $^{19}F\{^1H\}$  NMR ( $CD_2Cl_2$ , 376 MHz, 298 K):  $\delta = -181.5$  (br. s),  $-173.16$  (br. s),  $-145.98$  (br. s). FTIR (KBr disc, Nujol mull):  $\tilde{\nu} = 2370$  (w), 2357 (w), 1649 (m), 1626 (w), 1605 (br. w), 1560 (w), 1520 (m), 1418 (w), 1393 (w), 1337 (w), 1273 (m), 1263 (w), 1240 (w), 1204 (w), 1084 (m), 1036 (w), 977 (m), 851 (w), 810 (br. w), 8756 (w), 704 (w), 683 (w), 662 (w)  $cm^{-1}$ . Raman (solid sample, quartz slide):  $\tilde{\nu} = 485$  (228), 707 (81), 2902 (115), 2962 (92)  $cm^{-1}$  (counts).

$Dy@[Y(Cp^{III})_2][B(C_6F_5)_4]$  (**2**). A solution of  $[H(SiEt_3)_2][B(C_6F_5)_4]$  (0.5348 g, 0.587 mmol) in benzene (10 mL) was added dropwise to a stirred solution of  $[Y(Cp^{III})_2(Cl)]$  (0.330 g, 0.558 mmol) and  $[Dy(Cp^{III})_2(Cl)]$  (0.0195 g, 0.03 mmol) in benzene (10 mL) at room temperature to immediately give a pale yellow reaction mixture. The mixture was stirred for 48 hours, forming a small amount of pale yellow precipitate. The volatiles were removed *in vacuo* to give a pale yellow powder, which was washed with hexane (10 mL) and benzene (10 mL). The crude material was dissolved in DCM (1 mL) at 4 °C, and layered with hexane (1 mL). Storage at –25 °C afforded **2** as pale yellow crystals (0.239 g, 38%). Magnetic measurements (see below) show that this sample has a doping level of 8 % Dy (molar percentage). Anal calcd (%) for

$C_{58}H_{58}BF_{20}Y_{0.92}Dy_{0.08} \cdot 0.5CH_2Cl_2$ : C, 54.87; H, 4.66; Found: C, 54.87; H, 4.64.  $^1H$  NMR ( $CD_2Cl_2$ , 400 MHz, 298 K):  $\delta$  = 1.40 (s, 18H, Cp-C( $CH_3$ )<sub>3</sub>), 1.51 (s, 36H, Cp-C( $CH_3$ )<sub>3</sub>), 6.42 (s, 4H, Cp-CH).  $^{13}C\{^1H\}$  NMR ( $CD_2Cl_2$ , 100 MHz, 298 K):  $\delta$  = 32.51 (Cp-C( $CH_3$ )<sub>3</sub>), 33.20 (Cp-C( $CH_3$ )<sub>3</sub>), 33.76 (Cp-C( $CH_3$ )<sub>3</sub>), 35.54 (Cp-C( $CH_3$ )<sub>3</sub>), 116.91 (d, Cp-CH,  $^1J_{YC}$  = 1.5 Hz), 141.51 (d, Cp-C,  $^1J_{YC}$  = 1.0 Hz), 146.38 (d, Cp-C,  $^1J_{YC}$  = 1.5 Hz), {B( $C_6F_5$ )<sub>4</sub>} *ipso*-carbon not observed.  $^{11}B\{^1H\}$  NMR ( $CD_2Cl_2$ , 128 MHz, 298 K):  $\delta$  = -18.27 (s).  $^{19}F\{^1H\}$  NMR ( $CD_2Cl_2$ , 376 MHz, 298 K):  $\delta$  = -169.37 (br. s), -164.86 (br. m), -134.64 (s). FTIR (KBr disc, Nujol mull)  $\tilde{\nu}$ : 1641 (w), 1624 (w), 1607 (w), 1560 (w), 1512 (m), 1417 (w), 1402 (w), 1346 (w), 1277 (m), 1240 (w), 1225 (w), 1202 (w), 1086 (m), 1038 (w), 1026 (w), 978 (m), 959 (w), 851 (w), 756 (w), 745 (m), 710 (w), 683 (w), 662 (w)  $cm^{-1}$ . Raman: compound decomposes.

$[Y(Cp^{ttt})_2][B(C_6F_5)_4]$  (**5**). A solution of  $[H(SiEt_3)_2][B(C_6F_5)_4]$  (0.4051 g, 0.445 mmol) in benzene (10 mL) was added dropwise to a stirred solution of  $[Y(Cp^{ttt})_2(Cl)]$  (0.263 g, 0.445 mmol) in benzene (10 mL) at room temperature. The colourless reaction mixture was stirred for 48 hours, forming a small amount of white precipitate. The volatiles were removed *in vacuo* to give a white powder, which was washed with hexane (10 mL) and benzene (10 mL). The crude material was dissolved in DCM (1 mL) at 4 °C, and layered with hexane (1 mL). Storage at -25 °C afforded **5** as colourless crystals (0.211 g, 39%). Anal calcd (%) for  $C_{58}H_{58}BF_{20}Y \cdot 0.5CH_2Cl_2$ : C, 54.87; H, 4.66; Found: C, 54.87; H, 4.64.  $^1H$  NMR ( $CD_2Cl_2$ , 400 MHz, 298 K):  $\delta$  = 1.40 (s, 18H, Cp-C( $CH_3$ )<sub>3</sub>), 1.51 (s, 36H, Cp-C( $CH_3$ )<sub>3</sub>), 6.42 (s, 4H, Cp-CH).  $^{13}C\{^1H\}$  NMR ( $CD_2Cl_2$ , 100 MHz, 298 K):  $\delta$  = 32.51 (Cp-C( $CH_3$ )<sub>3</sub>), 33.20 (Cp-C( $CH_3$ )<sub>3</sub>), 33.76 (Cp-C( $CH_3$ )<sub>3</sub>), 35.54 (Cp-C( $CH_3$ )<sub>3</sub>), 116.91 (d, Cp-CH,  $^1J_{YC}$  = 1.5 Hz), 141.51 (d, Cp-C,  $^1J_{YC}$  = 1.0 Hz), 146.38 (d, Cp-C,  $^1J_{YC}$  = 1.5 Hz), {B( $C_6F_5$ )<sub>4</sub>} *ipso*-carbon not observed.  $^{13}C\{^1H\}$  NMR ( $CD_2Cl_2$ , 125 MHz, 298 K):  $\delta$  = 136.87 (d, *m*-CF,  $^1J_{FC}$  = 247.1 Hz), 140.71 (d, *p*-CF,  $^1J_{FC}$  = 228.0 Hz), 148.74 (d, *o*-CF,  $^1J_{FC}$  = 241.6 Hz), {B( $C_6F_5$ )<sub>4</sub>} *ipso*-carbon not observed.  $^{13}C\{^{19}F\}$  NMR ( $CD_2Cl_2$ , 126 MHz, 298 K):  $\delta$  = 124.53 (q, B-C<sub>*ipso*</sub>,  $^1J_{BC}$  = 50.9 Hz).  $^{11}B\{^1H\}$  NMR ( $CD_2Cl_2$ , 128 MHz, 298 K):  $\delta$  = -16.66 (s).



$^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 376 MHz, 298 K):  $\delta = -167.44$  (br. s),  $-163.57$  (br. m),  $-132.98$  (s). FTIR (KBr disc, Nujol mull):  $\tilde{\nu} = 1640$  (w),  $1624$  (w),  $1605$  (br. w),  $1560$  (w),  $1514$  (w),  $1348$  (w),  $1279$  (w),  $1242$  (w),  $1205$  (w),  $1086$  (m),  $1026$  (w),  $980$  (m),  $851$  (w),  $802$  (w),  $775$  (w),  $754$  (w),  $683$  (w),  $660$  (w)  $\text{cm}^{-1}$ . Raman: compound decomposes.

$[\text{Dy}(\text{Cp}^{\text{ttt}})_2(\text{Cl})]$  (**6**). Adapted from a literature procedure of  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2(\text{Br})]^4$ . Toluene (10 mL) was added to a pre-cooled ( $-78\text{ }^\circ\text{C}$ ) mixture of  $\text{DyCl}_3$  (0.538 g, 2 mmol) and  $\text{KCp}^{\text{ttt}}$  (1.225 g) with stirring. The mixture was allowed to warm to room temperature and refluxed for 48 hours. The vessel was allowed to cool to room temperature, and white solids settled. The pale yellow solution was filtered and concentrated to 3 mL. Storage at room temperature afforded **6** as large pale yellow blocks; multiple crops were obtained (0.413 g, 31%). Anal calcd (%) for  $\text{C}_{38}\text{H}_{58}\text{ClDy}$ : C, 64.01; H, 8.21; Found: C, 59.20; H, 8.73; low C values were obtained reproducibly and this was attributed to carbide formation.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz, 298 K):  $\delta = -59.00$  to  $-29.00$  (br,  $\nu_{1/2} \sim 12,000$  Hz, 18H,  $\text{Cp-C}(\text{CH}_3)_3$ ),  $7.29$  (s,  $\nu_{1/2} = 300$  Hz, 4H,  $\text{Cp-CH}$ ),  $13.26$  (br,  $\nu_{1/2} = 600$  Hz, 36H,  $\text{Cp-C}(\text{CH}_3)_3$ ). The paramagnetism of **6** precluded assignment of its  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum. FTIR (KBr disc, Nujol mull):  $\tilde{\nu} = 3107$  (w),  $1389$  (s),  $1358$  (s),  $1240$  (s),  $1221$  (w),  $1190$  (w),  $1163$  (s),  $1115$  (m),  $1024$  (m),  $1001$  (s),  $960$  (m),  $926$  (w),  $843$  (m),  $829$  (s),  $777$  (s),  $725$  (m),  $677$  (s)  $\text{cm}^{-1}$ . Raman (solid sample, quartz slide):  $\tilde{\nu} = 485$  (172),  $707$  (46),  $2902$  (86),  $2962$  (73)  $\text{cm}^{-1}$  (counts).

$[\text{Y}(\text{Cp}^{\text{ttt}})_2(\text{Cl})]$  (**7**). Adapted from a literature procedure of  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2(\text{Br})]^4$ . Toluene (10 mL) was added to a pre-cooled ( $-78\text{ }^\circ\text{C}$ ) mixture of  $\text{YCl}_3$  (0.391 g, 2 mmol) and  $\text{KCp}^{\text{ttt}}$  (1.225 g) with stirring. The mixture was allowed to warm to room temperature and refluxed for 72 hours. The vessel was allowed to cool to room temperature, and white solids settled. The pale yellow solution was filtered and concentrated to 3 mL. Storage at room temperature afforded **7** as large colourless blocks; multiple crops were obtained (0.384 g, 32%).  $\text{C}_{38}\text{H}_{58}\text{ClY}$ : C, 71.38; H, 9.15;

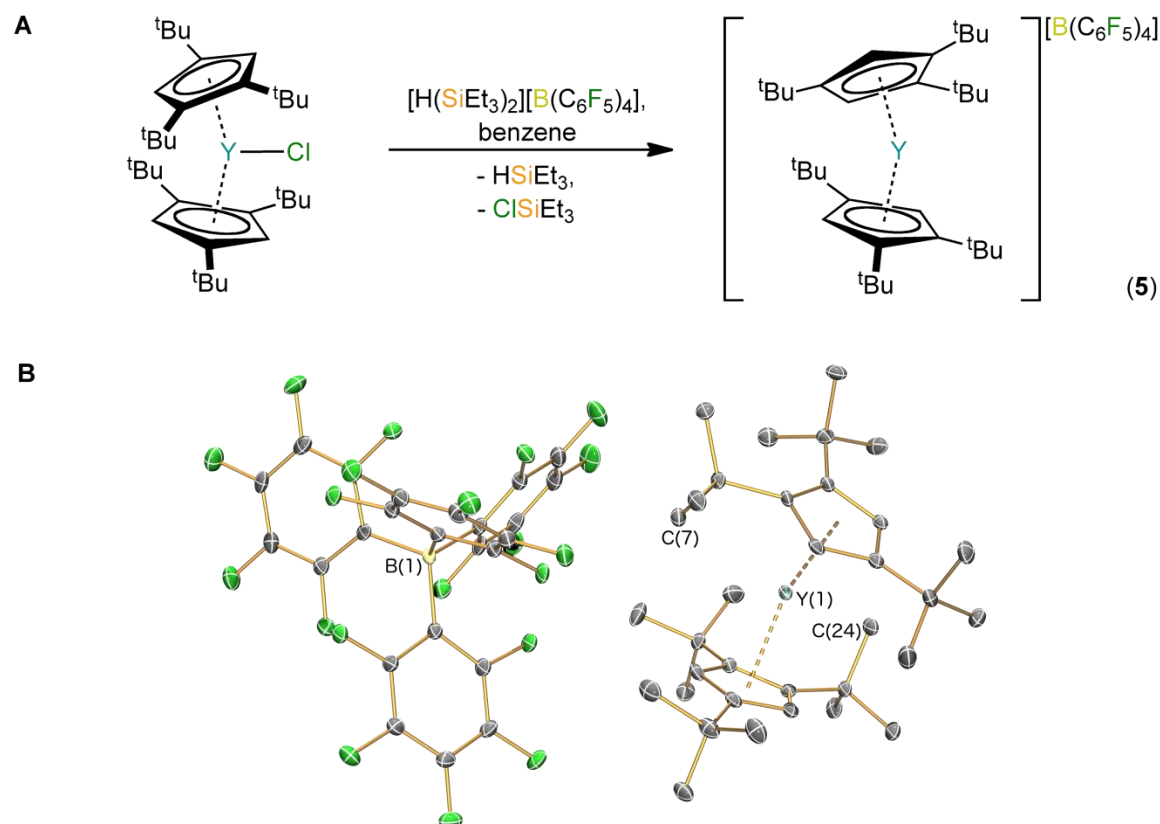
Found: C, 63.78; H, 9.54; low C values were obtained reproducibly and this was attributed to carbide formation.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz, 298 K):  $\delta$  = 1.21 (s, 18H, Cp-C( $\text{CH}_3$ )<sub>3</sub>), 1.53 (s, 36H, Cp-C( $\text{CH}_3$ )<sub>3</sub>), 6.67 (s, 4H, Cp-CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100 MHz, 298 K):  $\delta$  = 31.55 (Cp-C( $\text{CH}_3$ )<sub>3</sub>), 33.32 (Cp-C( $\text{CH}_3$ )<sub>3</sub>), 34.50 (Cp-C( $\text{CH}_3$ )<sub>3</sub>), 34.99 (Cp-C( $\text{CH}_3$ )<sub>3</sub>), 114.30 (br., Cp-CH), 136.87 (d, Cp-C,  $^1J_{\text{YC}} = 1.5$  Hz), 138.27 (Cp-C,  $^1J_{\text{YC}}$  not observed). FTIR (KBr disc, Nujol mull):  $\tilde{\nu}$  = 3107 (w), 1389 (s), 1358 (s), 1240 (s), 1221 (w), 1190 (w), 1163 (s), 1115 (m), 1024 (m), 1001 (s), 960 (m), 926 (w), 843 (m), 829 (s), 777 (s), 725 (m), 677 (s)  $\text{cm}^{-1}$ . Raman: compound decomposes.

### S3. Crystallography

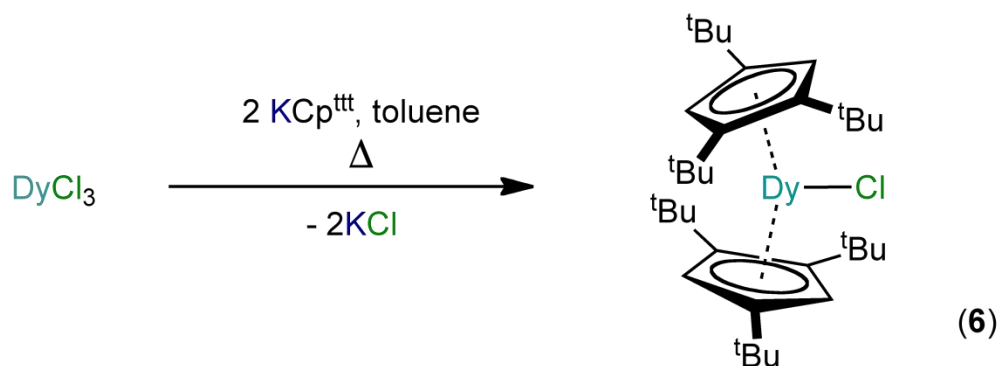
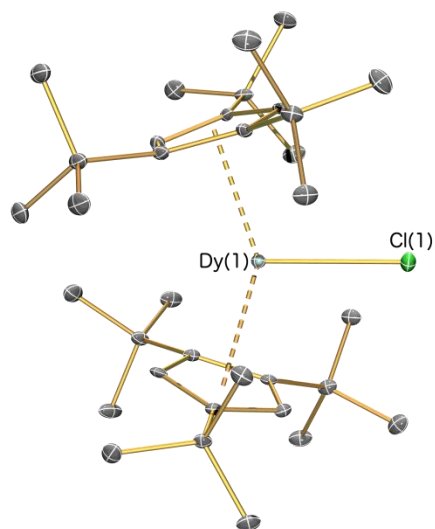
The crystal data for complexes **1**, **5**, **6** and **7** are compiled in Tables S1 and S2. Crystals of **1** were examined using an Oxford Diffraction Supernova diffractometer, equipped with CCD area detector and a mirror-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Crystals of **5** were examined with a Rigaku XtaLAB AFC11 diffractometer, equipped with CCD detector and a graphite-monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å). Crystals of **6** were examined using an Oxford Diffraction Xcalibur diffractometer, equipped with CCD area detector and a mirror-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Crystals of **7** were examined using a Bruker Apex II diffractometer, equipped with CCD area detector and a graphite-monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å). Intensities were integrated from data recorded on  $0.8^\circ$  (**1**, **6**),  $0.9^\circ$  (**7**) or  $1^\circ$  (**2**) frames by  $\omega$  rotation (**1**, **5**, **6**) or  $\omega$  and  $\phi$  rotation (**7**). Cell parameters were refined from the observed positions of all strong reflections in each data set. A Gaussian grid face-indexed (**1** and **5**), analytical (**6**) or multi-scan (**7**) absorption correction with a beam profile was applied<sup>5</sup>. The structures were solved variously using SHELXT (**1**)<sup>6</sup>, Superflip (**5**)<sup>7,8</sup> or by direct and heavy atom methods using SHELXS (**6**, **7**)<sup>9</sup>; the datasets were refined by full-matrix least-squares on all unique  $F^2$  values<sup>9</sup>, with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries;  $U_{\text{iso}}(\text{H})$  was set at 1.2 (1.5 for methyl groups) times  $U_{\text{eq}}$  of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. CrysAlisPro<sup>5</sup> was used for control and integration, and SHELX<sup>6,9</sup> was employed through OLEX2<sup>10</sup> for structure solution and refinement. ORTEP-3<sup>11</sup> and POV-Ray<sup>12</sup> were employed for molecular graphics. CCDC 1542354–1542357 (**1**, **5**, **6** and **7**) contain the supplementary crystal data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Despite the different unit cells of **1** and **5**, the cell parameters are complementary and related by inversion (transformation matrix: 1 0 0, 0  $-1$  0, 0 0 1). Structural analysis reveals that

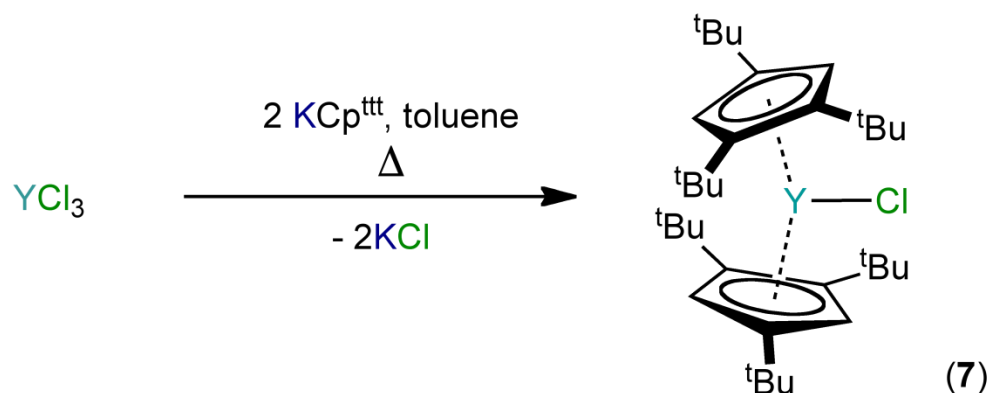
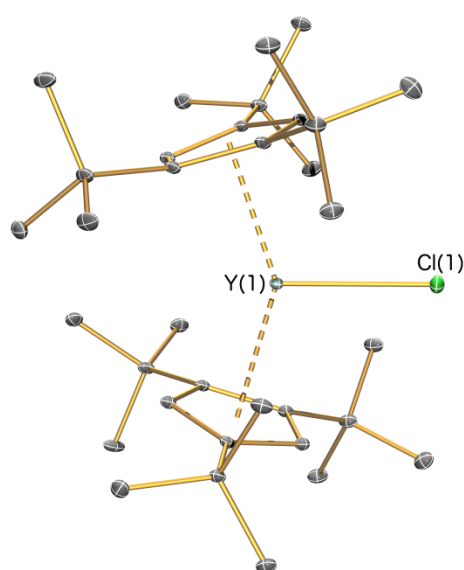
the two compounds have statistically identical metric parameters, thereby making them structurally analogous. This is confirmed by the identical IR spectra of **1** and **5** (Figs. S26 and S27). Single crystals of **2** were screened in order to verify the doped sample was of the correct structure; these afforded cell parameters consistent with those of **5**:  $a = 11.7373(7) \text{ \AA}$ ,  $b = 12.5111(6) \text{ \AA}$ ,  $c = 20.0385(10) \text{ \AA}$ ,  $\alpha = 82.967(4)^\circ$ ,  $\beta = 89.819(4)^\circ$ ,  $\gamma = 79.527(5)^\circ$ ,  $V = 2869.8(3) \text{ \AA}^3$ .



**Figure S1.** Synthesis and solid state characterisation of  $[Y(Cp^{ttt})_2][B(C_6F_5)_4]$  (**5**). **(A)** Synthesis of **5**. **(B)** Molecular structure of **5** with selective atom labelling (B = yellow, C = grey, Y = cyan, F = green). Displacement ellipsoids set at 30 % probability level and hydrogen atoms are omitted for clarity. Selected distances and angles:  $Y1 \cdots Cp_{\text{centroid1}}$ , 2.311(2) Å;  $Y1 \cdots Cp_{\text{centroid2}}$ , 2.313(2) Å;  $Y1 \cdots C7$ , 2.976(7) Å;  $Y1 \cdots C24$ , 2.981(6) Å;  $Y \cdots H$ , 2.522 and 2.539 Å;  $Cp_{\text{centroid1}} \cdots Y1 \cdots Cp_{\text{centroid2}}$ , 153.21(10)°;  $H \cdots Y \cdots H$ , 173.84°.

**A****B**

**Figure S2.** Synthesis and solid state characterisation of  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2(\text{Cl})]$  (**6**). **(A)** Synthesis of **6**. **(B)** Molecular structure of **6** with selective atom labelling (C = grey, Cl = green, Dy = cyan). Displacement ellipsoids set at 30 % probability level and hydrogen atoms are omitted for clarity. Selected distances and angles: Dy1 $\cdots$ Cp<sub>centroid1</sub>, 2.412(2) Å; Dy1 $\cdots$ Cp<sub>centroid2</sub>, 2.414(2) Å; Dy1–Cl1, 2.5480(12) Å; Cp<sub>centroid1</sub> $\cdots$ Dy1 $\cdots$ Cp<sub>centroid2</sub>, 146.67(7)°.

**A****B**

**Figure S3.** Synthesis and solid state characterisation of  $[\text{Y}(\text{Cp}^{\text{tBu}})_2\text{Cl}]$  (**7**). **(A)** Synthesis of **7**. **(B)** Molecular structure of **7** with selective atom labelling (C = grey, Cl = green, Y = cyan). Displacement ellipsoids set at 30 % probability level and hydrogen atoms are omitted for clarity. Selected distances and angles:  $\text{Y1}\cdots\text{Cp}_{\text{centroid1}}$ , 2.405(2) Å;  $\text{Y1}\cdots\text{Cp}_{\text{centroid2}}$ , 2.406(2) Å;  $\text{Y1}-\text{Cl1}$ , 2.5442(11) Å;  $\text{Cp}_{\text{centroid1}}\cdots\text{Y1}\cdots\text{Cp}_{\text{centroid2}}$ , 146.20(7)°.

**Table S1.** Crystallographic data for **1** and **5**.

<sup>a</sup>Conventional  $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ;  $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ ;  $S = [\Sigma w(F_o^2 - F_c^2)^2/\text{no. data} - \text{no. params}]^{1/2}$  for all data.

|                                                                                                         | <b>1</b>                                           | <b>5</b>                                           |
|---------------------------------------------------------------------------------------------------------|----------------------------------------------------|----------------------------------------------------|
| Formula                                                                                                 | C <sub>58</sub> H <sub>58</sub> BDyF <sub>20</sub> | C <sub>58</sub> H <sub>58</sub> BF <sub>20</sub> Y |
| Fw                                                                                                      | 1308.35                                            | 1233.75                                            |
| cryst size, mm                                                                                          | 0.04 × 0.10 × 0.20                                 | 0.09 × 0.12 × 0.52                                 |
| crystal syst                                                                                            | triclinic                                          | triclinic                                          |
| space group                                                                                             | <i>P</i> −1                                        | <i>P</i> −1                                        |
| <i>a</i> , Å                                                                                            | 11.7087(4)                                         | 11.7178(3)                                         |
| <i>b</i> , Å                                                                                            | 12.4957(4)                                         | 12.4990(3)                                         |
| <i>c</i> , Å                                                                                            | 20.0408(7)                                         | 20.0282(10)                                        |
| $\alpha$ , °                                                                                            | 96.933(3)                                          | 82.928(3)                                          |
| $\beta$ , °                                                                                             | 90.069(3)                                          | 89.873(3)                                          |
| $\gamma$ , °                                                                                            | 100.423(3)                                         | 76.605(2)                                          |
| <i>V</i> , Å <sup>3</sup>                                                                               | 2861.87(17)                                        | 2862.65(18)                                        |
| <i>Z</i>                                                                                                | 2                                                  | 2                                                  |
| $\rho_{\text{calcd}}$ , g cm <sup>3</sup>                                                               | 1.518                                              | 1.431                                              |
| $\mu$ , mm <sup>−1</sup>                                                                                | 1.407                                              | 2.344                                              |
| <i>F</i> (000)                                                                                          | 1314                                               | 1258                                               |
| no. of reflections (unique)                                                                             | 33899(10434)                                       | 27074 (10273)                                      |
| <i>S</i> <sup>a</sup>                                                                                   | 1.11                                               | 1.13                                               |
| <i>R</i> <sub>1</sub> ( <i>wR</i> <sub>2</sub> ) ( <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )) | 0.0401                                             | 0.0805(0.2148)                                     |
| <i>R</i> <sub>int</sub>                                                                                 | 0.0987                                             | 0.036                                              |
| min./max. diff map, Å <sup>−3</sup>                                                                     | −0.98, 1.66                                        | −0.86, 3.37                                        |



**Table S2.** Crystallographic data for **6** and **7**.

<sup>a</sup>Conventional  $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ;  $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ ;  $S = [\Sigma w(F_o^2 - F_c^2)^2/\text{no. data} - \text{no. params}]^{1/2}$  for all data.

|                                                                                                         | <b>6</b>                             | <b>7</b>                            |
|---------------------------------------------------------------------------------------------------------|--------------------------------------|-------------------------------------|
| Formula                                                                                                 | C <sub>34</sub> H <sub>58</sub> ClDy | C <sub>34</sub> H <sub>58</sub> ClY |
| Fw                                                                                                      | 664.75                               | 591.16                              |
| cryst size, mm                                                                                          | 0.25 × 0.25 × 0.44                   | 0.05 × 0.05 × 0.10                  |
| crystal syst                                                                                            | monoclinic                           | monoclinic                          |
| space group                                                                                             | <i>P</i> 2 <sub>1</sub> / <i>c</i>   | <i>P</i> 2 <sub>1</sub> / <i>c</i>  |
| <i>a</i> , Å                                                                                            | 10.339(3)                            | 10.3414(2)                          |
| <i>b</i> , Å                                                                                            | 15.3846(4)                           | 15.3511(3)                          |
| <i>c</i> , Å                                                                                            | 20.3495(7)                           | 20.3475(4)                          |
| $\alpha$ , °                                                                                            | 90                                   | 90                                  |
| $\beta$ , °                                                                                             | 99.477(3)                            | 99.4776(17)                         |
| $\gamma$ , °                                                                                            | 90                                   | 90                                  |
| <i>V</i> , Å <sup>3</sup>                                                                               | 3192.92(17)                          | 3486.11(11)                         |
| <i>Z</i>                                                                                                | 4                                    | 4                                   |
| $\rho_{\text{calcd}}$ , g cm <sup>3</sup>                                                               | 1.383                                | 1.232                               |
| $\mu$ , mm <sup>-1</sup>                                                                                | 2.444                                | 3.469                               |
| <i>F</i> (000)                                                                                          | 1380                                 | 1272                                |
| no. of reflections (unique)                                                                             | 15466(5834)                          | 25300(5813)                         |
| <i>S</i> <sup>a</sup>                                                                                   | 1.16                                 | 1.03                                |
| <i>R</i> <sub>1</sub> ( <i>wR</i> <sub>2</sub> ) ( <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )) | 0.0341(0.0872)                       | 0.0504(0.1434)                      |
| <i>R</i> <sub>int</sub>                                                                                 | 0.032                                | 0.070                               |
| min./max. diff map, Å <sup>-3</sup>                                                                     | -0.81, 1.28                          | -0.65, 1.27                         |

# Datablock: 1

---

Bond precision: C-C = 0.0063 Å Wavelength=0.71073

Cell: a=11.7087(4) b=12.4957(4) c=20.0408(7)  
 alpha=96.933(3) beta=90.069(3) gamma=100.423(3)

Temperature: 150 K

|                        | Calculated                           | Reported              |
|------------------------|--------------------------------------|-----------------------|
| Volume                 | 2861.87(17)                          | 2861.87(17)           |
| Space group            | P -1                                 | P -1                  |
| Hall group             | -P 1                                 | -P 1                  |
| Moiety formula         | C24 B F20, C34 H58 Dy [+<br>solvent] | C34 H58 Dy, B C24 F20 |
| Sum formula            | C58 H58 B Dy F20 [+ solvent]         | C58 H58 B Dy F20      |
| Mr                     | 1308.35                              | 1308.35               |
| Dx, g cm <sup>-3</sup> | 1.518                                | 1.518                 |
| Z                      | 2                                    | 2                     |
| Mu (mm <sup>-1</sup> ) | 1.407                                | 1.407                 |
| F000                   | 1314.0                               | 1314.0                |
| F000'                  | 1314.53                              |                       |
| h, k, lmax             | 14, 15, 24                           | 14, 15, 24            |
| Nref                   | 10466                                | 10434                 |
| Tmin, Tmax             | 0.845, 0.941                         | 0.900, 0.973          |
| Tmin'                  | 0.749                                |                       |

Correction method= # Reported T Limits: Tmin=0.900

Tmax=0.973 AbsCorr = GAUSSIAN

Data completeness= 0.997      Theta(max)= 25.350  
 R(reflections)= 0.0401( 9162)      wR2(reflections)= 0.0987( 10434)  
 S = 1.107      Npar= 769

The following ALERTS were generated. Each ALERT has the format

**test-name\_ALERT\_alert-type\_alert-level.**

Click on the hyperlinks for more details of the test.

## 🚨 Alert level B

[PLAT910\\_ALERT\\_3\\_B](#) Missing # of FCF Reflection(s) Below Theta(Min)      22 Note

**Author Response: Reduction of beam stop mask did not yield significant improvement. Most of those missing strong reflections appeared to be very strong and were treated as overflows.**

## 🚨 Alert level C

[PLAT242\\_ALERT\\_2\\_C](#) Low 'MainMol' Ueq as Compared to Neighbors of      C31 Check

[PLAT906\\_ALERT\\_3\\_C](#) Large K value in the Analysis of Variance .....      2.106 Check

[PLAT911\\_ALERT\\_3\\_C](#) Missing # FCF Refl Between THmin & STh/L= 0.600      9 Report

## 🚨 Alert level G

[PLAT002\\_ALERT\\_2\\_G](#) Number of Distance or Angle Restraints on AtSite      7 Note

[PLAT003\\_ALERT\\_2\\_G](#) Number of Uiso or Uij Restrained non-H Atoms ...      7 Report

[PLAT042\\_ALERT\\_1\\_G](#) Calc. and Reported MoietyFormula Strings Differ      Please Check

[PLAT154\\_ALERT\\_1\\_G](#) The s.u.'s on the Cell Angles are Equal ..(Note)      0.003 Degree

[PLAT176\\_ALERT\\_4\\_G](#) The CIF-Embedded .res File Contains SADI Records      1 Report

[PLAT177\\_ALERT\\_4\\_G](#) The CIF-Embedded .res File Contains DELU Records      1 Report

[PLAT178\\_ALERT\\_4\\_G](#) The CIF-Embedded .res File Contains SIMU Records      1 Report

[PLAT302\\_ALERT\\_4\\_G](#) Anion/Solvent/Minor-Residue Disorder (Resd 2)..      9 % Note

|                                   |                                                  |          |
|-----------------------------------|--------------------------------------------------|----------|
| <a href="#">PLAT605 ALERT 4 G</a> | Largest Solvent Accessible VOID in the Structure | 218 A**3 |
| <a href="#">PLAT860 ALERT 3 G</a> | Number of Least-Squares Restraints .....         | 106 Note |
| <a href="#">PLAT869 ALERT 4 G</a> | ALERTS Related to the use of SQUEEZE Suppressed  | ! Info   |
| <a href="#">PLAT913 ALERT 3 G</a> | Missing # of Very Strong Reflections in FCF .... | 1 Note   |
| <a href="#">PLAT933 ALERT 2 G</a> | Number of OMIT Records in Embedded .res File ... | 2 Note   |
| <a href="#">PLAT978 ALERT 2 G</a> | Number C-C Bonds with Positive Residual Density. | 2 Note   |

0 **ALERT level A** = Most likely a serious problem - resolve or explain

1 **ALERT level B** = A potentially serious problem, consider carefully

3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

14 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

5 ALERT type 2 Indicator that the structure model may be wrong or deficient

5 ALERT type 3 Indicator that the structure quality may be low

6 ALERT type 4 Improvement, methodology, query or suggestion

0 ALERT type 5 Informative message, check

## Datablock: 5

Bond precision: C-C = 0.0082 Å Wavelength=1.54184

Cell: a=11.7178 (3) b=12.4990 (3) c=20.0282 (10)

alpha=82.928 (3) beta=89.873 (3) gamma=79.605 (2)

Temperature: 100 K

|             | Calculated   | Reported     |
|-------------|--------------|--------------|
| Volume      | 2862.65 (18) | 2862.65 (17) |
| Space group | P -1         | P -1         |

|                                                                     |                                  |                      |
|---------------------------------------------------------------------|----------------------------------|----------------------|
| Hall group                                                          | -P 1                             | -P 1                 |
| Moiety formula                                                      | C24 B F20, C34 H57 Y [+ solvent] | C34 H57 Y, B C24 F20 |
| Sum formula                                                         | C58 H57 B F20 Y [+ solvent]      | C58 H57 B F20 Y      |
| Mr                                                                  | 1233.76                          | 1233.75              |
| Dx, g cm <sup>-3</sup>                                              | 1.431                            | 1.431                |
| Z                                                                   | 2                                | 2                    |
| Mu (mm <sup>-1</sup> )                                              | 2.344                            | 2.344                |
| F000                                                                | 1258.0                           | 1258.0               |
| F000'                                                               | 1262.33                          |                      |
| h, k, lmax                                                          | 14, 15, 24                       | 14, 15, 24           |
| Nref                                                                | 10466                            | 10273                |
| Tmin, Tmax                                                          | 0.760, 0.819                     | 0.396, 1.000         |
| Tmin'                                                               | 0.281                            |                      |
| Correction method= # Reported T Limits: Tmin=0.396                  |                                  |                      |
| Tmax=1.000 AbsCorr = GAUSSIAN                                       |                                  |                      |
| Data completeness= 0.982      Theta(max)= 68.242                    |                                  |                      |
| R(reflections)= 0.0805( 9467)      wR2(reflections)= 0.2148( 10273) |                                  |                      |
| S = 1.131      Npar= 795                                            |                                  |                      |

The following ALERTS were generated. Each ALERT has the format

**test-name\_ALERT\_alert-type\_alert-level.**

Click on the hyperlinks for more details of the test.

## ● Alert level C

DIFMX02\_ALERT\_1\_C The maximum difference density is > 0.1\*ZMAX\*0.75

The relevant atom site should be identified.

|                                   |                                                  |              |
|-----------------------------------|--------------------------------------------------|--------------|
| <a href="#">PLAT094 ALERT 2 C</a> | Ratio of Maximum / Minimum Residual Density .... | 3.93 Report  |
| <a href="#">PLAT097 ALERT 2 C</a> | Large Reported Max. (Positive) Residual Density  | 3.37 eA-3    |
| <a href="#">PLAT341 ALERT 3 C</a> | Low Bond Precision on C-C Bonds .....            | 0.00823 Ang. |
| <a href="#">PLAT412 ALERT 2 C</a> | Short Intra XH3 .. XHn H8C .. H12C ..            | 1.88 Ang.    |
| <a href="#">PLAT412 ALERT 2 C</a> | Short Intra XH3 .. XHn H25C .. H28C ..           | 1.86 Ang.    |
| <a href="#">PLAT906 ALERT 3 C</a> | Large K value in the Analysis of Variance .....  | 5.004 Check  |
| <a href="#">PLAT911 ALERT 3 C</a> | Missing # FCF Refl Between THmin & STh/L= 0.600  | 184 Report   |
| <a href="#">PLAT977 ALERT 2 C</a> | Check the Negative Difference Density on H13A    | -0.36 eA-3   |
| <a href="#">PLAT978 ALERT 2 C</a> | Number C-C Bonds with Positive Residual Density. | 0 Note       |

## ●Alert level G

|                                   |                                                  |              |
|-----------------------------------|--------------------------------------------------|--------------|
| <a href="#">PLAT002 ALERT 2 G</a> | Number of Distance or Angle Restraints on AtSite | 14 Note      |
| <a href="#">PLAT003 ALERT 2 G</a> | Number of Uiso or Uij Restrained non-H Atoms ... | 86 Report    |
| <a href="#">PLAT042 ALERT 1 G</a> | Calc. and Reported MoietyFormula Strings Differ  | Please Check |
| <a href="#">PLAT083 ALERT 2 G</a> | SHELXL Second Parameter in WGHT Unusually Large  | 11.31 Why ?  |
| <a href="#">PLAT172 ALERT 4 G</a> | The CIF-Embedded .res File Contains DFIX Records | 3 Report     |
| <a href="#">PLAT176 ALERT 4 G</a> | The CIF-Embedded .res File Contains SADI Records | 4 Report     |
| <a href="#">PLAT178 ALERT 4 G</a> | The CIF-Embedded .res File Contains SIMU Records | 3 Report     |
| <a href="#">PLAT187 ALERT 4 G</a> | The CIF-Embedded .res File Contains RIGU Records | 1 Report     |
| <a href="#">PLAT302 ALERT 4 G</a> | Anion/Solvent/Minor-Residue Disorder (Resd 2)..  | 17 % Note    |
| <a href="#">PLAT343 ALERT 2 G</a> | Unusual sp? Angle Range in Main Residue for      | C20 Check    |
| <a href="#">PLAT605 ALERT 4 G</a> | Largest Solvent Accessible VOID in the Structure | 219 A**3     |
| <a href="#">PLAT802 ALERT 4 G</a> | CIF Input Record(s) with more than 80 Characters | 1 Info       |
| <a href="#">PLAT860 ALERT 3 G</a> | Number of Least-Squares Restraints .....         | 984 Note     |
| <a href="#">PLAT869 ALERT 4 G</a> | ALERTS Related to the use of SQUEEZE Suppressed  | ! Info       |
| <a href="#">PLAT912 ALERT 4 G</a> | Missing # of FCF Reflections Above STh/L= 0.600  | 10 Note      |
| <a href="#">PLAT933 ALERT 2 G</a> | Number of OMIT Records in Embedded .res File ... | 5 Note       |

0 **ALERT level A** = Most likely a serious problem - resolve or explain

0 **ALERT level B** = A potentially serious problem, consider carefully

10 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

16 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

11 ALERT type 2 Indicator that the structure model may be wrong or deficient

4 ALERT type 3 Indicator that the structure quality may be low

9 ALERT type 4 Improvement, methodology, query or suggestion

0 ALERT type 5 Informative message, check

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## Datablock: 6

---

Bond precision: C-C = 0.0000 Å Wavelength=0.71073

Cell: a=10.3399 (3) b=15.3846 (4) c=20.3495 (7)

alpha=90 beta=99.477 (3) gamma=90

Temperature: 150 K

|                        | Calculated    | Reported            |
|------------------------|---------------|---------------------|
| Volume                 | 3192.92 (17)  | 3192.93 (18)        |
| Space group            | P 21/c        | P 1 21/c 1          |
| Hall group             | -P 2ybc       | -P 2ybc             |
| Moiety formula         | C34 H58 Cl Dy | 1 (C34 H58 Cl1 Dy1) |
| Sum formula            | C34 H58 Cl Dy | C34 H58 Cl Dy       |
| Mr                     | 664.75        | 664.75              |
| Dx, g cm <sup>-3</sup> | 1.383         | 1.383               |
| Z                      | 4             | 4                   |
| Mu (mm <sup>-1</sup> ) | 2.444         | 2.444               |

|            |              |              |
|------------|--------------|--------------|
| F000       | 1380.0       | 1380.0       |
| F000'      | 1380.16      |              |
| h, k, lmax | 12, 18, 24   | 12, 18, 24   |
| Nref       | 5850         | 5834         |
| Tmin, Tmax | 0.481, 0.540 | 0.841, 0.889 |
| Tmin'      | 0.338        |              |

Correction method= # Reported T Limits: Tmin=0.841

Tmax=0.889 AbsCorr = ANALYTICAL

Data completeness= 0.997      Theta(max)= 25.349

R(reflections)= 0.0341( 4812)      wR2(reflections)= 0.0872( 5834)

S = 1.160      Npar= 641

The following ALERTS were generated. Each ALERT has the format

**test-name\_ALERT\_alert-type\_alert-level.**

Click on the hyperlinks for more details of the test.

## 🟡 Alert level B

[PLAT910\\_ALERT\\_3\\_B](#) Missing # of FCF Reflection(s) Below Theta(Min)      14 Note

**Author Response: Reduction of beam stop mask did not yield significant improvement. Most of those missing strong reflections appeared to be very strong and were treated as overflows.**

## 🟡 Alert level C

[PLAT088\\_ALERT\\_3\\_C](#) Poor Data / Parameter Ratio .....      9.10 Note

[PLAT213\\_ALERT\\_2\\_C](#) Atom C9A      has ADP max/min Ratio .....      3.1 oblate

[PLAT213\\_ALERT\\_2\\_C](#) Atom C13A      has ADP max/min Ratio .....      3.1 oblate

[PLAT906\\_ALERT\\_3\\_C](#) Large K value in the Analysis of Variance .....      2.534 Check

[PLAT911\\_ALERT\\_3\\_C](#) Missing # FCF Refl Between THmin & STh/L= 0.600      2 Report



## ● Alert level G

|                                   |                                                  |       |              |
|-----------------------------------|--------------------------------------------------|-------|--------------|
| <a href="#">PLAT002 ALERT 2 G</a> | Number of Distance or Angle Restraints on AtSite | 69    | Note         |
| <a href="#">PLAT003 ALERT 2 G</a> | Number of Uiso or Uij Restrained non-H Atoms ... | 72    | Report       |
| <a href="#">PLAT042 ALERT 1 G</a> | Calc. and Reported MoietyFormula Strings Differ  |       | Please Check |
| <a href="#">PLAT083 ALERT 2 G</a> | SHELXL Second Parameter in WGHT Unusually Large  | 5.33  | Why ?        |
| <a href="#">PLAT172 ALERT 4 G</a> | The CIF-Embedded .res File Contains DFIX Records | 2     | Report       |
| <a href="#">PLAT174 ALERT 4 G</a> | The CIF-Embedded .res File Contains FLAT Records | 2     | Report       |
| <a href="#">PLAT175 ALERT 4 G</a> | The CIF-Embedded .res File Contains SAME Records | 2     | Report       |
| <a href="#">PLAT178 ALERT 4 G</a> | The CIF-Embedded .res File Contains SIMU Records | 1     | Report       |
| <a href="#">PLAT186 ALERT 4 G</a> | The CIF-Embedded .res File Contains ISOR Records | 2     | Report       |
| <a href="#">PLAT187 ALERT 4 G</a> | The CIF-Embedded .res File Contains RIGU Records | 1     | Report       |
| <a href="#">PLAT301 ALERT 3 G</a> | Main Residue Disorder .....(Resd 1)..            | 100 % | Note         |
| <a href="#">PLAT301 ALERT 3 G</a> | Main Residue Disorder .....(Resd 2)..            | 100 % | Note         |
| <a href="#">PLAT304 ALERT 4 G</a> | Non-Integer Number of Atoms ( 89.31) in Resd. #  | 1     | Check        |
| <a href="#">PLAT304 ALERT 4 G</a> | Non-Integer Number of Atoms ( 4.69) in Resd. #   | 2     | Check        |
| <a href="#">PLAT720 ALERT 4 G</a> | Number of Unusual/Non-Standard Labels .....      | 9     | Note         |
| <a href="#">PLAT789 ALERT 4 G</a> | Atoms with Negative _atom_site_disorder_group #  | 94    | Check        |
| <a href="#">PLAT802 ALERT 4 G</a> | CIF Input Record(s) with more than 80 Characters | 3     | Info         |
| <a href="#">PLAT860 ALERT 3 G</a> | Number of Least-Squares Restraints .....         | 1835  | Note         |
| <a href="#">PLAT933 ALERT 2 G</a> | Number of OMIT Records in Embedded .res File ... | 2     | Note         |
| <a href="#">PLAT978 ALERT 2 G</a> | Number C-C Bonds with Positive Residual Density. | 5     | Note         |

0 **ALERT level A** = Most likely a serious problem - resolve or explain

1 **ALERT level B** = A potentially serious problem, consider carefully

5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

20 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

7 ALERT type 2 Indicator that the structure model may be wrong or deficient

7 ALERT type 3 Indicator that the structure quality may be low

11 ALERT type 4 Improvement, methodology, query or suggestion

0 ALERT type 5 Informative message, check

## Datablock: 7

Bond precision: C-C = 0.0000 Å Wavelength=1.54184

Cell: a=10.3414(2) b=15.3511(3) c=20.3475(4)

alpha=90 beta=99.4776(17) gamma=90

Temperature: 100 K

|                        | Calculated   | Reported     |
|------------------------|--------------|--------------|
| Volume                 | 3186.11(11)  | 3186.10(11)  |
| Space group            | P 21/c       | P 1 21/c 1   |
| Hall group             | -P 2ybc      | -P 2ybc      |
| Moiety formula         | C34 H58 Cl Y | C34 H58 Cl Y |
| Sum formula            | C34 H58 Cl Y | C34 H58 Cl Y |
| Mr                     | 591.16       | 591.16       |
| Dx, g cm <sup>-3</sup> | 1.232        | 1.232        |
| Z                      | 4            | 4            |
| Mu (mm <sup>-1</sup> ) | 3.469        | 3.469        |
| F000                   | 1272.0       | 1272.0       |
| F000'                  | 1274.69      |              |
| h, k, lmax             | 12, 18, 24   | 12, 18, 24   |
| Nref                   | 5838         | 5813         |

Tmin, Tmax 0.812, 0.841 0.422, 1.000  
 Tmin' 0.707  
 Correction method= # Reported T Limits: Tmin=0.422  
 Tmax=1.000 AbsCorr = MULTI-SCAN  
 Data completeness= 0.996 Theta (max)= 68.250  
 R(reflections)= 0.0504( 4059) wR2(reflections)= 0.1429( 5813)  
 S = 1.028 Npar= 650

The following ALERTS were generated. Each ALERT has the format

**test-name\_ALERT\_alert-type\_alert-level.**

Click on the hyperlinks for more details of the test.

## ● Alert level C

[PLAT088\\_ALERT\\_3\\_C](#) Poor Data / Parameter Ratio ..... 8.94 Note  
[PLAT905\\_ALERT\\_3\\_C](#) Negative K value in the Analysis of Variance ... -0.460 Report  
[PLAT911\\_ALERT\\_3\\_C](#) Missing # FCF Refl Between THmin & STh/L= 0.600 14 Report  
[PLAT973\\_ALERT\\_2\\_C](#) Check Calcd Positive Residual Density on Y1A 1.10 eA-3  
[PLAT977\\_ALERT\\_2\\_C](#) Check the Negative Difference Density on H16A -0.42 eA-3

## ● Alert level G

[PLAT002\\_ALERT\\_2\\_G](#) Number of Distance or Angle Restraints on AtSite 74 Note  
[PLAT003\\_ALERT\\_2\\_G](#) Number of Uiso or Uij Restrained non-H Atoms ... 72 Report  
[PLAT083\\_ALERT\\_2\\_G](#) SHELXL Second Parameter in WGHT Unusually Large 8.00 Why ?  
[PLAT172\\_ALERT\\_4\\_G](#) The CIF-Embedded .res File Contains DFIX Records 1 Report  
[PLAT175\\_ALERT\\_4\\_G](#) The CIF-Embedded .res File Contains SAME Records 1 Report  
[PLAT178\\_ALERT\\_4\\_G](#) The CIF-Embedded .res File Contains SIMU Records 1 Report  
[PLAT187\\_ALERT\\_4\\_G](#) The CIF-Embedded .res File Contains RIGU Records 1 Report

|                                   |                                                  |            |
|-----------------------------------|--------------------------------------------------|------------|
| <a href="#">PLAT301 ALERT 3 G</a> | Main Residue Disorder .....(Resd 1)..            | 100 % Note |
| <a href="#">PLAT301 ALERT 3 G</a> | Main Residue Disorder .....(Resd 2)..            | 100 % Note |
| <a href="#">PLAT304 ALERT 4 G</a> | Non-Integer Number of Atoms ( 89.38) in Resd. #  | 1 Check    |
| <a href="#">PLAT304 ALERT 4 G</a> | Non-Integer Number of Atoms ( 4.62) in Resd. #   | 2 Check    |
| <a href="#">PLAT720 ALERT 4 G</a> | Number of Unusual/Non-Standard Labels .....      | 9 Note     |
| <a href="#">PLAT789 ALERT 4 G</a> | Atoms with Negative _atom_site_disorder_group #  | 94 Check   |
| <a href="#">PLAT802 ALERT 4 G</a> | CIF Input Record(s) with more than 80 Characters | 2 Info     |
| <a href="#">PLAT860 ALERT 3 G</a> | Number of Least-Squares Restraints .....         | 1932 Note  |
| <a href="#">PLAT912 ALERT 4 G</a> | Missing # of FCF Reflections Above STh/L= 0.600  | 11 Note    |
| <a href="#">PLAT933 ALERT 2 G</a> | Number of OMIT Records in Embedded .res File ... | 1 Note     |
| <a href="#">PLAT978 ALERT 2 G</a> | Number C-C Bonds with Positive Residual Density. | 9 Note     |

0 **ALERT level A** = Most likely a serious problem - resolve or explain

0 **ALERT level B** = A potentially serious problem, consider carefully

5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

18 **ALERT level G** = General information/check it is not something unexpected

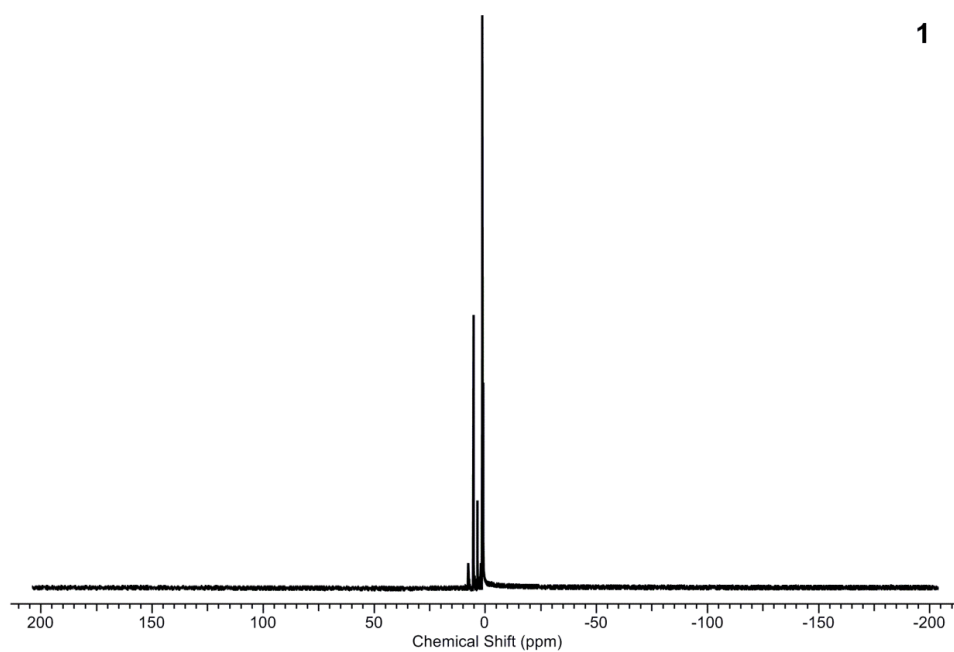
0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

7 ALERT type 2 Indicator that the structure model may be wrong or deficient

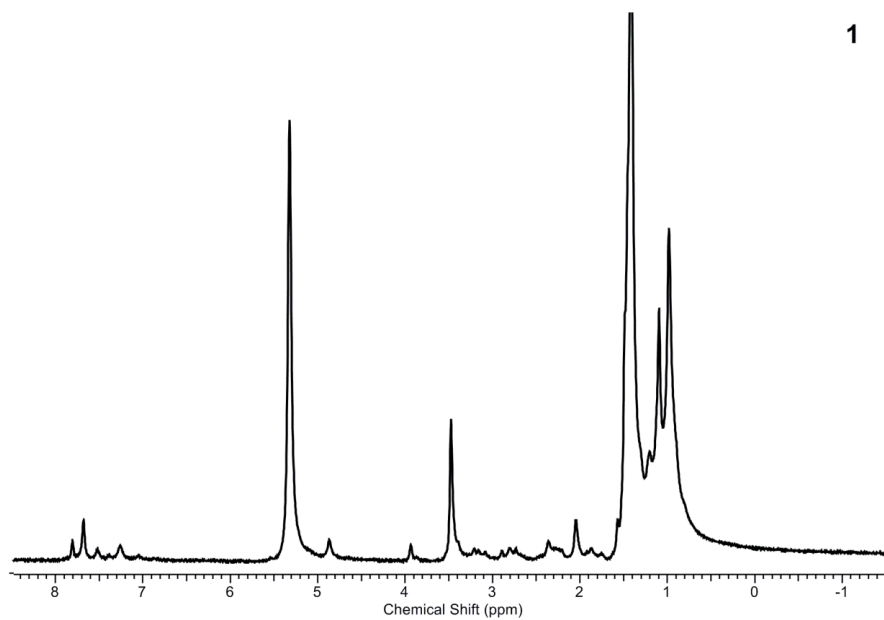
6 ALERT type 3 Indicator that the structure quality may be low

10 ALERT type 4 Improvement, methodology, query or suggestion

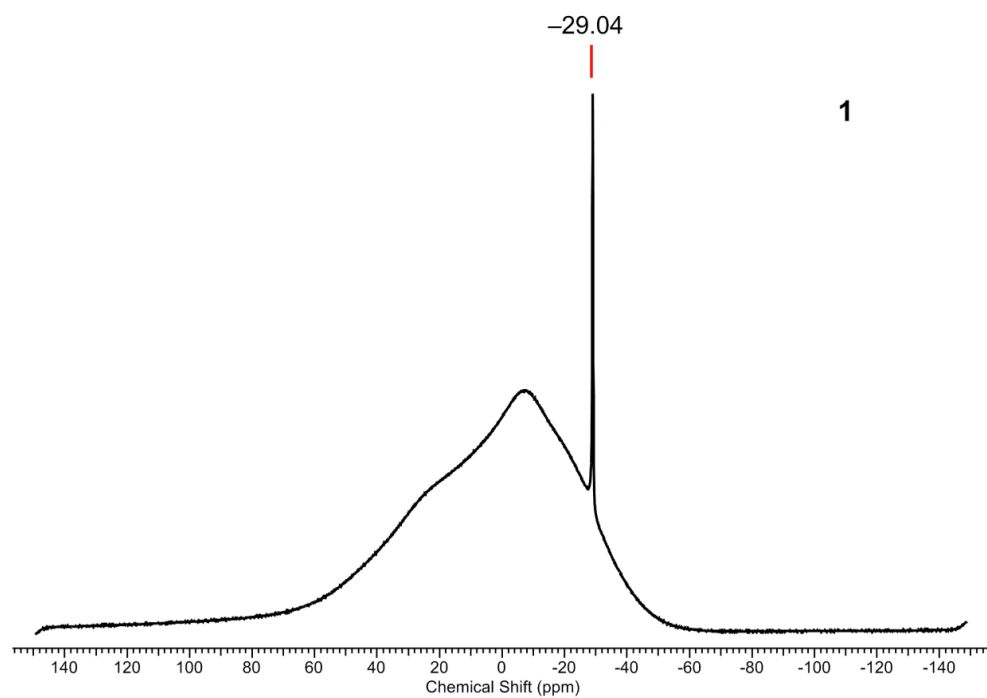
0 ALERT type 5 Informative message, check

**S4. NMR spectra**

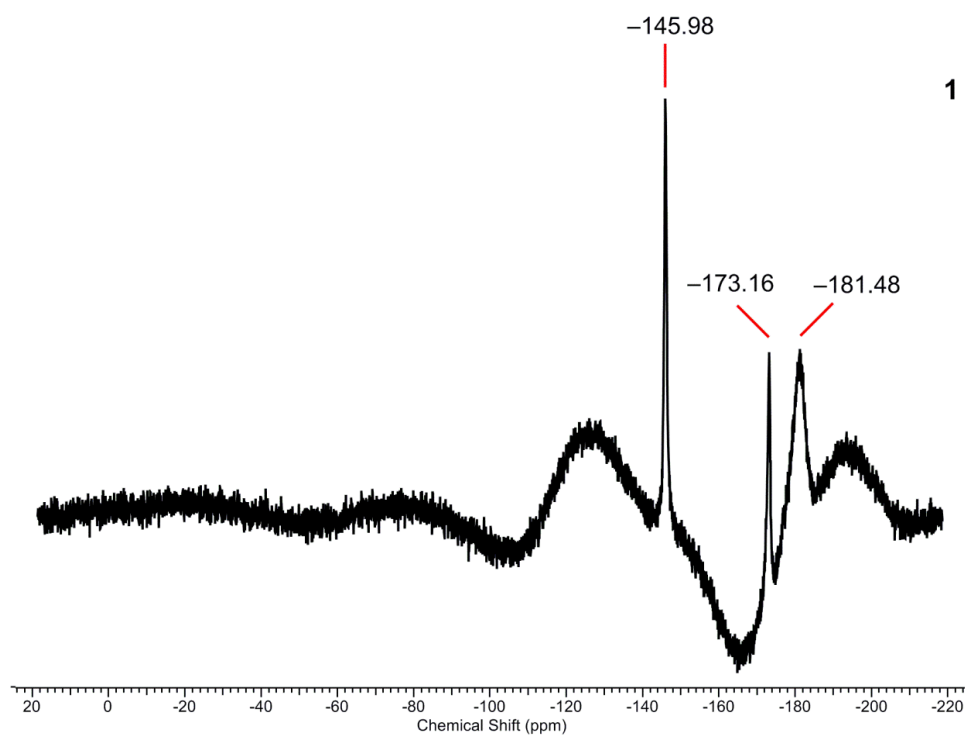
**Figure S4.**  $^1\text{H}$  NMR spectrum of complex **1** in  $\text{CD}_2\text{Cl}_2$ .



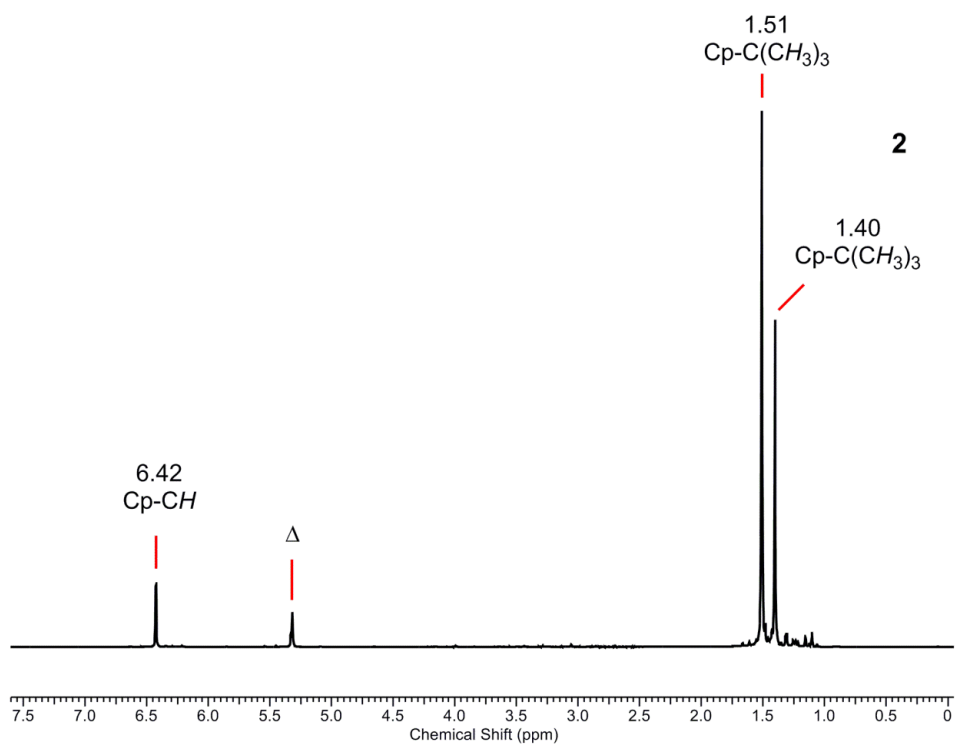
**Figure S5.**  $^1\text{H}$  NMR spectrum of complex **1** in  $\text{CD}_2\text{Cl}_2$  zoomed in the region between -1 and 8 ppm.



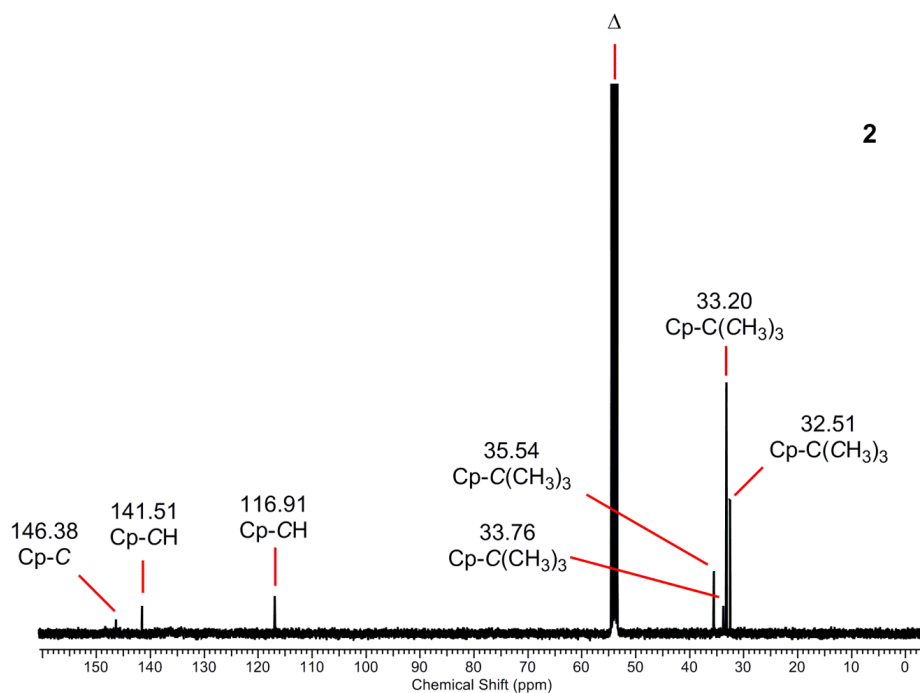
**Figure S6.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of complex **1** in  $\text{CD}_2\text{Cl}_2$ .



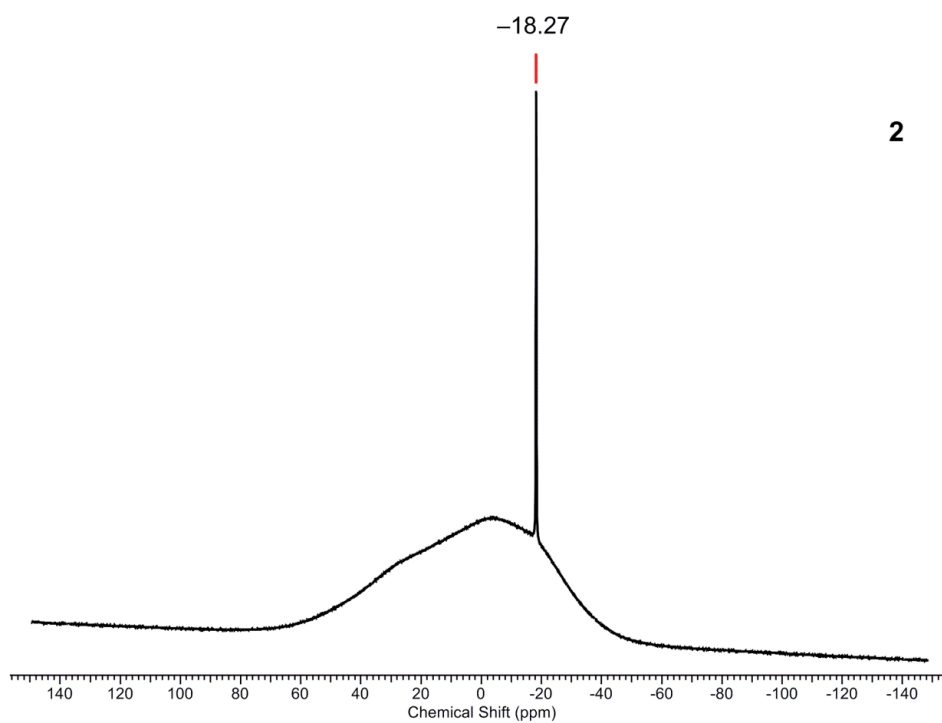
**Figure S7.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of complex **1** in  $\text{CD}_2\text{Cl}_2$ .



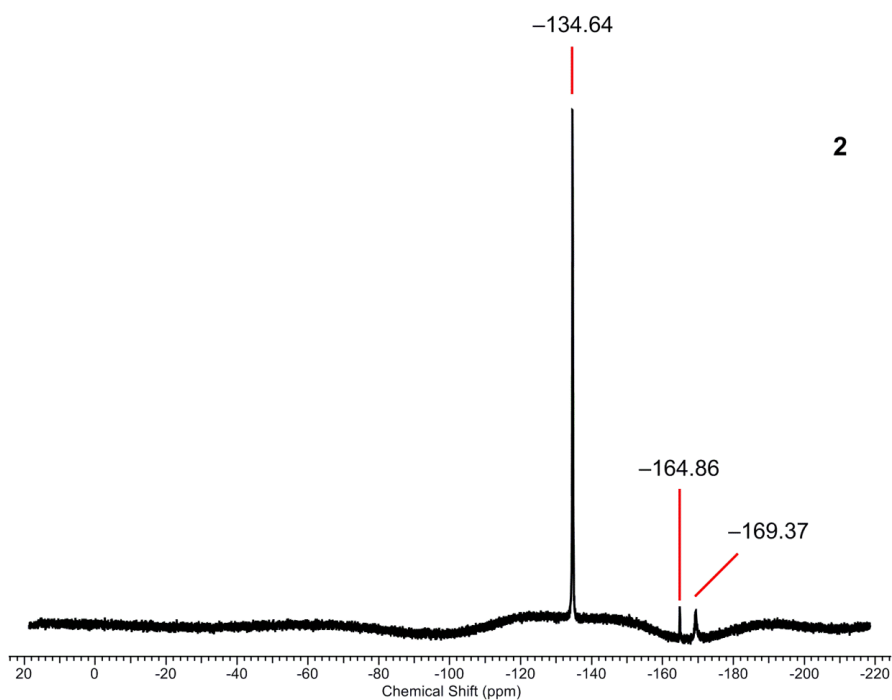
**Figure S8.** <sup>1</sup>H NMR spectrum of complex **2** in CD<sub>2</sub>Cl<sub>2</sub>. Δ denotes CH<sub>2</sub>Cl<sub>2</sub>.



**Figure S9.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of complex **2** in CD<sub>2</sub>Cl<sub>2</sub>. Δ denotes CH<sub>2</sub>Cl<sub>2</sub>.

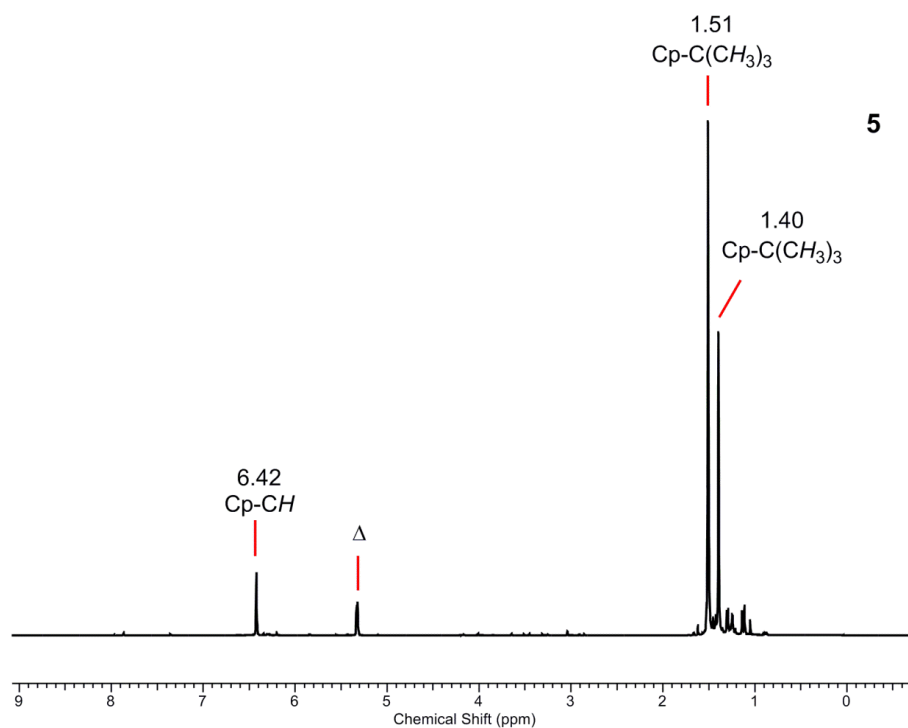


**Figure S10.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of complex **2** in  $\text{CD}_2\text{Cl}_2$ .

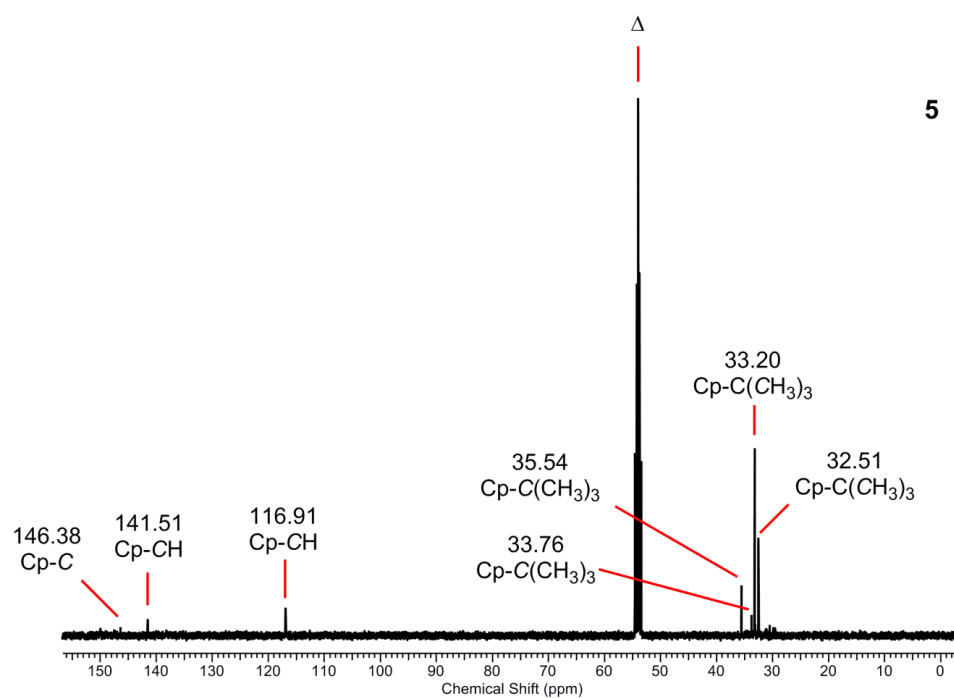


**Figure S11.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of complex **2** in  $\text{CD}_2\text{Cl}_2$ .

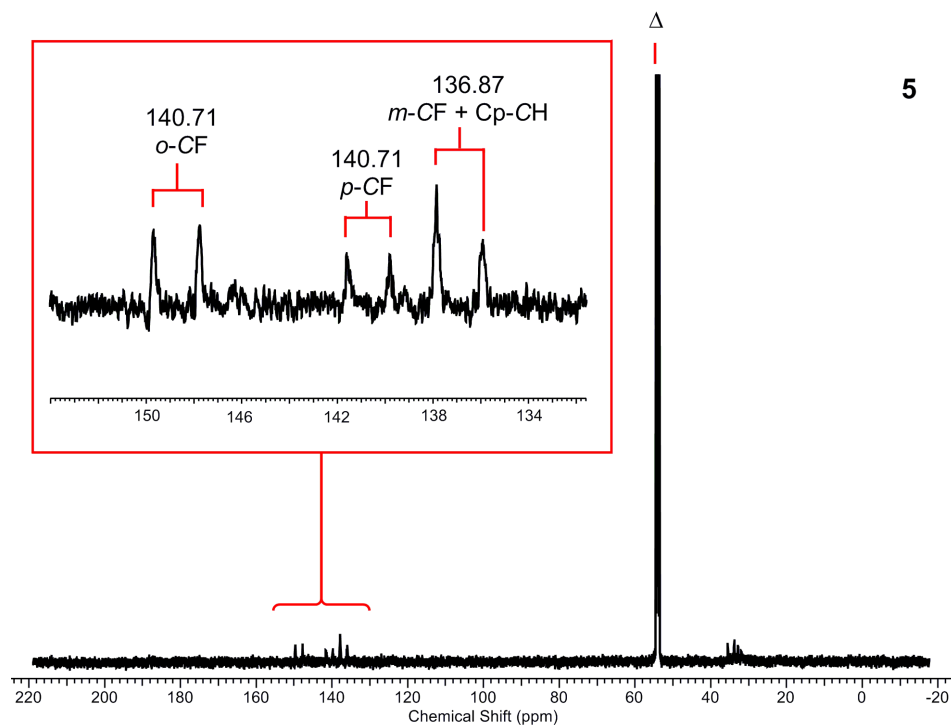




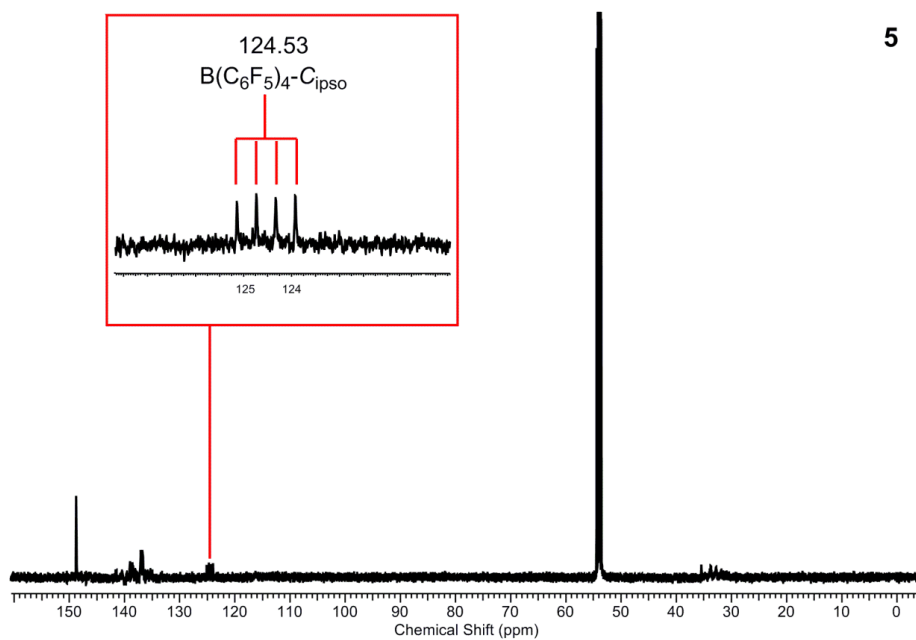
**Figure S12.** <sup>1</sup>H NMR spectrum of complex **5** in CD<sub>2</sub>Cl<sub>2</sub>. Δ denotes CH<sub>2</sub>Cl<sub>2</sub>.



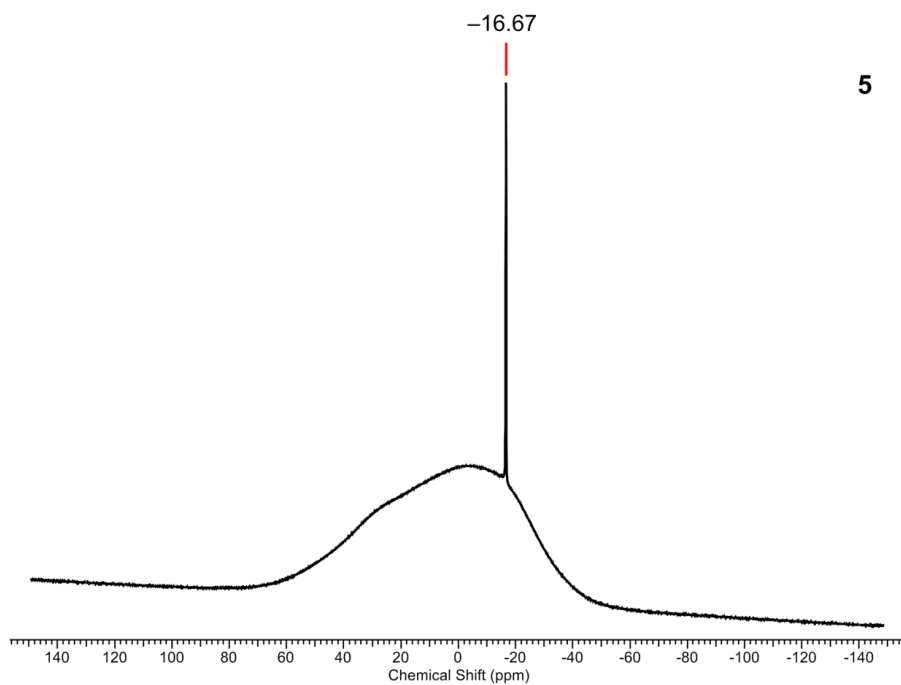
**Figure S13.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of complex **5** in CD<sub>2</sub>Cl<sub>2</sub>. Δ denotes CH<sub>2</sub>Cl<sub>2</sub>.



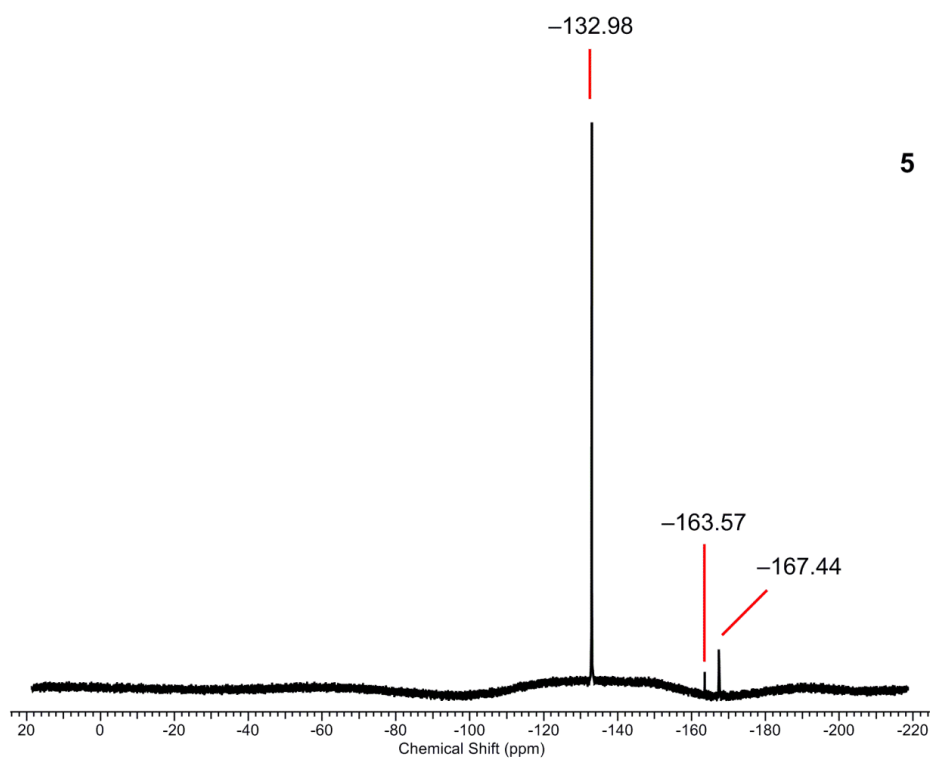
**Figure S14.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz) spectrum of complex **5** in  $\text{CD}_2\text{Cl}_2$  with increased relaxation time (1 s), which partially suppresses Cp–C resonances.  $\Delta$  denotes  $\text{CH}_2\text{Cl}_2$ .



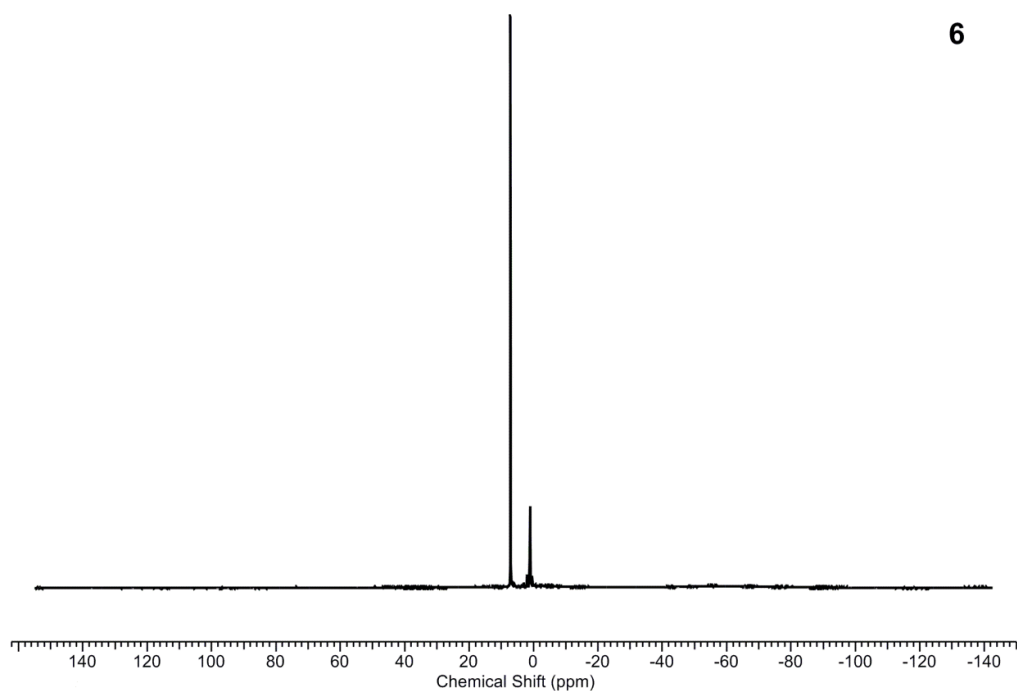
**Figure S15.**  $^{13}\text{C}\{^{19}\text{F}\}$  NMR spectrum of complex **5** in  $\text{CD}_2\text{Cl}_2$ .



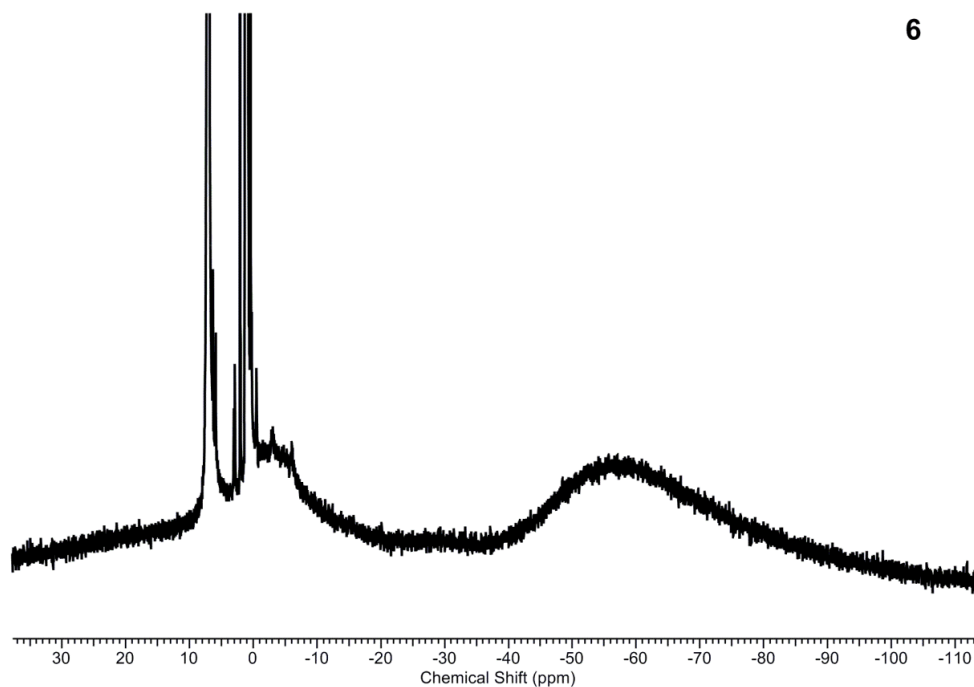
**Figure S16.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of complex **5** in  $\text{CD}_2\text{Cl}_2$ .



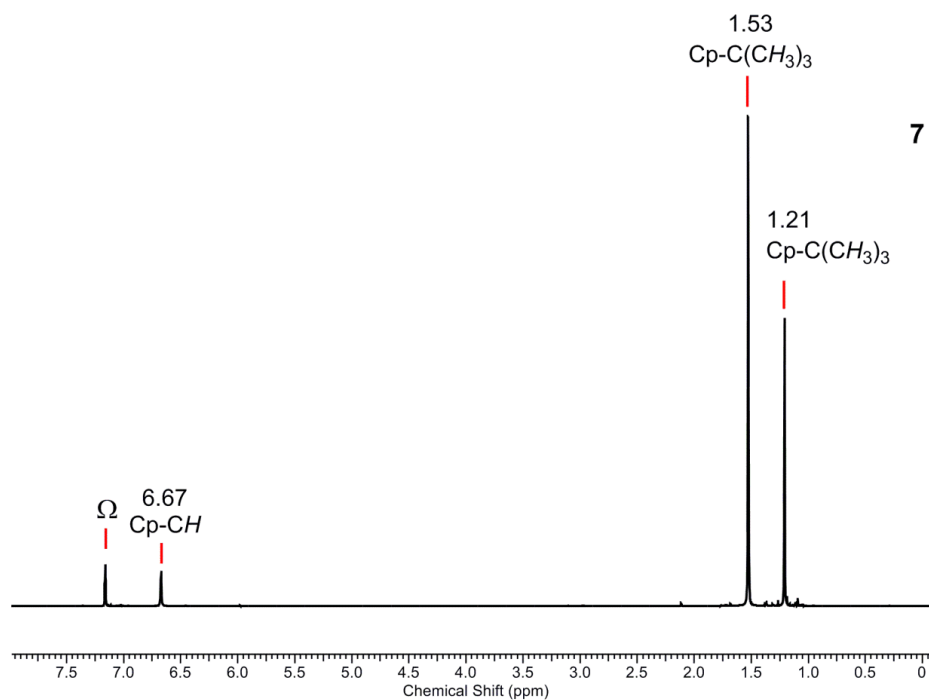
**Figure S17.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of complex **5** in  $\text{CD}_2\text{Cl}_2$ .



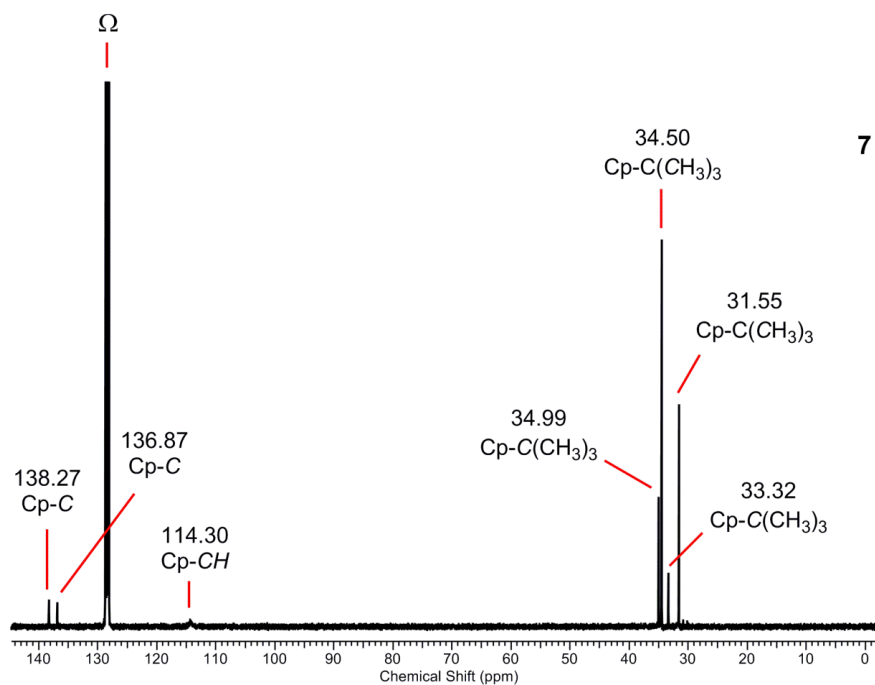
**Figure S18.**  $^1\text{H}$  NMR spectrum of complex **6** in  $\text{C}_6\text{D}_6$ .



**Figure S19.**  $^1\text{H}$  NMR spectrum of complex **6** in  $\text{C}_6\text{D}_6$  zoomed in the region between -110 and 30 ppm.

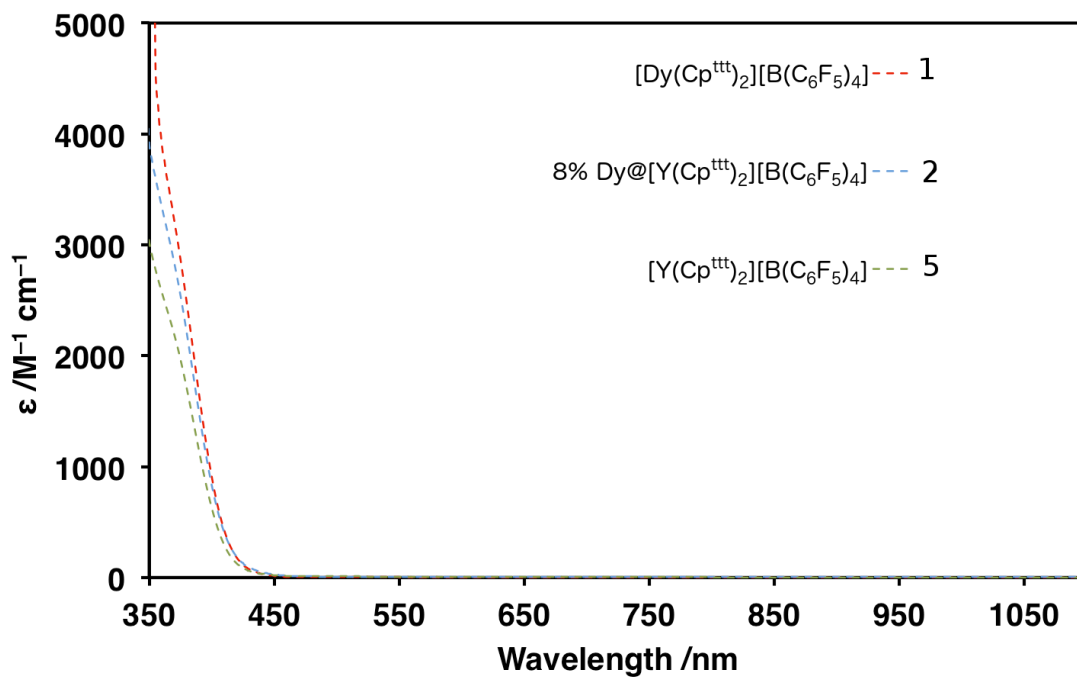


**Figure S20.** <sup>1</sup>H NMR spectrum of complex **7** in C<sub>6</sub>D<sub>6</sub>. Ω denotes C<sub>6</sub>H<sub>6</sub>.



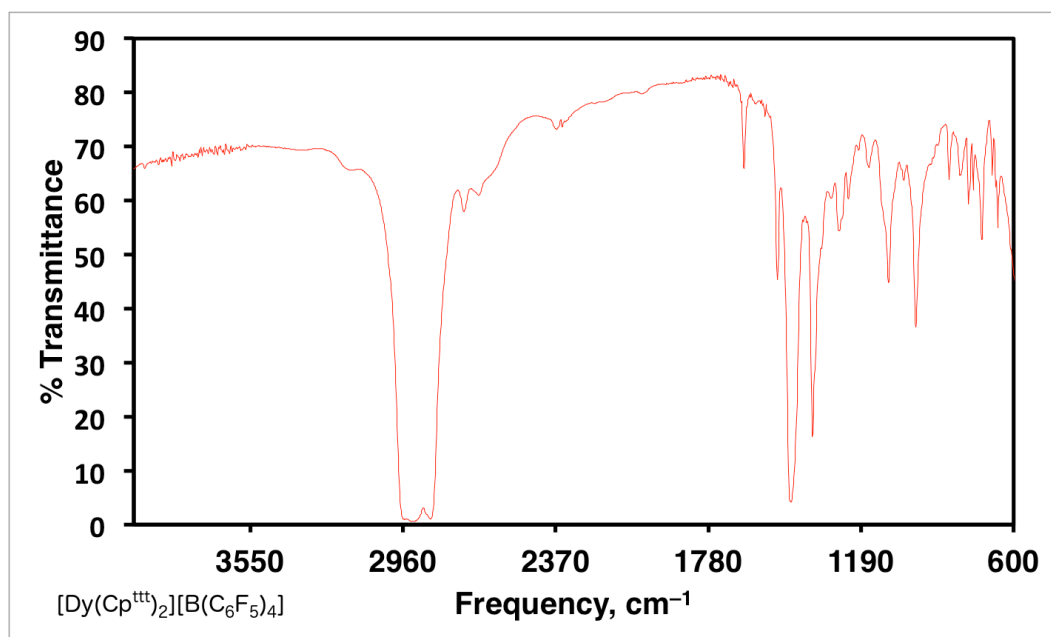
**Figure S21.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of complex **7** in C<sub>6</sub>D<sub>6</sub>.

## S5. UV-Vis-NIR spectra

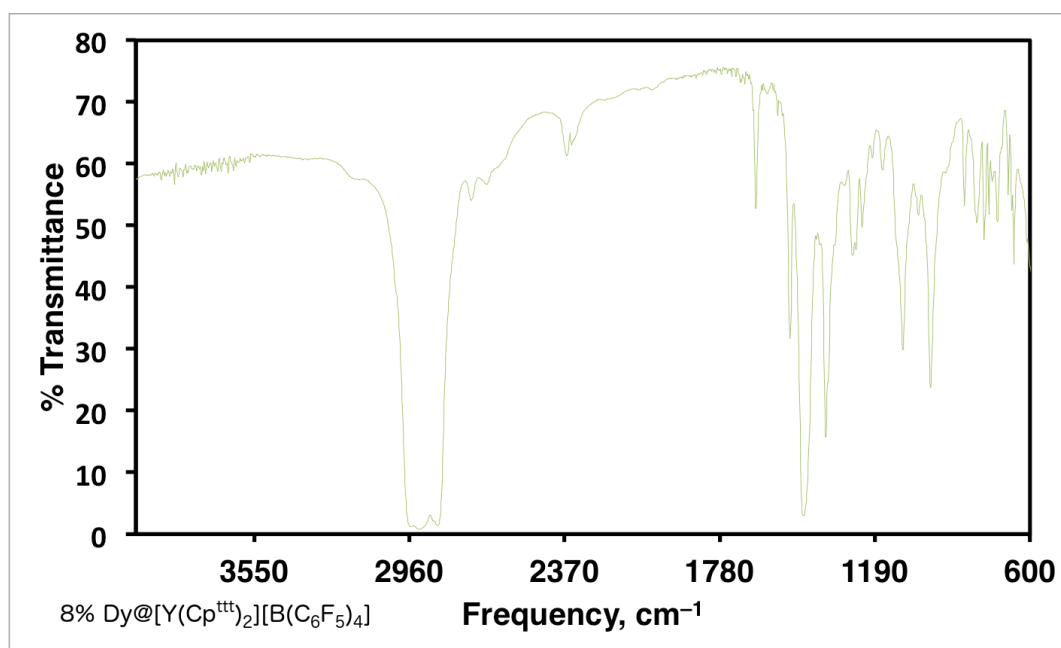


**Figure S22.** UV/Vis absorption spectra of complexes **1** (1.15 mM in DCM), **2** (0.99 mM in DCM) and **5** (1.00 mM in DCM).

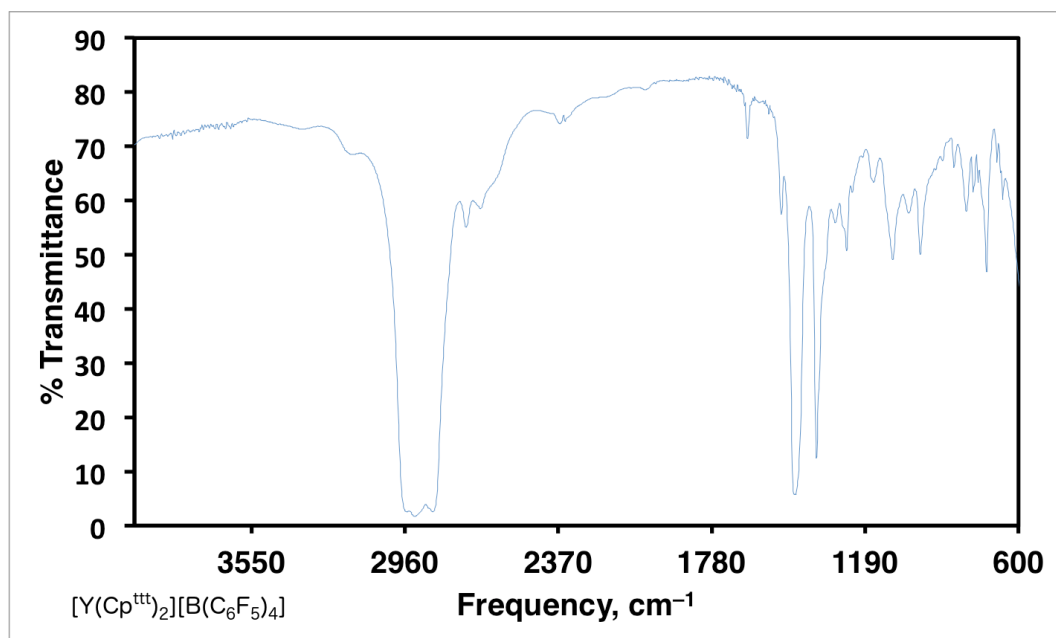
## S6. FTIR and Raman spectroscopy



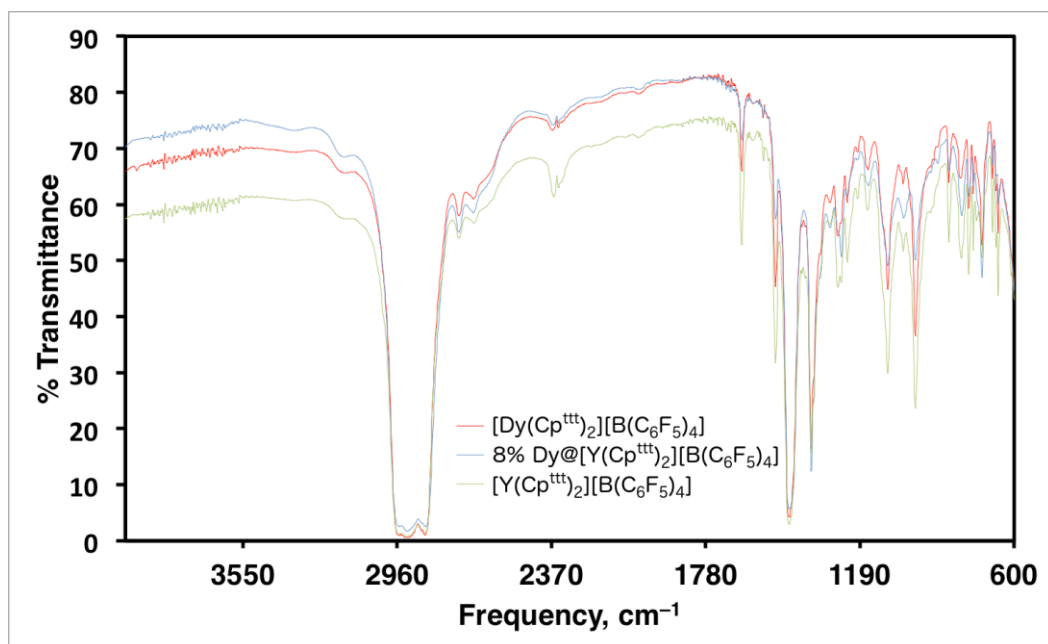
**Figure S23.** FTIR spectrum of complex 1 as a Nujol mull between KBr discs.



**Figure S24.** FTIR spectrum of complex 2 as a Nujol mull between KBr discs.

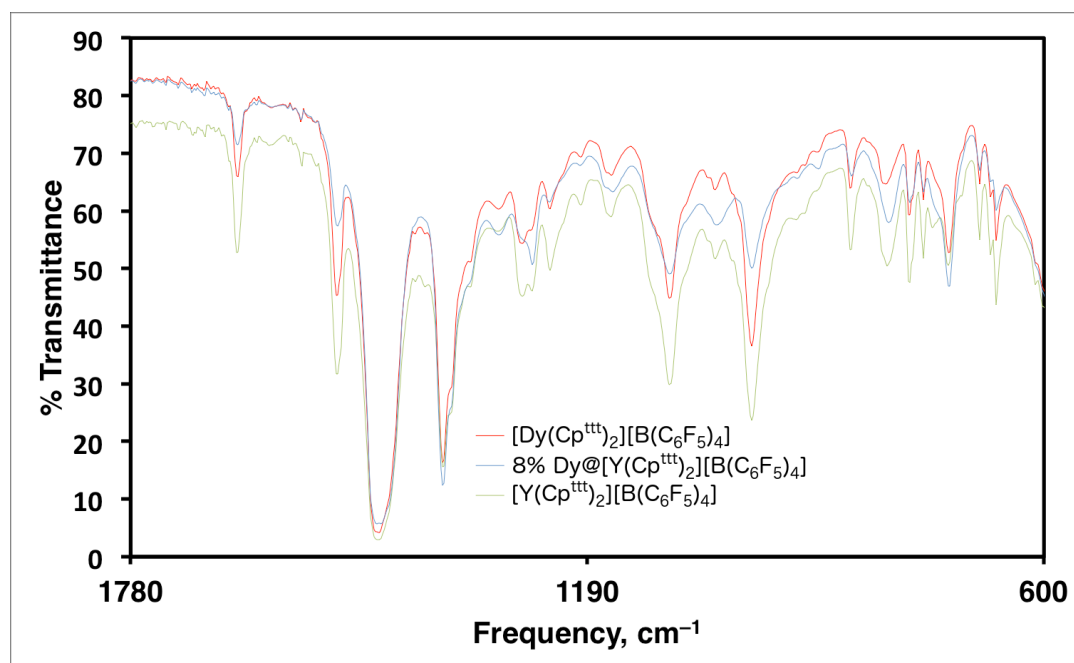


**Figure S25.** FTIR spectrum of complex 5 as a Nujol mull between KBr discs.

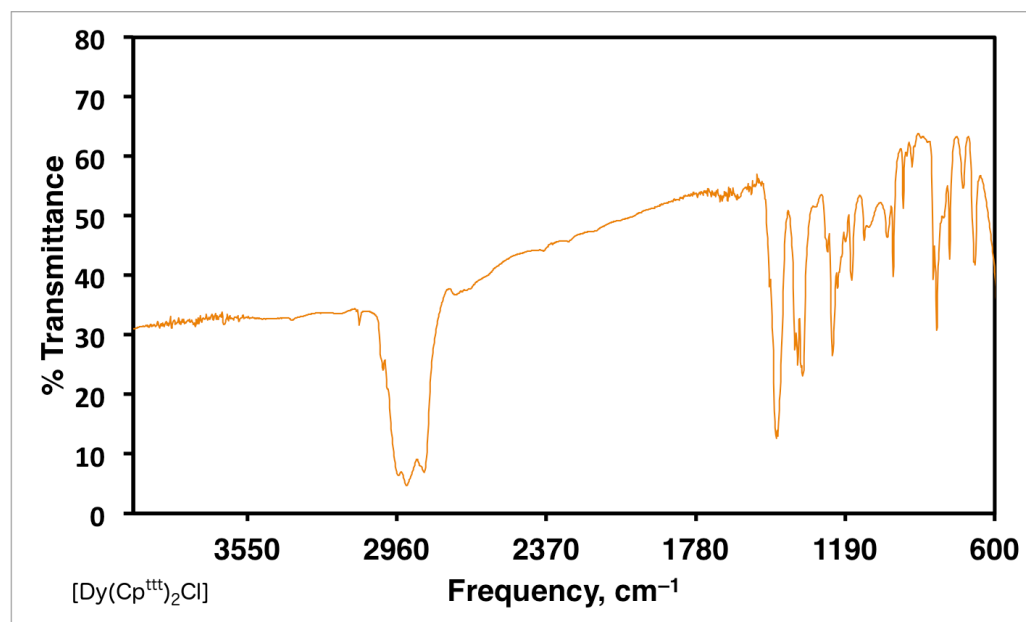


**Figure S26.** Overlaid FTIR spectra of complexes 1, 2 and 5 as Nujol mulls between KBr discs.

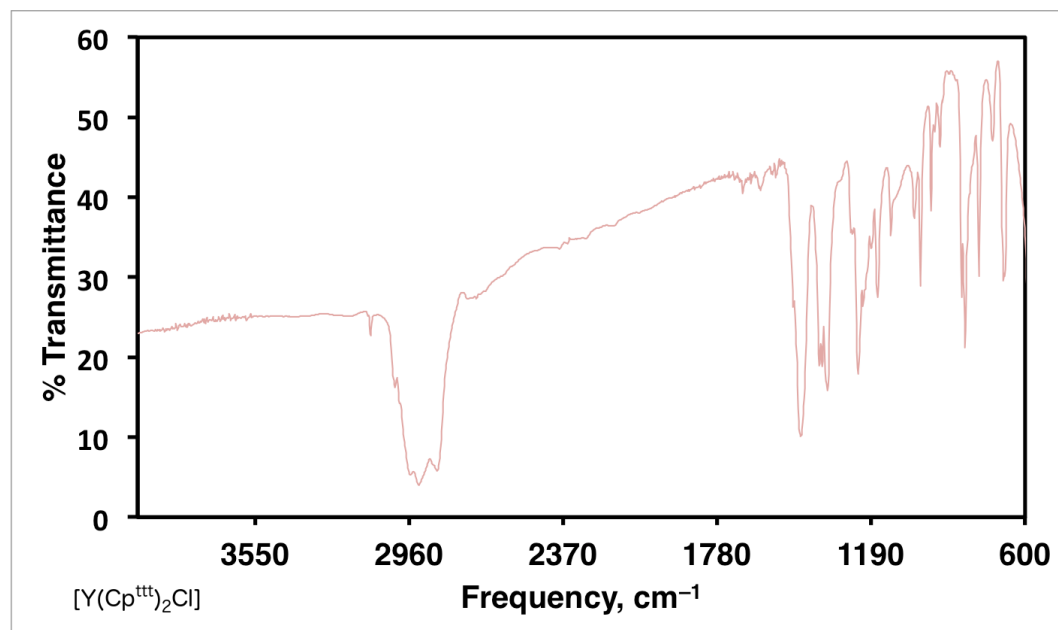




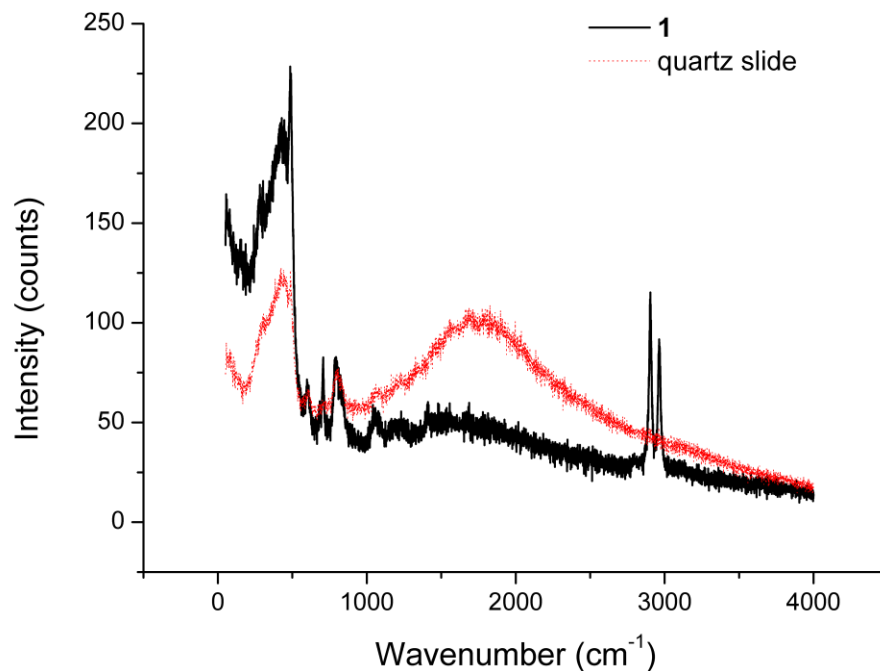
**Figure S27.** Overlaid FTIR spectra of complexes **1**, **2** and **5** as Nujol mulls between KBr discs zoomed in the region between 1780–600 cm<sup>-1</sup>.



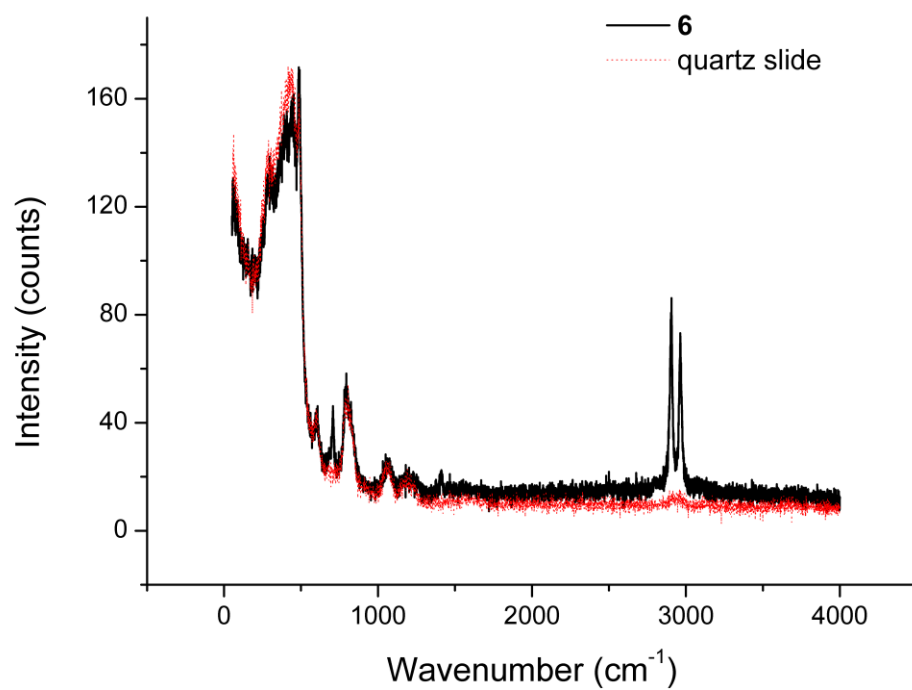
**Figure S28.** FTIR spectrum of complex **6** as a Nujol mull between KBr discs.



**Figure S29.** FTIR spectrum of complex **7** as a Nujol mull between KBr discs.



**Figure S30.** Raman spectrum of **1** (solid sample, quartz slide). The spectrum was acquired using a 532 nm green laser, 1800 g/mm grating, 1 s exposure and 5 accumulations.



**Figure S31.** Raman spectrum of **6** (solid sample, quartz slide). The spectrum was acquired using a 532 nm green laser, 1800 g/mm grating, 1 s exposure and 5 accumulations.

## S7. Magnetism

Magnetic measurements were made using a Quantum Design MPMS-XL7 superconducting quantum interference device (SQUID) magnetometer. For measurements on **1** and **2**, crystalline samples with mass ca. 30 mg were crushed with a mortar and pestle under an inert atmosphere. This was loaded into an NMR tube along with ca. 15 mg powdered eicosane, which was then evacuated and flame-sealed to a length of ca. 5 cm. The eicosane was melted by heating the tube gently with a low-power heat gun in order to immobilise the crystallites. The frozen solution samples were prepared by loading solutions of 2.9 mg (for **3**) or 21.0 mg (for **4**) of **1** in ca. 110 mg DCM (ca. 83  $\mu\text{L}$ ) into an NMR tube which was then frozen with liquid nitrogen, evacuated and flame-sealed to a length of ca. 5 cm. The NMR tube was then mounted in the centre of a drinking straw using friction by wrapping it with Kapton tape, and the straw was then fixed to the end of the sample rod.

The saturation magnetisation for **1** is 28419 emu mol<sup>-1</sup> at 2K (Table S3); the dilute crystalline sample **2**, and the solution samples **3** and **4** give  $M_{\text{sat}}$  values of 0.064, 0.048 and 0.39 emu at 2 K, respectively, which correspond to masses of  $[\text{Dy}(\text{Cp}^{\text{t}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$  of 2.9, 2.2 and 18.1 mg, respectively (Table S3). Note that due to slight mass inaccuracies in **1** (*cf.* CASSCF-SO calculations, see below), the magnetically-determined masses for **2-4** are underestimations.

**Table S3.** Sample specifications.

| Sample                     | 1<br>(mg)          | $M_{\text{sat}}$ 2 K<br>(emu) | 1<br>(mol)  | Solvent<br>(mg) | Concentration<br>(mmol L <sup>-1</sup> ) |
|----------------------------|--------------------|-------------------------------|-------------|-----------------|------------------------------------------|
| <b>1</b>                   | 34.2               | 7.42866E-01                   | 2.61396E-05 | -               | -                                        |
| <b>2</b>                   | 2.9 <sup>a,b</sup> | 6.40139E-02                   | 2.25249E-06 | -               | -                                        |
| <b>3 (DCM)</b>             | 2.2 <sup>a</sup>   | 4.82894E-02                   | 1.69919E-06 | 109.6           | 20.6                                     |
| <b>4 (DCM)</b>             | 18.1 <sup>a</sup>  | 3.92500E-01                   | 1.38111E-05 | 107.6           | 170                                      |
| <b>1,2-difluorobenzene</b> | 6.5 <sup>a</sup>   | 1.40355E-01                   | 4.93874E-06 | 139.4           | 41.1                                     |

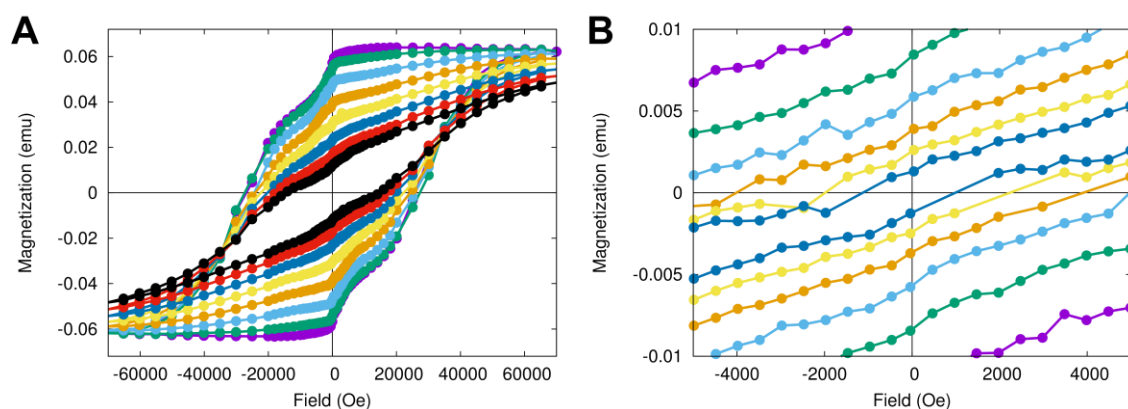
<sup>a</sup> Calculated from magnetic data rather than experimental masses.

<sup>b</sup> Total sample mass is 34.2 mg, therefore mass of  $[\text{Y}(\text{Cp}^{\text{tt}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$  is 31.3 mg.

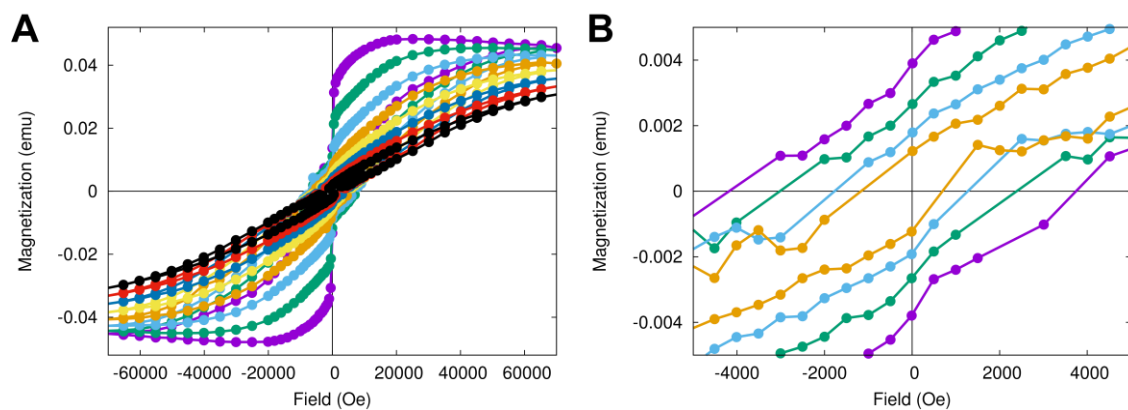
DC hysteresis measurements were collected by magnetising the samples at 70 kOe and sweeping the field through zero towards -70 kOe, and then sweeping the field back through zero towards 70 kOe, at a fixed temperature. The average field sweep rate was 22(9) Oe s<sup>-1</sup> for  $|\text{H}| < 10$  kOe, 54(15) Oe s<sup>-1</sup> for  $10 < |\text{H}| < 20$  kOe, and 91(17) Oe s<sup>-1</sup> for  $20 < |\text{H}| < 70$  kOe, giving an overall average sweep rate of 50(33) Oe s<sup>-1</sup>. Importantly, the sweep rate was very slow (22 Oe s<sup>-1</sup>) around zero field where the relaxation dynamics of single-molecule magnets (SMMs) are crucially dependent on sweep rate. For the doped sample **2** and the solution samples **3** and **4**, hysteresis measurements above 50, 34 and 54 K, respectively, were unreliable due to the very small magnetic fields and reasonably high temperatures giving very small magnetic moments. The hysteresis data for **1** are in excellent agreement with those reported by Guo *et al.*<sup>13</sup>.

It is interesting to note the opposite effect of magnetic dilution on the magnetic hysteresis between the solid state and solution samples; dilution in the solid state reduces the step at zero field, whilst the more dilute solution appears to have a larger step at zero field (Fig. S35). In order to check the significant change in the 2 K hysteresis of the DCM solution samples **3** and **4** *cf.* the solid-state samples, we also prepared an alternative solution sample of **1** dissolved in

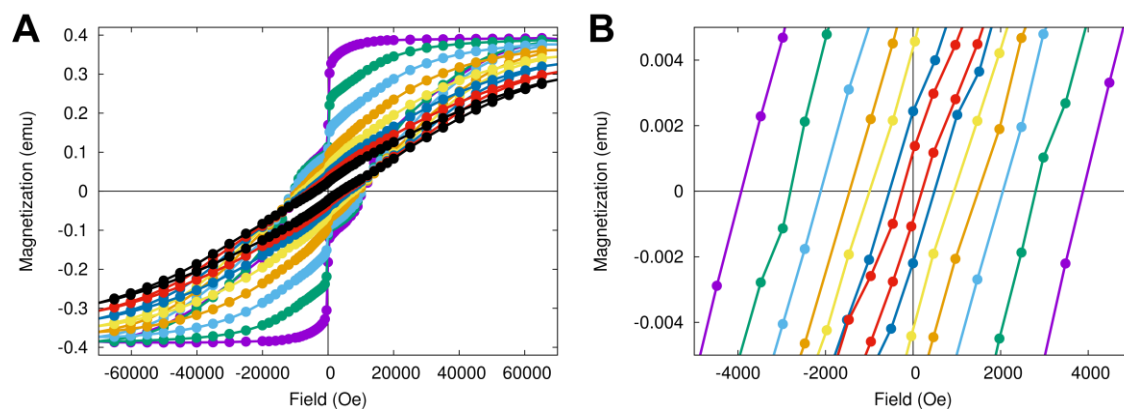
1,2-difluorobenzene. The 1,2-difluorobenzene sample shows nearly identical hysteresis at 2 K as the DCM sample **3**, which has a similar concentration (Figure S35). The resemblance of these data, despite the different steric and electronic properties of these solvents, indicate that the more significant zero field step in the solution samples compared to the solid state is not due to equatorial solvent interactions. Therefore we propose that this observation is due to either relaxation of molecular geometry or the different phonon modes available in frozen solution.



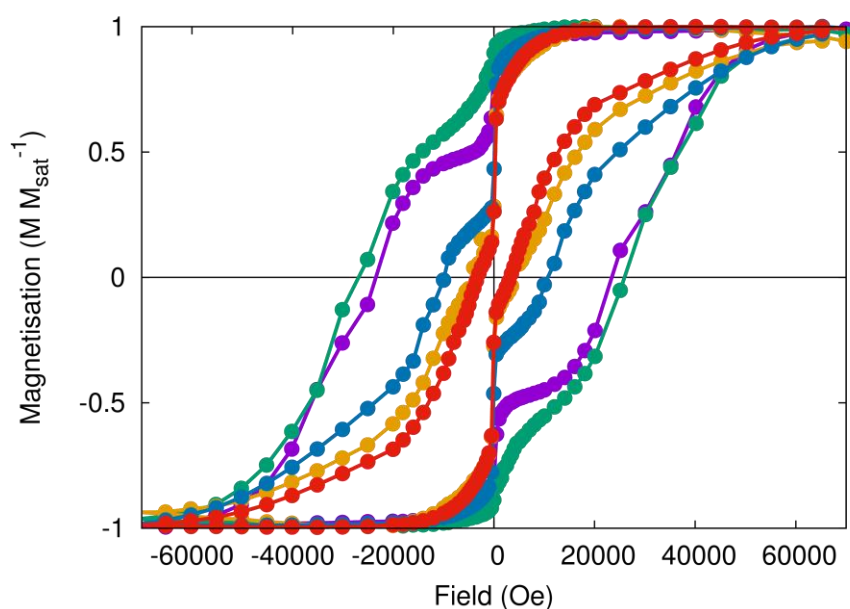
**Figure S32.** Magnetic hysteresis for **2**. (A) Hysteresis loops recorded at 2 (purple) – 30 K (black) in 4 K steps. (B) Hysteresis loops recorded at 30 (purple) – 50 K (dark blue) in 4 K steps.



**Figure S33.** Magnetic hysteresis for **3**. (A) Hysteresis loops recorded at 2 (purple) – 30 K (black) in 4 K steps. (B) Hysteresis loops recorded at 22 (purple) – 34 K (orange) in 4 K steps.



**Figure S34.** Magnetic hysteresis for **4**. (A) Hysteresis loops recorded at 2 (purple) – 30 K (black) in 4 K steps. (B) Hysteresis loops recorded at 30 (purple) – 54 K (red) in 4 K steps.



**Figure S35.** Magnetic hysteresis at 2 K for **1** (purple), **2** (green), **3** (orange), **4** (blue) and a ca. 40 mM 1,2-difluorobenzene solution of **1** (red).

The field cooled (FC) magnetic susceptibilities were collected at a cooling rate of  $-1.7 \text{ K min}^{-1}$  between 280 K and 100 K, and then at a rate of  $-0.8 \text{ K min}^{-1}$  between 100 and 2 K, for

fields of 1 kOe and 500 Oe. The zero field cooled (ZFC) magnetic susceptibilities were collected at a warming rate of  $+0.9 \text{ K min}^{-1}$  between 2 and 100 K, for fields of 1 kOe and 500 Oe. Magnetic data for the solution samples **3** and **4** were only measured at and below 170 K so that the dichloromethane solvent was frozen at all temperatures.

The measurements for **1** were corrected for the diamagnetism of the straw, borosilicate tube and eicosane using calibrated blanks, and the intrinsic diamagnetism of the sample using Pascals constants. The CASSCF-SO-calculated magnetic susceptibility for **1** is slightly lower than the experimental values (Fig. S36A). This is most likely due to small weighing errors reducing the accuracy of the sample mass, and a simple scaling of the calculated curve by a factor of 1.08 brings it into excellent agreement with the experimental data (Figure S36B).

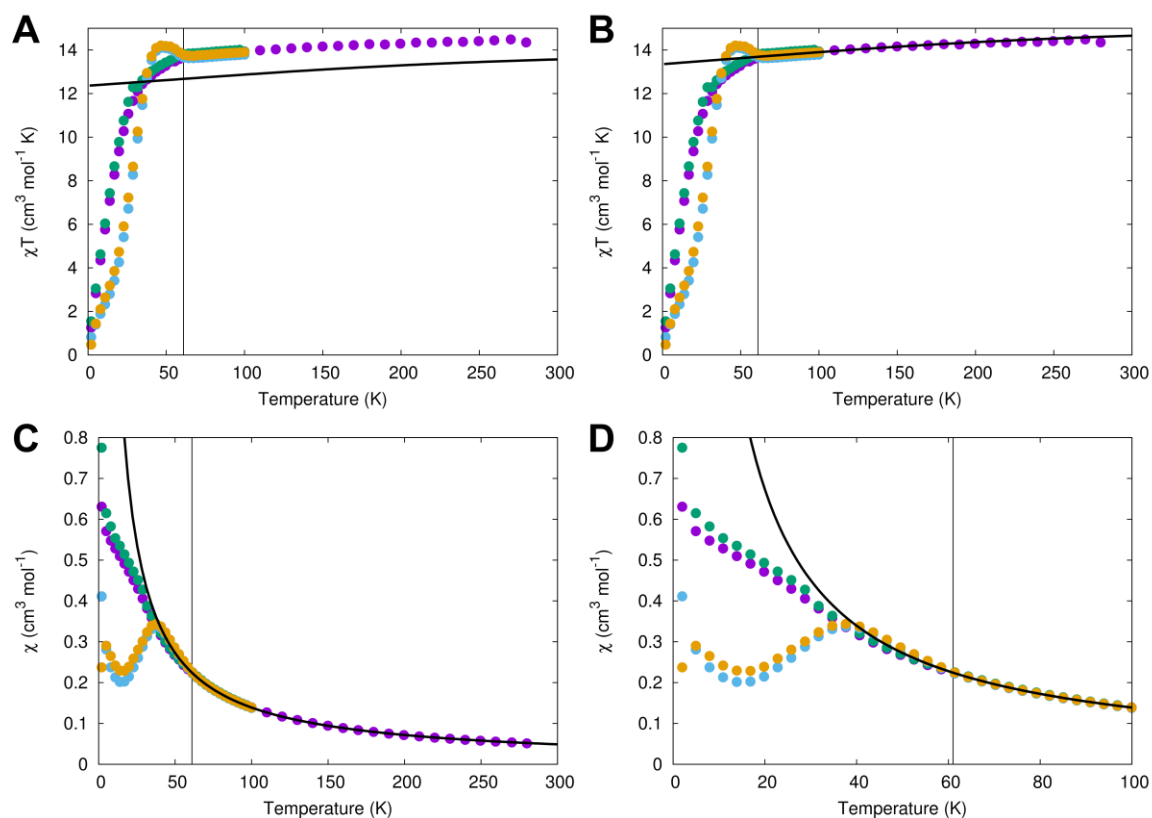
The ZFC  $\chi$  shows a maximum at 38 K and is higher than the equilibrium trace between 40 and 61 K; such a large separation between the ZFC maximum and the FC/ZFC bifurcation along with greater-than-equilibrium ZFC values have been observed for SMMs with large barriers previously<sup>14,15</sup>, yet their origin remains unexplained. Notably, this behaviour differs from the report of Guo *et al.*<sup>13</sup>, who do not observe ZFC > FC traces. Importantly, the temperature sweep rate used here is two times slower than that employed by Guo *et al.*; given that our investigation here includes measurement of many samples of different paramagnetic concentrations, different volumes and masses, and different phases, and all samples show a similar ZFC > FC effect, we believe this to be a real feature of the spin dynamics of **1**. Therefore, we suggest that the discrepancy between our report and that of Guo *et al.* is due to the difference in cooling rate, which seems to have a profound effect on the spin dynamics of this molecule below 61 K. We also observe a rise in the ZFC data for **1** at the lowest temperatures; this has been observed previously for other highly air-sensitive samples<sup>16,17</sup>. Whilst every precaution has been taken to ensure no sample decomposition, we cannot completely discount the presence of trace amounts of O<sub>2</sub> leading to minor sample degradation, which could be the origin of this feature. For the FC/ZFC data of samples **2-4**, the diamagnetic



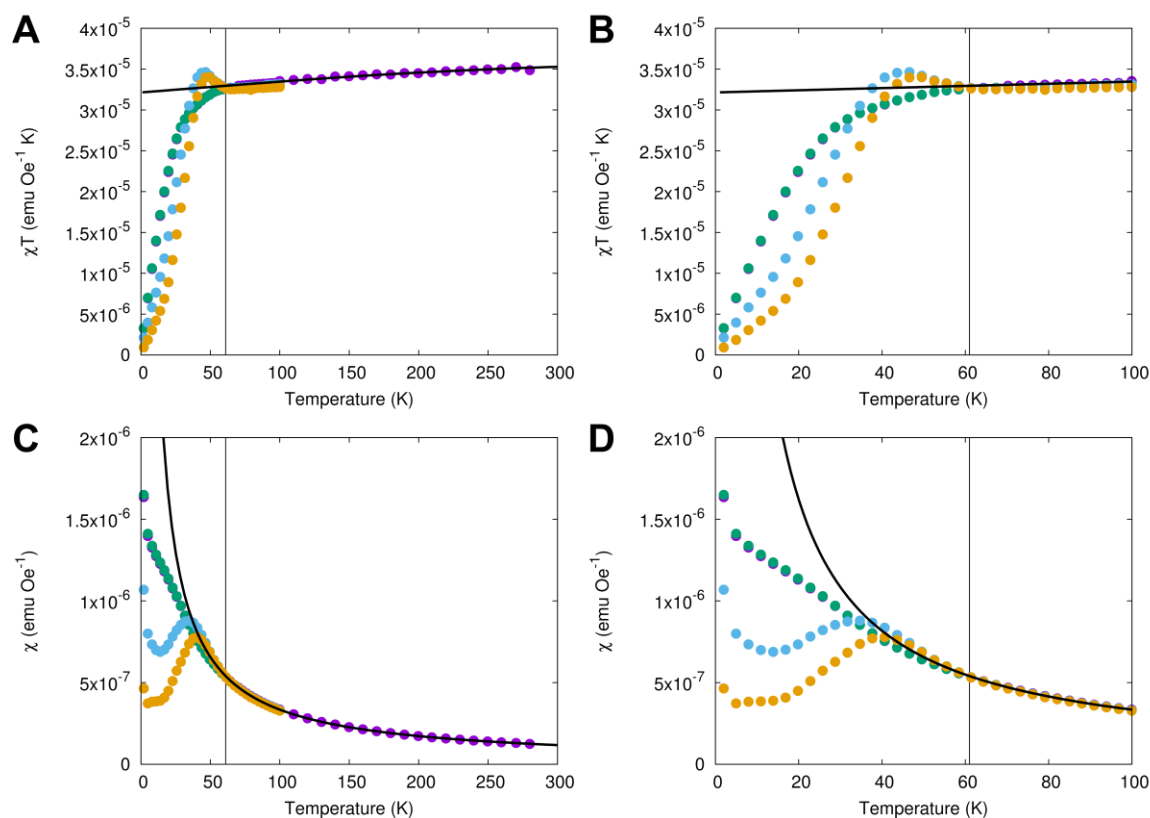
corrections have been estimated in comparison to the CASSCF-SO-calculated data (Table S4); we observe non-linear field dependence of the diamagnetism for the most dilute solution sample **3**, likely due to the large contribution from the dichloromethane solvent. The amounts of **1** in each sample determined from the CASSCF-SO scale factors are in excellent agreement with those from the saturation magnetisation data (Table S4 *cf.* Table S3). The data for samples **2-4** show the same bifurcation point at 61 K as the pure sample **1** (Fig. S36-S39), confirming that this FC/ZFC behaviour is intrinsic to the molecule and not an extrinsic feature of its environment. These diluted samples also show the ZFC data crossing the FC data below 60 K, just as for **1**, however the ZFC maxima disappear for the most dilute solution **3** and is only observed for the 1 kOe data in **4**. The disappearance of these maxima is consistent with the faster zero field relaxation at low temperatures in frozen solution, however the origin of the concentration dependence of these dynamics is not yet understood.

**Table S4.** Magnetic susceptibility corrections.

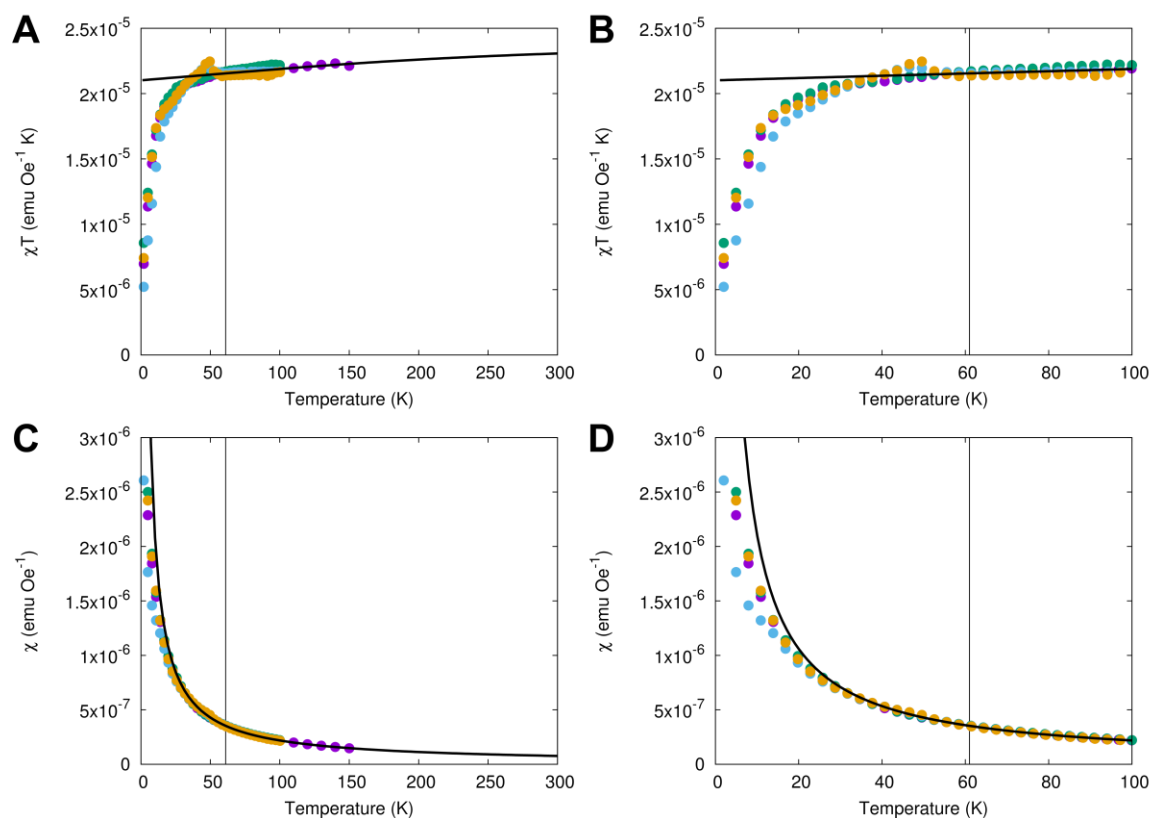
| Sample   | $\chi_{\text{dia}}$ (emu Oe <sup>-1</sup> )                     | CASSCF-SO scale factor | <b>1</b> (mol)       |
|----------|-----------------------------------------------------------------|------------------------|----------------------|
| <b>2</b> | $-5.3 \times 10^{-8}$                                           | $2.6 \times 10^{-6}$   | $2.4 \times 10^{-6}$ |
| <b>3</b> | $-2.9 \times 10^{-8}$ (1 kOe)<br>$-1.0 \times 10^{-8}$ (500 Oe) | $1.7 \times 10^{-6}$   | $1.6 \times 10^{-6}$ |
| <b>4</b> | $-1.6 \times 10^{-7}$                                           | $1.5 \times 10^{-5}$   | $1.4 \times 10^{-5}$ |



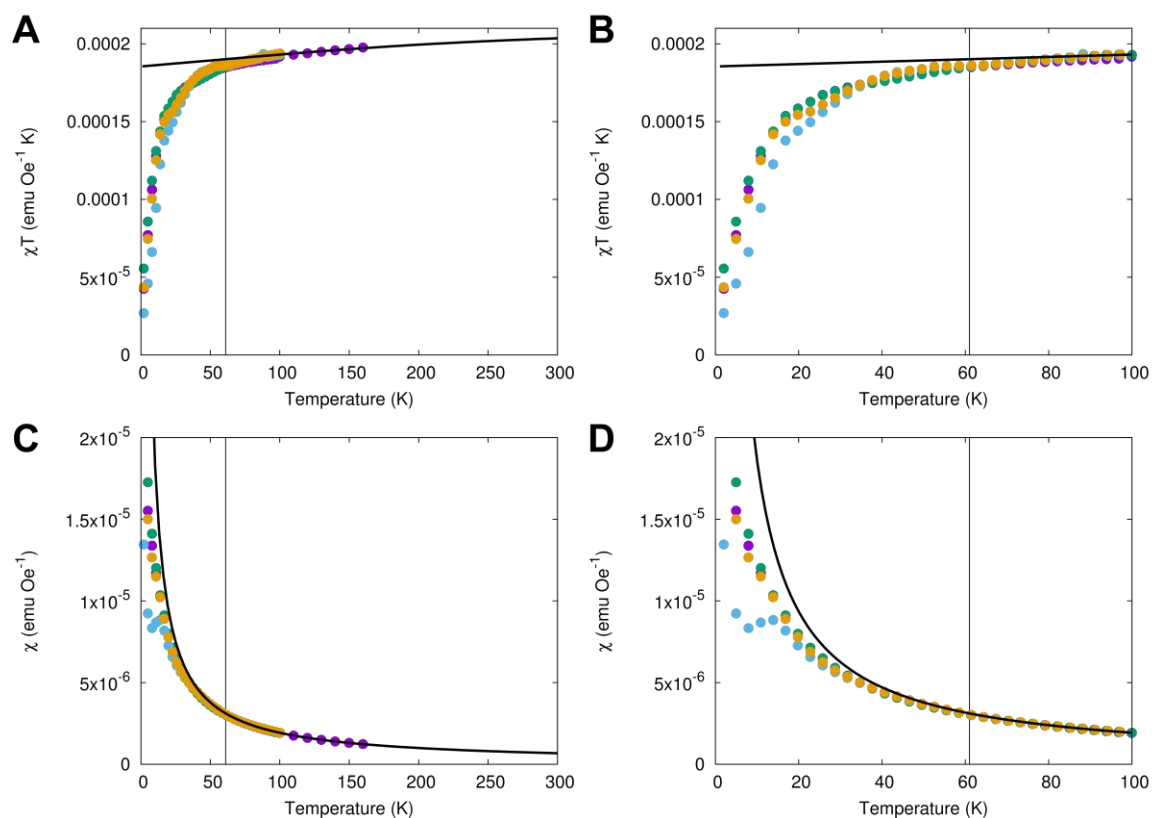
**Figure S36.** Field cooled (FC) and zero field cooled (ZFC) magnetic susceptibilities for **1**, vertical line showing bifurcation point at 61 K. **(A)** The  $\chi T$  product as a function of temperature for 1 kOe FC (purple), 500 Oe FC (green), 1 kOe ZFC (light blue), 500 Oe ZFC (orange) and the CASSCF-SO-calculated curve (black line). **(B)** Same as **A** however CASSCF-SO-calculated trace is scaled by 1.08. **(C)**  $\chi$  as a function of temperature with scaled CASSCF-SO-calculated data. **(D)** Same as **C** but with a truncated x-axis.



**Figure S37.** Field cooled (FC) and zero field cooled (ZFC) magnetic susceptibilities for **2**, vertical line showing bifurcation point at 61 K. **(A)** The  $\chi T$  product as a function of temperature for 1 kOe FC (purple), 500 Oe FC (green), 1 kOe ZFC (light blue), 500 Oe ZFC (orange) and the CASSCF-SO-calculated trace scaled by  $2.6 \times 10^{-6}$  (black line). **(B)** Same as **A** but with a truncated x-axis. **(C)**  $\chi$  as a function of temperature with scaled CASSCF-SO-calculated data. **(D)** Same as **C** but with a truncated x-axis.



**Figure S38.** Field cooled (FC) and zero field cooled (ZFC) magnetic susceptibilities for **3**, vertical line showing bifurcation point at 61 K. **(A)** The  $\chi T$  product as a function of temperature for 1 kOe FC (purple), 500 Oe FC (green), 1 kOe ZFC (light blue), 500 Oe ZFC (orange) and the CASSCF-SO-calculated trace scaled by  $1.7 \times 10^{-6}$  (black line). **(B)** Same as **A** but with a truncated x-axis. **(C)**  $\chi$  as a function of temperature with scaled CASSCF-SO-calculated data. **(D)** Same as **C** but with a truncated x-axis.



**Figure S39.** Field cooled (FC) and zero field cooled (ZFC) magnetic susceptibilities for **4**, vertical line showing bifurcation point at 61 K. **(A)** The  $\chi T$  product as a function of temperature for 1 kOe FC (purple), 500 Oe FC (green), 1 kOe ZFC (light blue), 500 Oe ZFC (orange) and the CASSCF-SO-calculated trace scaled by  $1.5 \times 10^{-5}$  (black line). **(B)** Same as **A** but with a truncated x-axis. **(C)**  $\chi$  as a function of temperature with scaled CASSCF-SO-calculated data. **(D)** Same as **C** but with a truncated x-axis.

Alternating current (AC) magnetic data was collected under zero applied direct current (DC) field with an oscillating field of 1.55 Oe for **1** and 3 Oe for **2-4**; however, the magnetic moment of **3** was too small to obtain reliable AC data. The AC data were fit using the Debye model, below<sup>18</sup>, where the real part is the in-phase magnetic susceptibility  $\chi'$  and the imaginary part is the out-of-phase magnetic susceptibility  $\chi''$ .  $\chi_s$  and  $\chi_T$  represent the adiabatic and isothermal susceptibilities, respectively, while  $\tau$  and  $\omega = 2\pi\nu$  represent the magnetic relaxation time and the angular AC frequency, respectively. The best fits of the data for **1** gives  $\chi_s = 0.15(2) \text{ cm}^3 \text{ mol}^{-1}$ , with the  $\chi_T$  and  $\tau$  values given in Table S5, and best fits in Fig. S40. The best fits of the data for **2** give  $\chi_s \sim 0 \text{ emu Oe}^{-1}$ , with the  $\chi_T$  and  $\tau$  values given in Table S6 and best fits in Fig. S41.

$$\begin{aligned}\chi(\omega) &= \chi_s + \frac{\chi_T - \chi_s}{1 + i\omega\tau} \\ \chi' = \text{Re}[\chi(\omega)] &= \chi_s + \frac{\chi_T - \chi_s}{1 + \omega^2\tau^2} \\ \chi'' = \text{Im}[\chi(\omega)] &= \frac{\omega\tau(\chi_T - \chi_s)}{1 + \omega^2\tau^2}\end{aligned}$$

For the concentrated solution sample **4**, we observe two unique relaxation processes in the AC data. These are fit using the Debye model for two relaxation processes, below<sup>18,19</sup> where  $\chi_{s,\text{tot}}$  is the total adiabatic susceptibility and  $\Delta\chi_a$  and  $\Delta\chi_b$  are the differences between the adiabatic and isothermal susceptibilities for each process, respectively, while  $\tau_a$  and  $\tau_b$  are the relaxation times for the two processes, respectively. The best fits of the data for **4** give  $\chi_{s,\text{tot}} \sim 4.2(6) \times 10^{-7} \text{ emu Oe}^{-1}$ , with the other parameters given in Table S7 and best fits in Fig. S42.

$$\begin{aligned}\chi(\omega) &= \chi_{s,\text{tot}} + \frac{\Delta\chi_a}{1 + i\omega\tau_a} + \frac{\Delta\chi_b}{1 + i\omega\tau_b} \\ \chi' = \text{Re}[\chi(\omega)] &= \chi_{s,\text{tot}} + \frac{\Delta\chi_a}{1 + \omega^2\tau_a^2} + \frac{\Delta\chi_b}{1 + \omega^2\tau_b^2} \\ \chi'' = \text{Im}[\chi(\omega)] &= \frac{\Delta\chi_a\omega\tau_a}{1 + \omega^2\tau_a^2} + \frac{\Delta\chi_b\omega\tau_b}{1 + \omega^2\tau_b^2}\end{aligned}$$

**Table S5.** Isothermal susceptibility and magnetic relaxation times extracted from AC magnetic data for **1**.

| Temperature (K) | $\chi_T$ (cm <sup>3</sup> mol <sup>-1</sup> ) | $\tau$ (s)  |
|-----------------|-----------------------------------------------|-------------|
| 72.0            | 1.83854E-01                                   | 6.79654E-01 |
| 76.0            | 1.74667E-01                                   | 2.12057E-01 |
| 80.0            | 1.67777E-01                                   | 7.27558E-02 |
| 85.0            | 1.51160E-01                                   | 2.33864E-02 |
| 89.4            | 1.45360E-01                                   | 8.32495E-03 |
| 93.8            | 1.38742E-01                                   | 3.17665E-03 |
| 98.2            | 1.33115E-01                                   | 1.27100E-03 |
| 102.5           | 1.27201E-01                                   | 5.35689E-04 |
| 106.9           | 1.22706E-01                                   | 2.73642E-04 |
| 111.3           | 1.18025E-01                                   | 1.20111E-04 |

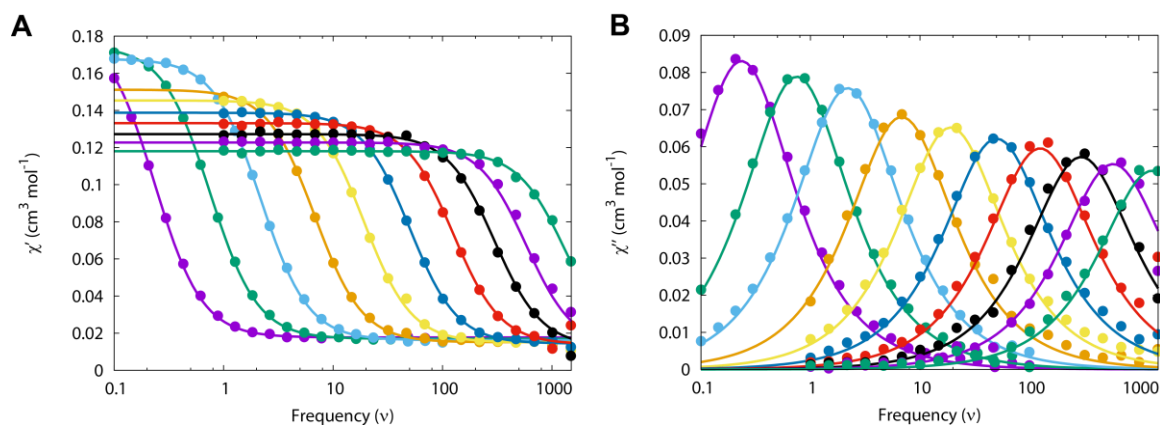
**Table S6.** Isothermal susceptibility and magnetic relaxation times extracted from AC magnetic data for **2**.

| Temperature (K) | $\chi_T$ (emu Oe <sup>-1</sup> ) | $\tau$ (s)  |
|-----------------|----------------------------------|-------------|
| 76.0            | 2.92085E-07                      | 2.08980E-01 |
| 80.0            | 2.78704E-07                      | 6.75112E-02 |
| 84.0            | 2.72538E-07                      | 2.70575E-02 |
| 88.0            | 2.58069E-07                      | 9.58652E-03 |
| 92.0            | 2.41578E-07                      | 3.69268E-03 |
| 96.0            | 2.36115E-07                      | 1.76892E-03 |

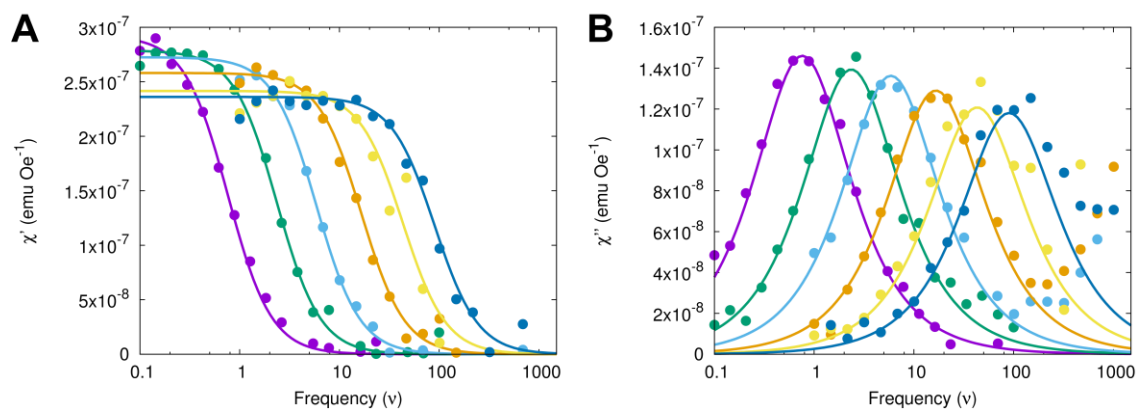
**Table S7.** Isothermal susceptibilities and magnetic relaxation times extracted from AC magnetic data for **4**.

| Temperature (K) | $\Delta\chi_a$ (emu Oe <sup>-1</sup> ) | $\tau_a$ (s) | $\Delta\chi_b$ (emu Oe <sup>-1</sup> ) | $\tau_b$ (s) |
|-----------------|----------------------------------------|--------------|----------------------------------------|--------------|
| 68              | 8.87067E-07                            | 5.13787E-02  | 9.87740E-07                            | 8.02220E-01  |
| 72              | 8.50917E-07                            | 1.91659E-02  | 1.02421E-06                            | 3.49561E-01  |
| 76              | 8.00753E-07                            | 6.85610E-03  | 1.00586E-06                            | 1.23495E-01  |
| 80              | 7.28017E-07                            | 2.99526E-03  | 9.22960E-07                            | 4.56677E-02  |
| 84              | 7.57760E-07                            | 8.99872E-04  | 8.98457E-07                            | 1.56786E-02  |
| 88              | 7.13750E-07                            | 3.76510E-04  | 8.59507E-07                            | 6.17652E-03  |
| 92              | 7.10440E-07                            | 1.82839E-04  | 7.95013E-07                            | 2.64436E-03  |
| 96              | 7.72867E-07                            | 1.00212E-04  | 7.21323E-07                            | 1.27320E-03  |
| 100             | 8.87067E-07                            | 5.13787E-02  | 9.87740E-07                            | 8.02220E-01  |
| 104             | 8.50917E-07                            | 1.91659E-02  | 1.02421E-06                            | 3.49561E-01  |
| 108             | 8.00753E-07                            | 6.85610E-03  | 1.00586E-06                            | 1.23495E-01  |
| 112             | 7.28017E-07                            | 2.99526E-03  | 9.22960E-07                            | 4.56677E-02  |
| 116             | 7.57760E-07                            | 8.99872E-04  | 8.98457E-07                            | 1.56786E-02  |

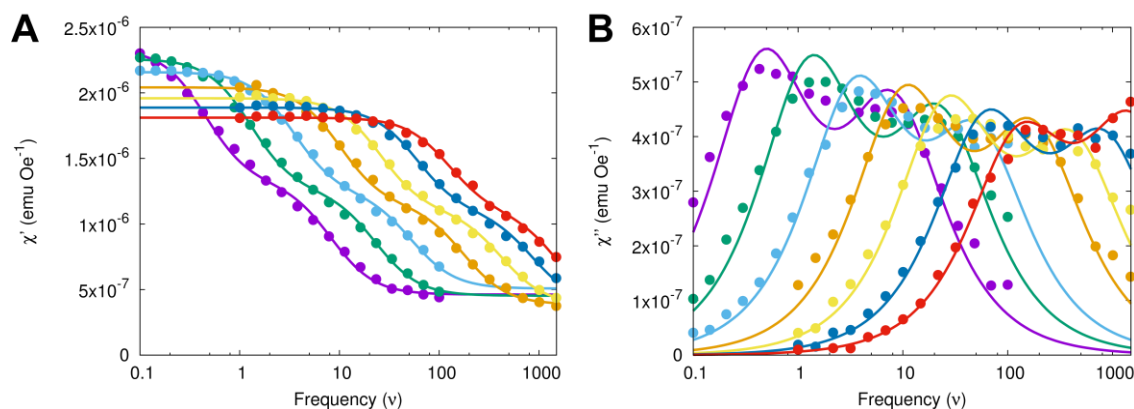




**Figure S40.** (A) In-phase and (B) out-of-phase AC susceptibility data for **1**. Solid points are the experimental data recorded at 72 (purple) – 103 K (black) and 107 (purple) – 111 K (green). Solid lines are fits with the Debye model and parameters given in Table S5.



**Figure S41.** (A) In-phase and (B) out-of-phase AC susceptibility data for **2**. Solid points are the experimental data recorded at 76 (purple) – 96 K (dark blue). Solid lines are fits with the Debye model and parameters given in Table S6.



**Figure S42.** (A) In-phase and (B) out-of-phase AC susceptibility data for **4**. Solid points are the experimental data recorded at 68 (purple) – 96 K (black) and 104 K (purple). Solid lines are fits with the Debye model for two relaxation processes and parameters given in Table S7.

DC decay measurements were collected by magnetising samples at 1 kOe and allowing 5 minutes for equilibration, then returning the field to 0 Oe (no-overshoot, hi-res disabled) and measuring the magnetisation as a function of time. The DC decay data were fitted with an exponential function, below<sup>18</sup>, where  $M_0$  is the first value of the magnetisation measured after the field has been removed (defining  $t = 0$  s),  $M_1$  is the final value of the magnetisation at  $t = \infty$  s, and  $\tau$  is the magnetic relaxation time. While  $M_1$  should equal zero for measurements in zero field, we find non-zero values for **1** in the cases where we have collected the full decay, which likely arise due to a small remnant field in the superconducting magnet. At high temperatures, where the relaxation is relatively fast, it is simple to observe the full decay. However when the relaxation times become long, full measurement of such decay curves take many hours and thus we were only able to do this for a limited number of temperatures. We have collected DC magnetisation decay curves to completion for **1** for temperatures between 50 and 62 K, as well as one full curve at 26 K, the lowest temperature investigated by this technique here, Figs. S43 – S46; these  $M_1$  values are consistent with a remnant field of ca. 0.01 Oe. We use the resulting  $M_1$  values to interpolate those expected for intermediate temperatures 30 to 46 K (Table S8),

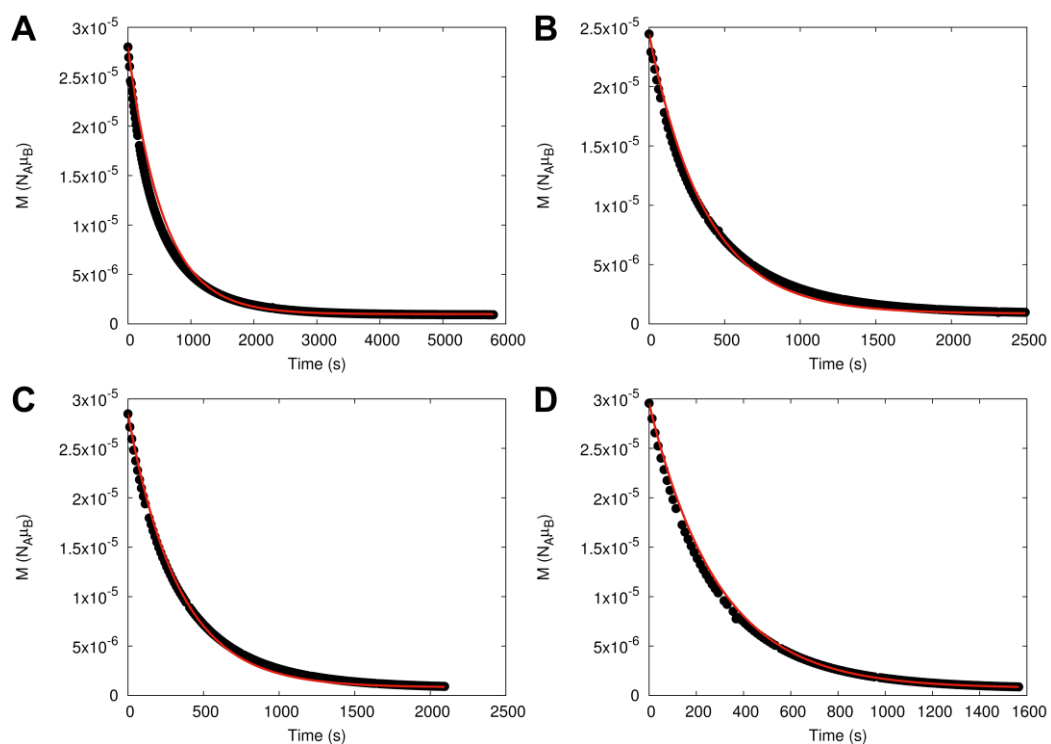
fixing these in order to extract more accurate relaxation times. We note that the decay data become less well described by a single exponential at the lowest temperatures, indicating more complicated relaxation dynamics below ca. 30 K.

$$M(t) = M_1 + (M_0 - M_1)\exp[-t/\tau]$$

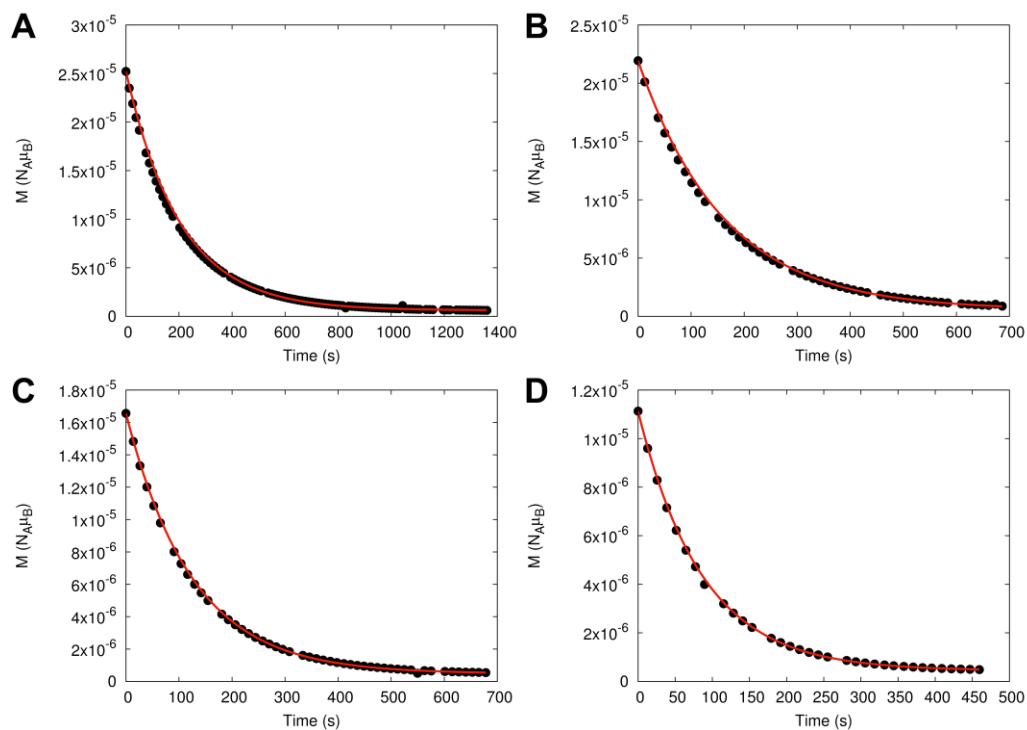
**Table S8.** Equilibrium magnetisation values and magnetic relaxation times extracted from DC magnetisation decay data for **1**.

| Temperature (K) | $M_1$ ( $N_A \mu_B$ )    | $\tau$ (s)  |
|-----------------|--------------------------|-------------|
| 26.0            | 9.90208E-07              | 5.58819E+02 |
| 30.0            | 8.72379E-07 <sup>a</sup> | 3.70924E+02 |
| 32.0            | 8.24559E-07 <sup>a</sup> | 3.34351E+02 |
| 36.0            | 7.36639E-07 <sup>a</sup> | 2.91284E+02 |
| 42.0            | 6.22019E-07 <sup>a</sup> | 2.03521E+02 |
| 46.0            | 5.55695E-07 <sup>a</sup> | 1.61447E+02 |
| 50.0            | 4.79487E-07              | 1.24691E+02 |
| 54.0            | 4.45442E-07              | 8.60514E+01 |
| 56.0            | 4.10205E-07              | 6.61379E+01 |
| 58.0            | 3.95513E-07              | 4.65376E+01 |
| 59.0            | 3.86057E-07              | 3.74331E+01 |
| 60.0            | 3.74936E-07              | 2.96048E+01 |
| 61.0            | 3.67172E-07              | 2.27924E+01 |
| 62.0            | 3.64060E-07              | 1.61433E+01 |

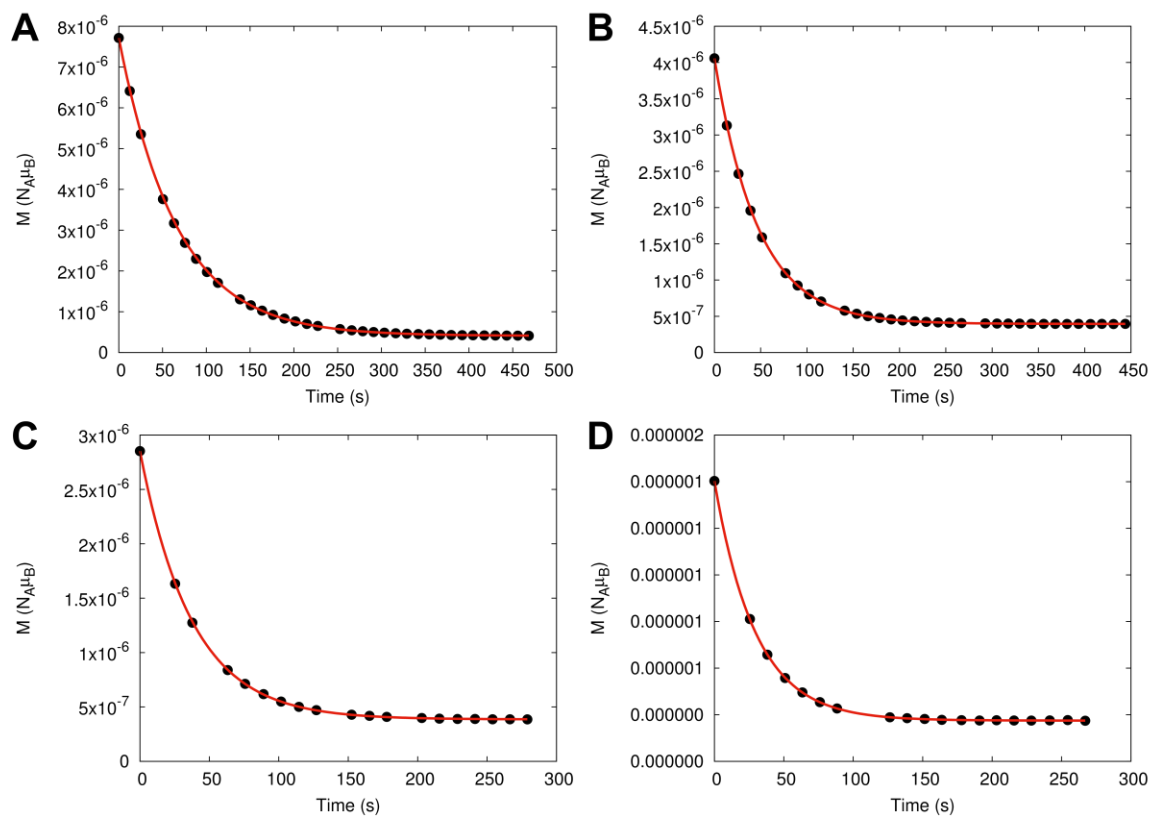
<sup>a</sup> $M_1$  values are interpolated from those directly measured using the empirical function  $M_1(T) = 2.03216 \times 10^{-6} \exp[-2.81877 \times 10^{-2} \times T] N_A \mu_B$ , which has an  $R^2$  value of 0.997 for the measured data points.



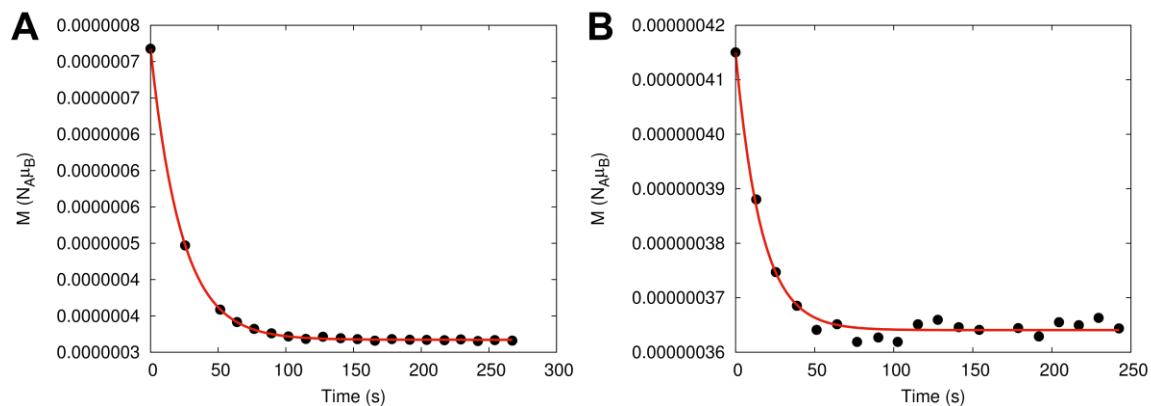
**Figure S43.** Magnetisation decay for **1** at (A) 26 K, (B) 30 K, (C) 32 K and (D) 36 K.



**Figure S44.** Magnetisation decay for **1** at (A) 42 K, (B) 46 K, (C) 50 K and (D) 54 K.



**Figure S45.** Magnetisation decay for **1** at (A) 56 K, (B) 58 K, (C) 59 K and (D) 60 K.

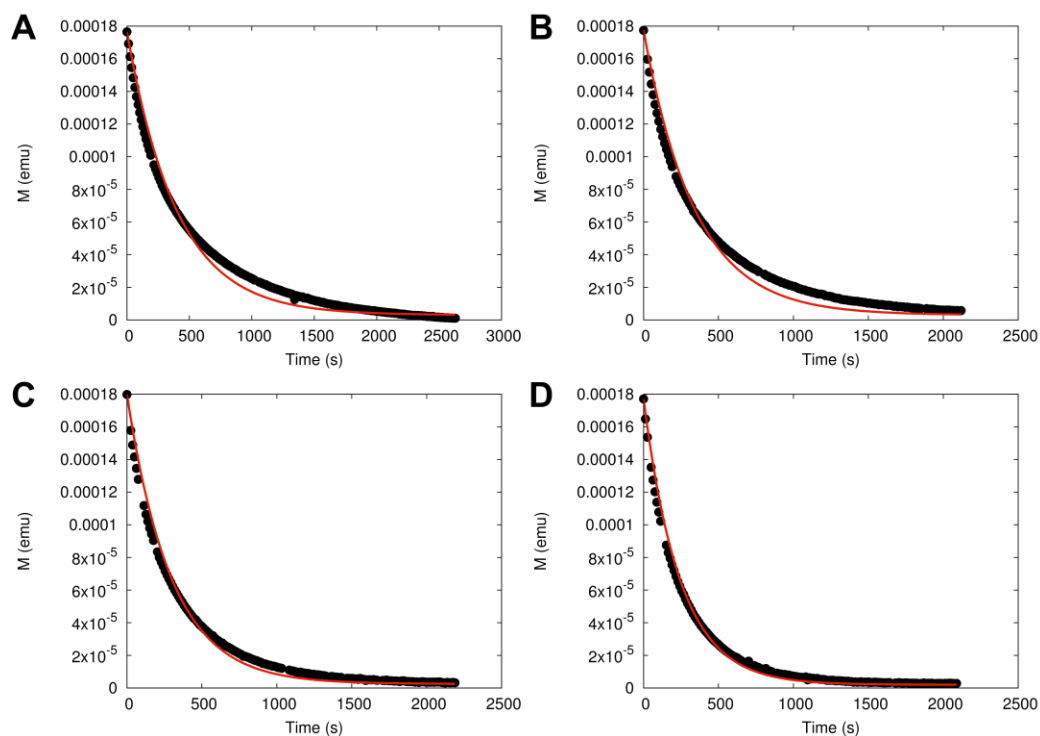


**Figure S46.** Magnetisation decay for **1** at (A) 61 K and (B) 62 K.

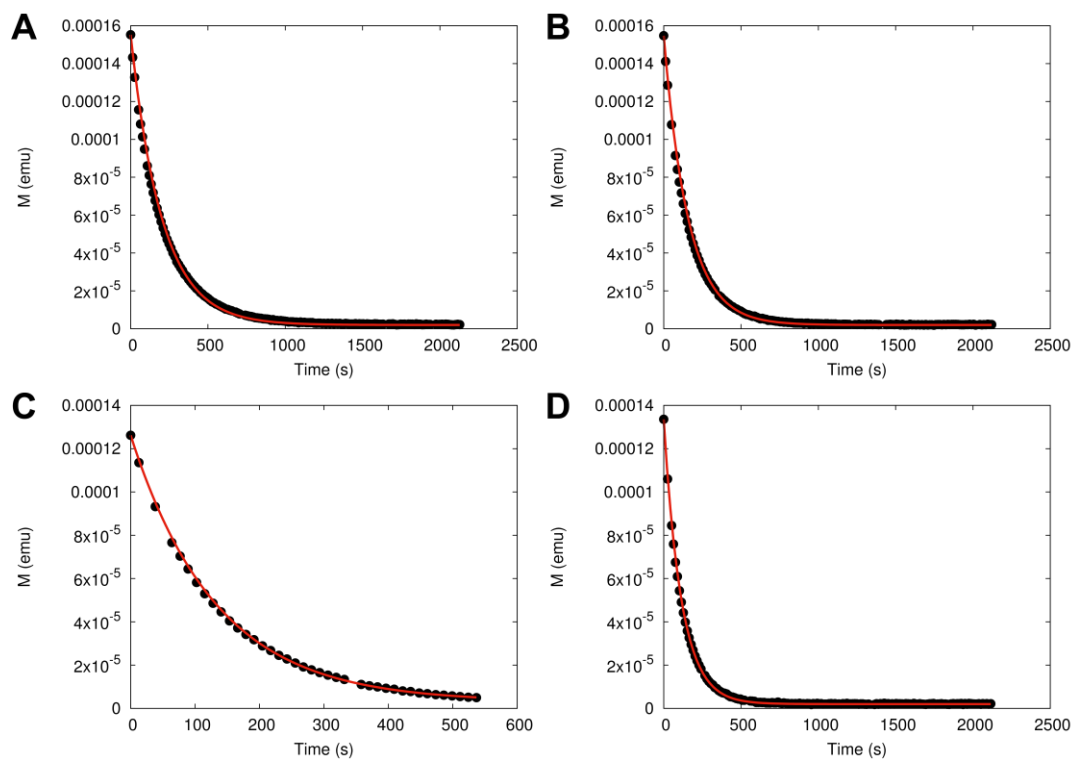
**Table S9.** Equilibrium magnetisation values and magnetic relaxation times extracted from DC magnetisation decay data for **2**.

| Temperature (K) | $M_1$ (emu)              | $\tau$ (s)               |
|-----------------|--------------------------|--------------------------|
| 28.0            | 3.00000E-06 <sup>a</sup> | 4.00000E+02 <sup>a</sup> |
| 32.0            | 3.00000E-06 <sup>a</sup> | 3.44138E+02              |
| 36.0            | 2.50000E-06 <sup>a</sup> | 2.94904E+02              |
| 40.0            | 2.00000E-06 <sup>a</sup> | 2.43346E+02              |
| 44.0            | 2.00000E-06 <sup>a</sup> | 2.02202E+02              |
| 48.0            | 2.00000E-06 <sup>a</sup> | 1.58335E+02              |
| 50.0            | 2.98421E-06              | 1.32186E+02              |
| 52.0            | 2.00000E-06 <sup>a</sup> | 1.14164E+02              |
| 54.0            | 2.09018E-06              | 9.21635E+01              |
| 56.0            | 2.00615E-06              | 7.09280E+01              |
| 58.0            | 1.83836E-06              | 4.83311E+01              |
| 60.0            | 1.80838E-06              | 3.06327E+01              |
| 62.0            | 1.72681E-06              | 1.51717E+01              |

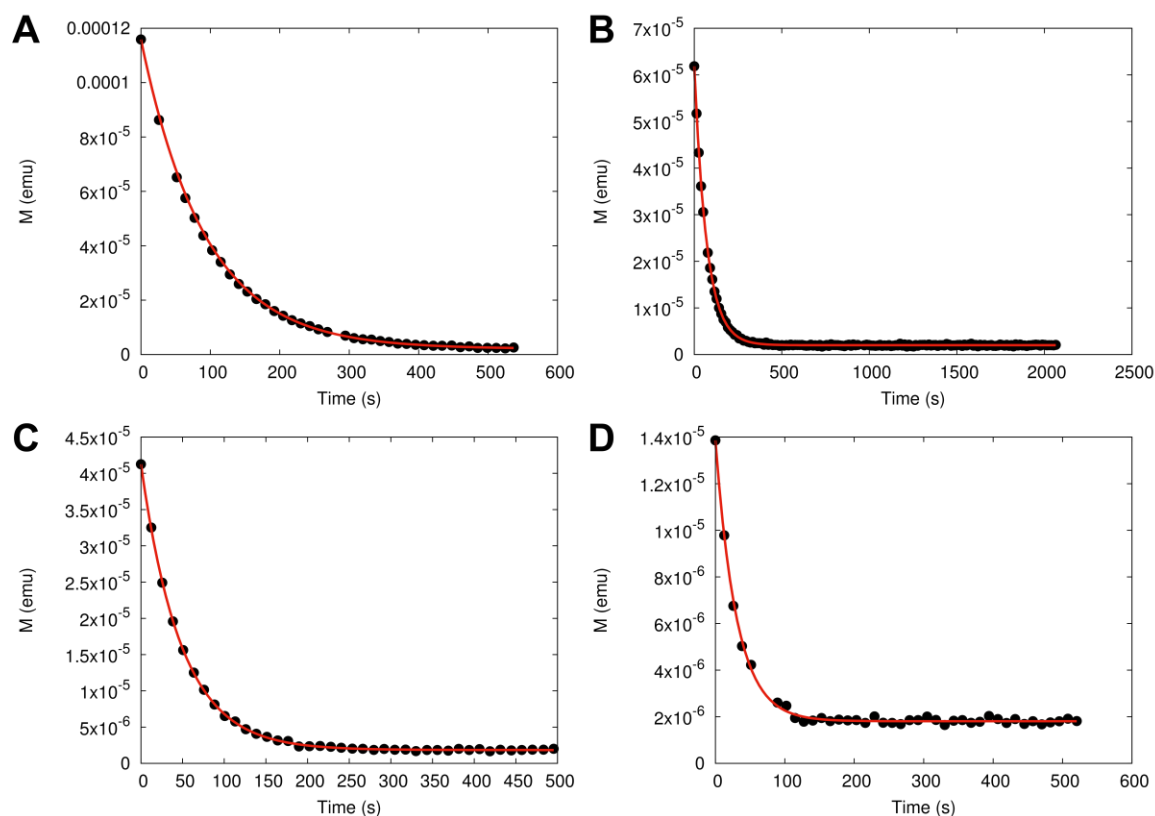
<sup>a</sup> Values are fixed to replicate the experimental data as best as possible.



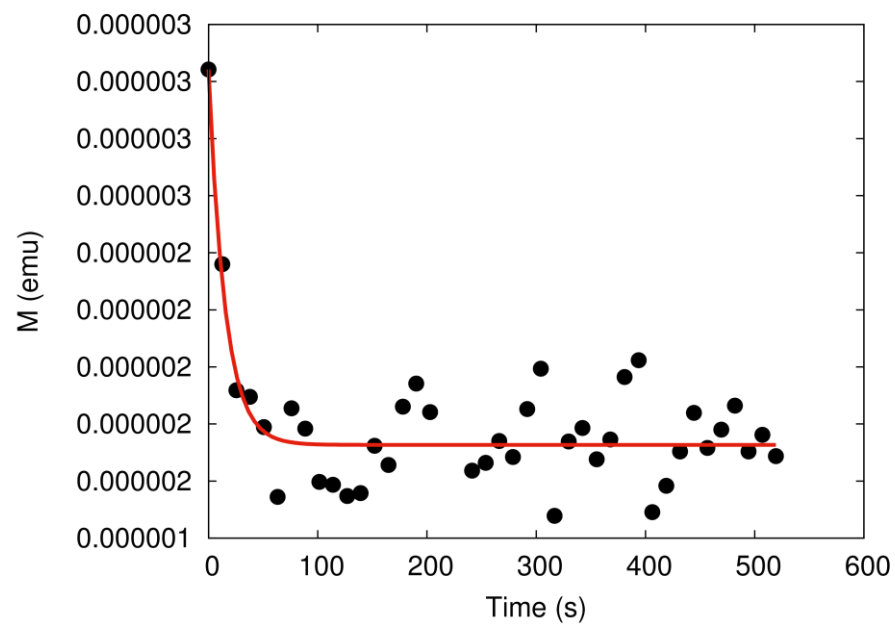
**Figure S47.** Magnetisation decay for **2** at (A) 28 K, (B) 32 K, (C) 36 K and (D) 40 K.



**Figure S48.** Magnetisation decay for **2** at (A) 44 K, (B) 48 K, (C) 50 K and (D) 52 K.



**Figure S49.** Magnetisation decay for **2** at (A) 54 K, (B) 56 K, (C) 58 K and (D) 60 K.

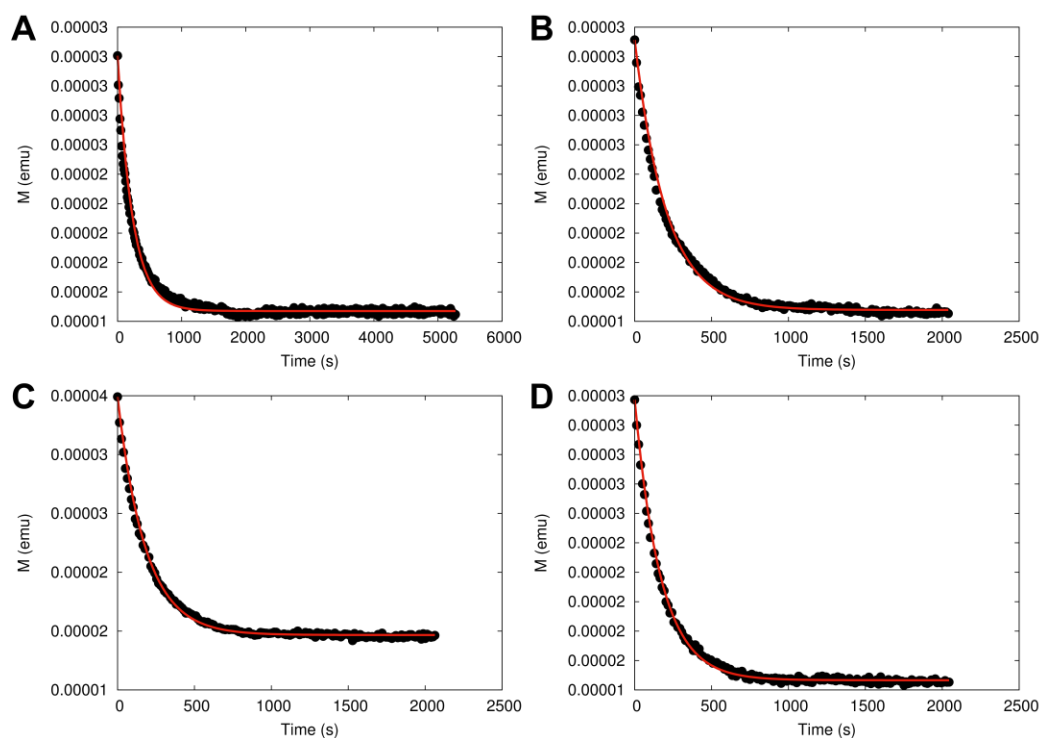


**Figure S50.** Magnetisation decay for **2** at 62 K.

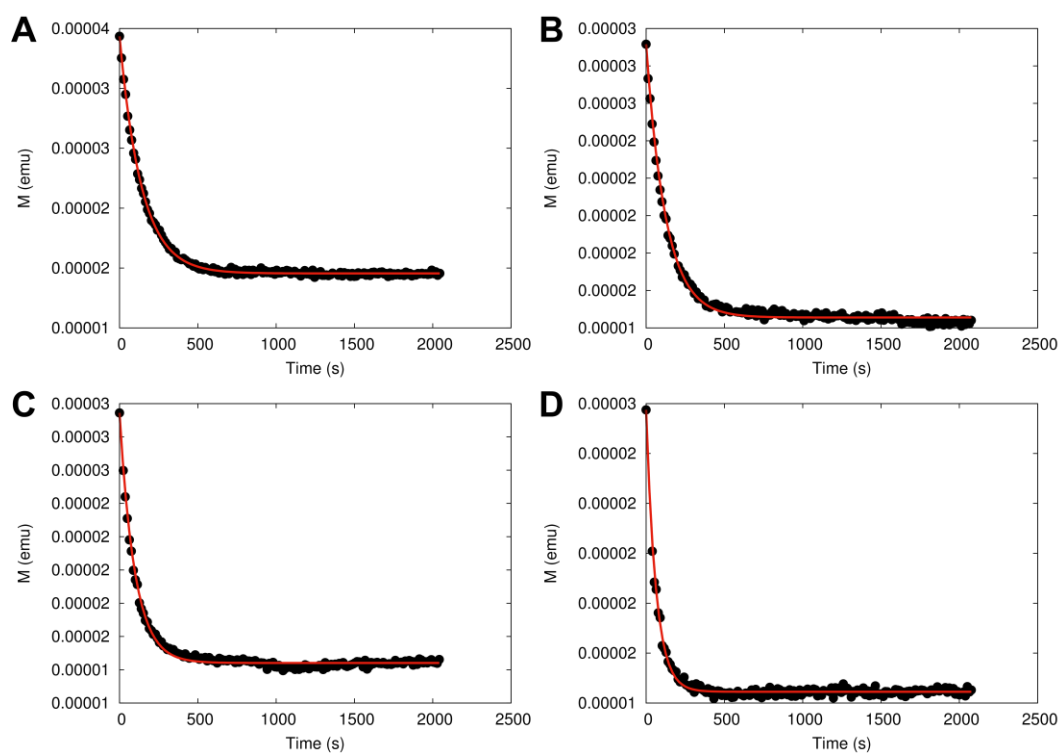


**Table S10.** Equilibrium magnetisation values and magnetic relaxation times extracted from DC magnetisation decay data for **3**.

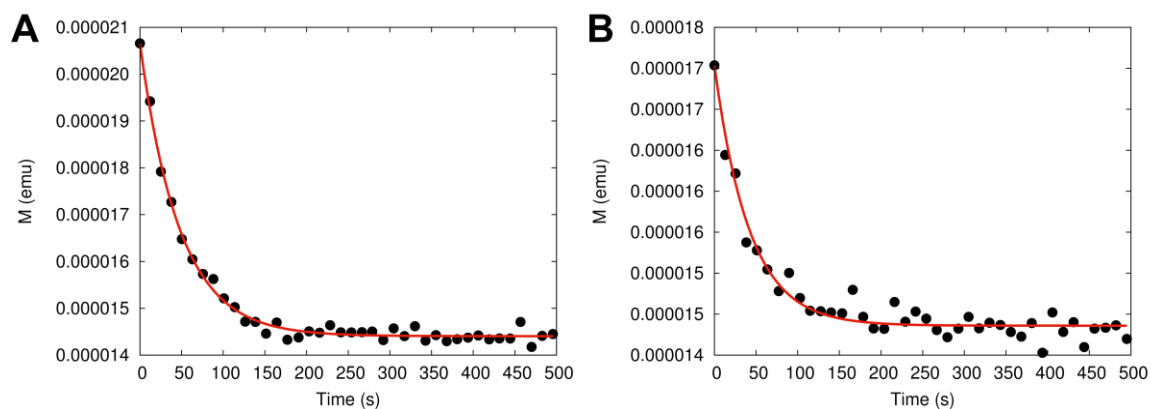
| Temperature (K) | $M_1$ (emu) | $\tau$ (s)  |
|-----------------|-------------|-------------|
| 26.0            | 1.47038E-05 | 2.34261E+02 |
| 30.0            | 1.47742E-05 | 2.04955E+02 |
| 34.0            | 1.46689E-05 | 1.81177E+02 |
| 38.0            | 1.46594E-05 | 1.70012E+02 |
| 42.0            | 1.45486E-05 | 1.40589E+02 |
| 46.0            | 1.45569E-05 | 1.25283E+02 |
| 50.0            | 1.44083E-05 | 9.74085E+01 |
| 54.0            | 1.44513E-05 | 6.28440E+01 |
| 56.0            | 1.44043E-05 | 4.75641E+01 |
| 58.0            | 1.43590E-05 | 4.19987E+01 |



**Figure S51.** Magnetisation decay for **3** at (A) 26 K, (B) 30 K, (C) 34 K and (D) 38 K.



**Figure S52.** Magnetisation decay for **3** at (A) 42 K, (B) 46 K, (C) 50 K and (D) 54 K.

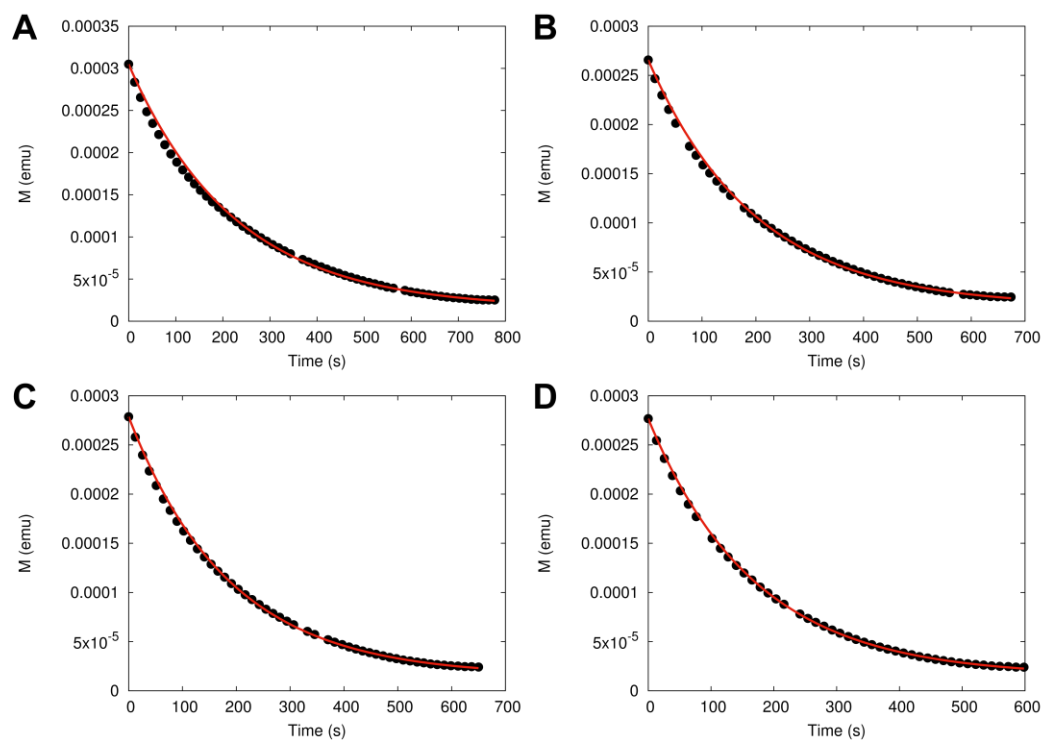


**Figure S53.** Magnetisation decay for **3** at (A) 56 K and (B) 58 K.

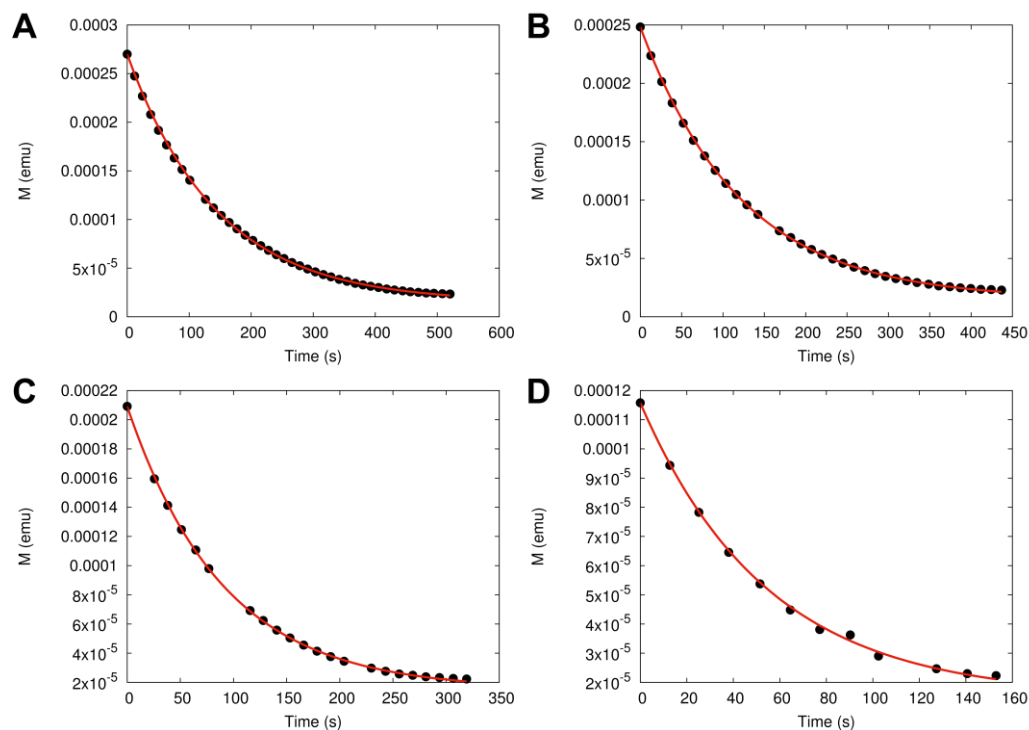
**Table S11.** Equilibrium magnetisation values and magnetic relaxation times extracted from DC magnetisation decay data for **4**.

| Temperature (K) | $M_1$ (emu)              | $\tau$ (s)  |
|-----------------|--------------------------|-------------|
| 28.0            | 1.50000E-05 <sup>a</sup> | 2.25632E+02 |
| 32.0            | 1.50000E-05 <sup>a</sup> | 1.98395E+02 |
| 36.0            | 1.50000E-05 <sup>a</sup> | 1.86259E+02 |
| 40.0            | 1.50000E-05 <sup>a</sup> | 1.69024E+02 |
| 44.0            | 1.50000E-05 <sup>a</sup> | 1.44677E+02 |
| 48.0            | 1.50000E-05 <sup>a</sup> | 1.21598E+02 |
| 52.0            | 1.50000E-05 <sup>a</sup> | 9.00548E+01 |
| 56.0            | 1.50000E-05 <sup>a</sup> | 5.45290E+01 |

<sup>a</sup> Values are fixed to replicate the experimental data as best as possible



**Figure S54.** Magnetisation decay for **4** at (A) 28 K, (B) 32 K, (C) 36 K and (D) 40 K.



**Figure S55.** Magnetisation decay for **4** at (A) 44 K, (B) 48 K, (C) 52 K and (D) 56 K.

The magnetic relaxation times extracted from the AC data for **1** show an exponential dependence on temperature, which is characteristic of the Orbach process<sup>18</sup> (Figs. 3b and S56). These data are well modelled using the familiar Arrhenius law, below, representing slow magnetic relaxation over a potential barrier,  $U_{\text{eff}}$ . The best fit for these data between 72 and 111 K gives  $U_{\text{eff}} = 1223 \text{ cm}^{-1}$  (1760 K) and  $\tau_0 = 1.986 \times 10^{-11} \text{ s}$  (Figs. 3b and S56, Table S12). These data can also be well modelled by a power law ( $\tau^{-1} = CT^n$ ) with parameters  $C = 3 \times 10^{-37} \text{ s}^{-1} \text{ K}^{-20}$  and  $n = 20$ , however these are not physically sensible parameters for a two-phonon Raman relaxation process and therefore this interpretation is discounted.

$$\tau^{-1} = \tau_0^{-1} \exp[-U_{\text{eff}}/kT]$$

The magnetic relaxation rates extracted from the DC data for **1** at the lowest temperatures between 26 and 50 K show a power-law dependence on temperature (Figs. 3b and S57). These data are well modelled using the power-law relation, below, with  $C = 1.664 \times 10^{-6} \text{ s}^{-1} \text{ K}^{-n}$  and  $n = 2.151$  (Figs. 3b and S57, Table S12). These data can also be fit reasonably well using the Arrhenius law with parameters  $U_{\text{eff}} = 53 \text{ cm}^{-1}$  (76 K) and  $\tau_0 = 20 \text{ s}$ , however according to the CASSCF-SO calculations there is no electronic state at  $53 \text{ cm}^{-1}$  and furthermore the  $\tau_0$  value is orders of magnitude too large to represent a real Orbach process. However, it is possible that such an exponential profile could be due to a non-resonant direct transition between the lowest two doublets<sup>20</sup>; while we do not experimentally observe a vibrational mode at  $53 \text{ cm}^{-1}$  (see Spin Dynamics), there may be vibrational modes existing near this energy which might facilitate such a process. Under the assumption that this rate shows power-law temperature dependence, the  $n$  parameter takes a value near 2; this is similar to that expected for a phonon bottleneck<sup>21</sup> that can occur when the mean-free-path of the phonons that allow magnetic relaxation *via* the Orbach mechanism is much shorter than the crystallite dimensions due to a high concentration of paramagnetic centres or large crystals<sup>22-24</sup>. In the case of a phonon bottleneck the measured

relaxation rate actually corresponds to the phonon-bath relaxation rate and not the spin-phonon relaxation rate intrinsic to the molecule.

$$\tau^{-1} = CT^n$$

In order to examine the possibility of a phonon bottleneck, we have also measured the relaxation rates for the doped sample **2** and the frozen solution samples **3** and **4**. The relaxation rates for **2** extracted from AC measurements between 76 and 96 K are best-fit by  $U_{\text{eff}} = 1219 \text{ cm}^{-1}$  (1754 K) and  $\tau_0 = 2.060 \times 10^{-11} \text{ s}$ , and those from DC magnetisation decay measurements between 28 and 50 K are best-fit by  $C = 4.287 \times 10^{-6} \text{ s}^{-1} \text{ K}^{-n}$  and  $n = 1.881$  (Fig. S58, Table S12). The relaxation rates for **3** extracted from DC magnetisation decay measurements between 26 and 50 K are best-fit by  $C = 6.780 \times 10^{-6} \text{ s}^{-1} \text{ K}^{-n}$  and  $n = 1.254$  (Fig. S59, Table S12). For **4** we observe two distinct relaxation processes in the AC measurements; between 72 and 96 K these are best-fit by  $U_{\text{eff,a}} = 1080 \text{ cm}^{-1}$  (1554 K),  $\tau_{0,\text{a}} = 8.855 \times 10^{-12} \text{ s}$ ,  $U_{\text{eff,b}} = 1141 \text{ cm}^{-1}$  (1641 K) and  $\tau_{0,\text{b}} = 4.945 \times 10^{-11} \text{ s}$  (Fig. S60, Table S12). The relaxation rates from DC magnetisation decay measurements for **4** between 28 and 48 K are best-fit by  $C = 1.157 \times 10^{-4} \text{ s}^{-1} \text{ K}^{-n}$  and  $n = 1.084$  (Fig. S60, Table S12).

Despite the differing best-fit parameters for **2-4** *cf.* **1**, the relaxation rates themselves are nearly superimposable with those for **1** (Fig. S61). This clearly indicates that the power-law temperature dependence with small exponent is not due to a phonon bottleneck, and confirms the suggestion of Gill that the Orbach mechanism should not be subject to a phonon bottleneck in zero magnetic field<sup>25</sup>. Furthermore, the coincidence of these data imply that the observed behaviour is intrinsic to the molecule and not a feature of the lattice, which therefore suggests that the relaxation mechanism owes to local molecular vibrations (optical phonons).

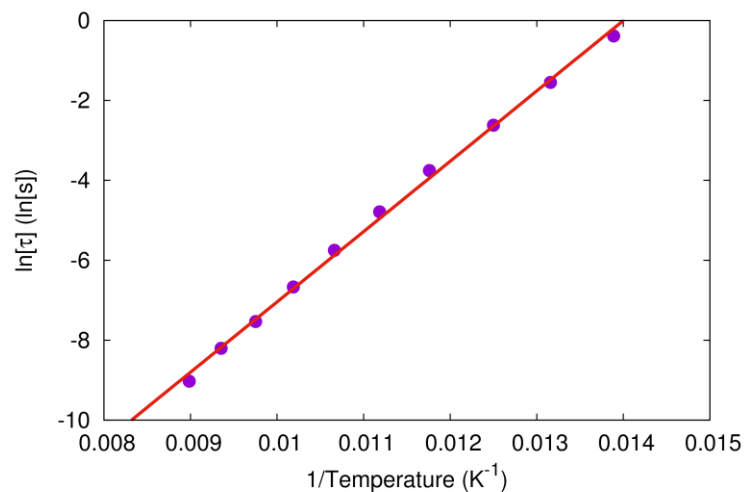
It is plausible that the fast Orbach process for **4** could in fact have the same  $U_{\text{eff}}$  as for **1**, **2** and the slow process for **4**, despite the best-fit parameter  $U_{\text{eff,a}}$ ; this would imply that both the fast and slow processes for **4** involved the same intrinsic energy barrier, but have distinct  $\tau_0$  pre-

factors. This situation could conceivably arise due to the continuum of phonon modes available in the amorphous frozen solution phase, compared to the crystalline lattices of **1** and **2**.

The temperature dependence of the relaxation rate for **1** is similar to that reported by Guo *et al.*<sup>13</sup>; we observe  $U_{\text{eff}} = 1223 \text{ cm}^{-1}$  and  $\tau_0 = 1.986 \times 10^{-11} \text{ s}$  while they report  $U_{\text{eff}} = 1277$  or  $1256 \text{ cm}^{-1}$  and  $\tau_0 = 8.12 \times 10^{-12}$  or  $1.02 \times 10^{-11} \text{ s}$ , respectively. The main difference between the two reports is that we find  $n = 2.151$  with  $C = 1.664 \times 10^{-6} \text{ s}^{-1} \text{ K}^{-n}$ , while Guo *et al.* find  $n = 3.92$  with  $C = 1.81 \times 10^{-9} \text{ s}^{-1} \text{ K}^{-n}$ . We find a consistently lower power-law exponent across multiple samples, and hence we believe this feature to be real (Fig. S61); the orders-of-magnitude difference between the two values of  $C$  owes to the significant difference in the power-law exponent.

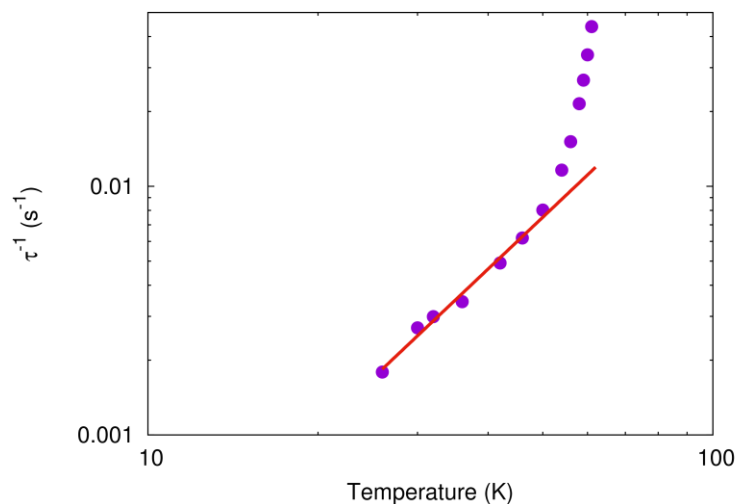
**Table S12.** Parameterisation of relaxation dynamics

| Sample   | $U_{\text{eff}} (\text{cm}^{-1})$ | $\tau_0 (\text{s})$                                              | $C (\text{s}^{-1} \text{ K}^{-n})$ | $n$   |
|----------|-----------------------------------|------------------------------------------------------------------|------------------------------------|-------|
| <b>1</b> | 1223                              | $1.986 \times 10^{-11}$                                          | $1.664 \times 10^{-6}$             | 2.151 |
| <b>2</b> | 1219                              | $2.060 \times 10^{-11}$                                          | $4.287 \times 10^{-6}$             | 1.881 |
| <b>3</b> | -                                 | -                                                                | $6.780 \times 10^{-5}$             | 1.254 |
| <b>4</b> | 1080 (fast)<br>1141 (slow)        | $8.855 \times 10^{-12}$ (fast)<br>$4.945 \times 10^{-11}$ (slow) | $1.157 \times 10^{-4}$             | 1.084 |

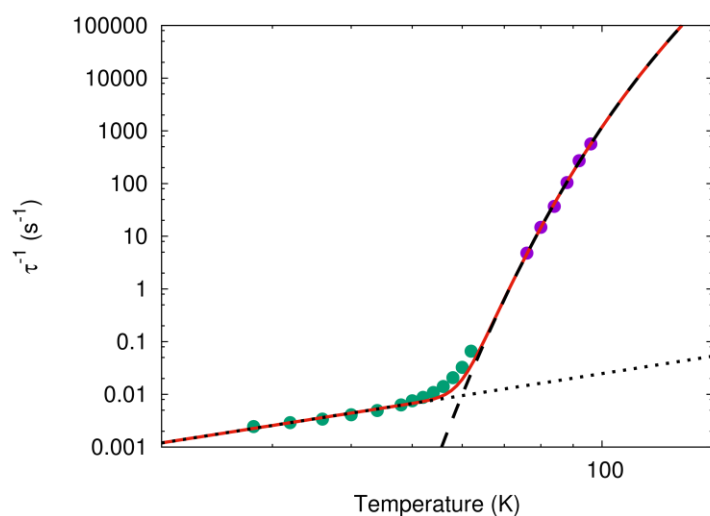


**Figure S56.** Exponential temperature dependence of the magnetic relaxation time between 72 and 111 K for **1**. Points are the relaxation times extracted from AC susceptibility and the red line is a fit to  $\tau^{-1} = \tau_0^{-1} \exp[-U_{\text{eff}}/kT]$  with  $U_{\text{eff}} = 1223 \text{ cm}^{-1}$  (1760 K) and  $\tau_0 = 1.986 \times 10^{-11} \text{ s}$ .

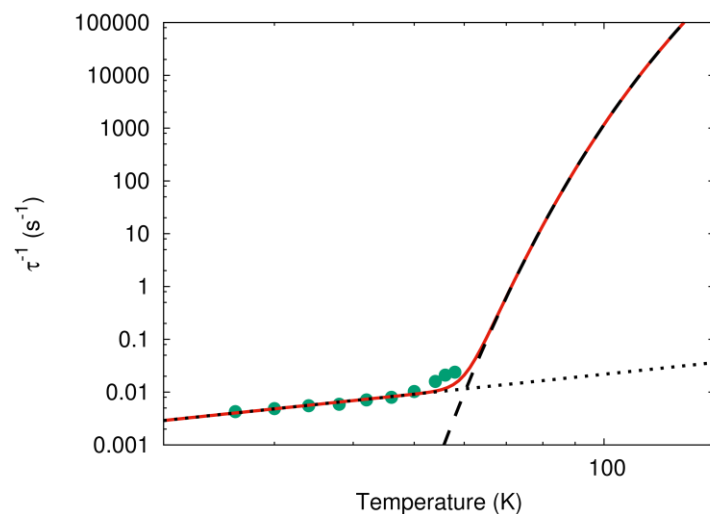




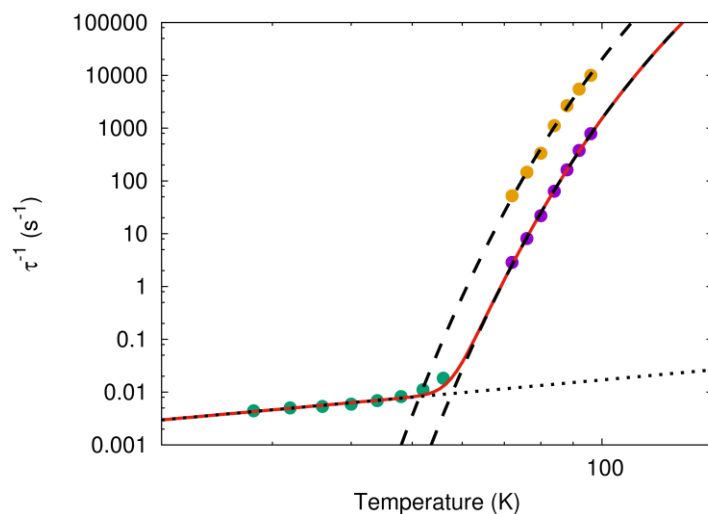
**Figure S57.** Power-law temperature dependence of the magnetic relaxation rate between 26 and 50 K for **1**. Points are the relaxation rates extracted from DC magnetisation decay experiments and the red line is a fit to  $\tau^{-1} = CT^n$  with  $C = 1.664 \times 10^{-6} \text{ s}^{-1} \text{ K}^{-n}$  and  $n = 2.151$ .



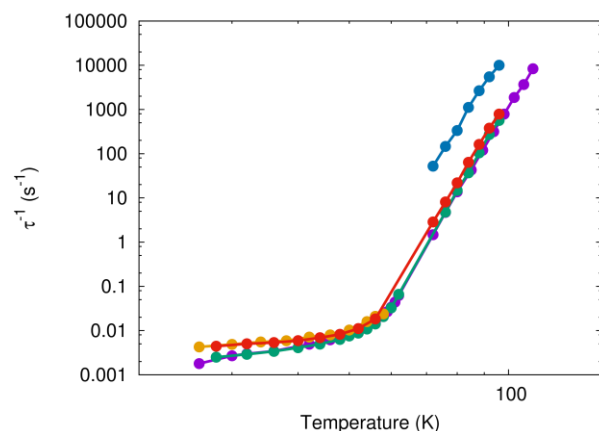
**Figure S58.** Temperature dependence of the magnetic relaxation rate for **2**. Solid purple points are the relaxation rates extracted from AC susceptibility data and solid green points from DC magnetisation decay data. Solid red line is given by  $\tau^{-1} = \tau_0^{-1} \exp[-U_{\text{eff}}/kT] + CT^n$ , dashed black line is given by  $\tau^{-1} = \tau_0^{-1} \exp[-U_{\text{eff}}/kT]$  and dotted black line is given by  $\tau^{-1} = CT^n$  with  $U_{\text{eff}} = 1219 \text{ cm}^{-1}$  (1754 K),  $\tau_0 = 2.060 \times 10^{-11} \text{ s}$ ,  $C = 4.287 \times 10^{-6} \text{ s}^{-1} \text{ K}^{-n}$  and  $n = 1.881$ .



**Figure S59.** Temperature dependence of the magnetic relaxation rate for **3**. Solid green points are the relaxation rates extracted from DC magnetisation decay data. Solid red line is given by  $\tau^{-1} = \tau_0^{-1} \exp[-U_{\text{eff}}/kT] + CT^n$ , dashed black line is given by  $\tau^{-1} = \tau_0^{-1} \exp[-U_{\text{eff}}/kT]$  and dotted black line is given by  $\tau^{-1} = CT^n$  with  $U_{\text{eff}} = 1221 \text{ cm}^{-1}$  (1757 K) (average of **1** and **2**),  $\tau_0 = 2.023 \times 10^{-11} \text{ s}$  (average of **1** and **2**),  $C = 6.780 \times 10^{-5} \text{ s}^{-1} \text{ K}^{-n}$  and  $n = 1.254$ .

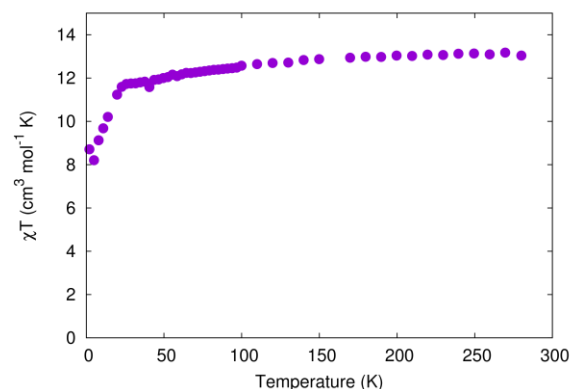


**Figure S60.** Temperature dependence of the magnetic relaxation rate for **4**. Solid purple and orange points are the relaxation rates extracted from AC susceptibility data (fast and slow process, respectively) and solid green points from DC magnetisation decay data. Dashed black lines are given by  $\tau^{-1} = \tau_0^{-1} \exp[-U_{\text{eff}}/kT]$  and dotted black line is given by  $\tau^{-1} = CT^n$  with  $U_{\text{eff,a}} = 1080 \text{ cm}^{-1}$  (1554 K),  $\tau_{0,\text{a}} = 8.855 \times 10^{-12} \text{ s}$ ,  $U_{\text{eff,b}} = 1141 \text{ cm}^{-1}$  (1641 K),  $\tau_{0,\text{b}} = 4.945 \times 10^{-11} \text{ s}$  and  $C = 1.157 \times 10^{-4} \text{ s}^{-1} \text{ K}^{-n}$  and  $n = 1.084$ . Solid red line is given by  $\tau^{-1} = \tau_0^{-1} \exp[-U_{\text{eff}}/kT] + CT^n$ , with  $U_{\text{eff,b}} = 1141 \text{ cm}^{-1}$  (1641 K),  $\tau_{0,\text{b}} = 4.945 \times 10^{-11} \text{ s}$  and  $C = 1.157 \times 10^{-4} \text{ s}^{-1} \text{ K}^{-n}$  and  $n = 1.084$ .



**Figure S61.** Temperature dependence of the magnetic relaxation rate for **1** (purple), **2** (green), **3** (orange) and **4** (fast AC process: blue, slow AC process and DC: red). Lines are just a guide for the eye.

We have measured the  $\chi T$  product for **6** in FC mode under a 1 kOe field (Fig. S62). These data show a value of ca.  $13 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 280 K, which is slightly lower than that for **1** and also lower than that for an isolated Dy(III) ion of  $14.17 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ; this could be due to a small inaccuracy in the mass of the complex or to the crystal field (CF) splitting of **6**. The sharp decrease below approximately 20 K may be due to slow magnetisation dynamics, but we have not studied this precursor compound any further. Additional magnetic data for **6** have been simultaneously reported by Guo *et al.*<sup>13</sup>.



**Figure S62.** The  $\chi T$  product as a function of temperature for **6** in a 1 kOe field.

## S8. Electronic Structure

We used MOLCAS 8.0<sup>26</sup> to perform CASSCF-SO calculations of **1**. We employed the molecular geometry of the  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  cation from the single crystal X-ray structure with no optimisation, taking the largest disorder component only. Basis sets from ANO-RCC library<sup>27,28</sup> were employed with VQZP quality for Dy, VTZP quality for the cyclopentadienyl C atoms, and VDZP quality for all remaining atoms, employing the second-order DKH transformation. Cholesky decomposition of the two-electron integrals with a threshold of  $10^{-8}$  was performed to save disk space and reduce computational demand. The molecular orbitals (MOs) were optimised in state-averaged CASSCF calculations, where the active space was defined by the nine 4f electrons in the seven 4f orbitals of Dy(III). Three such calculations were performed independently for each possible spin state, where 21 roots were included for  $S = 5/2$ , 224 roots were included for  $S = 3/2$ , and 490 roots were included for  $S = 1/2$ . The wavefunctions obtained from these CASSCF calculations were then mixed by spin orbit coupling, where all 21  $S = 5/2$  states, 128 of the  $S = 3/2$  states, and 130 of the  $S = 1/2$  states were included. The resulting spin orbit wavefunctions were decomposed into their CF wavefunctions, and the magnetic susceptibility calculated (see Magnetism) using SINGLE\_ANISO<sup>29</sup>.

Our calculations show that the strong axial ligand field generated by the  $\text{Cp}^{\text{ttt}}$  ligands splits the  $J = 15/2$  total angular momentum ground state where the five lowest-lying doublets are very well described as the free-ion  $m_J = \pm 15/2, \pm 13/2, \pm 11/2, \pm 9/2, \pm 7/2$  and  $\pm 5/2$  states, respectively (Fig. 4b, Table S13 and S20), quantised along the Cp-Dy-Cp axis. These results are practically identical to those reported by Guo *et al.*<sup>13</sup> The only differences are in the energies of the Kramers doublets (higher here by ca.  $30 - 140 \text{ cm}^{-1}$ ) and in the composition of the two most energetic states; these small differences likely result from using slightly different crystal structures, the partial structural optimisation by Guo *et al.*, and differing basis sets and relativistic Hamiltonians.

In order to examine the effect of the local geometry of  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  on its electronic structure, we have performed a number of CASSCF-SO calculations on model complexes: (i) X-ray geometry of  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  with  $^t\text{Bu}$  groups replaced by Me groups (C-H distances in Me groups set to 1.07 Å), (ii)  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  with  $^t\text{Bu}$  groups replaced by Me groups and Cp-Dy-Cp angle forced to  $180^\circ$  (Cp rings remain eclipsed), (iii)  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  with  $^t\text{Bu}$  groups replaced by Me groups, Cp-Dy-Cp angle forced to  $180^\circ$  and one Cp ring rotated  $36^\circ$  to be in a staggered conformation (Tables S14 – S16). Modification (i) shows little difference to the experimental  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  complex, with only a small increase in the energies of the Kramers doublets on the order of  $40 - 80 \text{ cm}^{-1}$ , showing that the close equatorial H atoms are not playing a significant role in the electronic structure of **1** (Table S14 *cf.* Table S13). Modification (ii) shows a further increase in the energies of the Kramers doublets over modification (i), as well as slight changes to the character of the two most energetic Kramers doublets; however, these changes are relatively minor and therefore show that the bent nature of the Cp-Dy-Cp geometry in **1** does not greatly influence its electronic structure (Table S15 *cf.* Table S14) – this result echoes a previous communication by one of us<sup>30</sup>. Modification (iii) provides an electronic structure that is nearly identical to that of modification (ii), showing that the eclipsed vs. staggered nature of the Cp rings is of no consequence for the electronic structure of **1** (Table S16 *cf.* Table S15); this is likely due to the main donor contribution of the Cp ring arising from the delocalised  $\pi$ -system of the ligand and not the individual carbon atoms.

**Table S13.** Electronic structure of  $[\text{Dy}(\text{Cp}^{\text{tt}})_2]^+$  calculated with CASSCF-SO using solid-state geometry from **1**.

| Energy ( $\text{cm}^{-1}$ ) | Energy (K) | $g_x$ | $g_y$ | $g_z$ | $g_z$ angle (degrees) | Wavefunction                                                                                                                                                                                    |
|-----------------------------|------------|-------|-------|-------|-----------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 0.0                         | 0.0        | 0.00  | 0.00  | 19.89 | -                     | 99.5% $ \pm 15/2\rangle$<br>+ 0.3% $ \pm 13/2\rangle$<br>+ 0.2% $ \pm 11/2\rangle$                                                                                                              |
| 488.6                       | 703.0      | 0.00  | 0.00  | 17.02 | 1.9                   | 99.5% $ \pm 13/2\rangle$<br>+ 0.2% $ \pm 15/2\rangle$<br>+ 0.1% $ \pm 11/2\rangle$<br>+ 0.1% $ \pm 9/2\rangle$                                                                                  |
| 771.0                       | 1109.3     | 0.00  | 0.00  | 14.40 | 2.9                   | 99.5% $ \pm 11/2\rangle$<br>+ 0.2% $ \pm 15/2\rangle$<br>+ 0.2% $ \pm 7/2\rangle$<br>+ 0.1% $ \pm 13/2\rangle$                                                                                  |
| 956.5                       | 1376.2     | 0.00  | 0.01  | 11.76 | 3.3                   | 99.0% $ \pm 9/2\rangle$<br>+ 0.6% $ \pm 5/2\rangle$<br>+ 0.2% $ \pm 7/2\rangle$<br>+ 0.1% $ \pm 13/2\rangle$<br>+ 0.1% $ \pm 3/2\rangle$                                                        |
| 1122.2                      | 1614.5     | 0.05  | 0.05  | 9.11  | 4.9                   | 98.2% $ \pm 7/2\rangle$<br>+ 0.9% $ \pm 5/2\rangle$<br>+ 0.3% $ \pm 9/2\rangle$<br>+ 0.3% $ \pm 3/2\rangle$<br>+ 0.2% $ \pm 11/2\rangle$<br>+ 0.1% $ \pm 1/2\rangle$                            |
| 1277.5                      | 1838.1     | 0.83  | 1.01  | 6.44  | 3.4                   | 96.4% $ \pm 5/2\rangle$<br>+ 1.6% $ \pm 3/2\rangle$<br>+ 1.1% $ \pm 7/2\rangle$<br>+ 0.5% $ \pm 9/2\rangle$<br>+ 0.2% $ \mp 3/2\rangle$<br>+ 0.1% $ \mp 1/2\rangle$                             |
| 1399.3                      | 2013.3     | 2.84  | 3.67  | 5.39  | 89.4                  | 91.6% $ \pm 3/2\rangle$<br>+ 3.7% $ \mp 1/2\rangle$<br>+ 2.4% $ \pm 1/2\rangle$<br>+ 1.4% $ \pm 5/2\rangle$<br>+ 0.3% $ \pm 7/2\rangle$<br>+ 0.3% $ \mp 5/2\rangle$<br>+ 0.2% $ \mp 3/2\rangle$ |
| 1476.1                      | 2123.7     | 1.07  | 6.11  | 14.28 | 89.4                  | 89.4% $ \pm 1/2\rangle$<br>+ 4.2% $ \mp 1/2\rangle$<br>+ 3.9% $ \pm 3/2\rangle$<br>+ 2.1% $ \mp 3/2\rangle$<br>+ 0.2% $ \mp 5/2\rangle$<br>+ 0.1% $ \pm 7/2\rangle$<br>+ 0.1% $ \pm 5/2\rangle$ |

**Table S14.** Electronic structure of  $[\text{Dy}(\text{Cp}^{\text{tt}})_2]^+$  calculated with CASSCF-SO using solid-state geometry from **1**, where  $^t\text{Bu}$  groups have been replaced with Me groups (modification (i)).

| Energy ( $\text{cm}^{-1}$ ) | Energy (K) | $g_x$ | $g_y$ | $g_z$ | $g_z$ angle (degrees) | Wavefunction                                                                                                                                                                                      |
|-----------------------------|------------|-------|-------|-------|-----------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 0.0                         | 0.0        | 0.00  | 0.00  | 19.89 | -                     | 99.7% $ \pm 15/2\rangle$<br>+ 0.2% $ \pm 11/2\rangle$<br>+ 0.1% $ \pm 13/2\rangle$                                                                                                                |
| 496.1                       | 713.8      | 0.00  | 0.00  | 17.01 | 1.46                  | 99.6% $ \pm 13/2\rangle$<br>+ 0.2% $ \pm 9/2\rangle$<br>+ 0.1% $ \pm 15/2\rangle$                                                                                                                 |
| 797.2                       | 1147.0     | 0.00  | 0.00  | 14.39 | 1.77                  | 99.7% $ \pm 11/2\rangle$<br>+ 0.2% $ \pm 15/2\rangle$                                                                                                                                             |
| 1003.2                      | 1443.3     | 0.00  | 0.01  | 11.77 | 2.55                  | 99.6% $ \pm 9/2\rangle$<br>+ 0.2% $ \pm 13/2\rangle$<br>+ 0.1% $ \pm 7/2\rangle$                                                                                                                  |
| 1180.9                      | 1699.0     | 0.31  | 0.32  | 9.08  | 4.47                  | 98.9% $ \pm 7/2\rangle$<br>+ 0.7% $ \pm 5/2\rangle$<br>+ 0.2% $ \pm 3/2\rangle$<br>+ 0.1% $ \pm 9/2\rangle$                                                                                       |
| 1340.9                      | 1929.3     | 0.14  | 0.83  | 6.29  | 3.89                  | 95.1% $ \pm 5/2\rangle$<br>+ 2.2% $ \pm 1/2\rangle$<br>+ 1.5% $ \pm 3/2\rangle$<br>+ 0.5% $ \pm 7/2\rangle$<br>+ 0.5% $ \mp 5/2\rangle$                                                           |
| 1457.5                      | 2097.1     | 2.88  | 7.57  | 8.37  | 89.91                 | 77.3% $ \pm 3/2\rangle$<br>+ 18.2% $ \mp 1/2\rangle$<br>+ 2.2% $ \mp 3/2\rangle$<br>+ 0.8% $ \pm 5/2\rangle$<br>+ 0.8% $ \pm 1/2\rangle$<br>+ 0.3% $ \mp 5/2\rangle$<br>+ 0.2% $ \pm 7/2\rangle$  |
| 1581.5                      | 2275.3     | 0.46  | 1.69  | 17.63 | 88.92                 | 47.0% $ \pm 1/2\rangle$<br>+ 31.7% $ \mp 1/2\rangle$<br>+ 16.4% $ \mp 3/2\rangle$<br>+ 2.3% $ \pm 3/2\rangle$<br>+ 1.9% $ \mp 5/2\rangle$<br>+ 0.6% $ \pm 5/2\rangle$<br>+ 0.2% $ \mp 7/2\rangle$ |



**Table S15.** Electronic structure of  $[\text{Dy}(\text{Cp}^{\text{ttb}})_2]^+$  calculated with CASSCF-SO using solid-state geometry from **1**, where  $^t\text{Bu}$  groups have been replaced with Me groups and Cp-Dy-Cp angle has been forced to  $180^\circ$  (Cp rings remain eclipsed, modification (ii)).

| Energy ( $\text{cm}^{-1}$ ) | Energy (K) | $g_x$ | $g_y$ | $g_z$ | $g_z$ angle (degrees) | Wavefunction                                                                                                                                                         |
|-----------------------------|------------|-------|-------|-------|-----------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 0.0                         | 0.0        | 0.00  | 0.00  | 19.91 | -                     | 99.8% $ \pm 15/2\rangle$<br>+ 0.2% $ \pm 13/2\rangle$                                                                                                                |
| 601.5                       | 865.4      | 0.00  | 0.00  | 16.96 | 1.84                  | 99.6% $ \pm 13/2\rangle$<br>+ 0.2% $ \pm 15/2\rangle$<br>+ 0.1% $ \pm 11/2\rangle$<br>+ 0.1% $ \pm 9/2\rangle$                                                       |
| 885.7                       | 1274.4     | 0.00  | 0.00  | 14.41 | 2.63                  | 99.7% $ \pm 11/2\rangle$<br>+ 0.2% $ \pm 7/2\rangle$<br>+ 0.1% $ \pm 13/2\rangle$                                                                                    |
| 1052.5                      | 1514.3     | 0.00  | 0.00  | 11.82 | 3.47                  | 99.5% $ \pm 9/2\rangle$<br>+ 0.3% $ \pm 7/2\rangle$<br>+ 0.1% $ \pm 13/2\rangle$<br>+ 0.1% $ \pm 5/2\rangle$                                                         |
| 1224.2                      | 1761.3     | 0.01  | 0.01  | 9.11  | 5.75                  | 98.4% $ \pm 7/2\rangle$<br>+ 1.1% $ \pm 5/2\rangle$<br>+ 0.2% $ \pm 9/2\rangle$<br>+ 0.2% $ \pm 11/2\rangle$<br>+ 0.1% $ \pm 3/2\rangle$                             |
| 1416.7                      | 2038.3     | 0.13  | 0.15  | 6.36  | 5.11                  | 96.5% $ \pm 5/2\rangle$<br>+ 2.2% $ \pm 3/2\rangle$<br>+ 1.0% $ \pm 7/2\rangle$<br>+ 0.2% $ \pm 1/2\rangle$<br>+ 0.1% $ \pm 9/2\rangle$                              |
| 1592.3                      | 2290.9     | 2.82  | 3.34  | 3.68  | 15.67                 | 92.8% $ \pm 3/2\rangle$<br>+ 3.3% $ \pm 1/2\rangle$<br>+ 2.0% $ \mp 1/2\rangle$<br>+ 1.7% $ \pm 5/2\rangle$<br>+ 0.2% $ \pm 7/2\rangle$<br>+ 0.1% $ \mp 3/2\rangle$  |
| 1706.0                      | 2454.6     | 1.13  | 7.30  | 13.51 | 89.00                 | 80.3% $ \pm 1/2\rangle$<br>+ 14.1% $ \mp 1/2\rangle$<br>+ 4.6% $ \pm 3/2\rangle$<br>+ 0.6% $ \pm 5/2\rangle$<br>+ 0.3% $ \mp 3/2\rangle$<br>+ 0.1% $ \pm 7/2\rangle$ |

**Table S16.** Electronic structure of  $[\text{Dy}(\text{Cp}^{\text{ttb}})_2]^+$  calculated with CASSCF-SO using solid-state geometry from **1**, where  $^t\text{Bu}$  groups have been replaced with Me groups, Cp-Dy-Cp angle has been forced to  $180^\circ$ , and one Cp ring has been rotated by  $36^\circ$  (staggered, modification (iii)).

| Energy ( $\text{cm}^{-1}$ ) | Energy (K) | $g_x$ | $g_y$ | $g_z$ | $g_z$ angle (degrees) | Wavefunction                                                                                                                                                        |
|-----------------------------|------------|-------|-------|-------|-----------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 0.0                         | 0.0        | 0.00  | 0.00  | 19.91 | -                     | 99.7% $ \pm 15/2\rangle$<br>+ 0.3% $ \pm 13/2\rangle$                                                                                                               |
| 601.9                       | 866.0      | 0.00  | 0.00  | 16.96 | 2.27                  | 99.5% $ \pm 13/2\rangle$<br>+ 0.3% $ \pm 15/2\rangle$<br>+ 0.1% $ \pm 11/2\rangle$                                                                                  |
| 886.5                       | 1275.5     | 0.01  | 0.01  | 14.41 | 3.21                  | 99.8% $ \pm 11/2\rangle$<br>+ 0.1% $ \pm 7/2\rangle$<br>+ 0.1% $ \pm 13/2\rangle$                                                                                   |
| 1053.8                      | 1516.2     | 0.01  | 0.02  | 11.84 | 4.28                  | 99.5% $ \pm 9/2\rangle$<br>+ 0.4% $ \pm 7/2\rangle$                                                                                                                 |
| 1225.2                      | 1762.8     | 0.07  | 0.11  | 9.13  | 6.87                  | 97.9% $ \pm 7/2\rangle$<br>+ 1.6% $ \pm 5/2\rangle$<br>+ 0.3% $ \pm 9/2\rangle$<br>+ 0.1% $ \pm 11/2\rangle$                                                        |
| 1417.9                      | 2040.0     | 0.32  | 0.50  | 6.37  | 6.00                  | 95.3% $ \pm 5/2\rangle$<br>+ 3.0% $ \pm 3/2\rangle$<br>+ 1.5% $ \pm 7/2\rangle$<br>+ 0.1% $ \pm 9/2\rangle$<br>+ 0.2% $ \mp 1/2\rangle$                             |
| 1594.9                      | 2294.7     | 1.47  | 2.35  | 3.71  | 7.81                  | 91.9% $ \pm 3/2\rangle$<br>+ 4.6% $ \pm 1/2\rangle$<br>+ 2.6% $ \pm 5/2\rangle$<br>+ 0.4% $ \mp 1/2\rangle$<br>+ 0.3% $ \mp 3/2\rangle$<br>+ 0.1% $ \pm 7/2\rangle$ |
| 1705.4                      | 2453.6     | 1.19  | 8.55  | 12.39 | 88.87                 | 90.6% $ \pm 1/2\rangle$<br>+ 4.7% $ \pm 3/2\rangle$<br>+ 4.2% $ \mp 1/2\rangle$<br>+ 0.3% $ \pm 5/2\rangle$<br>+ 0.1% $ \mp 3/2\rangle$<br>+ 0.1% $ \pm 7/2\rangle$ |

## S9. Spin Dynamics

As outlined in the main text, we perform our calculation of the spin dynamics using the gas-phase vibrational modes of the  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  cation as determined by density functional theory (DFT). In order to facilitate convergence of the self-consistent field, we replaced dysprosium(III) with yttrium(III) in the DFT calculations; this is justified because they possess similar ionic radii and they are chemically very similar as demonstrated by the analogous yttrium(III) complex **5**. Thus, the geometry of  $[\text{Y}(\text{Cp}^{\text{ttt}})_2]^+$  was optimised using Gaussian09d<sup>31</sup> with the pure exchange-correlation PBE functional<sup>32,33</sup> and Grimme's dispersion corrections<sup>34-36</sup>. We employed the cc-pVDZ basis set for all non-metal atoms<sup>37,38</sup>, while the 28 core electrons of yttrium were treated with the Stuttgart RSC 1997<sup>39-41</sup> effective core potential (ECP) and its remaining valence electrons were described with the corresponding valence basis set. Calculation of the hessian confirmed that the optimised structure corresponds to a minimum in the potential energy surface, as all frequencies are positive and the force constants are close to zero.

The optimised coordinates of  $[\text{Y}(\text{Cp}^{\text{ttt}})_2]^+$  (Table S17) are nearly identical to the experimental coordinates of  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  in **1**. The optimised geometry shows a symmetric distance between the yttrium atom and the centroids of the two  $\text{Cp}^{\text{ttt}}$  ligands of 2.309 Å, compared to 2.318 and 2.314 Å for **1**. The angle between by the centroids of the two  $\text{Cp}^{\text{ttt}}$  ligands and the yttrium atom optimises to 151.45°, which compares very well to the experimental value of 152.56° for **1**. Aside from a slight depression of the energies of the Kramers doublets on the order of 40 – 80  $\text{cm}^{-1}$ , the electronic structure of the DFT optimised  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  is essentially the same as for **1** (Table S18 *cf.* Table S13).

**Table S17.** Optimised coordinates of  $[\text{Y}(\text{Cp}^{\text{ttt}})_2]^+$ .

| Atom | x (Å)    | y (Å)    | z (Å)    |
|------|----------|----------|----------|
| Y    | 0.00000  | -0.22042 | 0.00001  |
| C    | -2.46791 | -0.86675 | -0.34553 |
| C    | -2.42746 | 0.02333  | 0.81495  |
| C    | -2.06343 | 1.32596  | 0.32272  |
| H    | -1.99609 | 2.22783  | 0.93839  |
| C    | -1.92568 | 1.30565  | -1.10178 |
| C    | -2.16037 | -0.04330 | -1.48635 |
| H    | -2.17570 | -0.39313 | -2.52295 |
| C    | -2.85685 | -2.35328 | -0.54546 |
| C    | -2.15003 | -3.31914 | 0.43154  |
| H    | -1.03948 | -3.24696 | 0.35212  |
| H    | -2.40597 | -4.36838 | 0.18268  |
| H    | -2.42435 | -3.15969 | 1.48870  |
| C    | -2.46249 | -2.82538 | -1.96665 |
| H    | -3.00972 | -2.28177 | -2.76037 |
| H    | -2.70887 | -3.89917 | -2.07976 |
| H    | -1.37364 | -2.71460 | -2.16225 |
| C    | -4.39364 | -2.49445 | -0.42928 |
| H    | -4.76951 | -2.19877 | 0.56571  |
| H    | -4.69870 | -3.54500 | -0.61384 |
| H    | -4.89476 | -1.85389 | -1.18182 |
| C    | -2.51718 | -0.24450 | 2.33555  |
| C    | -3.73661 | -1.09402 | 2.74351  |
| H    | -3.71794 | -2.11719 | 2.33113  |
| H    | -4.67483 | -0.60909 | 2.40913  |
| H    | -3.77704 | -1.18577 | 3.84755  |
| C    | -2.63365 | 1.08815  | 3.11149  |
| H    | -1.75099 | 1.74313  | 2.97426  |
| H    | -2.71885 | 0.87969  | 4.19609  |
| H    | -3.53450 | 1.65318  | 2.80185  |
| C    | -1.19686 | -0.92415 | 2.77797  |
| H    | -0.31584 | -0.25638 | 2.59952  |
| H    | -1.02499 | -1.90525 | 2.28747  |
| H    | -1.16936 | -1.11638 | 3.87094  |

|   |          |          |          |
|---|----------|----------|----------|
| C | -1.90106 | 2.51246  | -2.04052 |
| C | 2.42746  | 0.02330  | -0.81495 |
| C | 2.46790  | -0.86679 | 0.34552  |
| C | 2.16037  | -0.04334 | 1.48635  |
| H | 2.17571  | -0.39318 | 2.52295  |
| C | 1.92570  | 1.30562  | 1.10179  |
| C | 2.06345  | 1.32593  | -0.32271 |
| H | 1.99611  | 2.22780  | -0.93837 |
| C | 2.51719  | -0.24451 | -2.33555 |
| C | 1.19686  | -0.92411 | -2.77801 |
| H | 0.31585  | -0.25631 | -2.59956 |
| H | 1.02495  | -1.90521 | -2.28754 |
| H | 1.16937  | -1.11630 | -3.87099 |
| C | 2.63372  | 1.08815  | -3.11147 |
| H | 2.71894  | 0.87971  | -4.19607 |
| H | 3.53458  | 1.65315  | -2.80179 |
| H | 1.75109  | 1.74316  | -2.97424 |
| C | 3.73660  | -1.09406 | -2.74351 |
| H | 3.71789  | -2.11724 | -2.33115 |
| H | 4.67483  | -0.60917 | -2.40911 |
| H | 3.77704  | -1.18580 | -3.84755 |
| C | 2.85680  | -2.35333 | 0.54544  |
| C | 4.39358  | -2.49456 | 0.42925  |
| H | 4.89473  | -1.85403 | 1.18181  |
| H | 4.69860  | -3.54512 | 0.61379  |
| H | 4.76946  | -2.19887 | -0.56574 |
| C | 2.46242  | -2.82543 | 1.96662  |
| H | 1.37358  | -2.71464 | 2.16222  |
| H | 3.00966  | -2.28185 | 2.76035  |
| H | 2.70878  | -3.89923 | 2.07971  |
| C | 2.14994  | -3.31915 | -0.43158 |
| H | 1.03939  | -3.24691 | -0.35215 |
| H | 2.40582  | -4.36840 | -0.18272 |
| H | 2.42426  | -3.15970 | -1.48873 |
| C | 1.90111  | 2.51242  | 2.04054  |
| C | 3.35960  | 3.03356  | 2.11899  |
| H | 3.72466  | 3.34869  | 1.12106  |

|   |          |         |          |
|---|----------|---------|----------|
| H | 4.04277  | 2.24834 | 2.50017  |
| H | 3.42077  | 3.90669 | 2.80024  |
| C | 1.43811  | 2.11802 | 3.45569  |
| H | 0.40086  | 1.72519 | 3.45392  |
| H | 1.45445  | 3.00396 | 4.12079  |
| H | 2.09703  | 1.35398 | 3.91451  |
| C | 0.99498  | 3.63542 | 1.50820  |
| H | 1.30411  | 3.97596 | 0.50062  |
| H | 1.03774  | 4.51475 | 2.18129  |
| H | -0.06057 | 3.30377 | 1.44711  |
| C | -1.43803 | 2.11807 | -3.45566 |
| H | -0.40078 | 1.72524 | -3.45387 |
| H | -1.45437 | 3.00401 | -4.12076 |
| H | -2.09694 | 1.35403 | -3.91450 |
| C | -3.35955 | 3.03360 | -2.11900 |
| H | -4.04272 | 2.24838 | -2.50020 |
| H | -3.42072 | 3.90673 | -2.80024 |
| H | -3.72464 | 3.34871 | -1.12108 |
| C | -0.99495 | 3.63546 | -1.50816 |
| H | -1.03770 | 4.51479 | -2.18124 |
| H | 0.06060  | 3.30381 | -1.44706 |
| H | -1.30410 | 3.97599 | -0.50058 |

**Table S18.** Electronic structure of  $[\text{Dy}(\text{Cp}^{\text{tBu}})_2]^+$  calculated with CASSCF-SO using DFT optimised geometry (Table S17).

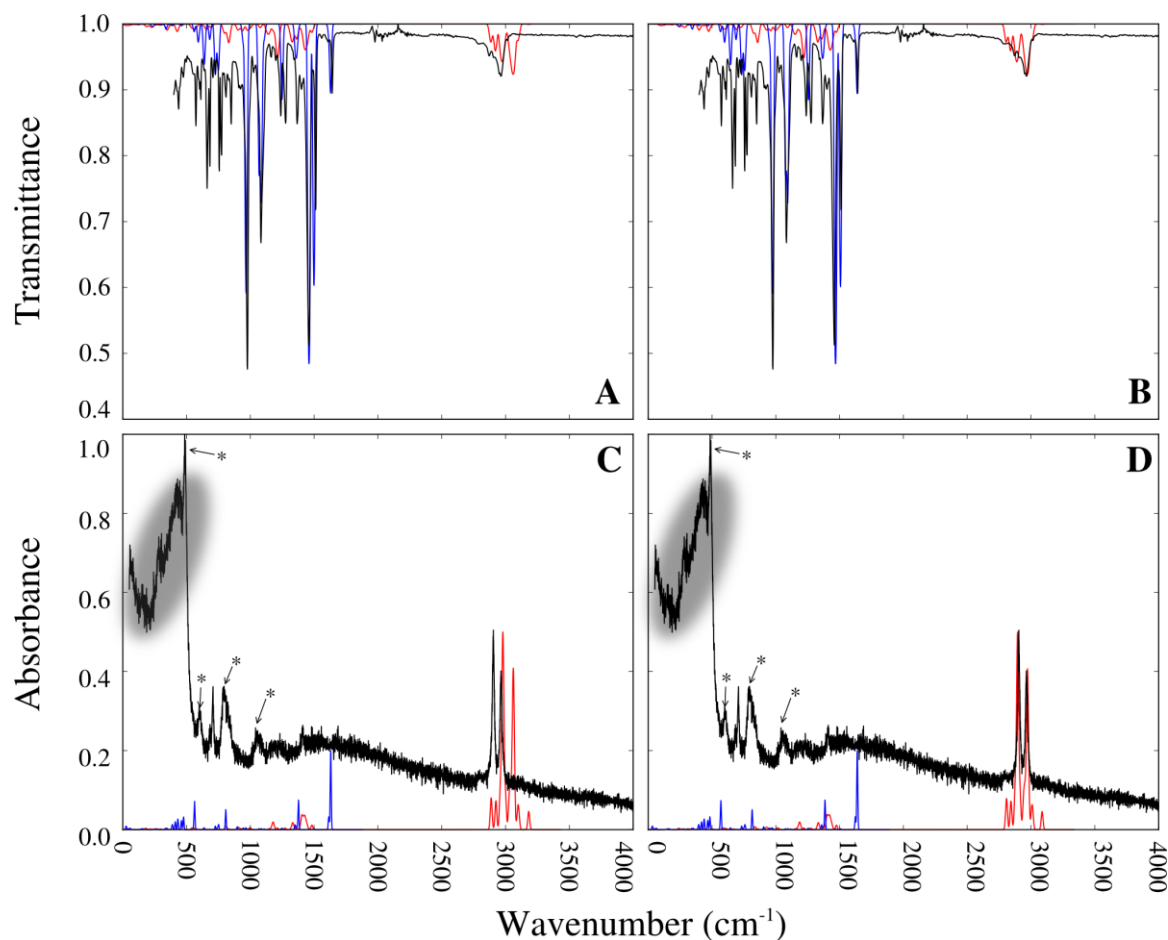
| Energy ( $\text{cm}^{-1}$ ) | Energy (K) | $g_x$ | $g_y$ | $g_z$ | $g_z$ angle (degrees) | Wavefunction                                                                                                                                                                                                                 |
|-----------------------------|------------|-------|-------|-------|-----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 0.0                         | 0.0        | 0.00  | 0.00  | 19.89 | -                     | 99.6% $ \pm 15/2\rangle$<br>+ 0.2% $ \pm 13/2\rangle$<br>+ 0.2% $ \pm 11/2\rangle$                                                                                                                                           |
| 460.6                       | 662.7      | 0.00  | 0.00  | 17.03 | 1.57                  | 99.7% $ \pm 13/2\rangle$<br>+ 0.2% $ \pm 15/2\rangle$<br>+ 0.1% $ \pm 11/2\rangle$<br>+ 0.1% $ \pm 9/2\rangle$                                                                                                               |
| 727.3                       | 1046.3     | 0.00  | 0.00  | 14.40 | 2.39                  | 99.4% $ \pm 11/2\rangle$<br>+ 0.2% $ \pm 15/2\rangle$<br>+ 0.3% $ \pm 7/2\rangle$<br>+ 0.1% $ \pm 13/2\rangle$                                                                                                               |
| 903.6                       | 1300.1     | 0.00  | 0.01  | 11.74 | 2.72                  | 98.9% $ \pm 9/2\rangle$<br>+ 0.8% $ \pm 5/2\rangle$<br>+ 0.1% $ \pm 7/2\rangle$<br>+ 0.1% $ \pm 13/2\rangle$<br>+ 0.1% $ \pm 3/2\rangle$                                                                                     |
| 1063.0                      | 1529.3     | 0.07  | 0.07  | 9.10  | 3.51                  | 98.3% $ \pm 7/2\rangle$<br>+ 0.5% $ \pm 5/2\rangle$<br>+ 0.5% $ \pm 3/2\rangle$<br>+ 0.3% $ \pm 11/2\rangle$<br>+ 0.2% $ \pm 9/2\rangle$<br>+ 0.1% $ \pm 1/2\rangle$                                                         |
| 1211.1                      | 1742.5     | 1.03  | 1.28  | 6.45  | 2.05                  | 96.8% $ \pm 5/2\rangle$<br>+ 0.8% $ \pm 9/2\rangle$<br>+ 0.8% $ \pm 3/2\rangle$<br>+ 0.7% $ \pm 7/2\rangle$<br>+ 0.3% $ \mp 5/2\rangle$<br>+ 0.3% $ \mp 3/2\rangle$<br>+ 0.2% $ \mp 1/2\rangle$                              |
| 1326.1                      | 1907.9     | 2.47  | 3.67  | 5.49  | 90.00                 | 81.6% $ \pm 3/2\rangle$<br>+ 11.8% $ \mp 3/2\rangle$<br>+ 4.6% $ \mp 1/2\rangle$<br>+ 0.8% $ \mp 5/2\rangle$<br>+ 0.4% $ \pm 5/2\rangle$<br>+ 0.4% $ \pm 7/2\rangle$<br>+ 0.3% $ \pm 1/2\rangle$<br>+ 0.1% $ \mp 7/2\rangle$ |
| 1397.0                      | 2010.0     | 1.09  | 6.28  | 14.11 | 89.64                 | 89.9% $ \pm 1/2\rangle$<br>+ 5.0% $ \mp 1/2\rangle$<br>+ 2.7% $ \pm 3/2\rangle$<br>+ 2.1% $ \mp 3/2\rangle$<br>+ 0.2% $ \mp 5/2\rangle$<br>+ 0.1% $ \pm 7/2\rangle$<br>+ 0.1% $ \pm 5/2\rangle$                              |

For the calculation of the harmonic vibrational modes and vibrational spectra, we gave the yttrium atom an isotopic mass of 162.5 (the natural abundance-weighted mass of dysprosium), in order to obtain the correct reduced masses. To compare the calculated vibrational spectra to the experimental IR and Raman data, we also optimised and determined the vibrational modes of the  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  anion using the same methods described above. Furthermore, we subsequently collected the IR spectrum of **1** using the attenuated total reflectance (ATR) technique in order to avoid contributions of the Nujol oil which may hamper our comparison (Figs. S63A and S63B *cf.* Fig. S23). The calculated data show that our gas-phase vibrational calculations already provide a good approximation of the solid-state spectra (Figs. S63A and S63C). First, we observe that the Raman mode with the most calculated intensity for  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  ( $1630\text{ cm}^{-1}$ ) does not appear in the experimental spectrum (Fig. S36C, Table S19); this allows us to safely assume that  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  does not give any distinguishable peaks in the Raman spectrum. Comparing the calculated IR spectrum of  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  with the experimental data, it is clear that most of the peaks in the range  $500 - 2000\text{ cm}^{-1}$  arise from this species (Fig. S36A). Fitting the calculated positions for  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  to the experimental values, we find a linear correction with a slope of 1.002 and an intercept of  $5.992\text{ cm}^{-1}$ ; applying this correction to the calculated Raman and IR spectra for  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  provides an excellent simulation of the data (Fig. S36B). The main features in the experimental Raman spectrum must therefore owe to  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  – we note that there is an experimental feature at ca.  $700\text{ cm}^{-1}$  that is not background, but does not seem to originate from  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  or  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ; this signal is also present in **6** and thus we attribute this peak to sample decomposition by the Raman laser during acquisition. Initially, we fit the calculated Raman peaks of  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  appearing at 1417, 2978 and  $3060\text{ cm}^{-1}$  to the experimentally observed peaks at 1411, 2904 and  $2963\text{ cm}^{-1}$ , respectively, and obtain a linear correction with a slope of 0.9499 and an intercept of  $65.44\text{ cm}^{-1}$ . Applying this correction to the IR spectrum for  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  and identifying the features that owe to  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , we can identify low energy IR transitions for  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  at 439, 475, 851, 1240 and



1403  $\text{cm}^{-1}$ . Including these transitions in our calibration (corresponding DFT calculated values of 389, 427, 831, 1214 and 1420  $\text{cm}^{-1}$ , respectively) gives a final linear correction with a slope of 0.9485 and an intercept of 69.33  $\text{cm}^{-1}$ ; with this correction, we see excellent agreement with the observed features (Figs. S36B and S36D).

We note that in our analysis of the spin dynamics below, the most energetic vibrations that contribute to magnetic relaxation are *ca.* 500  $\text{cm}^{-1}$ . While our calibration has encompassed modes of this energy, and thus we are confident that these are accurately described, our calibration is not directly based on experimental evidence of low energy modes < 400  $\text{cm}^{-1}$  as they are not observable in the IR and Raman spectra. However, given that the uncalibrated DFT calculations are in good agreement with the experimental vibrational spectra and the correction is quite small, we propose that we have made a reasonable calibration of the low energy modes.



**Figure S63.** Vibrational spectra for **1**; experimental data (black lines),  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  (red lines) and  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (blue lines). **(A)** ATR-IR spectra with uncalibrated calculated data. **(B)** ATR-IR spectra with calibrated calculated data. **(C)** Raman spectra with uncalibrated calculated data. **(D)** Raman spectra with calibrated calculated data. Intensities of the calculated data have been scaled to best reproduce the experimental data. Peaks labelled with asterisks and the region shaded in grey correspond to background signals from the silica slide.

**Table S19.** Vibrational modes of  $[\text{Dy}(\text{Cp}^{\text{III}})_2]^+$ .

| Mode number | DFT Energy (cm <sup>-1</sup> ) | Calibrated Energy (cm <sup>-1</sup> ) | Normalized IR Intensity | Normalized Raman Intensity | Reduced mass (a.u.) |
|-------------|--------------------------------|---------------------------------------|-------------------------|----------------------------|---------------------|
| 1           | 23.1                           | 91.3                                  | 0.0402                  | 0.0005                     | 3.5423              |
| 2           | 26.0                           | 94.0                                  | 0.0003                  | 0.0007                     | 3.4714              |
| 3           | 36.2                           | 103.7                                 | 0.0001                  | 0.0003                     | 2.7772              |
| 4           | 39.2                           | 106.5                                 | 0.0179                  | 0.0000                     | 3.0111              |
| 5           | 46.7                           | 113.6                                 | 0.0003                  | 0.0011                     | 3.8497              |
| 6           | 54.9                           | 121.4                                 | 0.0304                  | 0.0002                     | 5.0893              |
| 7           | 58.2                           | 124.5                                 | 0.0023                  | 0.0010                     | 3.2190              |
| 8           | 58.4                           | 124.7                                 | 0.0001                  | 0.0008                     | 3.0880              |
| 9           | 73.6                           | 139.2                                 | 0.0041                  | 0.0013                     | 4.3585              |
| 10          | 79.9                           | 145.1                                 | 0.0044                  | 0.0025                     | 3.7468              |
| 11          | 89.4                           | 154.2                                 | 0.0008                  | 0.0033                     | 3.4266              |
| 12          | 93.1                           | 157.6                                 | 0.0068                  | 0.0029                     | 4.9284              |
| 13          | 94.5                           | 159.0                                 | 0.0037                  | 0.0004                     | 3.6043              |
| 14          | 119.1                          | 182.3                                 | 0.0108                  | 0.0004                     | 2.7754              |
| 15          | 124.2                          | 187.1                                 | 0.0020                  | 0.0003                     | 2.5691              |
| 16          | 125.6                          | 188.5                                 | 0.0130                  | 0.0002                     | 3.1850              |
| 17          | 135.8                          | 198.1                                 | 0.0011                  | 0.0015                     | 3.1026              |
| 18          | 173.4                          | 233.8                                 | 0.0049                  | 0.0024                     | 2.6997              |
| 19          | 174.0                          | 234.4                                 | 0.0052                  | 0.0023                     | 2.5805              |
| 20          | 180.0                          | 240.1                                 | 0.0044                  | 0.0173                     | 3.6922              |
| 21          | 186.6                          | 246.3                                 | 0.0597                  | 0.0028                     | 2.9056              |
| 22          | 199.2                          | 258.2                                 | 0.0121                  | 0.0029                     | 2.5692              |
| 23          | 202.3                          | 261.2                                 | 0.0011                  | 0.0003                     | 1.3730              |
| 24          | 202.6                          | 261.5                                 | 0.0053                  | 0.0016                     | 1.3297              |
| 25          | 215.7                          | 273.9                                 | 0.0168                  | 0.0015                     | 2.8928              |
| 26          | 217.4                          | 275.6                                 | 0.0001                  | 0.0071                     | 2.5416              |
| 27          | 224.4                          | 282.2                                 | 0.0497                  | 0.0006                     | 1.7249              |
| 28          | 226.3                          | 284.0                                 | 0.0001                  | 0.0002                     | 1.1399              |

|    |       |       |        |        |        |
|----|-------|-------|--------|--------|--------|
| 29 | 228.9 | 286.5 | 0.0261 | 0.0002 | 1.4832 |
| 30 | 236.3 | 293.4 | 0.0212 | 0.0014 | 1.6888 |
| 31 | 244.4 | 301.1 | 0.0028 | 0.0037 | 1.5566 |
| 32 | 252.6 | 308.9 | 0.0001 | 0.0015 | 1.5767 |
| 33 | 253.1 | 309.4 | 0.0041 | 0.0000 | 2.3045 |
| 34 | 255.1 | 311.2 | 0.0093 | 0.0005 | 1.3498 |
| 35 | 255.4 | 311.6 | 0.0036 | 0.0091 | 1.8684 |
| 36 | 266.0 | 321.7 | 0.0001 | 0.0042 | 1.7598 |
| 37 | 268.5 | 324.0 | 0.0026 | 0.0008 | 1.7556 |
| 38 | 271.1 | 326.5 | 0.0053 | 0.0009 | 1.2697 |
| 39 | 272.3 | 327.6 | 0.0046 | 0.0001 | 1.2889 |
| 40 | 285.3 | 339.9 | 0.0048 | 0.0001 | 1.1409 |
| 41 | 285.7 | 340.4 | 0.0050 | 0.0009 | 1.1258 |
| 42 | 291.7 | 346.0 | 0.0009 | 0.0022 | 1.2288 |
| 43 | 292.2 | 346.5 | 0.0064 | 0.0037 | 1.6103 |
| 44 | 296.1 | 350.1 | 0.0000 | 0.0019 | 1.4610 |
| 45 | 297.1 | 351.1 | 0.0200 | 0.0006 | 1.1172 |
| 46 | 299.8 | 353.7 | 0.0011 | 0.0020 | 1.1764 |
| 47 | 300.3 | 354.2 | 0.0011 | 0.0002 | 1.1567 |
| 48 | 328.8 | 381.2 | 0.0000 | 0.0010 | 1.2367 |
| 49 | 330.2 | 382.5 | 0.0038 | 0.0007 | 1.2549 |
| 50 | 341.2 | 393.0 | 0.0066 | 0.0006 | 1.8527 |
| 51 | 342.7 | 394.3 | 0.0012 | 0.0015 | 1.2841 |
| 52 | 344.3 | 395.9 | 0.0055 | 0.0047 | 2.4874 |
| 53 | 345.0 | 396.5 | 0.0133 | 0.0000 | 1.5585 |
| 54 | 347.4 | 398.8 | 0.1467 | 0.0002 | 2.5218 |
| 55 | 348.6 | 400.0 | 0.0057 | 0.0044 | 2.5038 |
| 56 | 359.4 | 410.2 | 0.0040 | 0.0017 | 2.1550 |
| 57 | 359.5 | 410.3 | 0.0030 | 0.0001 | 2.1450 |
| 58 | 371.2 | 421.4 | 0.0056 | 0.0004 | 2.1384 |
| 59 | 375.3 | 425.3 | 0.0062 | 0.0003 | 2.1178 |

|    |       |       |        |        |        |
|----|-------|-------|--------|--------|--------|
| 60 | 382.2 | 431.9 | 0.0074 | 0.0017 | 2.3793 |
| 61 | 382.4 | 432.0 | 0.0010 | 0.0013 | 2.3485 |
| 62 | 388.7 | 438.0 | 0.0001 | 0.0021 | 2.2288 |
| 63 | 388.8 | 438.1 | 0.0343 | 0.0004 | 2.2130 |
| 64 | 413.2 | 461.3 | 0.0026 | 0.0001 | 2.3972 |
| 65 | 417.4 | 465.2 | 0.0001 | 0.0008 | 2.4803 |
| 66 | 425.5 | 473.0 | 0.0004 | 0.0020 | 3.0526 |
| 67 | 426.5 | 473.9 | 0.2216 | 0.0002 | 3.1920 |
| 68 | 452.7 | 498.7 | 0.0032 | 0.0039 | 2.3614 |
| 69 | 455.0 | 500.9 | 0.0057 | 0.0036 | 2.3581 |
| 70 | 464.2 | 509.6 | 0.0109 | 0.0013 | 2.7965 |
| 71 | 464.4 | 509.9 | 0.0010 | 0.0017 | 2.7970 |
| 72 | 536.9 | 578.6 | 0.0336 | 0.0008 | 2.9536 |
| 73 | 539.1 | 580.7 | 0.0129 | 0.0028 | 2.9486 |
| 74 | 542.3 | 583.7 | 0.0446 | 0.0014 | 2.8193 |
| 75 | 543.4 | 584.8 | 0.0162 | 0.0246 | 2.7106 |
| 76 | 561.4 | 601.8 | 0.0367 | 0.0022 | 3.8550 |
| 77 | 563.8 | 604.1 | 0.0861 | 0.0190 | 4.0396 |
| 78 | 579.4 | 618.9 | 0.0536 | 0.0007 | 3.5357 |
| 79 | 580.3 | 619.7 | 0.0004 | 0.0057 | 3.5723 |
| 80 | 630.3 | 667.2 | 0.0041 | 0.0104 | 3.5784 |
| 81 | 630.5 | 667.3 | 0.0310 | 0.0004 | 3.5465 |
| 82 | 655.8 | 691.3 | 0.1209 | 0.0017 | 5.3743 |
| 83 | 656.9 | 692.4 | 0.0405 | 0.0038 | 5.1569 |
| 84 | 687.9 | 721.8 | 0.0440 | 0.0001 | 5.0172 |
| 85 | 694.9 | 728.4 | 0.0610 | 0.0036 | 4.8382 |
| 86 | 794.0 | 822.4 | 0.1838 | 0.0011 | 1.3885 |
| 87 | 798.0 | 826.3 | 0.0001 | 0.0009 | 1.3930 |
| 88 | 802.3 | 830.3 | 0.0834 | 0.0000 | 2.5685 |
| 89 | 802.3 | 830.3 | 0.0075 | 0.0042 | 2.4669 |
| 90 | 808.2 | 835.9 | 0.0034 | 0.0035 | 2.4364 |

|     |       |        |        |        |        |
|-----|-------|--------|--------|--------|--------|
| 91  | 808.5 | 836.2  | 0.0245 | 0.0408 | 2.6356 |
| 92  | 821.2 | 848.3  | 0.0120 | 0.0048 | 2.2555 |
| 93  | 821.9 | 848.9  | 0.0214 | 0.0002 | 2.2749 |
| 94  | 831.0 | 857.6  | 0.5515 | 0.0002 | 1.2485 |
| 95  | 831.4 | 857.9  | 0.0476 | 0.0080 | 1.2569 |
| 96  | 896.8 | 919.9  | 0.0000 | 0.0073 | 1.4903 |
| 97  | 897.0 | 920.2  | 0.0021 | 0.0031 | 1.4587 |
| 98  | 897.9 | 921.0  | 0.0262 | 0.0016 | 1.6081 |
| 99  | 898.2 | 921.3  | 0.0461 | 0.0025 | 1.6039 |
| 100 | 902.2 | 925.1  | 0.0098 | 0.0017 | 1.4498 |
| 101 | 902.2 | 925.1  | 0.0234 | 0.0039 | 1.4564 |
| 102 | 903.8 | 926.6  | 0.0001 | 0.0059 | 1.6976 |
| 103 | 904.6 | 927.3  | 0.0349 | 0.0079 | 1.6511 |
| 104 | 908.4 | 930.9  | 0.0044 | 0.0028 | 1.6160 |
| 105 | 908.6 | 931.1  | 0.0108 | 0.0044 | 1.6060 |
| 106 | 910.7 | 933.1  | 0.0006 | 0.0014 | 1.3046 |
| 107 | 910.8 | 933.2  | 0.0134 | 0.0026 | 1.3047 |
| 108 | 913.7 | 935.9  | 0.0009 | 0.0010 | 1.2504 |
| 109 | 915.8 | 938.0  | 0.0061 | 0.0024 | 1.3613 |
| 110 | 915.8 | 938.0  | 0.0155 | 0.0018 | 1.3658 |
| 111 | 917.7 | 939.8  | 0.0122 | 0.0003 | 1.4825 |
| 112 | 919.2 | 941.2  | 0.0028 | 0.0071 | 1.4906 |
| 113 | 920.0 | 942.0  | 0.0048 | 0.0020 | 1.2835 |
| 114 | 938.2 | 959.2  | 0.1165 | 0.0100 | 3.5942 |
| 115 | 940.2 | 961.1  | 0.0798 | 0.0004 | 3.7295 |
| 116 | 974.8 | 993.9  | 0.1033 | 0.0011 | 2.0038 |
| 117 | 975.8 | 994.9  | 0.0487 | 0.0015 | 1.9073 |
| 118 | 985.4 | 1004.0 | 0.0206 | 0.0011 | 1.5574 |
| 119 | 986.4 | 1005.0 | 0.0159 | 0.0027 | 1.5804 |
| 120 | 994.4 | 1012.5 | 0.0070 | 0.0047 | 1.4842 |
| 121 | 994.7 | 1012.8 | 0.0193 | 0.0010 | 1.4263 |

|     |        |        |        |        |        |
|-----|--------|--------|--------|--------|--------|
| 122 | 995.7  | 1013.8 | 0.0015 | 0.0021 | 1.4213 |
| 123 | 996.0  | 1014.0 | 0.0143 | 0.0077 | 1.4504 |
| 124 | 997.5  | 1015.5 | 0.0081 | 0.0066 | 1.4313 |
| 125 | 998.1  | 1016.0 | 0.0083 | 0.0009 | 1.4191 |
| 126 | 1000.1 | 1018.0 | 0.0003 | 0.0046 | 1.4549 |
| 127 | 1000.4 | 1018.2 | 0.0016 | 0.0016 | 1.4448 |
| 128 | 1005.9 | 1023.4 | 0.0218 | 0.0051 | 1.7782 |
| 129 | 1006.4 | 1023.9 | 0.0211 | 0.0002 | 1.7495 |
| 130 | 1077.1 | 1090.9 | 0.0599 | 0.0051 | 1.2792 |
| 131 | 1078.0 | 1091.8 | 0.0466 | 0.0016 | 1.2774 |
| 132 | 1129.4 | 1140.6 | 0.0813 | 0.0006 | 1.4241 |
| 133 | 1129.8 | 1140.9 | 0.1093 | 0.0045 | 1.4328 |
| 134 | 1146.8 | 1157.1 | 0.2316 | 0.0005 | 2.4919 |
| 135 | 1150.4 | 1160.5 | 0.0068 | 0.0178 | 2.5237 |
| 136 | 1167.4 | 1176.6 | 0.0072 | 0.0073 | 2.8962 |
| 137 | 1168.2 | 1177.4 | 0.0122 | 0.0148 | 2.9319 |
| 138 | 1173.8 | 1182.6 | 0.0052 | 0.0277 | 2.7863 |
| 139 | 1176.5 | 1185.2 | 0.0687 | 0.0128 | 2.6197 |
| 140 | 1178.1 | 1186.8 | 0.0110 | 0.0245 | 2.7223 |
| 141 | 1179.5 | 1188.1 | 0.0052 | 0.0301 | 2.8389 |
| 142 | 1181.1 | 1189.6 | 0.0010 | 0.0005 | 2.9774 |
| 143 | 1181.4 | 1189.9 | 0.0002 | 0.0168 | 2.7407 |
| 144 | 1185.4 | 1193.7 | 0.0929 | 0.0091 | 2.8390 |
| 145 | 1185.8 | 1194.0 | 0.0105 | 0.0100 | 2.7828 |
| 146 | 1200.8 | 1208.3 | 0.0318 | 0.0015 | 2.9136 |
| 147 | 1201.0 | 1208.4 | 0.0566 | 0.0018 | 2.8663 |
| 148 | 1208.7 | 1215.8 | 0.0638 | 0.0043 | 2.9709 |
| 149 | 1209.4 | 1216.5 | 0.0589 | 0.0085 | 3.0039 |
| 150 | 1213.6 | 1220.5 | 0.6954 | 0.0094 | 2.7335 |
| 151 | 1214.6 | 1221.4 | 0.5853 | 0.0050 | 2.7690 |
| 152 | 1269.3 | 1273.3 | 0.0085 | 0.0019 | 5.7713 |

|     |        |        |        |        |        |
|-----|--------|--------|--------|--------|--------|
| 153 | 1270.2 | 1274.1 | 0.0084 | 0.0237 | 5.7591 |
| 154 | 1310.5 | 1312.4 | 0.1222 | 0.0028 | 1.2669 |
| 155 | 1310.7 | 1312.5 | 0.0013 | 0.0021 | 1.2693 |
| 156 | 1324.4 | 1325.5 | 0.0008 | 0.0031 | 1.2689 |
| 157 | 1324.4 | 1325.6 | 0.1277 | 0.0003 | 1.2672 |
| 158 | 1326.0 | 1327.1 | 0.1348 | 0.0042 | 1.4521 |
| 159 | 1327.3 | 1328.3 | 0.0007 | 0.0220 | 1.4081 |
| 160 | 1328.7 | 1329.6 | 0.0381 | 0.0007 | 1.3005 |
| 161 | 1329.1 | 1330.0 | 0.0703 | 0.0005 | 1.3644 |
| 162 | 1329.2 | 1330.1 | 0.0002 | 0.0168 | 1.4026 |
| 163 | 1330.4 | 1331.2 | 0.0967 | 0.0045 | 1.3201 |
| 164 | 1331.8 | 1332.6 | 0.0627 | 0.0018 | 2.0751 |
| 165 | 1332.3 | 1333.0 | 0.0020 | 0.0469 | 1.9220 |
| 166 | 1337.8 | 1338.3 | 0.0227 | 0.0115 | 1.3584 |
| 167 | 1338.5 | 1338.9 | 0.0467 | 0.0219 | 1.4084 |
| 168 | 1354.8 | 1354.3 | 0.0769 | 0.0012 | 1.5894 |
| 169 | 1355.1 | 1354.6 | 0.0359 | 0.0035 | 1.4688 |
| 170 | 1359.8 | 1359.1 | 0.0247 | 0.0014 | 1.5240 |
| 171 | 1360.5 | 1359.7 | 0.0173 | 0.0007 | 1.4500 |
| 172 | 1362.8 | 1362.0 | 0.1800 | 0.0035 | 1.7872 |
| 173 | 1364.9 | 1364.0 | 0.1111 | 0.0017 | 2.1265 |
| 174 | 1368.0 | 1366.9 | 0.0585 | 0.0002 | 1.2904 |
| 175 | 1369.2 | 1368.0 | 0.0075 | 0.0162 | 1.2771 |
| 176 | 1387.8 | 1385.7 | 0.0110 | 0.0035 | 1.0433 |
| 177 | 1389.2 | 1387.0 | 0.0043 | 0.0057 | 1.0448 |
| 178 | 1389.8 | 1387.6 | 0.0001 | 0.0003 | 1.0724 |
| 179 | 1393.9 | 1391.4 | 0.0076 | 0.0115 | 1.0719 |
| 180 | 1395.6 | 1393.1 | 0.0234 | 0.0107 | 1.0443 |
| 181 | 1398.2 | 1395.5 | 0.0078 | 0.0099 | 1.3973 |
| 182 | 1398.7 | 1396.0 | 0.0002 | 0.0070 | 1.1392 |
| 183 | 1398.9 | 1396.1 | 0.0059 | 0.0077 | 1.0778 |



|     |        |        |        |        |        |
|-----|--------|--------|--------|--------|--------|
| 184 | 1399.5 | 1396.8 | 0.0010 | 0.0023 | 1.0941 |
| 185 | 1401.1 | 1398.3 | 0.0145 | 0.0058 | 1.0869 |
| 186 | 1401.5 | 1398.6 | 0.0047 | 0.0074 | 1.1774 |
| 187 | 1402.2 | 1399.3 | 0.0056 | 0.0471 | 1.2353 |
| 188 | 1402.6 | 1399.7 | 0.0115 | 0.0390 | 1.3694 |
| 189 | 1403.4 | 1400.4 | 0.0125 | 0.0009 | 1.1643 |
| 190 | 1404.6 | 1401.6 | 0.0003 | 0.0285 | 1.6262 |
| 191 | 1408.7 | 1405.5 | 0.0211 | 0.0484 | 1.0778 |
| 192 | 1409.2 | 1406.0 | 0.0133 | 0.0153 | 1.0605 |
| 193 | 1411.2 | 1407.8 | 0.0274 | 0.0209 | 1.0806 |
| 194 | 1412.4 | 1409.0 | 0.0099 | 0.0098 | 1.0492 |
| 195 | 1413.1 | 1409.7 | 0.0001 | 0.0243 | 1.0680 |
| 196 | 1420.4 | 1416.5 | 0.1356 | 0.0107 | 1.0622 |
| 197 | 1422.2 | 1418.3 | 0.0003 | 0.0607 | 1.0574 |
| 198 | 1423.1 | 1419.1 | 0.0947 | 0.0510 | 1.1050 |
| 199 | 1423.4 | 1419.5 | 0.1896 | 0.0011 | 1.0804 |
| 200 | 1425.3 | 1421.3 | 0.0089 | 0.0129 | 1.0856 |
| 201 | 1426.0 | 1421.9 | 0.1214 | 0.0290 | 1.0932 |
| 202 | 1429.5 | 1425.2 | 0.0079 | 0.0223 | 1.0856 |
| 203 | 1429.6 | 1425.3 | 0.1334 | 0.0079 | 1.0811 |
| 204 | 1432.5 | 1428.1 | 0.0222 | 0.0254 | 1.0695 |
| 205 | 1433.7 | 1429.2 | 0.0788 | 0.0342 | 1.0680 |
| 206 | 1435.1 | 1430.5 | 0.0184 | 0.0067 | 1.0728 |
| 207 | 1438.7 | 1434.0 | 0.0664 | 0.0024 | 1.0667 |
| 208 | 1440.1 | 1435.3 | 0.1158 | 0.0114 | 1.0754 |
| 209 | 1442.0 | 1437.1 | 0.1192 | 0.0166 | 1.0757 |
| 210 | 1443.9 | 1438.8 | 0.0118 | 0.0113 | 1.1049 |
| 211 | 1444.6 | 1439.5 | 0.0088 | 0.0279 | 1.1200 |
| 212 | 1450.5 | 1445.1 | 0.2280 | 0.0019 | 1.0865 |
| 213 | 1451.0 | 1445.6 | 0.0593 | 0.0054 | 1.0894 |
| 214 | 1481.3 | 1474.3 | 0.1118 | 0.0453 | 3.8318 |

|     |        |        |        |        |        |
|-----|--------|--------|--------|--------|--------|
| 215 | 1483.1 | 1476.1 | 0.1386 | 0.0288 | 3.8512 |
| 216 | 2884.3 | 2805.1 | 0.5895 | 0.0586 | 1.0553 |
| 217 | 2887.5 | 2808.2 | 0.0123 | 0.4597 | 1.0547 |
| 218 | 2920.3 | 2839.3 | 1.0000 | 0.0138 | 1.0556 |
| 219 | 2924.2 | 2843.0 | 0.0095 | 0.4565 | 1.0536 |
| 220 | 2958.1 | 2875.1 | 0.4992 | 0.0374 | 1.0421 |
| 221 | 2958.1 | 2875.1 | 0.0011 | 0.5119 | 1.0421 |
| 222 | 2967.5 | 2884.0 | 0.3793 | 0.0232 | 1.0350 |
| 223 | 2967.5 | 2884.0 | 0.1021 | 0.1350 | 1.0350 |
| 224 | 2970.4 | 2886.8 | 0.2354 | 0.0143 | 1.0361 |
| 225 | 2971.1 | 2887.4 | 0.0483 | 0.4147 | 1.0363 |
| 226 | 2976.1 | 2892.2 | 0.0999 | 0.1252 | 1.0368 |
| 227 | 2976.4 | 2892.5 | 0.0467 | 0.0035 | 1.0363 |
| 228 | 2976.4 | 2892.5 | 0.1815 | 0.3470 | 1.0363 |
| 229 | 2978.0 | 2894.0 | 0.1124 | 1.0000 | 1.0363 |
| 230 | 2979.6 | 2895.5 | 0.2530 | 0.1042 | 1.0398 |
| 231 | 2979.6 | 2895.5 | 0.0602 | 0.7953 | 1.0398 |
| 232 | 2985.0 | 2900.6 | 0.2719 | 0.0014 | 1.0404 |
| 233 | 2985.1 | 2900.7 | 0.0138 | 0.8238 | 1.0404 |
| 234 | 2998.8 | 2913.7 | 0.0990 | 0.0221 | 1.0779 |
| 235 | 2999.2 | 2914.1 | 0.1093 | 0.4971 | 1.0784 |
| 236 | 3026.8 | 2940.2 | 0.1536 | 0.0443 | 1.0847 |
| 237 | 3027.7 | 2941.1 | 0.2314 | 0.3529 | 1.0854 |
| 238 | 3036.2 | 2949.2 | 0.0523 | 0.1928 | 1.0992 |
| 239 | 3036.2 | 2949.2 | 0.2255 | 0.0794 | 1.0992 |
| 240 | 3042.4 | 2955.0 | 0.5110 | 0.0336 | 1.0948 |
| 241 | 3042.8 | 2955.4 | 0.1312 | 0.3243 | 1.0948 |
| 242 | 3052.8 | 2964.9 | 0.2896 | 0.0260 | 1.1011 |
| 243 | 3052.8 | 2965.0 | 0.0109 | 0.0785 | 1.1011 |
| 244 | 3054.6 | 2966.6 | 0.0697 | 0.0870 | 1.1025 |
| 245 | 3054.6 | 2966.6 | 0.0017 | 0.0529 | 1.1024 |

|     |        |        |        |        |        |
|-----|--------|--------|--------|--------|--------|
| 246 | 3055.5 | 2967.4 | 0.1802 | 0.0397 | 1.1022 |
| 247 | 3056.7 | 2968.6 | 0.0532 | 0.0464 | 1.1017 |
| 248 | 3057.0 | 2968.9 | 0.1738 | 0.0383 | 1.1015 |
| 249 | 3057.1 | 2968.9 | 0.1098 | 0.0256 | 1.1015 |
| 250 | 3057.3 | 2969.2 | 0.0039 | 0.2281 | 1.1017 |
| 251 | 3057.3 | 2969.2 | 0.1018 | 0.0963 | 1.1017 |
| 252 | 3059.7 | 2971.4 | 0.6167 | 0.4919 | 1.1009 |
| 253 | 3060.0 | 2971.7 | 0.0172 | 0.0712 | 1.1022 |
| 254 | 3060.1 | 2971.8 | 0.0437 | 0.1486 | 1.1021 |
| 255 | 3060.5 | 2972.2 | 0.1146 | 0.3046 | 1.1011 |
| 256 | 3060.5 | 2972.3 | 0.3237 | 0.0259 | 1.1011 |
| 257 | 3060.9 | 2972.6 | 0.6064 | 0.4547 | 1.1003 |
| 258 | 3064.0 | 2975.5 | 0.0049 | 0.1054 | 1.1006 |
| 259 | 3066.4 | 2977.8 | 0.0453 | 0.1428 | 1.1016 |
| 260 | 3066.6 | 2978.0 | 0.2888 | 0.1990 | 1.1015 |
| 261 | 3067.2 | 2978.6 | 0.3407 | 0.0531 | 1.1007 |
| 262 | 3068.2 | 2979.6 | 0.0033 | 0.1403 | 1.1025 |
| 263 | 3068.3 | 2979.6 | 0.2204 | 0.1459 | 1.1025 |
| 264 | 3093.6 | 3003.6 | 0.1867 | 0.0202 | 1.0962 |
| 265 | 3093.8 | 3003.8 | 0.0423 | 0.1614 | 1.0962 |
| 266 | 3099.4 | 3009.1 | 0.1346 | 0.0180 | 1.0981 |
| 267 | 3099.4 | 3009.1 | 0.0986 | 0.1449 | 1.0981 |
| 268 | 3104.5 | 3013.9 | 0.0872 | 0.0880 | 1.0955 |
| 269 | 3104.5 | 3014.0 | 0.0120 | 0.0521 | 1.0955 |
| 270 | 3181.2 | 3086.7 | 0.0018 | 0.0049 | 1.0913 |
| 271 | 3181.3 | 3086.8 | 0.0032 | 0.0934 | 1.0922 |
| 272 | 3181.3 | 3086.8 | 0.0008 | 0.1634 | 1.0926 |
| 273 | 3181.4 | 3086.9 | 0.0070 | 0.0342 | 1.0935 |

To calibrate the atomic displacements for each vibrational mode, we note that a harmonic oscillator possesses maximum potential energy and zero kinetic energy at its maximum displacement and thus we associate the zero-point energy of each vibrational mode (where  $\hbar\omega_j$  is the vibrational energy of mode  $j$ ) to the classical harmonic oscillator potential energy at the zero-point displacement:

$$E_{j,0} = \frac{1}{2} \hbar\omega_j = \frac{1}{2} k_j x_{j,0}^2$$

This allows us to determine the effective force-constant  $k_j$  for each vibrational mode under the harmonic approximation and therefore define the displacement for arbitrary vibrational excitations (vibrational quantum number labelled  $n$ ) in terms of the zero-point displacement. Here, we define the zero-point displacement of each mode as  $x_{j,0} = \beta \frac{a_0}{\sqrt{\mu_j}}$  where  $\mu_j$  is the effective reduced mass of the vibrational mode from DFT calculations (Table S19),  $a_0$  is the Bohr radius and  $\beta$  is our scaling parameter on the order of unity.

$$E_{j,n} = \hbar\omega_j \left( \frac{1}{2} + n \right) = \frac{1}{2} k_j x_{j,n}^2 = \frac{\hbar\omega_j}{2x_{j,0}^2} x_{j,n}^2$$

$$x_{j,n} = \sqrt{2x_{j,0}^2 \left( \frac{1}{2} + n \right)} = x_{j,0} \sqrt{1 + 2n}$$

Under the gas-phase harmonic approximation, the vibrational modes are uncoupled harmonic oscillators whose populations  $p_{j,n}$  are given by the Boltzmann distribution (we arbitrarily define  $E_{j,0} = 0$  for each mode when performing Boltzmann statistics). Thus, at a given temperature we are able to calculate the population of each vibrational state of each mode and associate a thermally-averaged displacement with each mode  $\bar{x}_j$ .

$$p_{j,n} = \frac{e^{-\hbar\omega_j n/k_B T}}{\sum_{n=0}^{\infty} e^{-\hbar\omega_j n/k_B T}}$$

$$\bar{x}_j = \sum_{n=0}^{\infty} p_{j,n} x_{j,n}$$

We then perform a time-average calculation of the root-mean-square (RMS) atomic displacements by simulating the motion of each atom under the simultaneous influence of all vibrational modes. Here, we assume that all modes undergo sinusoidal harmonic oscillations with amplitudes given by their thermally averaged displacements  $\bar{x}_j$ , and frequencies as calibrated above with randomly chosen initial phases. Repeating this calculation for different initial random phases to obtain reliable statistics allows us to directly compare to the experimental thermal parameters obtained from X-ray diffraction – for this analysis we compare only the average RMS displacement of the cyclopentadienyl C atoms and the Dy atom. In order to give good agreement to experiment we find that  $\beta = 0.85$ , which yields an average RMS displacement of 0.148(2) Å *cf.* the experimental value of 0.150(5) Å at 150 K.

To simulate the spin dynamics we must solve the set of differential equations known as the Master equation<sup>18,42</sup>, expressing the change in population of each electronic state as a function of time (where  $\gamma_{fi}$  is the transition rate between electronic states  $i$  and  $f$ , and we only consider states in the  $J = 15/2$  basis of the ground  ${}^6\text{H}_{15/2}$  term of dysprosium(III)):

$$\frac{d}{dt}p_i(t) = \sum_{f \neq i} [\gamma_{if}p_f(t) - \gamma_{fi}p_i(t)]$$

We define the vibrationally-induced transition rate between two electronic states for a single phonon process (the direct process) below. Here, we assume the electronic and nuclear dynamics are independent (Born-Oppenheimer approximation) and that the vibrations give rise

to a harmonic perturbation to the equilibrium electronic states resulting in non-adiabatic transitions ( $\varepsilon_j$  is the strain of a given mode and conservation of energy implies  $|E_f - E_i| = \hbar\omega$ )<sup>18,43,44</sup>.

$$\text{Phonon absorption:} \quad \gamma_{fi} = \frac{2\pi}{\hbar} \sum_j \left[ |\langle f | \hat{H}_j | i \rangle|^2 |\langle n_j - 1 | \varepsilon_j | n_j \rangle|^2 \delta(|E_f - E_i| - \hbar\omega) \rho_j(\hbar\omega) \right]$$

$$\text{Phonon emission:} \quad \gamma_{if} = \frac{2\pi}{\hbar} \sum_j \left[ |\langle i | \hat{H}_j | f \rangle|^2 |\langle n_j + 1 | \varepsilon_j | n_j \rangle|^2 \delta(|E_i - E_f| - \hbar\omega) \rho_j(\hbar\omega) \right]$$

Usually when considering solid-state phonons, these expressions must be integrated over the phonon wavevector, however as we are under the gas-phase approximation we ignore this integration; this is tantamount to assuming that there is no dispersion of the optical phonon modes with wavevector and that the gamma-point normal modes are consistent throughout reciprocal space. Furthermore, the acoustic phonon modes are undefined in the gas-phase and thus they are also ignored. For solid-state calculations, the matrix elements of phonon strain are usually related to their average values from Bose-Einstein statistics<sup>18,43,45</sup>:

$$|\langle n_j - 1 | \varepsilon_j | n_j \rangle|^2 \propto \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

$$|\langle n_j + 1 | \varepsilon_j | n_j \rangle|^2 \propto \frac{1}{1 - e^{-\hbar\omega/k_B T}}$$

However, as we are working under the gas-phase approximation, we prefer to define these matrix elements as the probability of being able to lose a vibrational quantum, and the probability of being able to gain a vibrational quantum, respectively. The probability of being able to lose a vibrational quantum is equal to the probability of being in a vibrationally excited state (i.e.  $n \geq 1$ ), and under the harmonic approximation an oscillator can always gain a vibrational quantum; thus, employing the Boltzman populations given above, we define:

$$|\langle n_j - 1 | \varepsilon_j | n_j \rangle|^2 = \frac{\sum_{n=1}^{\infty} e^{-\hbar\omega n/k_B T}}{\sum_{n=0}^{\infty} e^{-\hbar\omega n/k_B T}} = e^{-\hbar\omega/k_B T}$$

$$|\langle n_j + 1 | \varepsilon_j | n_j \rangle|^2 = 1$$

Indeed, employing either the Bose-Einstein or Boltzmann definitions results in the ratio of the forward and backwards rates between any two states obeying the detailed balance criterion below<sup>18</sup> (note  $|\langle f | \hat{H}_j | i \rangle|^2 = |\langle i | \hat{H}_j | f \rangle|^2$ ), and, importantly, using either convention in our calculations yields exactly the same simulation of the spin dynamics (Figs. 4a, S65 and S67).

$$\frac{\gamma_{fi}}{\gamma_{if}} = e^{-\hbar\omega/k_B T}$$

The delta-function in the definitions of  $\gamma_{fi}$  and  $\gamma_{if}$  implies the energy of the vibrational mode must equal the energy difference between the two electronic states involved in the transition; this simply expresses conservation of energy. Under the gas-phase approximation we have a discrete vibrational spectrum and thus it is highly unlikely we will have *exactly* the correct vibrational energies to make electronic transitions. Therefore, we assume that the vibrational density of states for each mode  $\rho_j(\hbar\omega)$  is given by a Gaussian-convoluted spectrum around the discrete vibrational energies – that is, we allow slightly anharmonic vibrational energies with a Gaussian density of states. In doing so we introduce a rather arbitrary linewidth parameter,  $\sigma$ , however we note that it can only lie within a certain range. If  $\sigma$  is too small then the Gaussian function approaches a delta function and therefore no relaxation dynamics are observed, however very large values would imply a continuously flat vibrational spectrum, in contrast to that observed for this molecular species. Examining the vibrational transitions in the IR and Raman spectra that arise from  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  (Fig. S63), we observe that the full-width-half-maximum linewidth is ca.  $20 \text{ cm}^{-1}$ ; this corresponds to  $\sigma \sim 10 \text{ cm}^{-1}$ .

$$\rho_j(\hbar\omega) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{\hbar\omega - \hbar\omega_j}{\sigma}\right)^2}$$

To calculate the electronic spin-phonon coupling elements  $\langle f|\hat{H}_j|i\rangle$ , we adopt the non-adiabatic or “quench” regime where transitions between eigenstates of the equilibrium Hamiltonian are caused by a periodic perturbing Hamiltonian. We define our equilibrium Hamiltonian, of which  $|i\rangle$  and  $|f\rangle$  are eigenstates (where  $B_{k_0}^q$  are the equilibrium CF parameters (CFPs),  $\theta_k$  are the operator equivalent factors,  $\theta_2 = -2/315$ ,  $\theta_4 = -8/135135$  and  $\theta_6 = 4/3864861$ , and  $\hat{O}_k^q$  are the extended Steven’s operator equivalents<sup>46</sup>) as:

$$\hat{H}_0 = \sum_{k=2,4,6} \sum_{q=-k}^k B_{k_0}^q \theta_k \hat{O}_k^q$$

To determine the equilibrium CFPs, we employ a very similar CASSCF-SO method to that used on the static molecules above. We employ basis sets from the ANO-RCC library<sup>27,28</sup> of VTZP quality for Dy, VDZP quality for the cyclopentadienyl C atoms, and VDZ quality for all remaining atoms, employing the second-order DKH transformation. Cholesky decomposition of the two-electron integrals with a threshold of  $10^{-4}$  was performed to save disk space and reduce computational demand. The molecular orbitals (MOs) were optimised in state-averaged CASSCF calculations, where the active space was defined by the nine 4f electrons in the seven 4f orbitals of Dy(III) and only the 21  $S = 5/2$  states were considered. The wavefunction was then mixed by spin orbit coupling where all 21  $S = 5/2$  states were included. The resulting spin orbit wavefunctions were decomposed into CFPs using SINGLE\_ANISO<sup>29</sup> with a fixed reference frame. Comparing the results of this modified CASSCF-SO method with the original one on the DFT optimised geometry of  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  (Table S20 *cf.* Table S18), we see virtually no difference



in the two sets of results, giving us confidence that our spin dynamics CASSCF-SO calculations provide accurate descriptions of the electronic structure of  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$ .

**Table S20.** Electronic structure of  $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$  calculated with CASSCF-SO (smaller basis sets, only sextets, lower Cholesky threshold) using DFT optimised geometry (Table S17).

| Energy ( $\text{cm}^{-1}$ ) | Energy (K) | $g_x$ | $g_y$ | $g_z$ | $g_z$ angle (degrees) | Wavefunction                                                                                                                                                                                                                |
|-----------------------------|------------|-------|-------|-------|-----------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 0.0                         | 0.0        | 0.00  | 0.00  | 19.99 | -                     | 99.5% $ \pm 15/2\rangle$<br>+ 0.3% $ \pm 13/2\rangle$<br>+ 0.3% $ \pm 11/2\rangle$                                                                                                                                          |
| 457.6                       | 658.3      | 0.00  | 0.00  | 17.08 | 1.72                  | 99.4% $ \pm 13/2\rangle$<br>+ 0.2% $ \pm 15/2\rangle$<br>+ 0.2% $ \pm 11/2\rangle$<br>+ 0.1% $ \pm 9/2\rangle$                                                                                                              |
| 725.1                       | 1043.3     | 0.00  | 0.00  | 14.45 | 3.19                  | 99.3% $ \pm 11/2\rangle$<br>+ 0.3% $ \pm 15/2\rangle$<br>+ 0.2% $ \pm 7/2\rangle$<br>+ 0.1% $ \pm 13/2\rangle$                                                                                                              |
| 898.4                       | 1292.6     | 0.01  | 0.01  | 11.79 | 2.84                  | 98.9% $ \pm 9/2\rangle$<br>+ 0.7% $ \pm 5/2\rangle$<br>+ 0.2% $ \pm 7/2\rangle$<br>+ 0.1% $ \pm 13/2\rangle$<br>+ 0.1% $ \pm 3/2\rangle$                                                                                    |
| 1056.2                      | 1519.7     | 0.00  | 0.01  | 9.12  | 3.93                  | 98.4% $ \pm 7/2\rangle$<br>+ 0.7% $ \pm 5/2\rangle$<br>+ 0.3% $ \pm 3/2\rangle$<br>+ 0.2% $ \pm 11/2\rangle$<br>+ 0.2% $ \pm 9/2\rangle$<br>+ 0.1% $ \pm 1/2\rangle$                                                        |
| 1205.7                      | 1734.8     | 0.92  | 1.05  | 6.44  | 2.19                  | 96.8% $ \pm 5/2\rangle$<br>+ 1.2% $ \pm 5/2\rangle$<br>+ 0.8% $ \pm 7/2\rangle$<br>+ 0.7% $ \pm 9/2\rangle$<br>+ 0.2% $ \mp 3/2\rangle$<br>+ 0.1% $ \mp 5/2\rangle$<br>+ 0.1% $ \mp 1/2\rangle$<br>+ 0.1% $ \pm 1/2\rangle$ |
| 1320.7                      | 1900.2     | 3.36  | 4.30  | 7.46  | 90.00                 | 72.8% $ \pm 3/2\rangle$<br>+ 15.8% $ \mp 3/2\rangle$<br>+ 9.9% $ \mp 1/2\rangle$<br>+ 0.6% $ \mp 5/2\rangle$<br>+ 0.5% $ \pm 5/2\rangle$<br>+ 0.2% $ \pm 7/2\rangle$<br>+ 0.1% $ \mp 7/2\rangle$                            |

|        |        |      |      |       |       |                                                                                                                                                                                                 |
|--------|--------|------|------|-------|-------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1404.8 | 2021.2 | 0.86 | 4.20 | 15.74 | 89.62 | 88.2% $ \pm 1/2\rangle$<br>+ 6.2% $ \mp 3/2\rangle$<br>+ 3.4% $ \pm 3/2\rangle$<br>+ 1.6% $ \mp 1/2\rangle$<br>+ 0.3% $ \pm 5/2\rangle$<br>+ 0.3% $ \mp 5/2\rangle$<br>+ 0.1% $ \pm 7/2\rangle$ |
|--------|--------|------|------|-------|-------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**Table S21.** Equilibrium crystal field parameters for  $[\text{Dy}(\text{Cp}^{\text{ttb}})_2]^+$ .

| CFP           | Value ( $\text{cm}^{-1}$ ) |
|---------------|----------------------------|
| $B_{20}^{-2}$ | 0.0                        |
| $B_{20}^{-1}$ | 0.0                        |
| $B_{20}^0$    | 1226.9                     |
| $B_{20}^1$    | -124.4                     |
| $B_{20}^2$    | -5.2                       |
| $B_{40}^{-4}$ | 0.0                        |
| $B_{40}^{-3}$ | 0.1                        |
| $B_{40}^{-2}$ | 0.0                        |
| $B_{40}^{-1}$ | 0.0                        |
| $B_{40}^0$    | 31.2                       |
| $B_{40}^1$    | -11.3                      |
| $B_{40}^2$    | -40.5                      |
| $B_{40}^3$    | -123.5                     |
| $B_{40}^4$    | 42.1                       |
| $B_{60}^{-6}$ | 0.0                        |
| $B_{60}^{-5}$ | 0.1                        |
| $B_{60}^{-4}$ | 0.0                        |
| $B_{60}^{-3}$ | 0.1                        |
| $B_{60}^{-2}$ | -0.1                       |
| $B_{60}^{-1}$ | 0.0                        |
| $B_{60}^0$    | -36.0                      |
| $B_{60}^1$    | 108.9                      |

|            |        |
|------------|--------|
| $B_{60}^2$ | 198.3  |
| $B_{60}^3$ | -141.1 |
| $B_{60}^4$ | -86.0  |
| $B_{60}^5$ | -23.8  |
| $B_{60}^6$ | -5.2   |

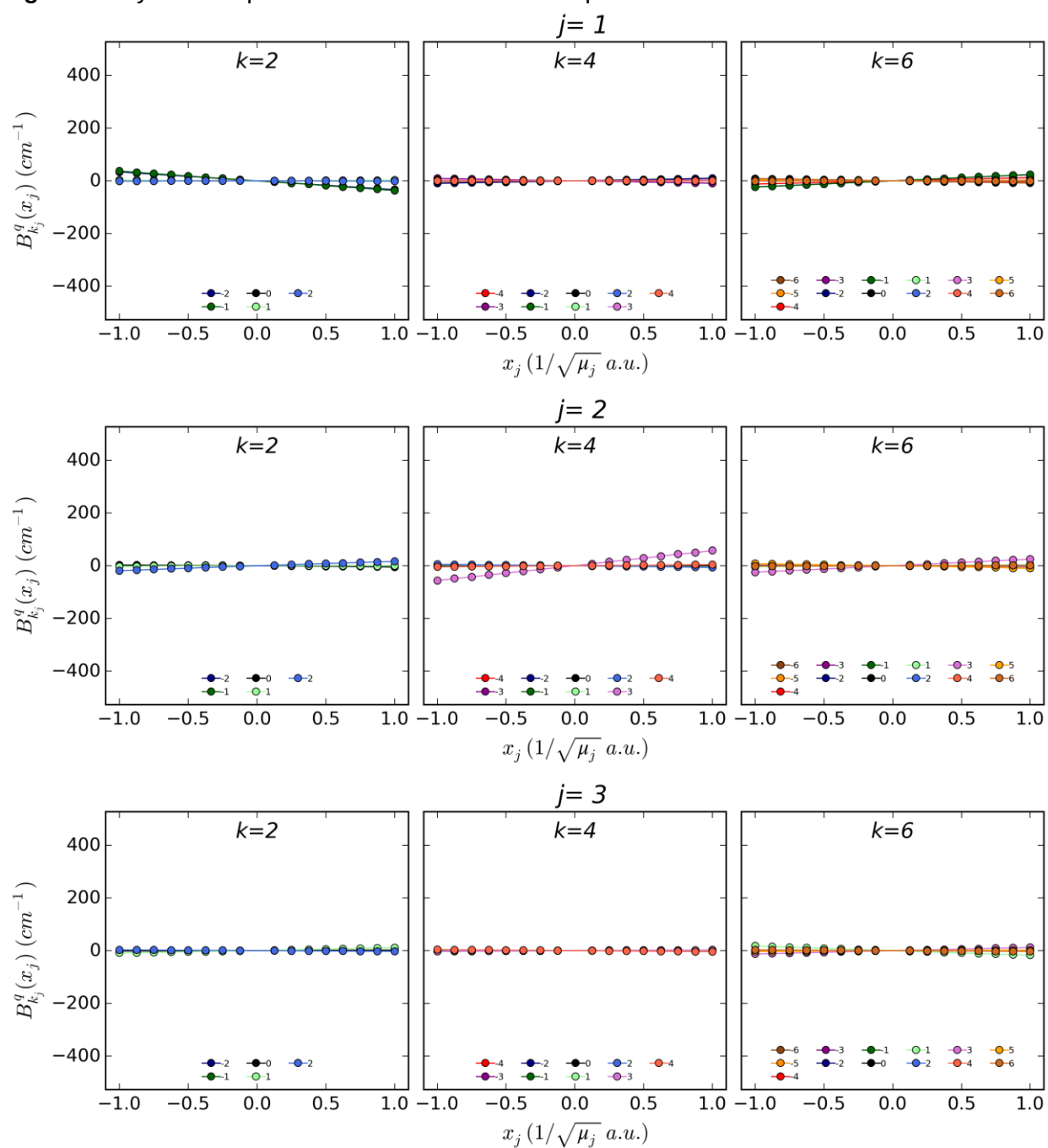
We then define the perturbation to the electronic structure from each vibrational mode, where the CFPs for each mode  $B_{kj}^q(x_j)$  are functions of the atomic displacement and give the changes from the equilibrium CFPs (i.e.  $B_{kj}^q(0) = 0$  for all  $j$ ,  $k$  and  $q$ ). Here, we define the atomic displacements to be harmonic in time:  $x_j(t) = \bar{x}_j \sin(\omega_j t)$ .

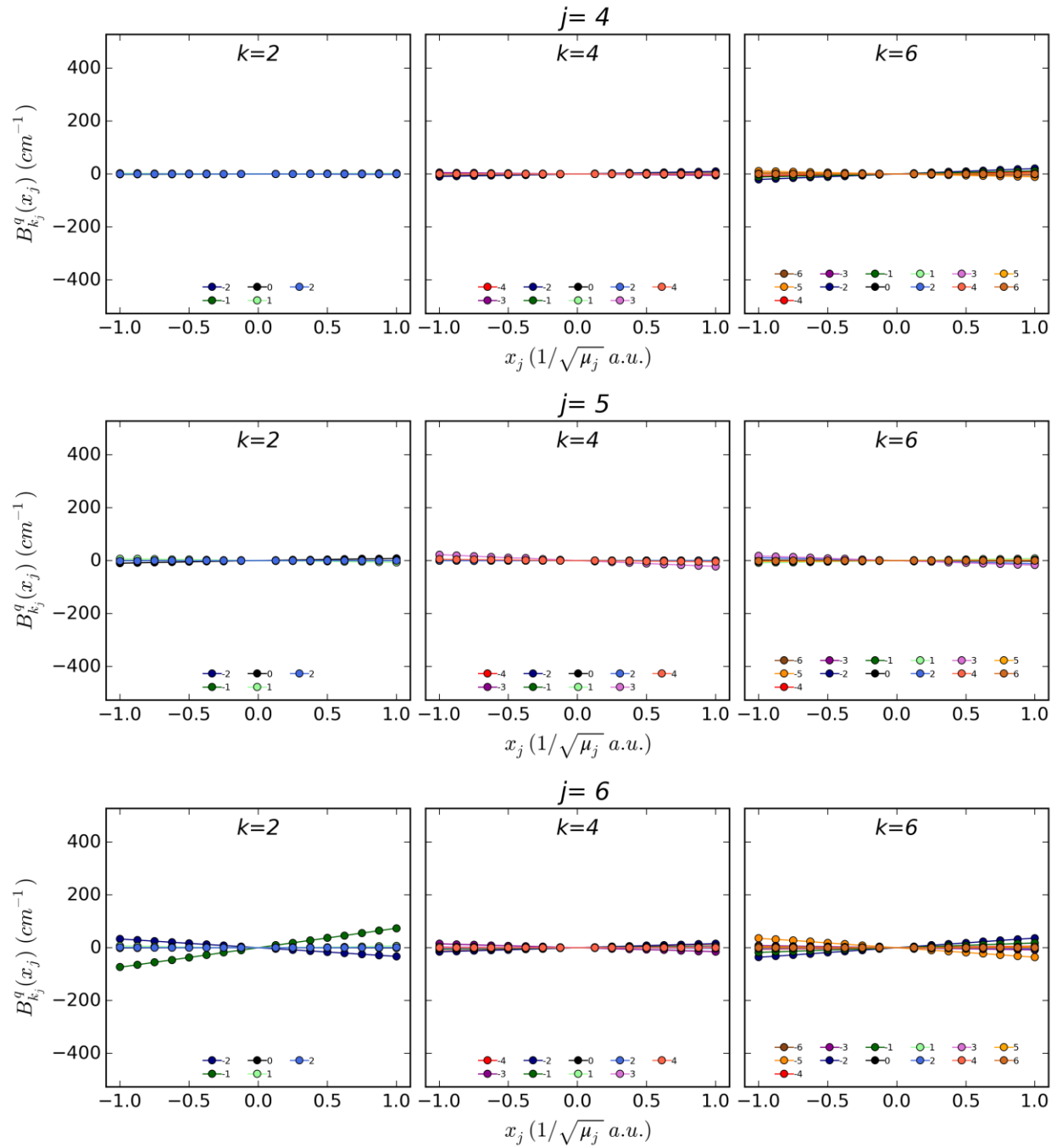
$$\hat{H}_j(x_j) = \sum_{k=2,4,6} \sum_{q=-k}^k B_{kj}^q(x_j) \theta_k \hat{O}_k^q$$

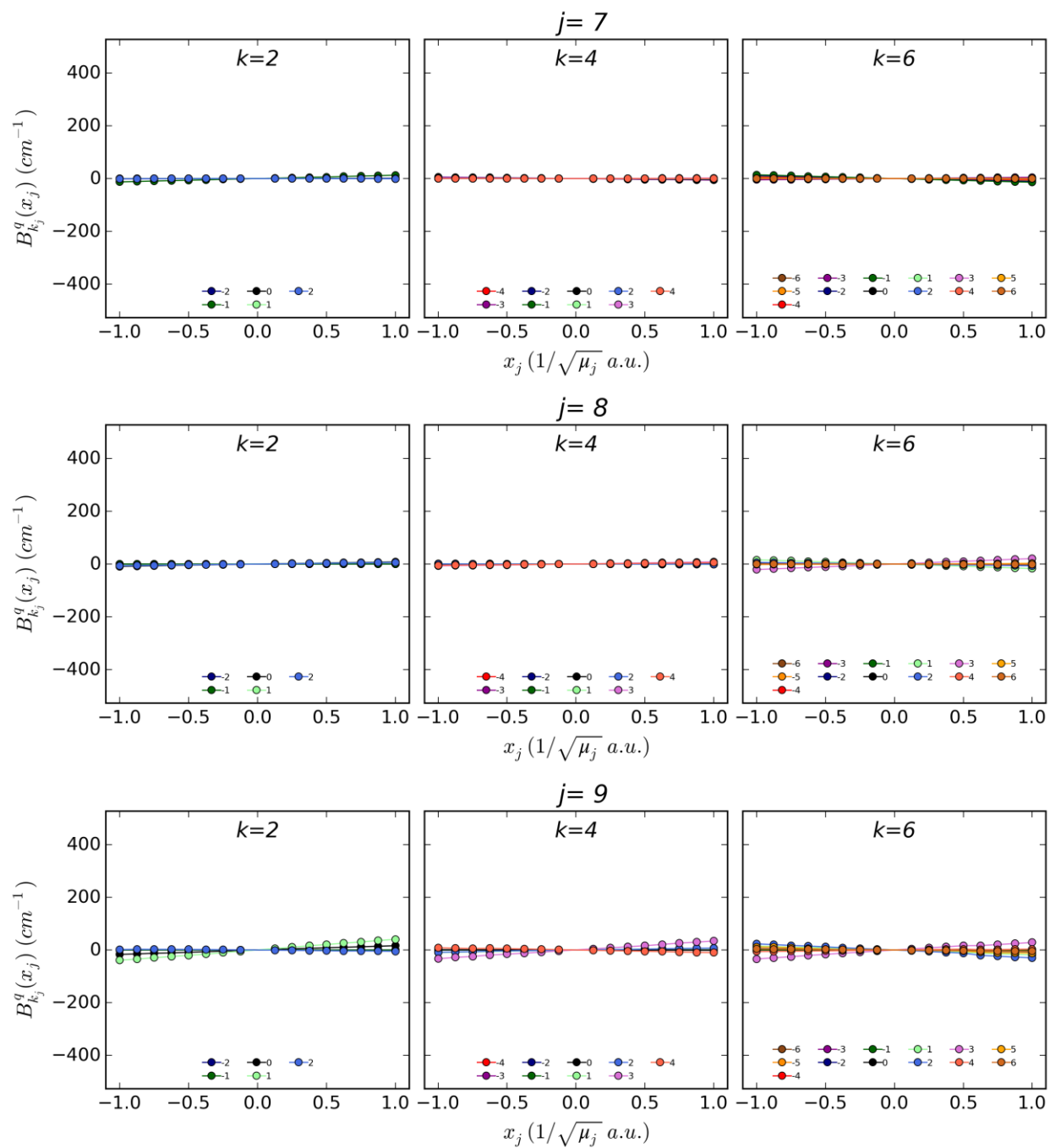
We have performed CASSCF-SO calculations for each of the 273 vibrational modes on molecular geometries distorted from the optimised equilibrium geometry along the relevant normal mode vector, in both positive and negative directions. For each calculation we have extracted the total CFPs and subtracted the equilibrium values to yield the  $B_{kj}^q(x_j)$  (Fig. S64); note that  $\bar{x}_j$  is dominated by the zero-point displacement and thus atomic displacements for each mode are on the order of  $\sim \pm 0.5 \frac{1}{\sqrt{\mu_j}}$  at temperatures of interest. We observe that most CFPs exhibiting the largest changes for each mode have a linear dependence on displacement, but some are markedly nonlinear (e.g. modes 82 – 84, 153, and 214 – 219). However, calculation of the overall matrix elements of  $\hat{H}_j(\pm \bar{x}_j)$  with PHI<sup>46</sup> reveals that the matrix elements for the positive and negative displacements have approximately equal magnitude but are  $\sim \pm \pi$  radians out of phase with one another: thus, despite some non-linear CFPs, the matrix elements

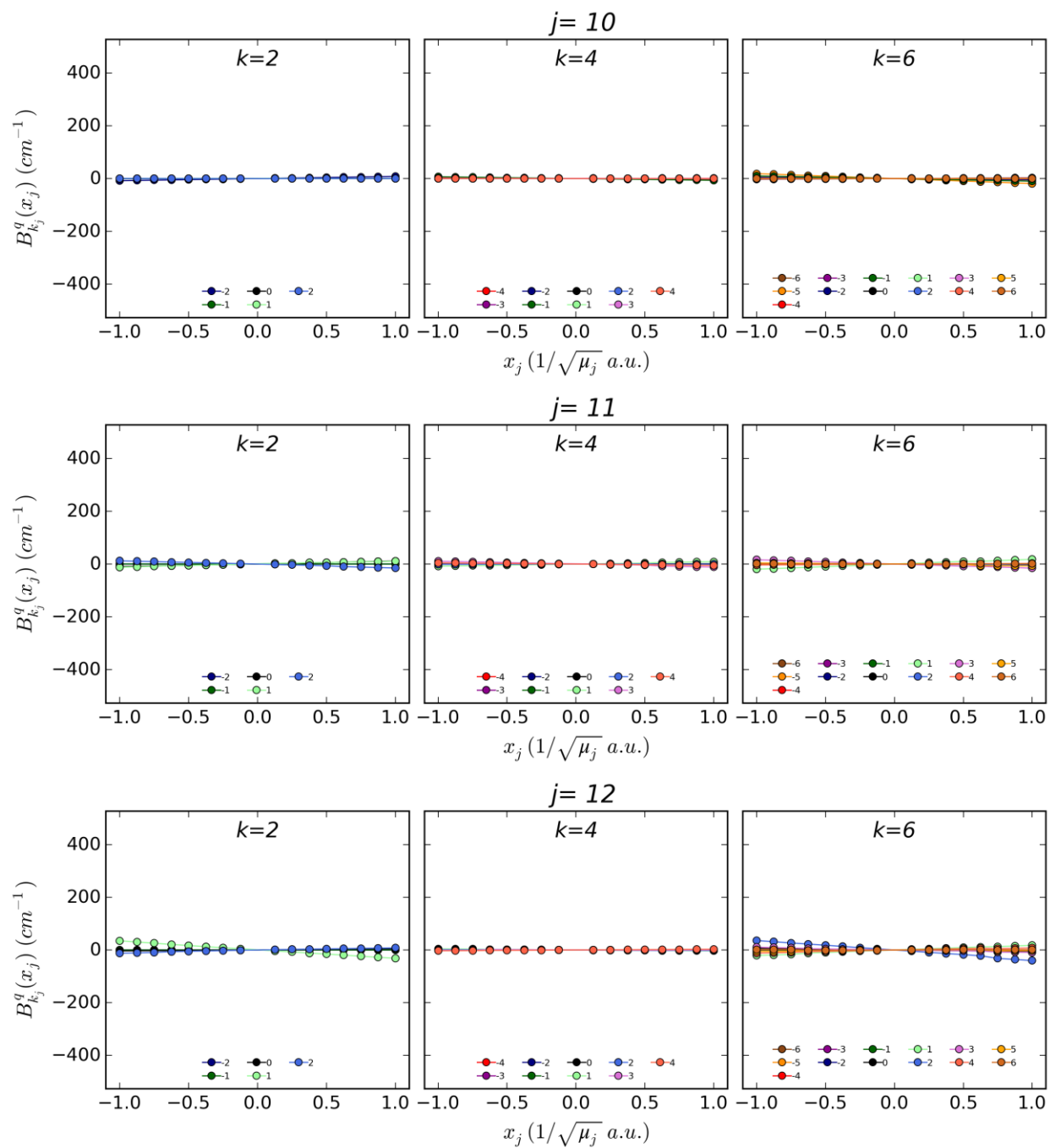
themselves oscillate harmonically with complex phase. As we take the square magnitude of these matrix elements in the expressions for  $\gamma_{fi}$  and  $\gamma_{if}$ , the phase is inconsequential and therefore we average the magnitude of the positive and negative matrix elements, and arbitrarily adopt the phase of the positive elements. Thus we define the electronic spin-phonon coupling elements at the thermally averaged displacement at 150 K as:

$$\langle f | \hat{H}_j | i \rangle = \frac{|\langle f | \hat{H}_j(+\bar{x}_j) | i \rangle| + |\langle f | \hat{H}_j(-\bar{x}_j) | i \rangle|}{2} e^{i \tan^{-1} \left( \frac{\text{Im}[\langle f | \hat{H}_j(+\bar{x}_j) | i \rangle]}{\text{Re}[\langle f | \hat{H}_j(+\bar{x}_j) | i \rangle]} \right)}$$

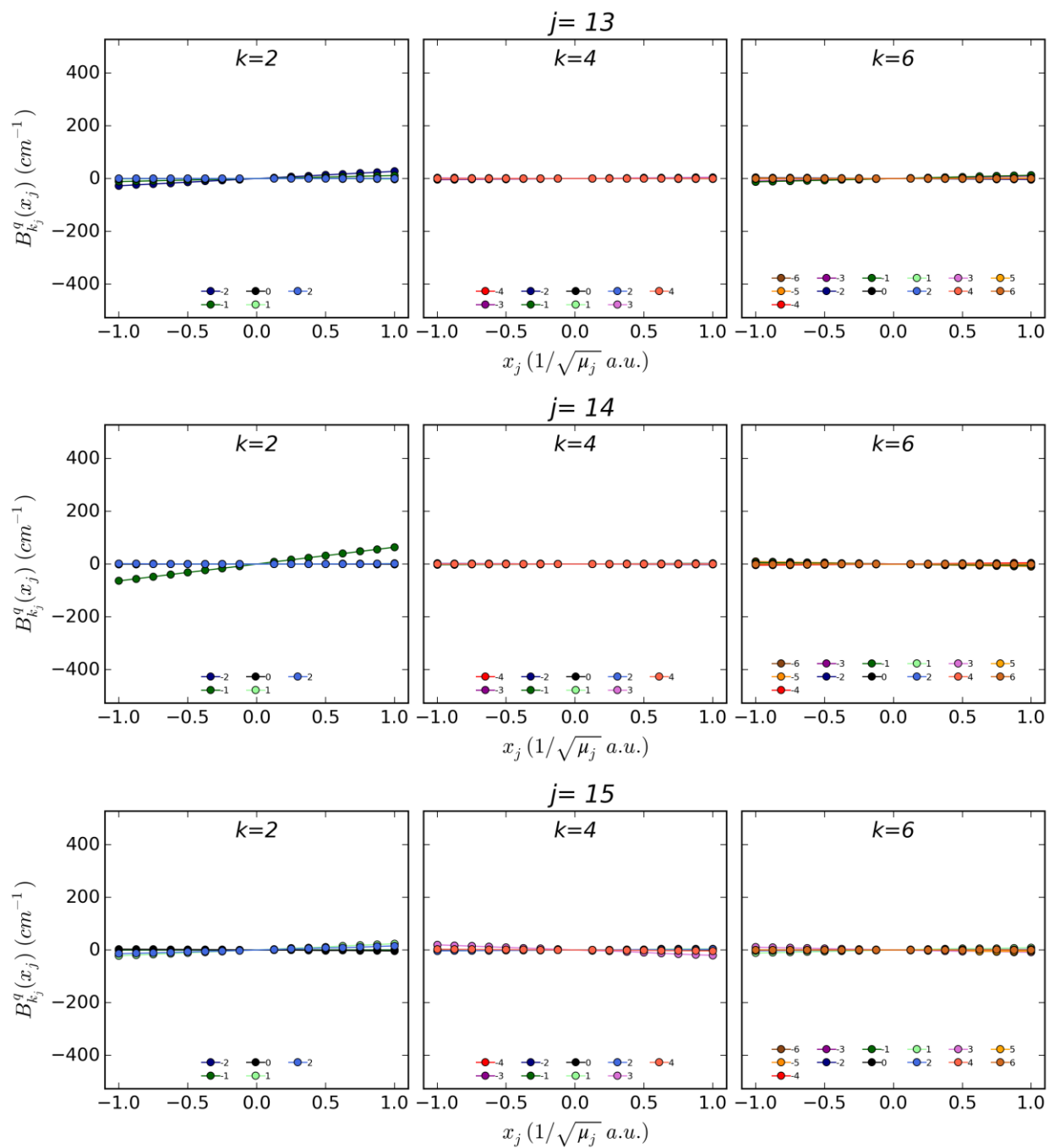
**Fig. S64.** Crystal field parameters as a function of displacement for all 273 vibrational modes.

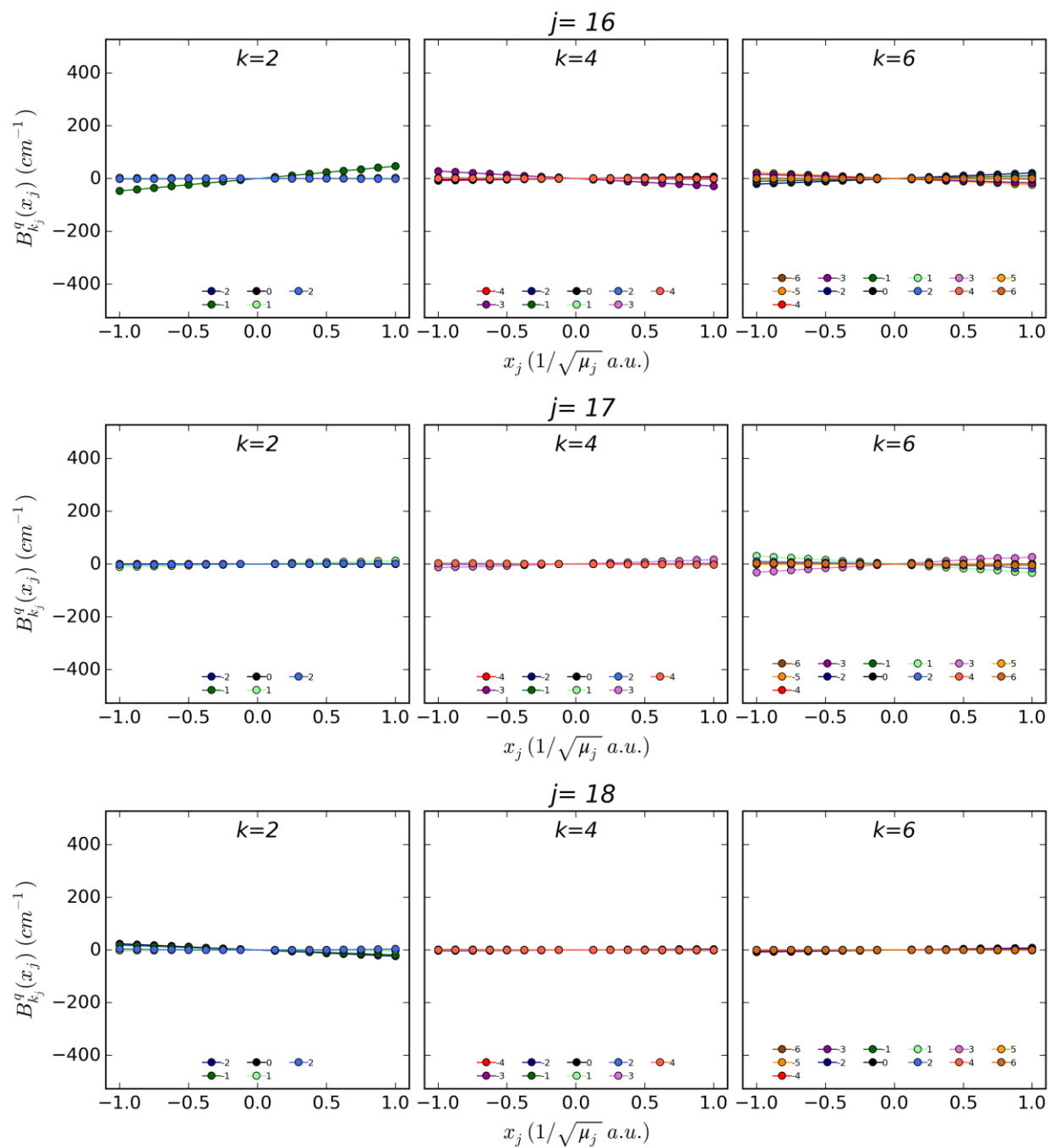


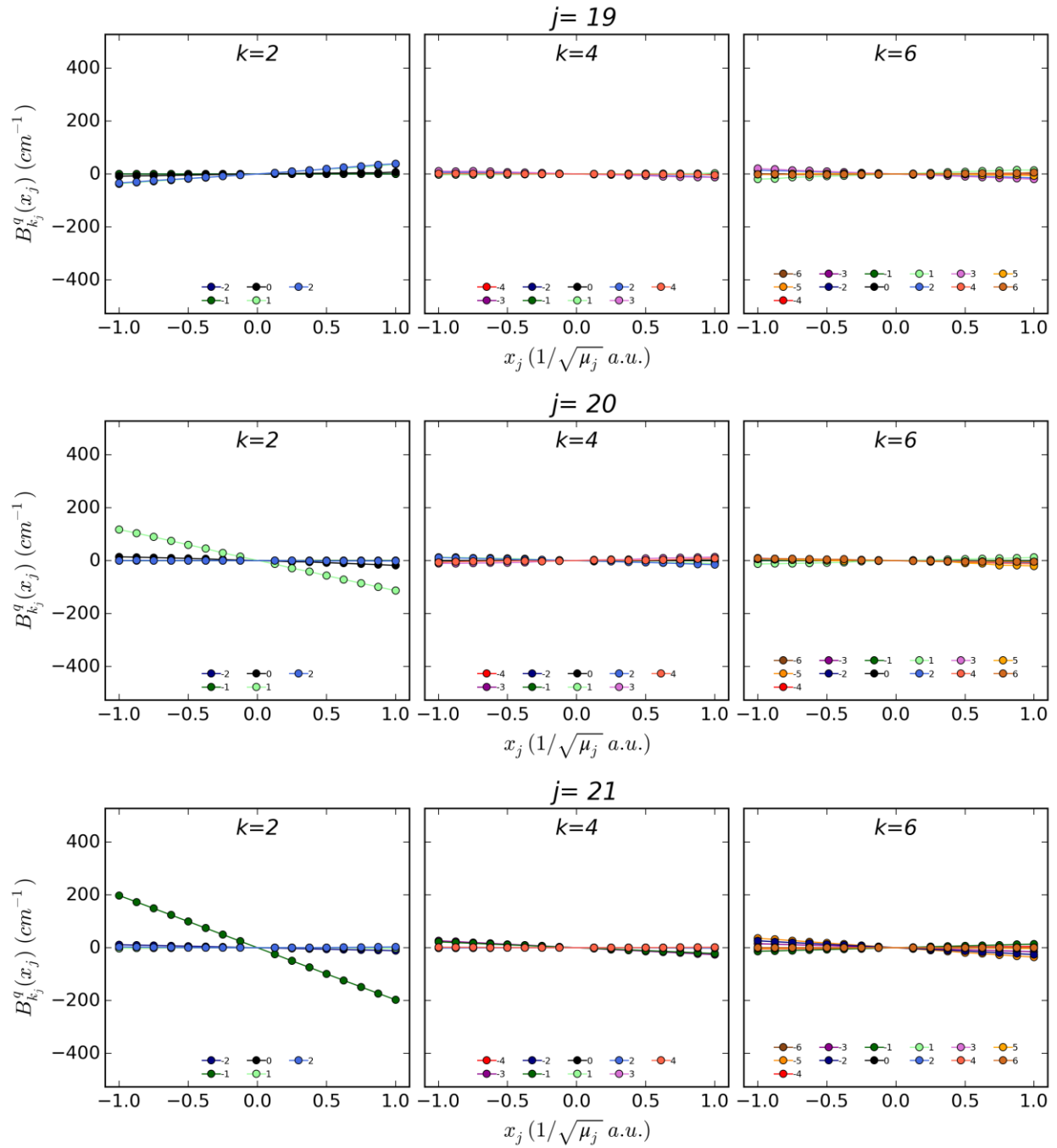


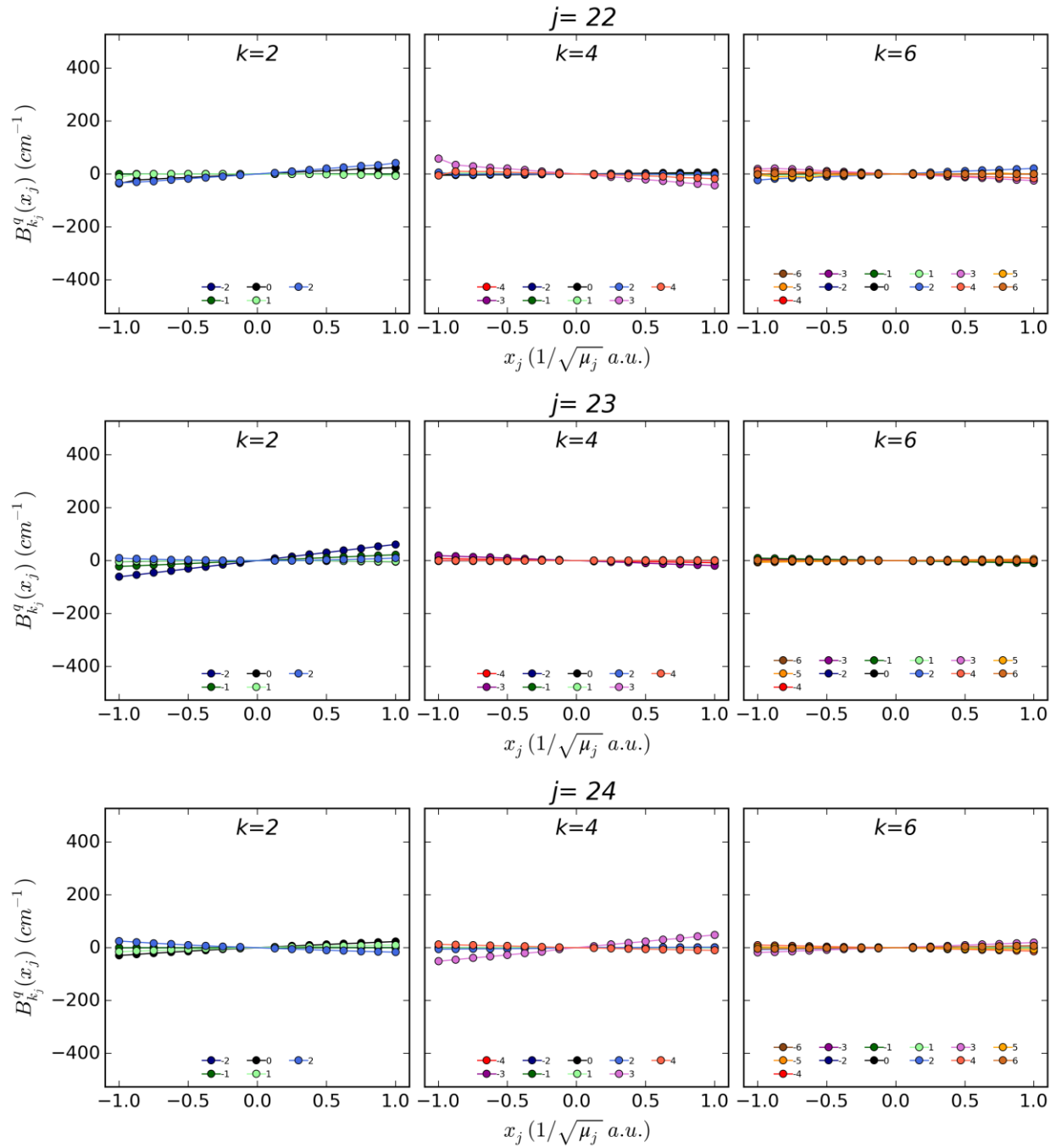


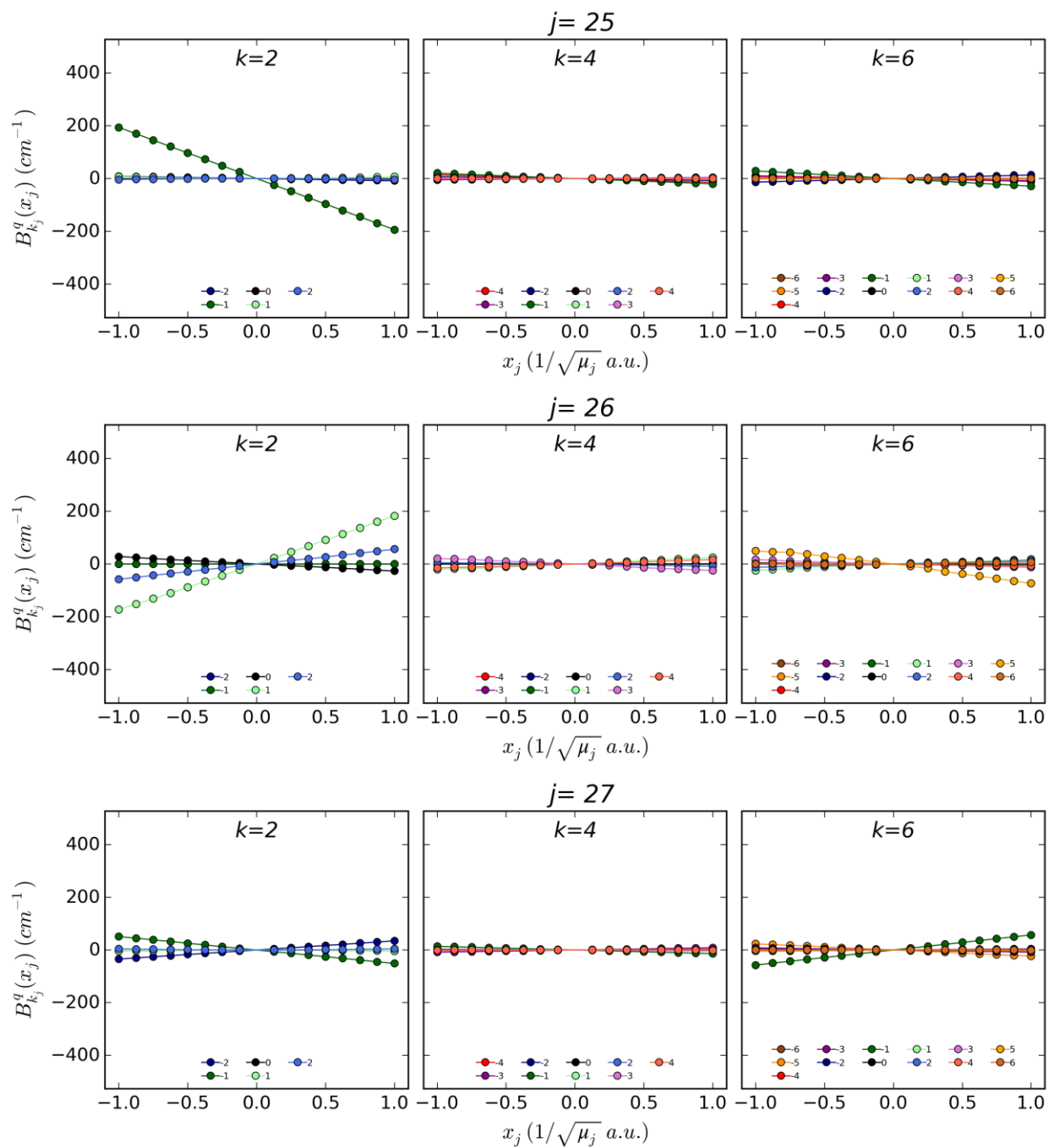


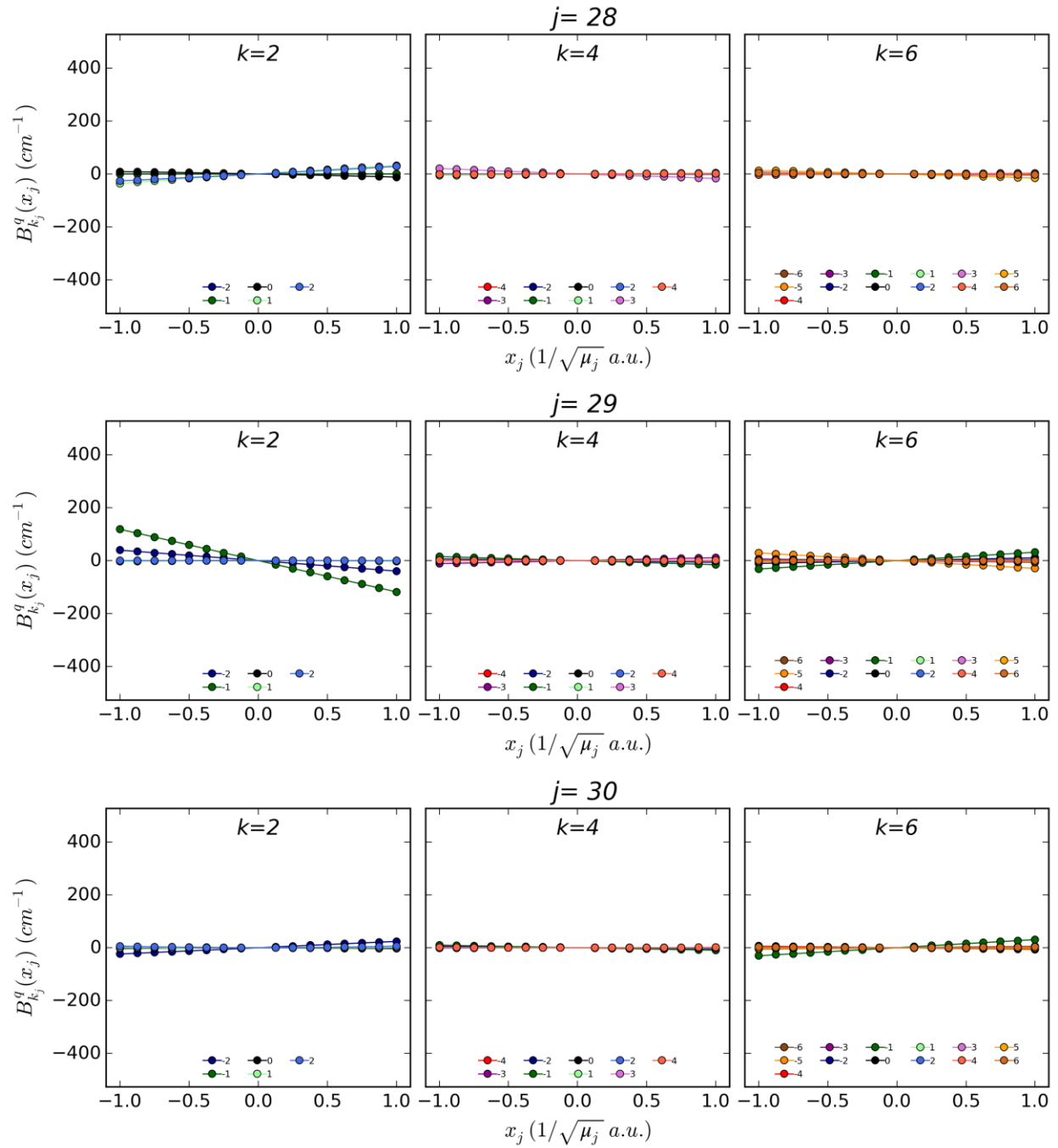


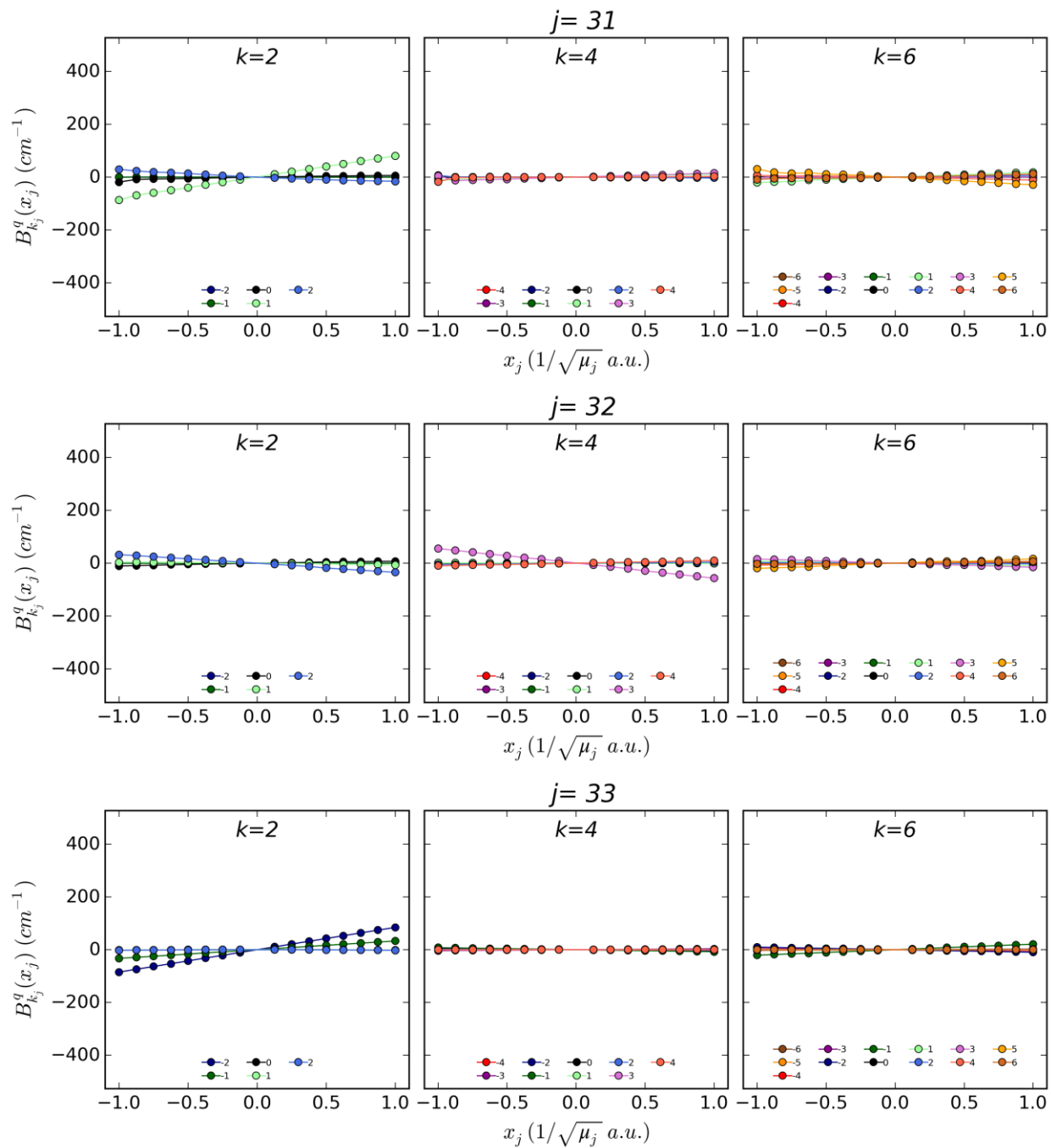


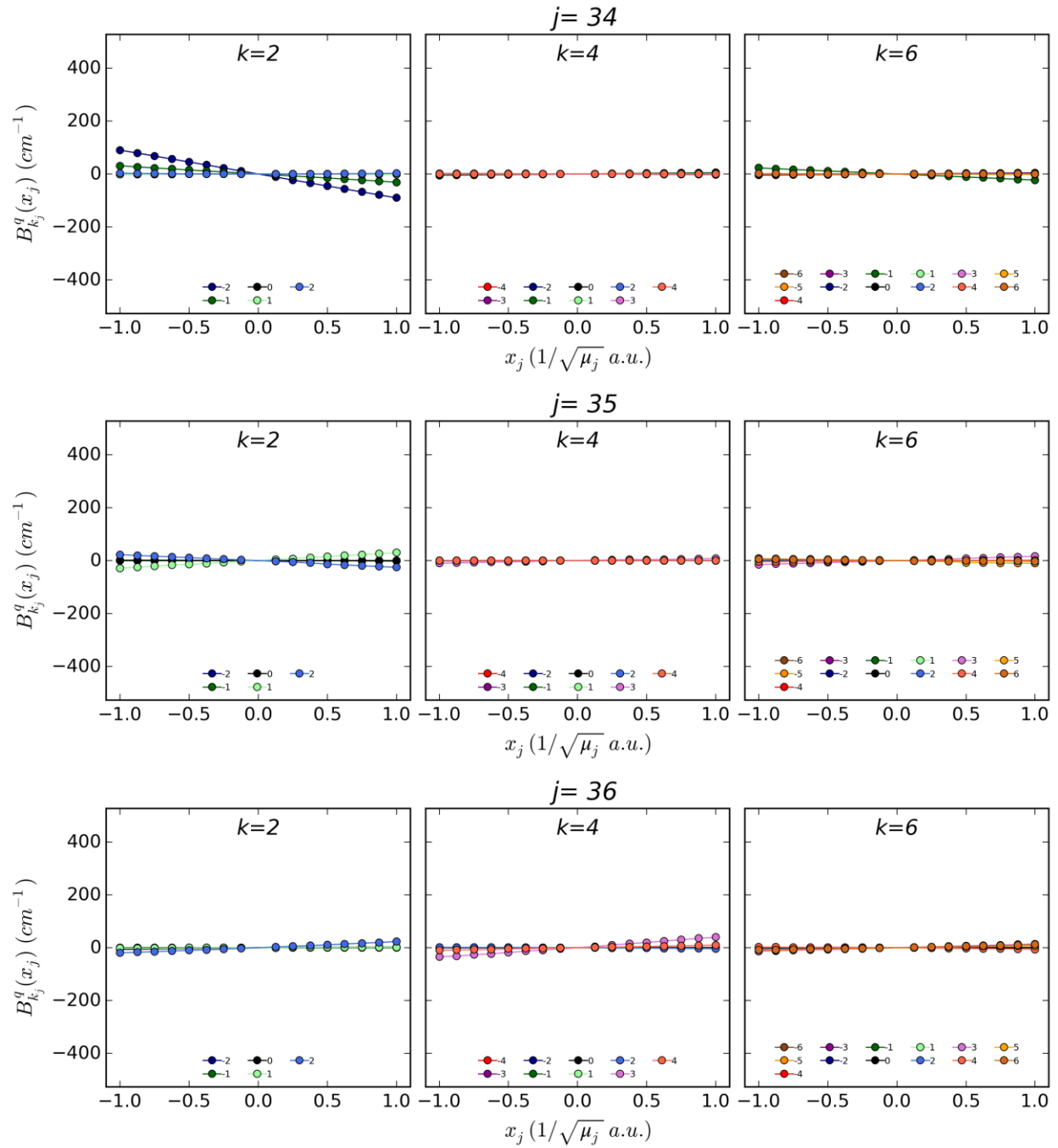




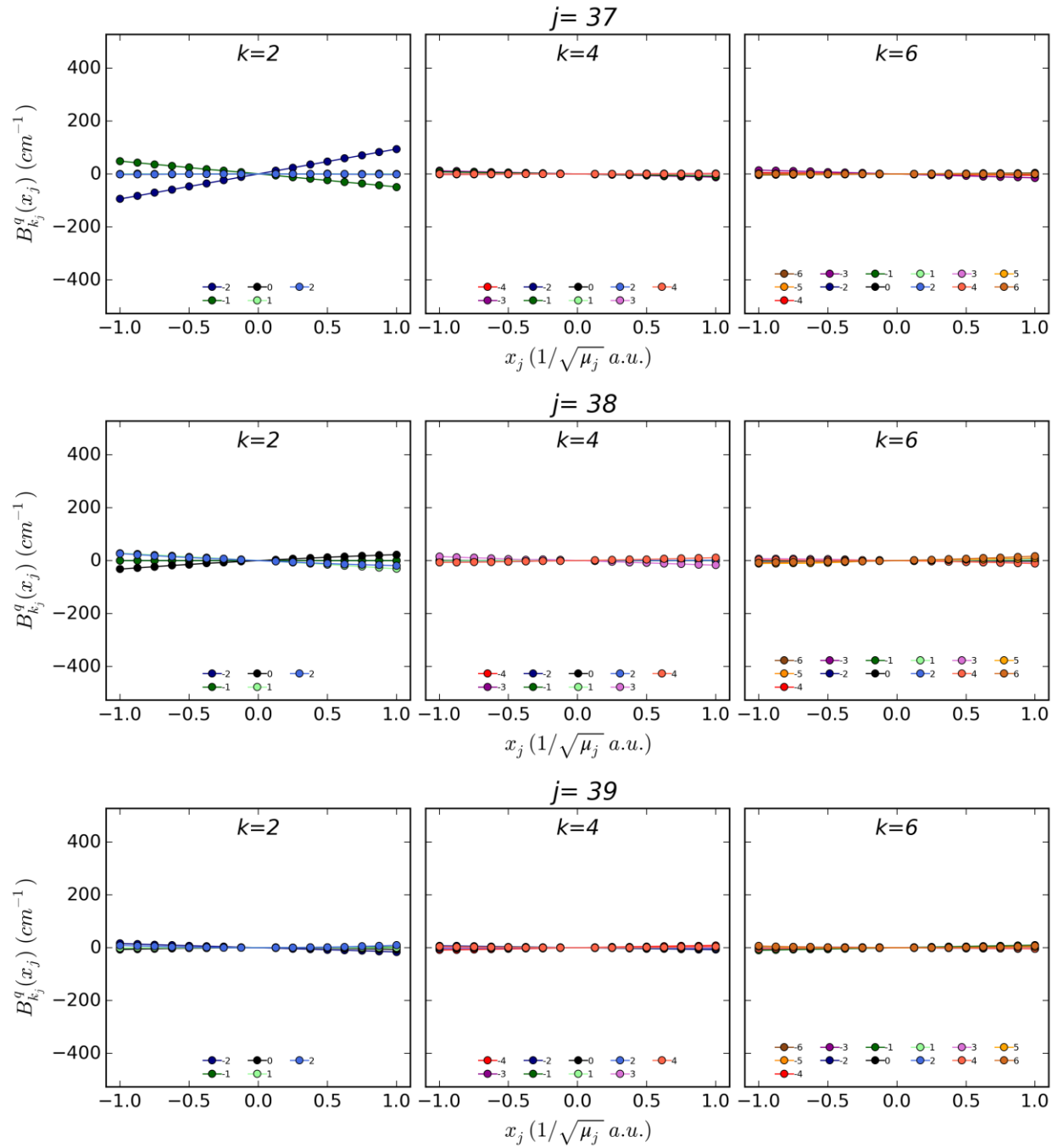


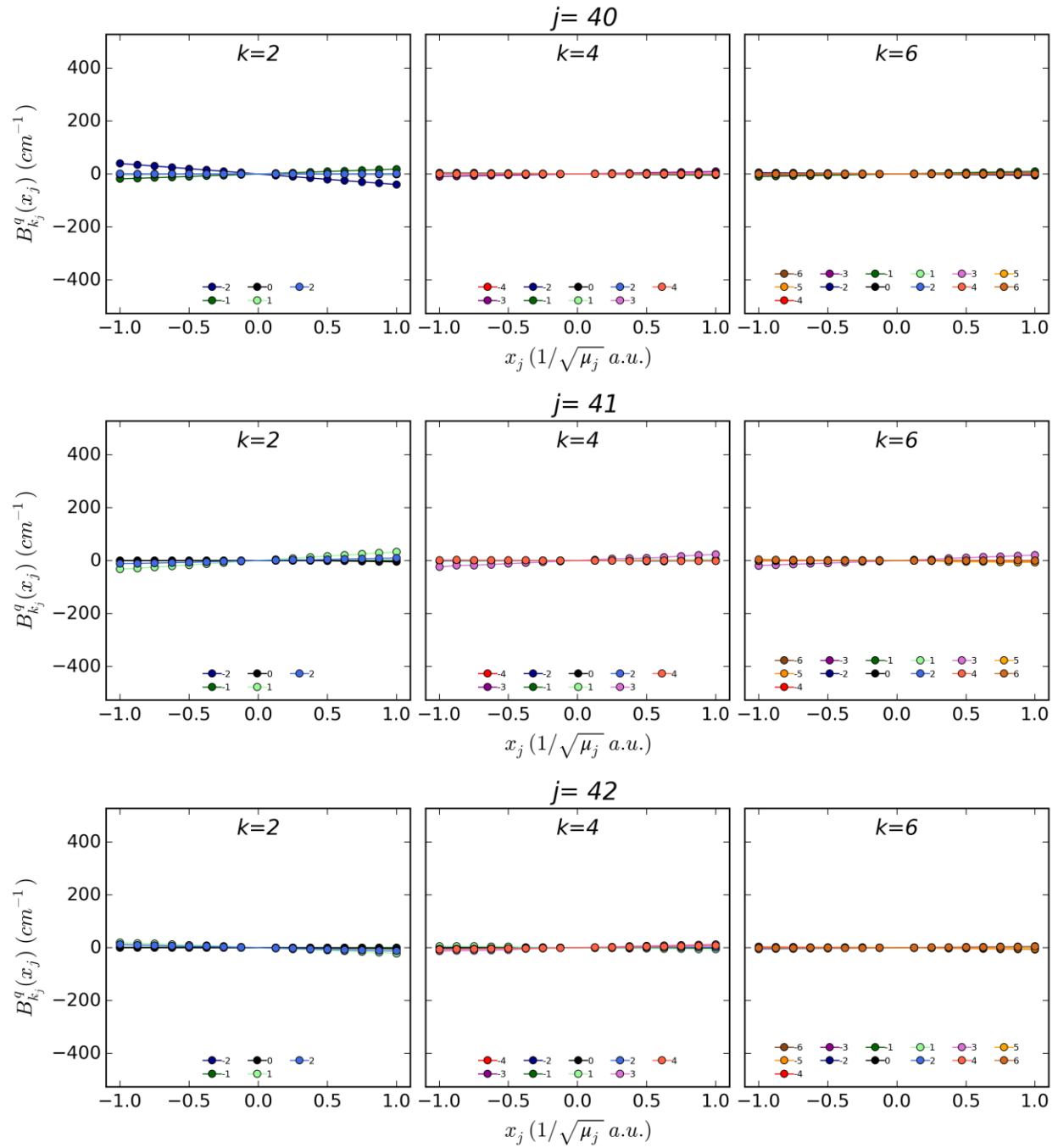


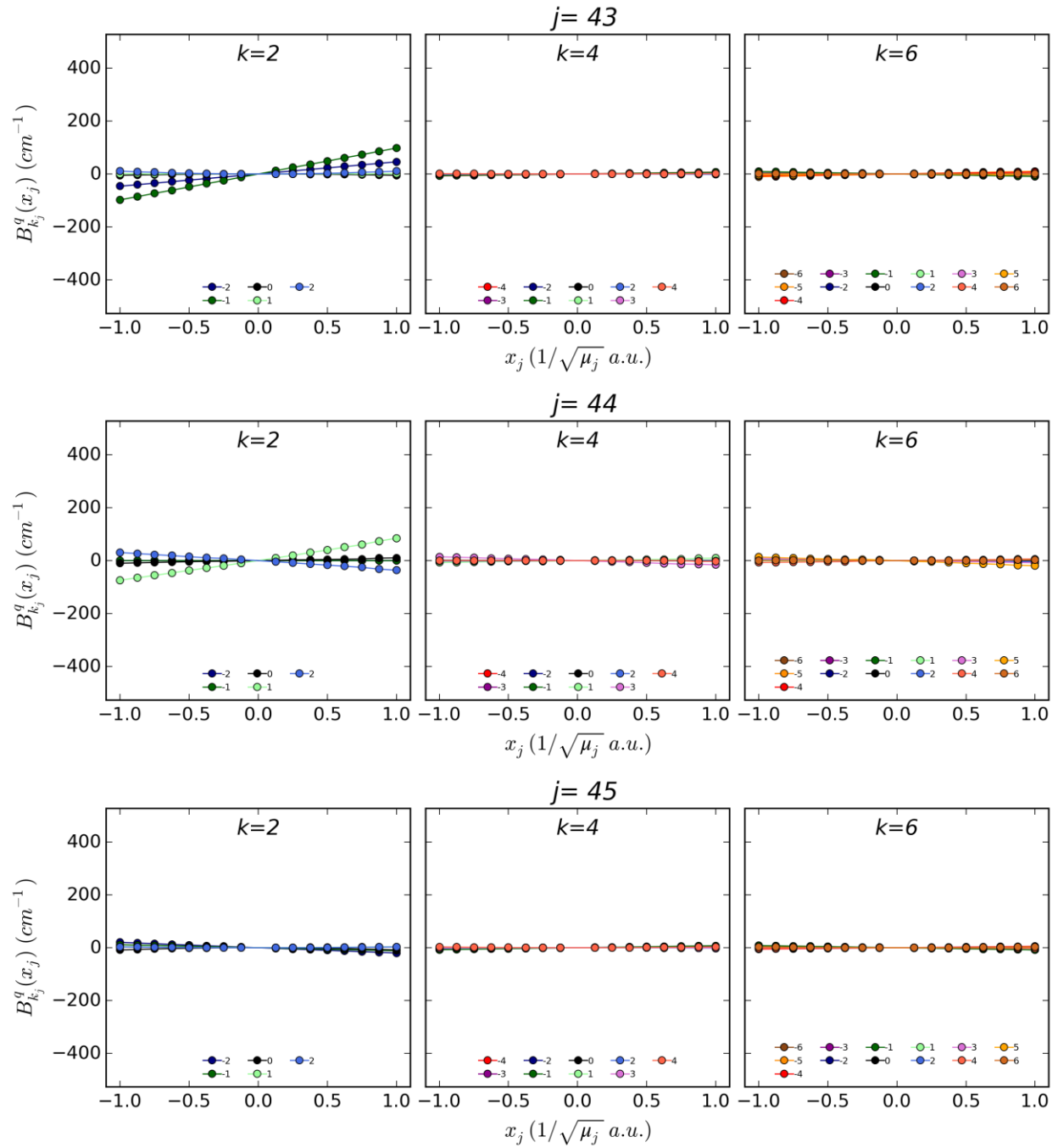


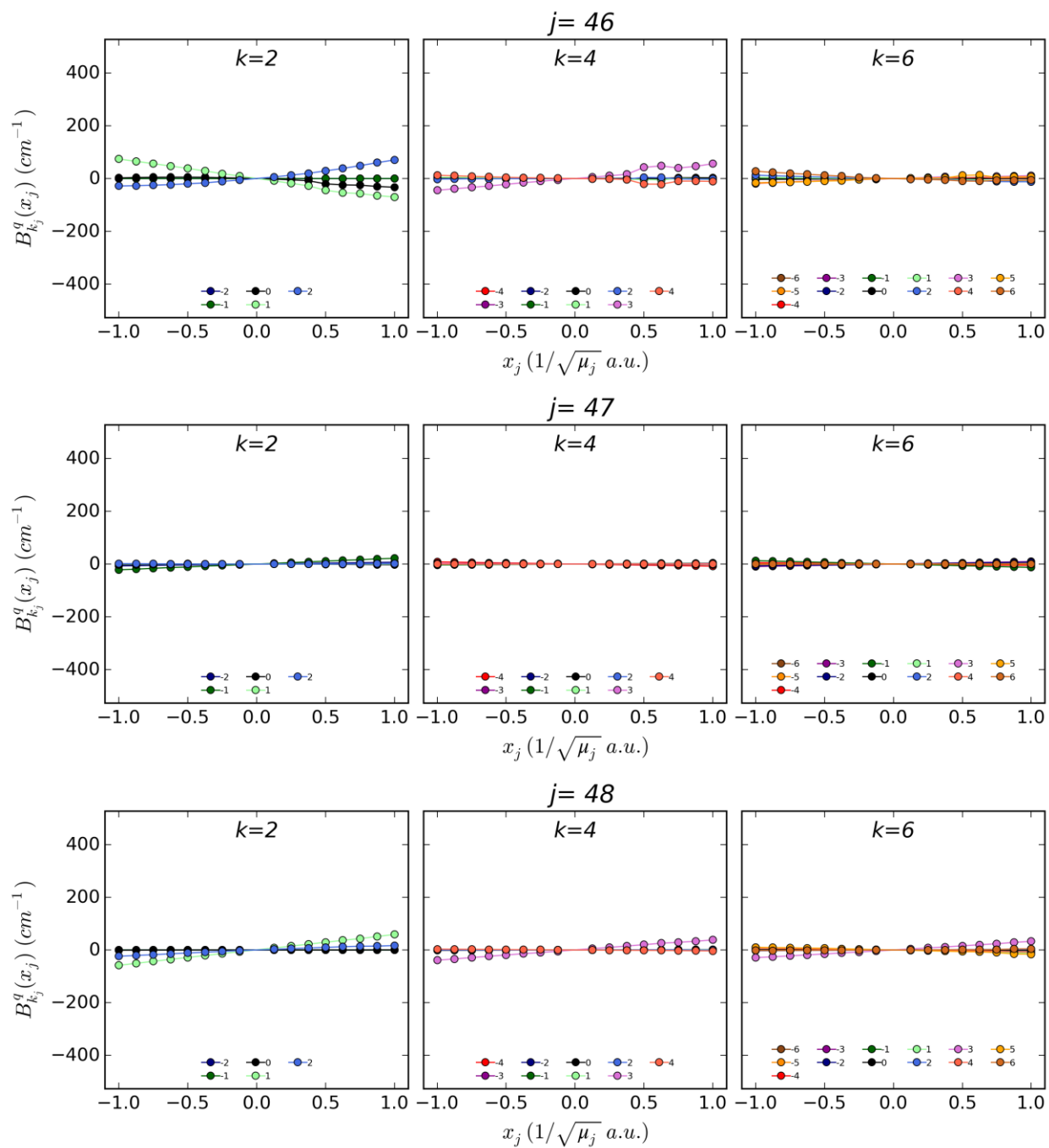


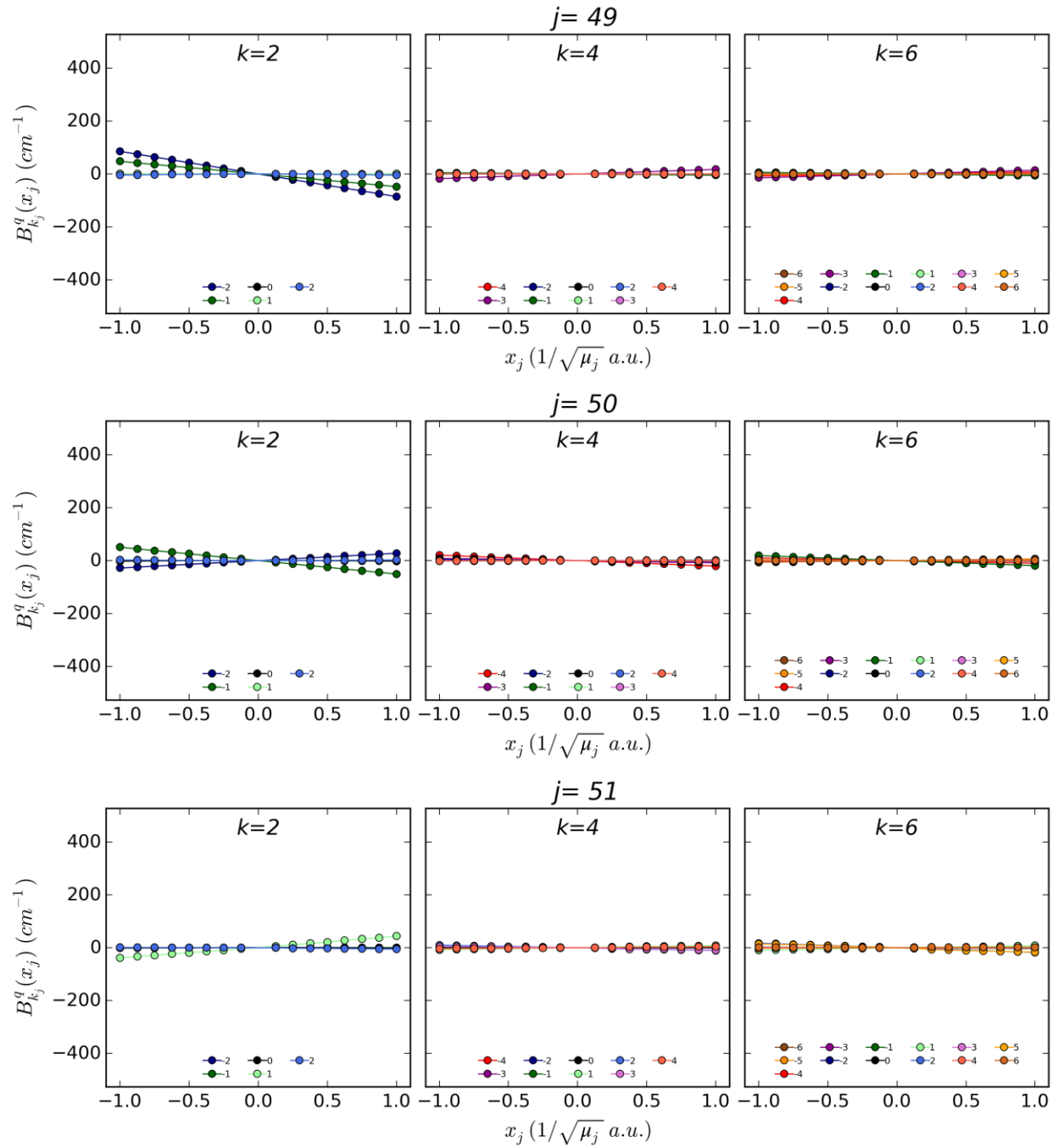


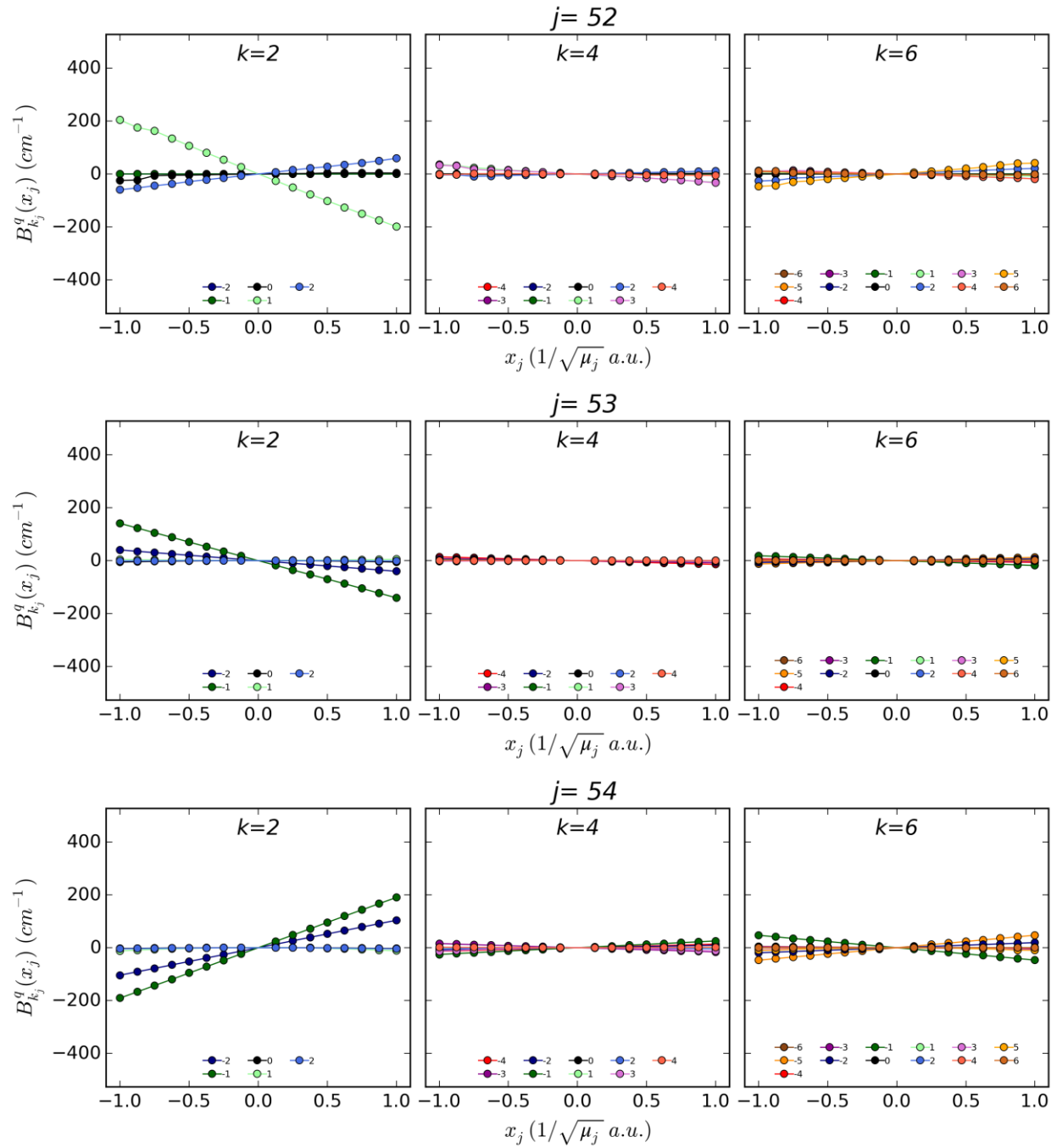


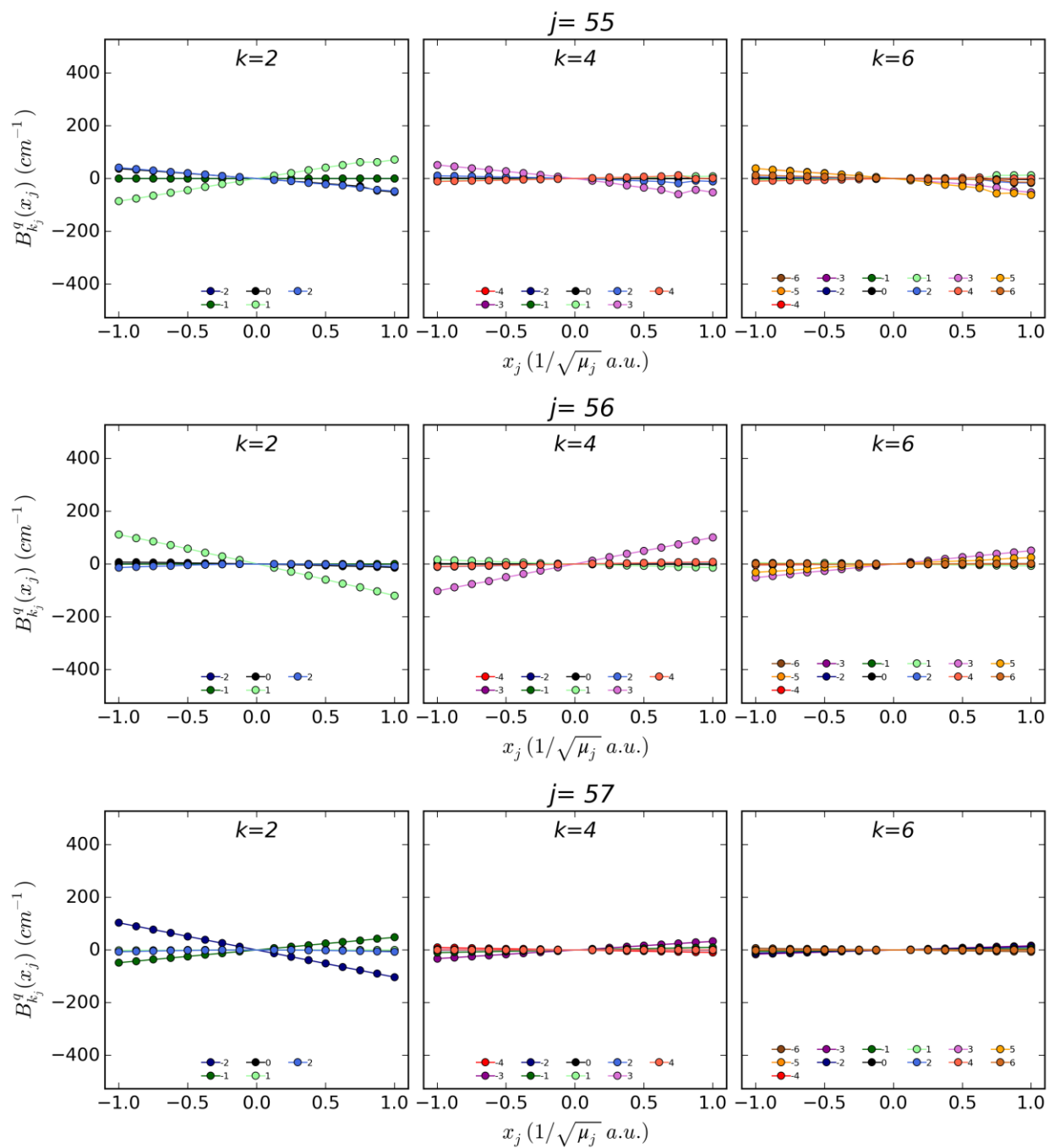


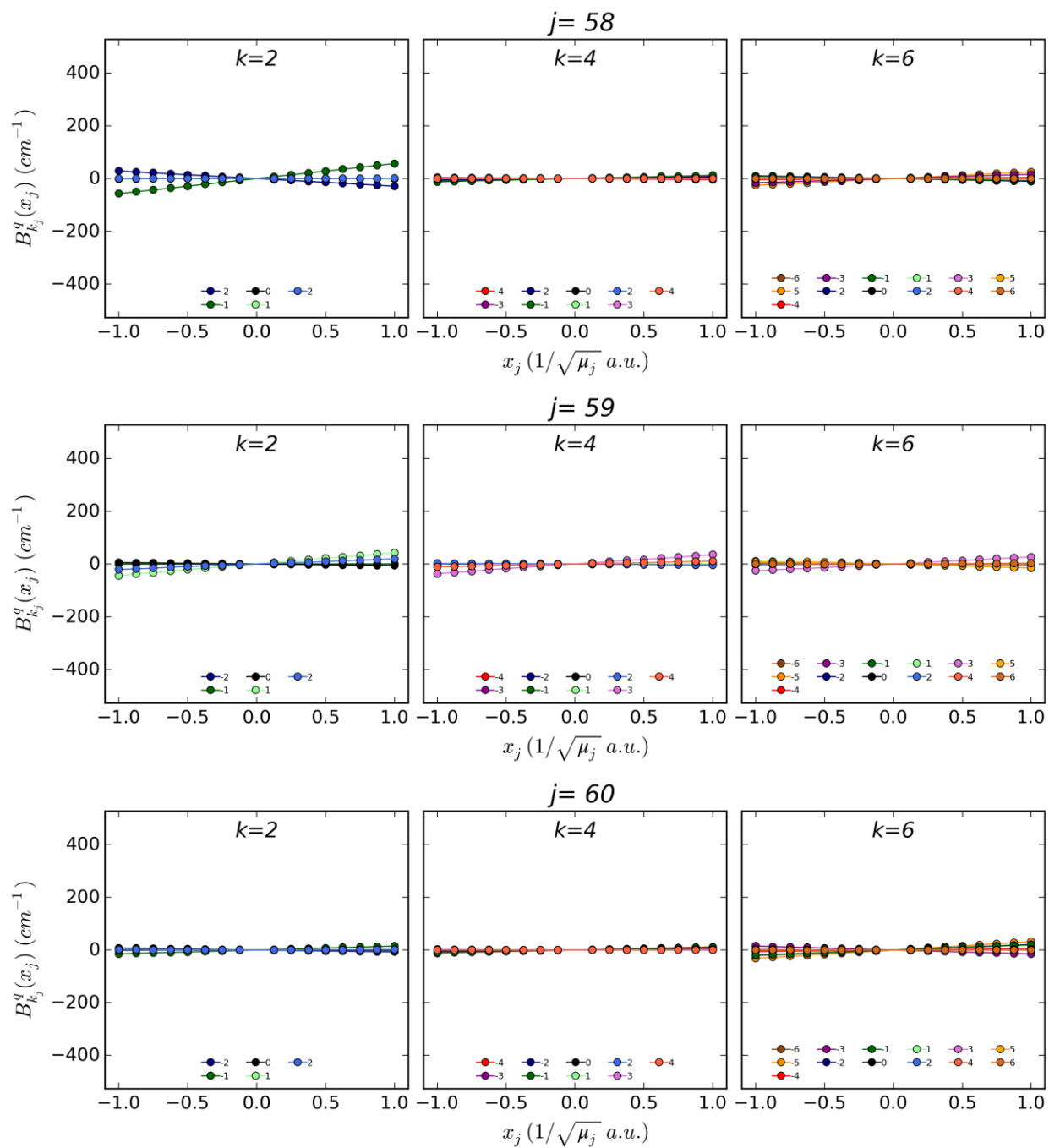




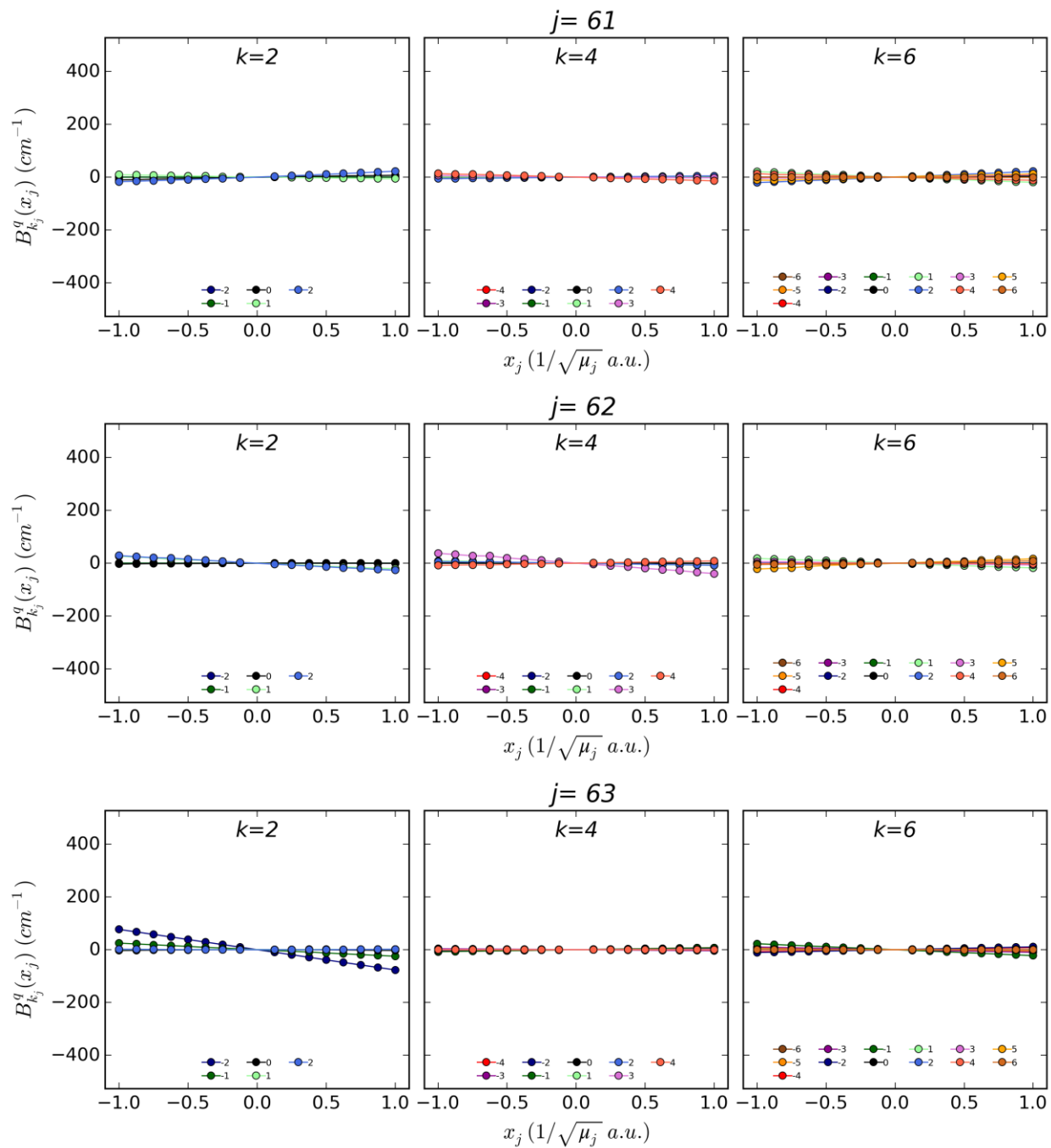


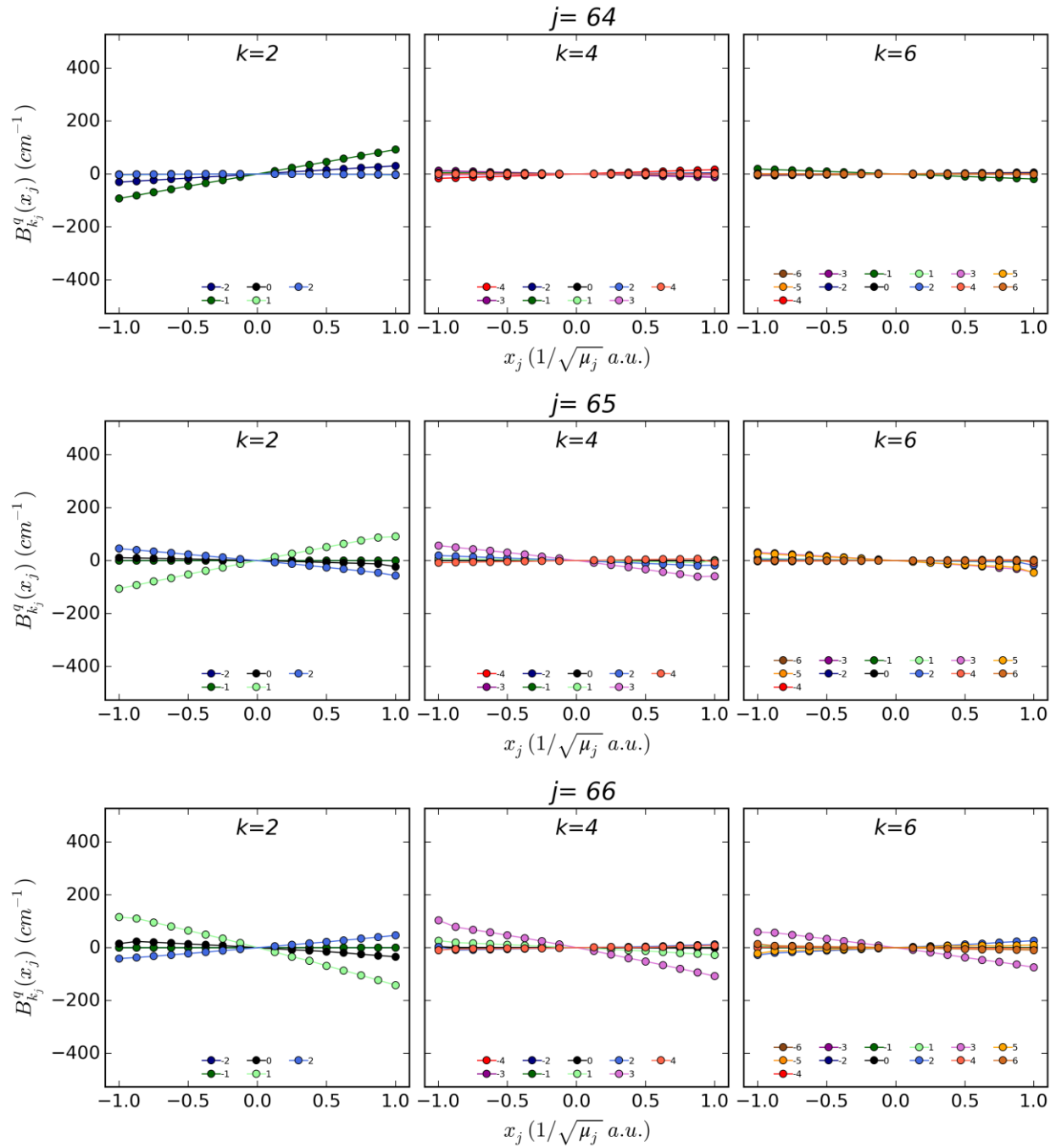


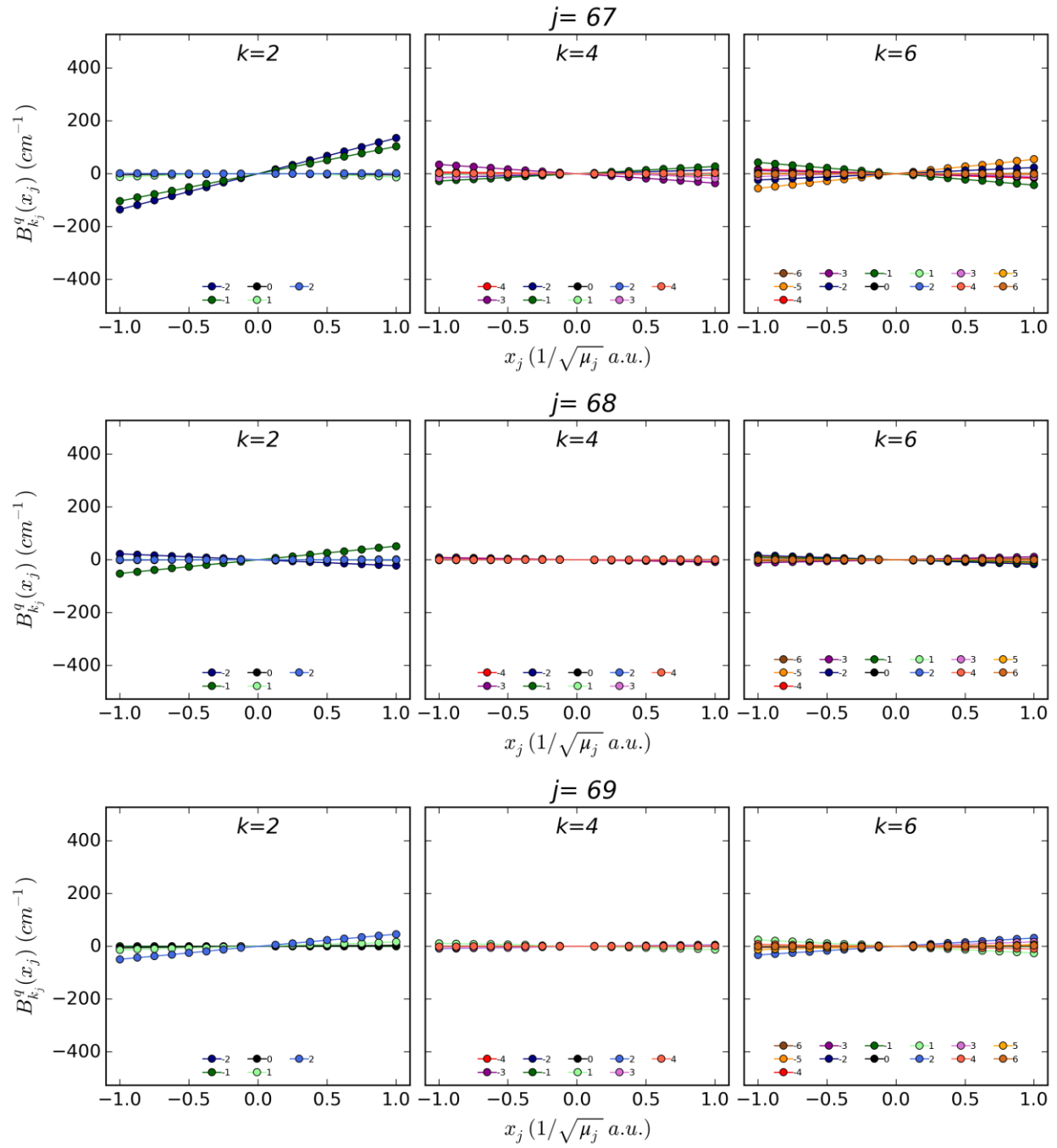


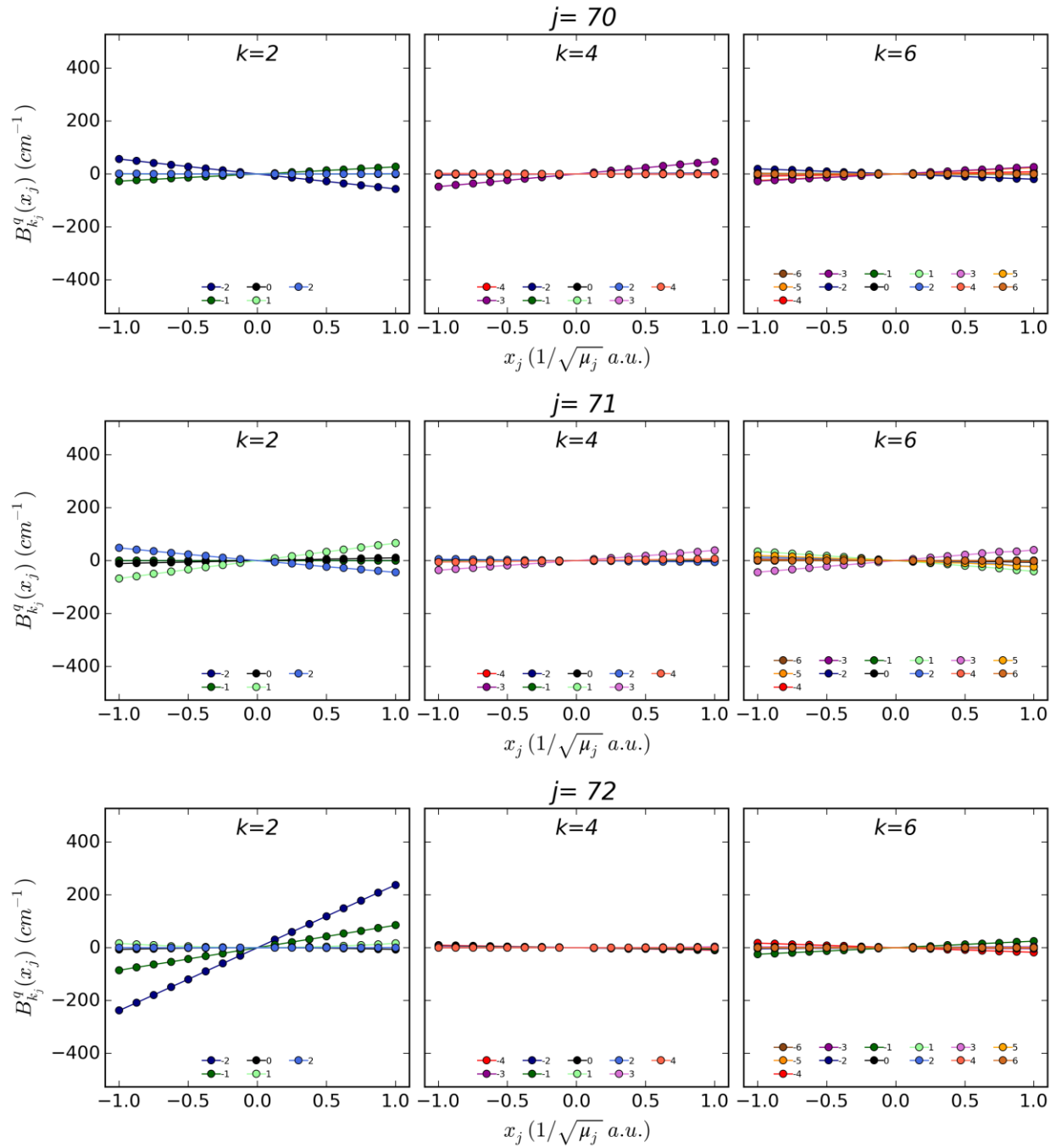


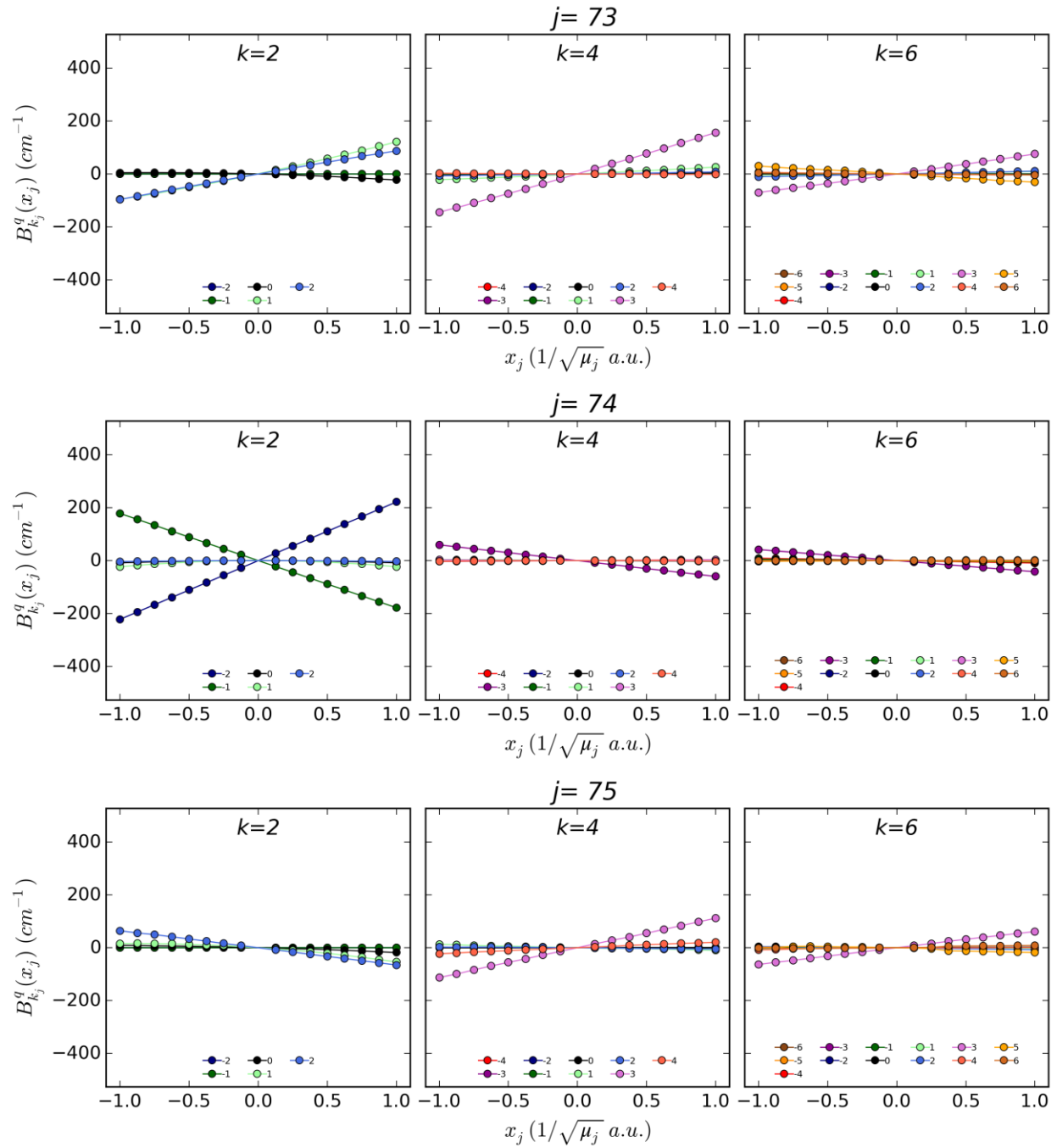


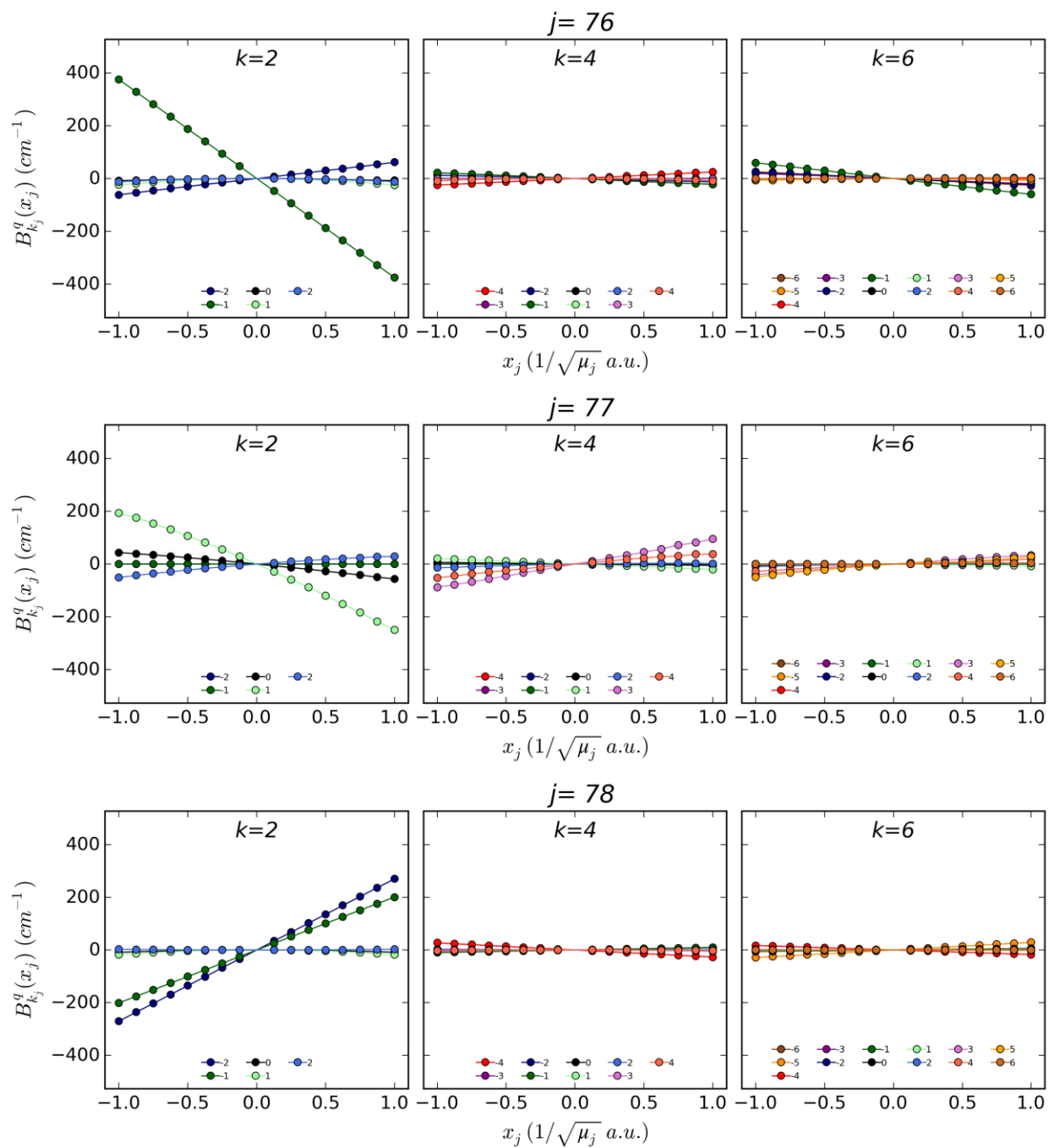


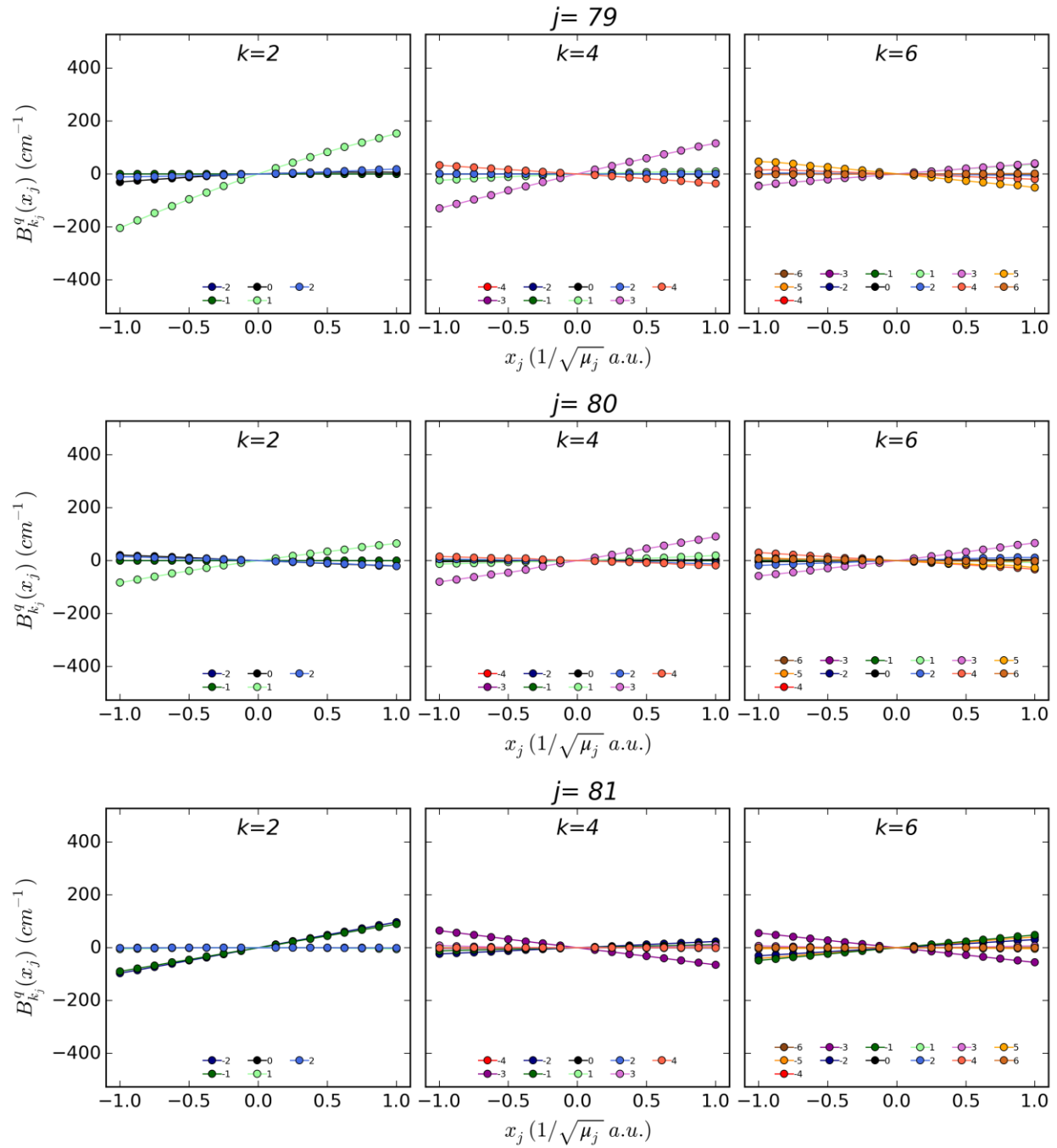


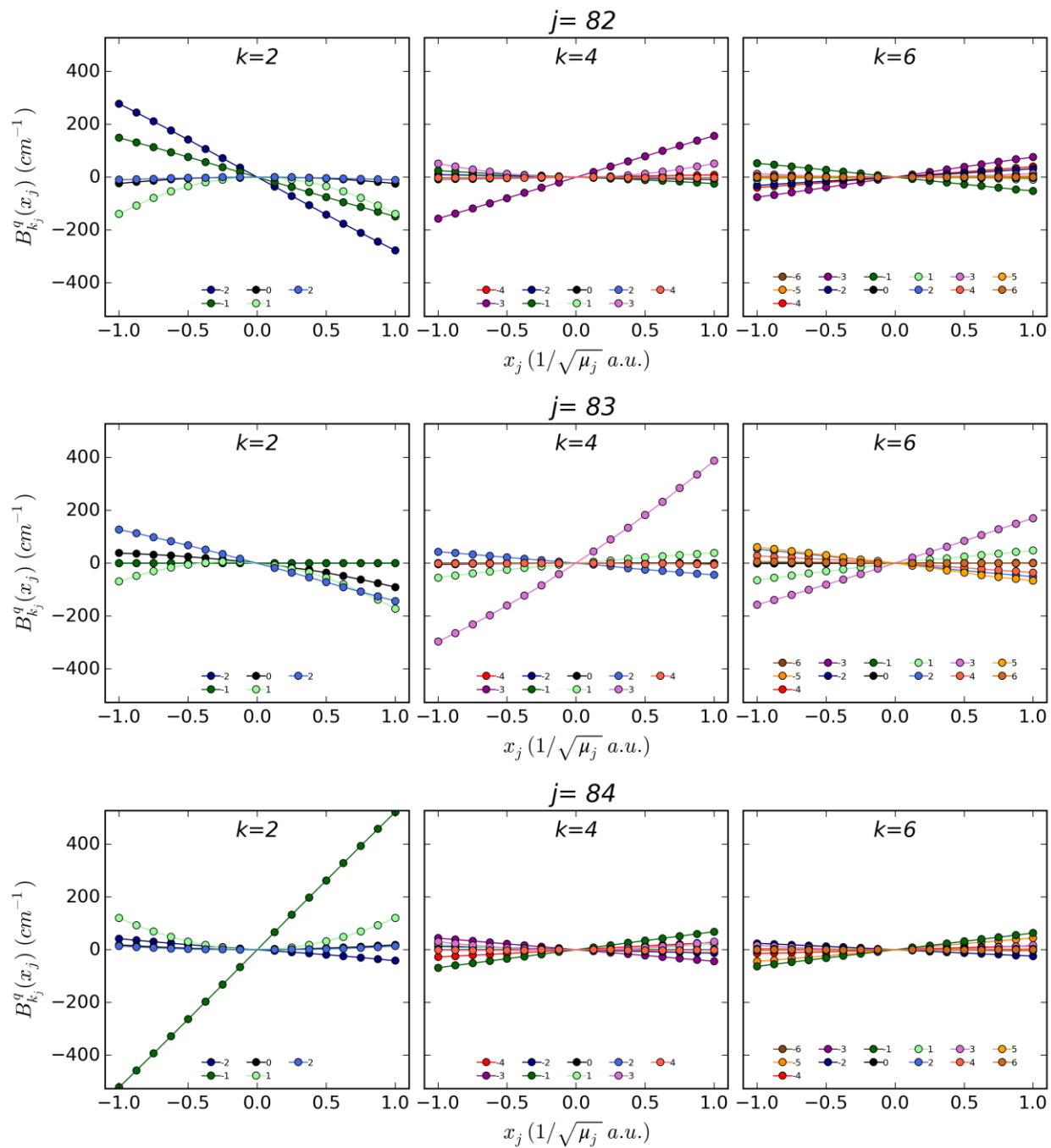




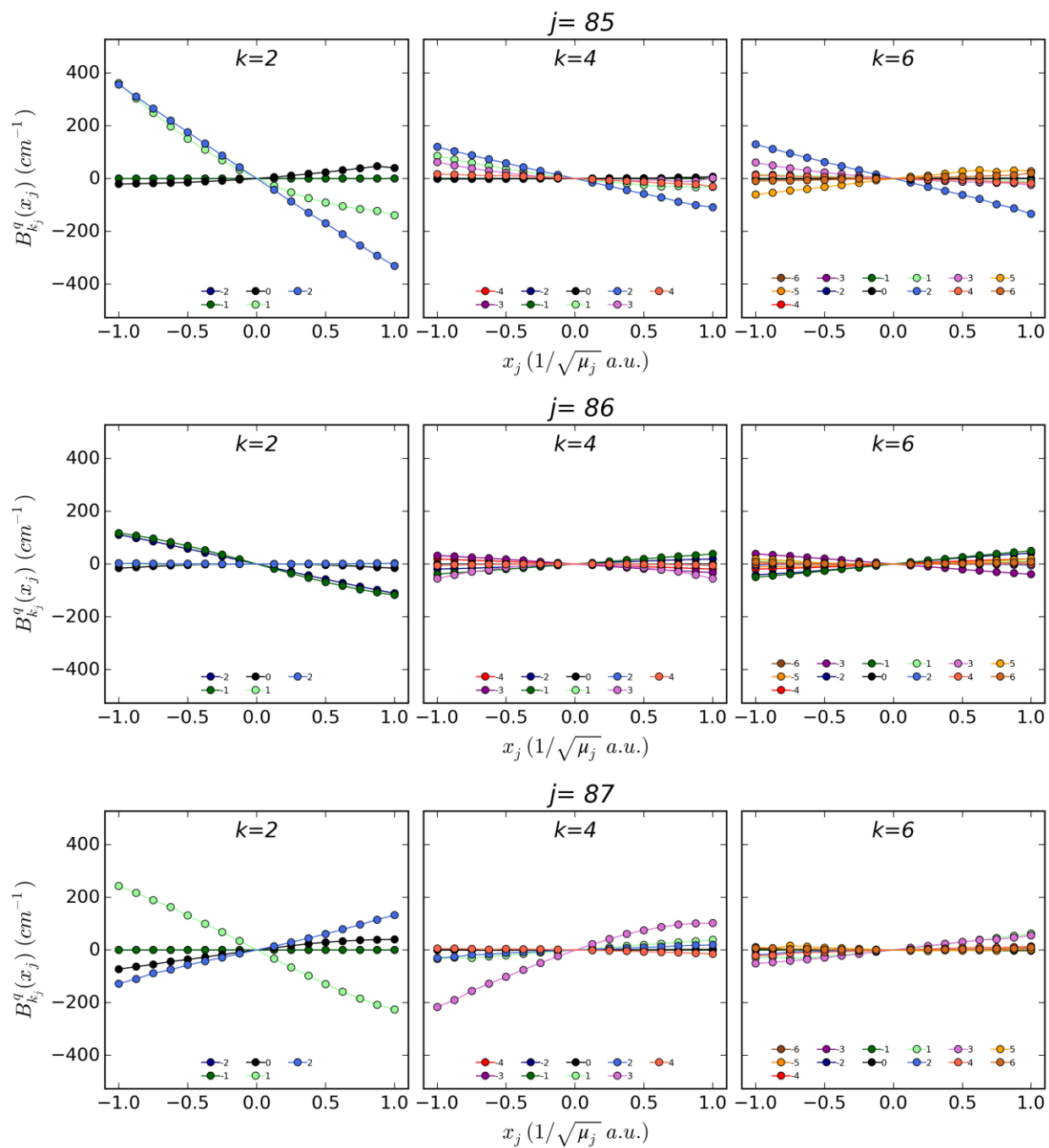


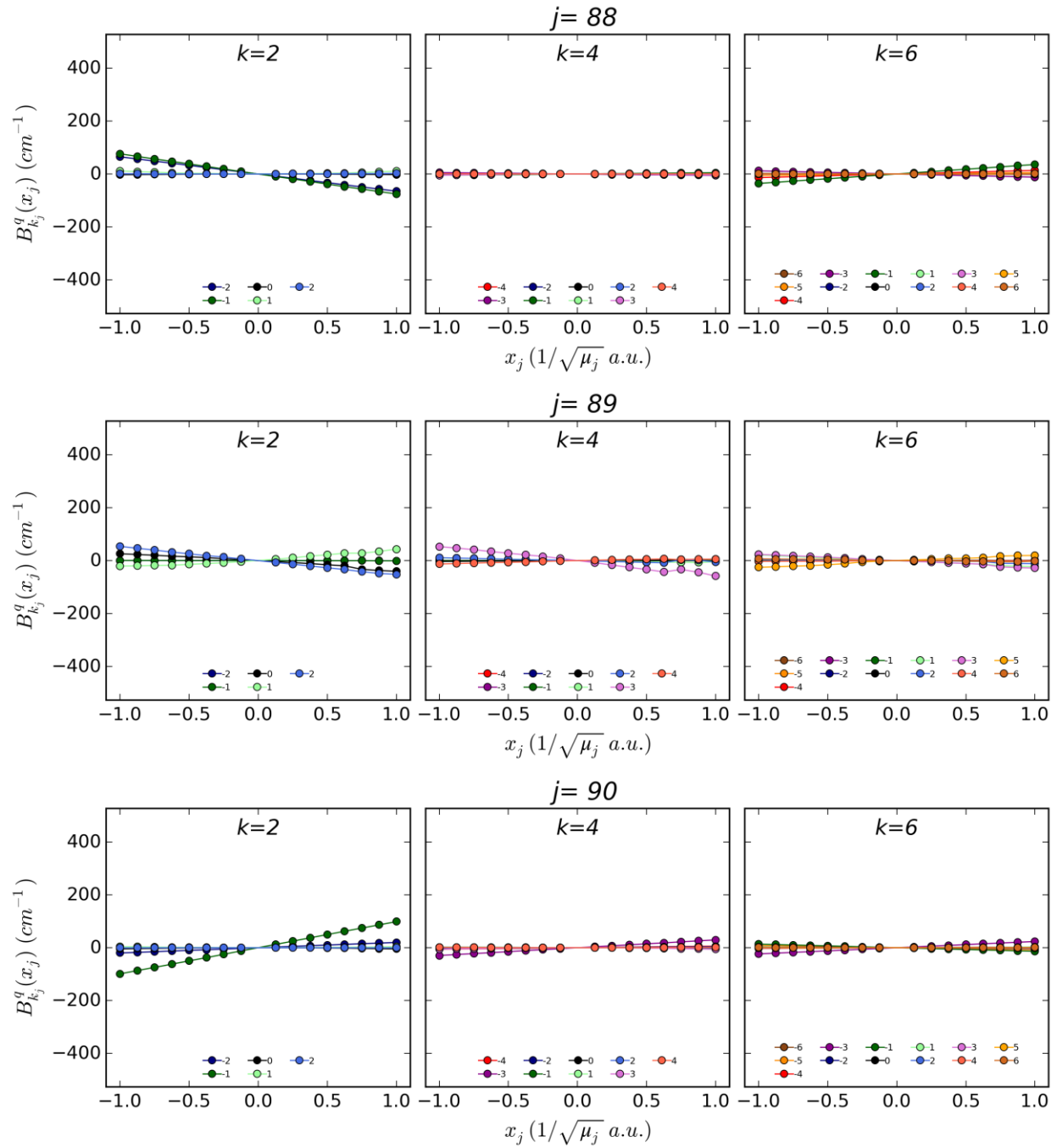


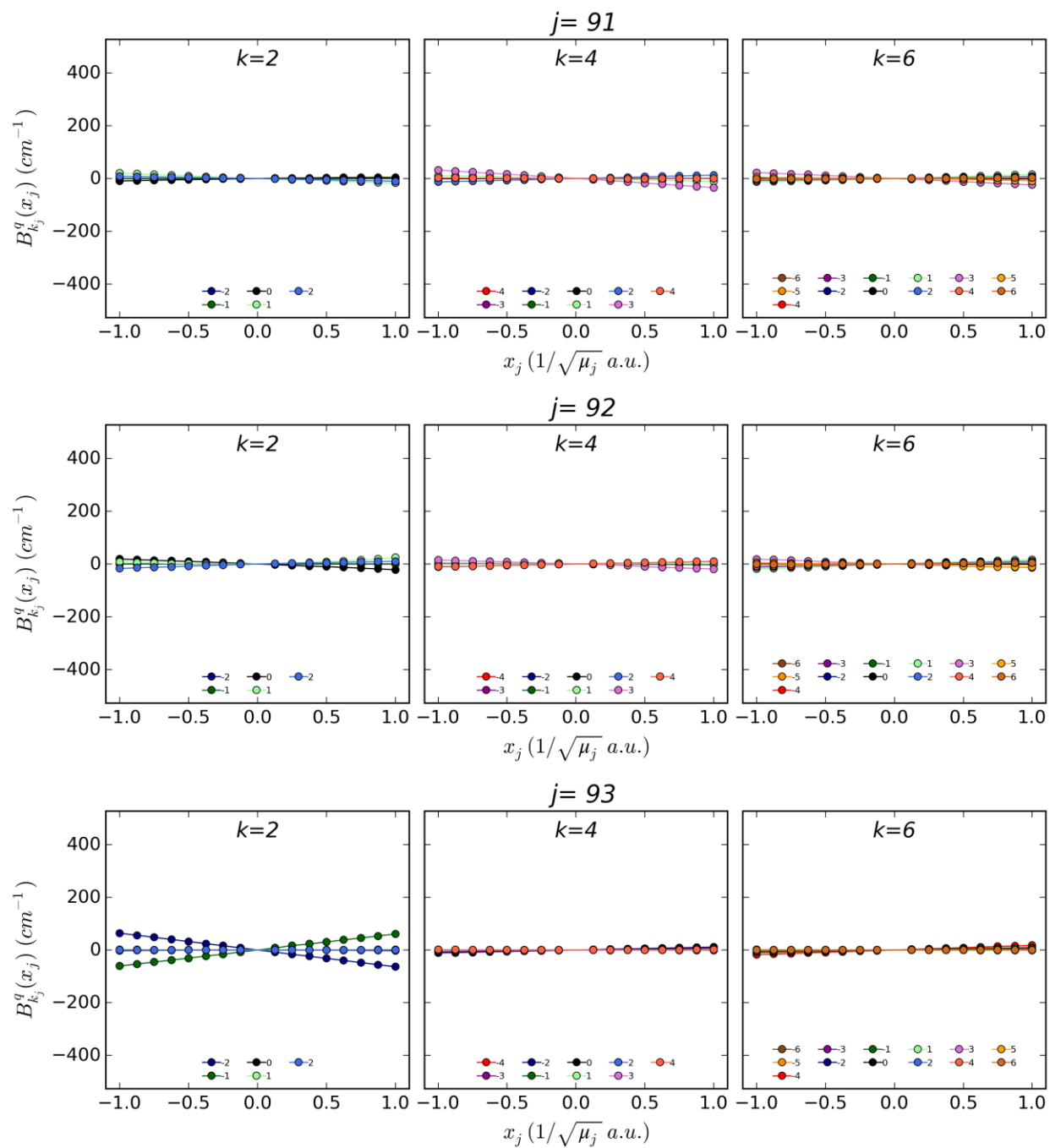


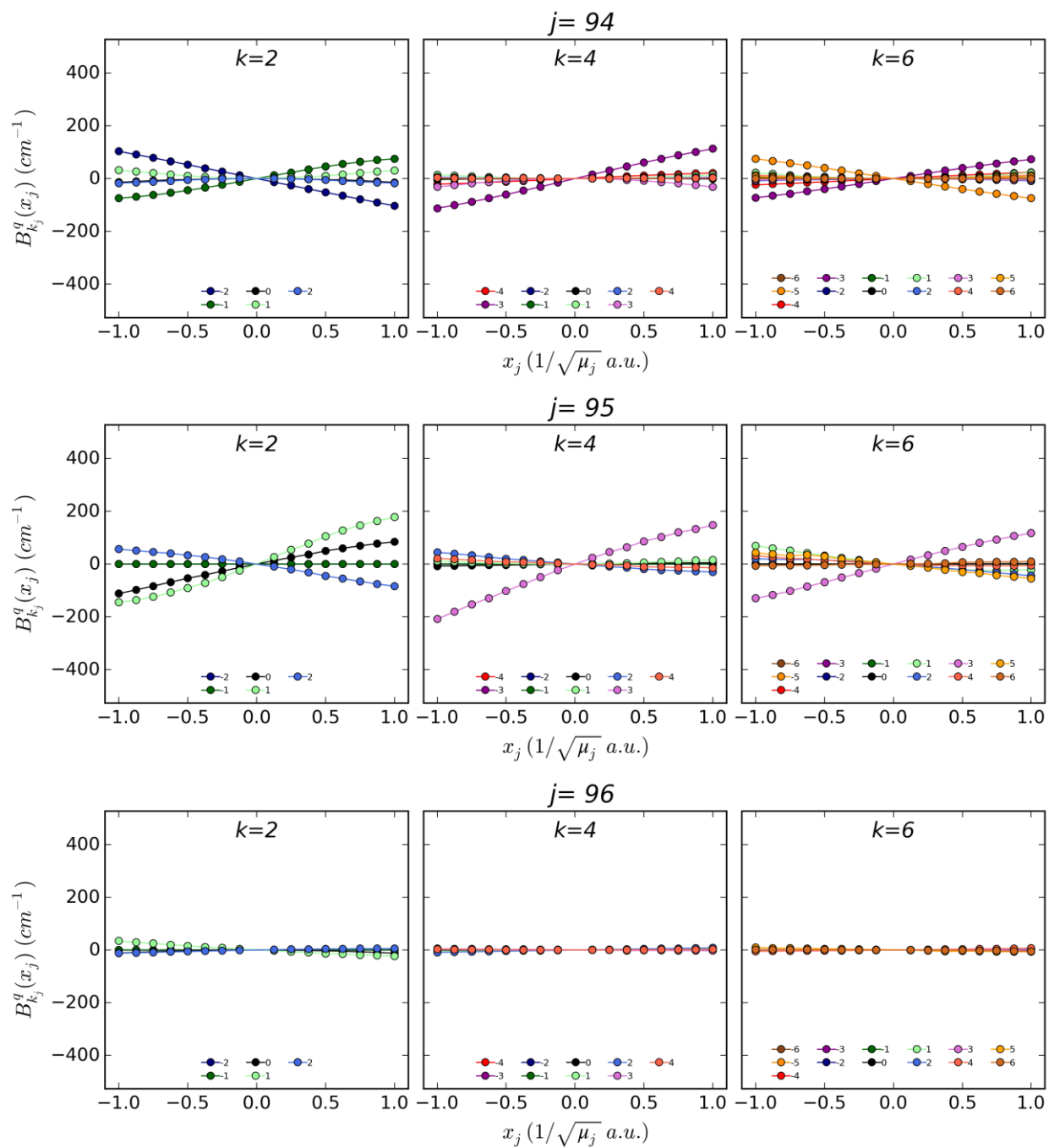


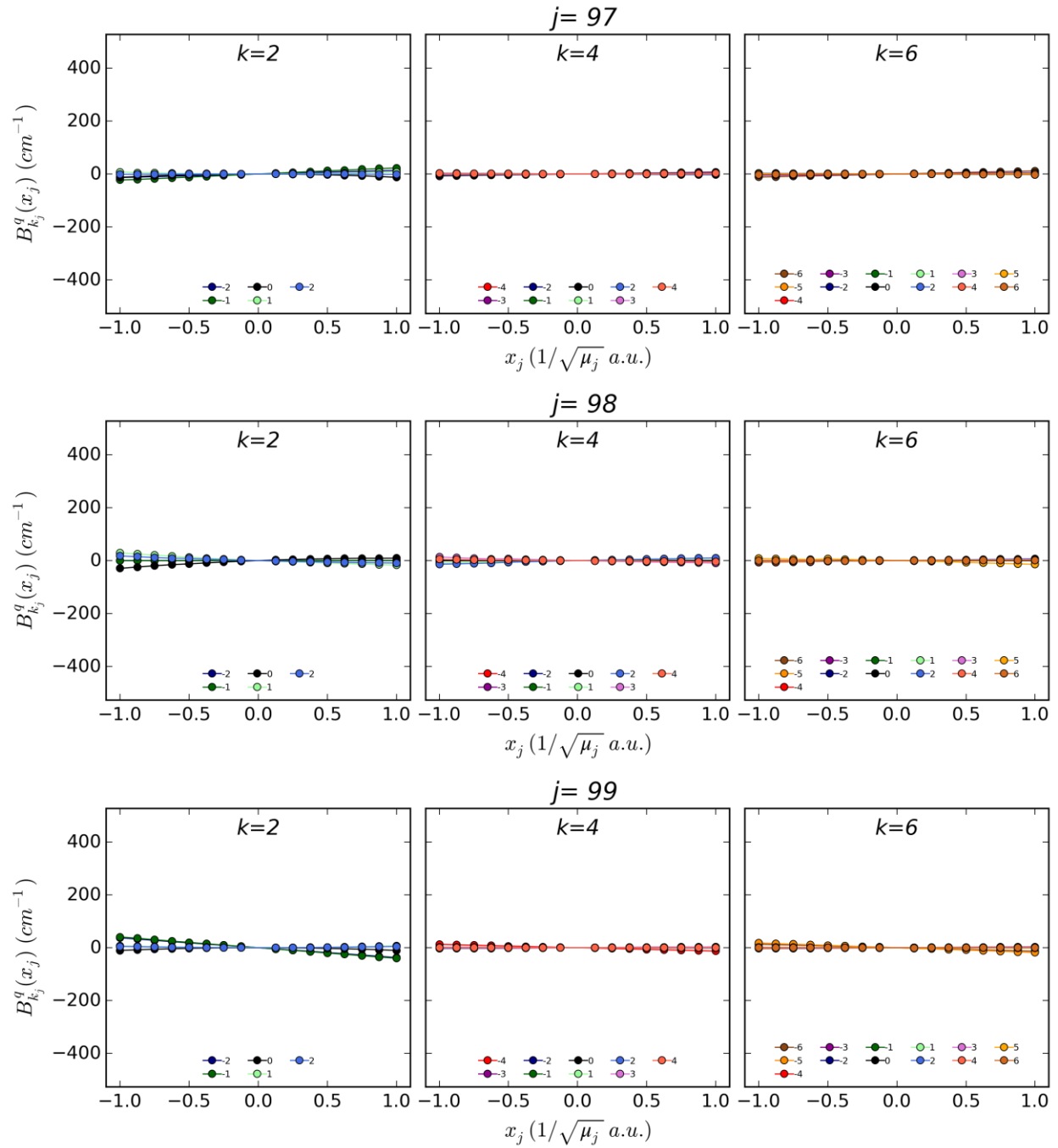


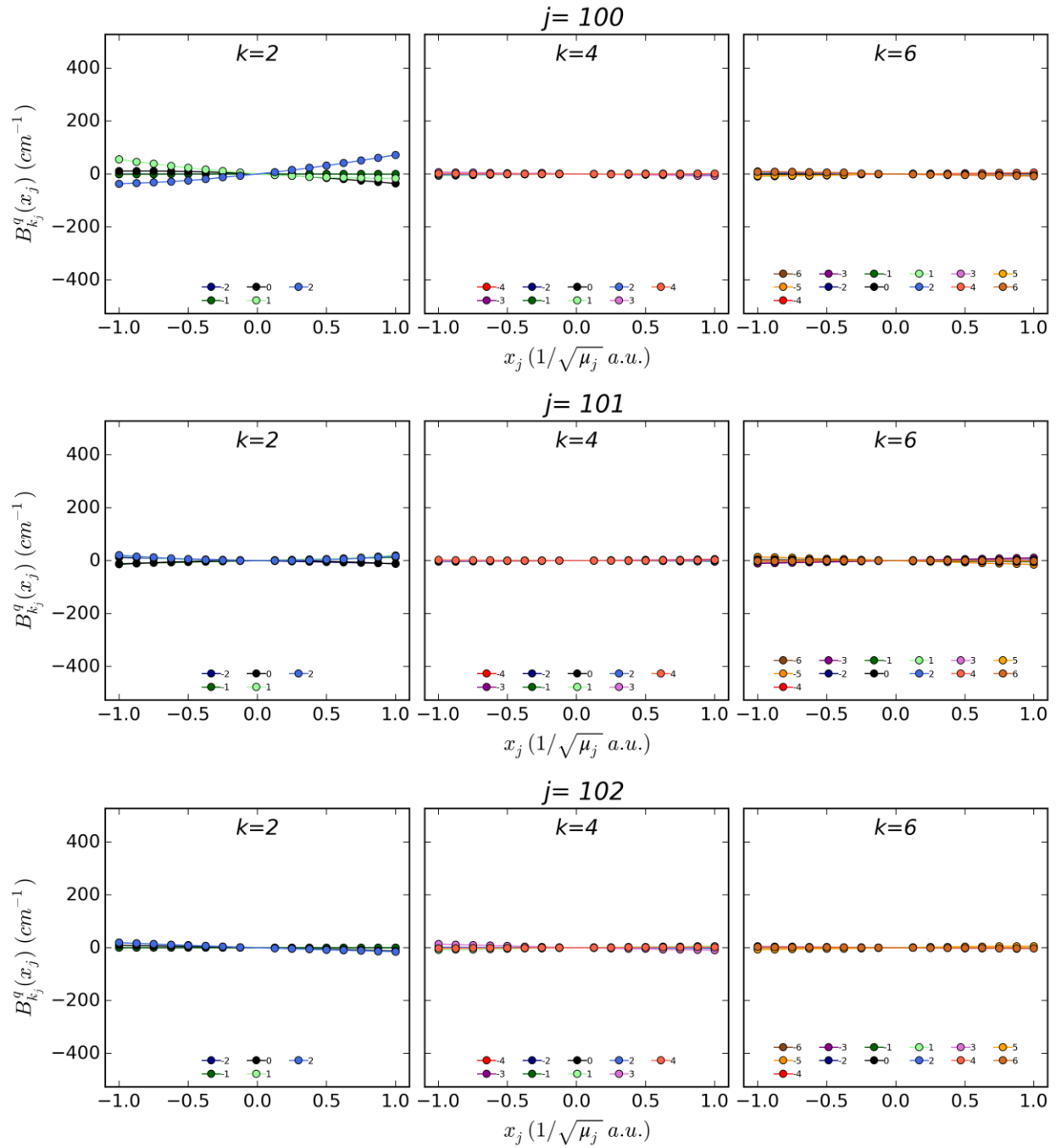


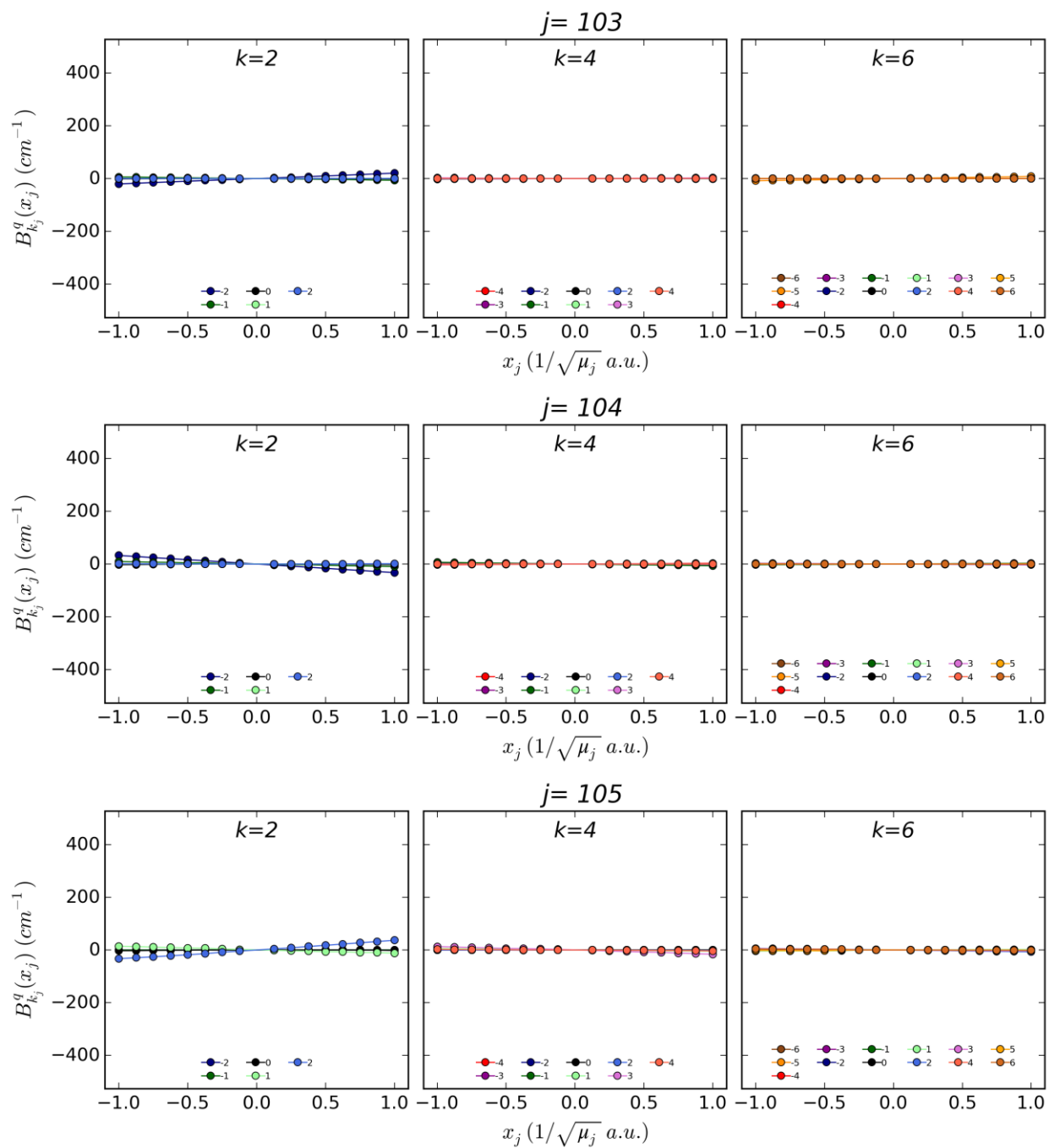


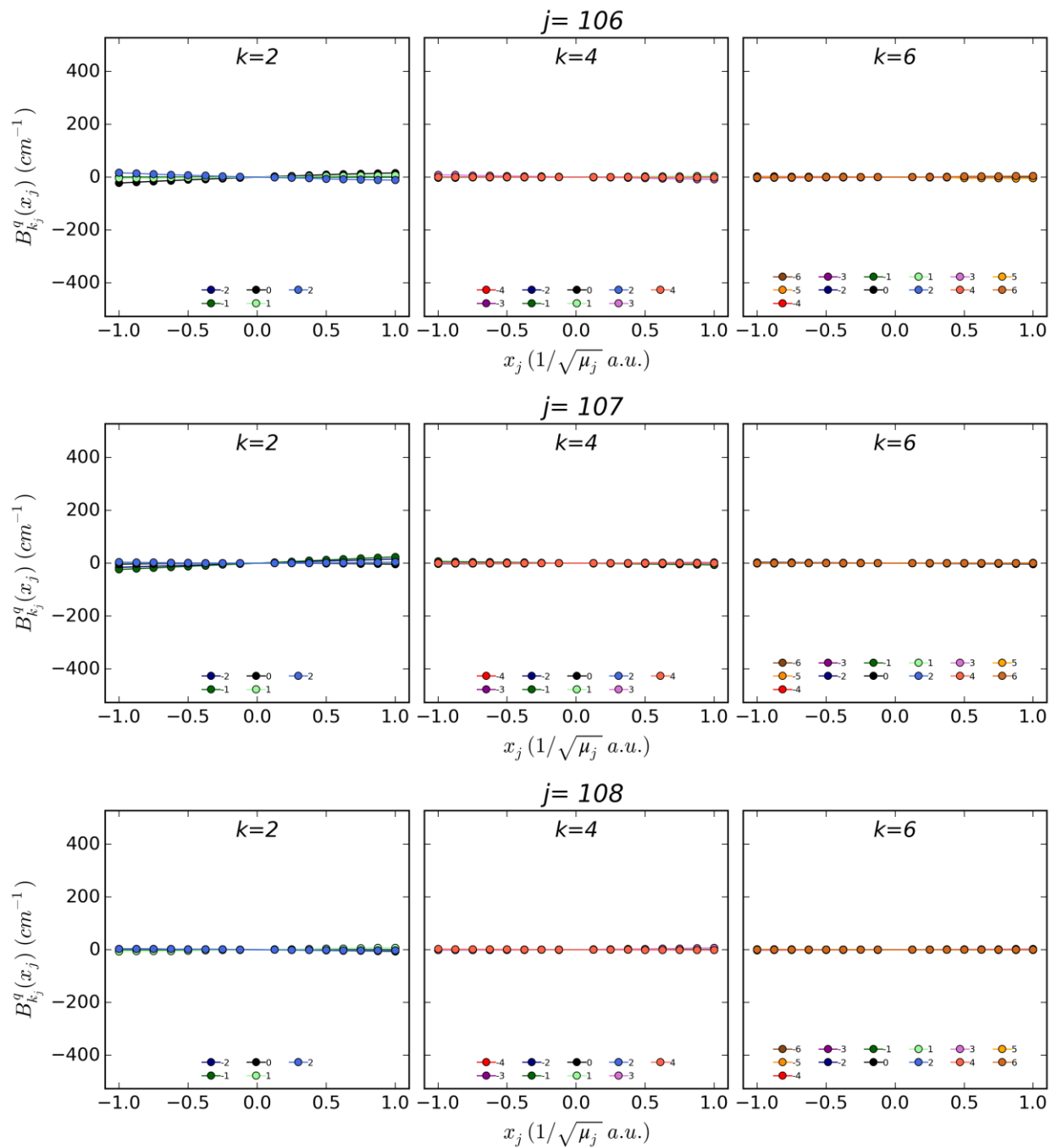




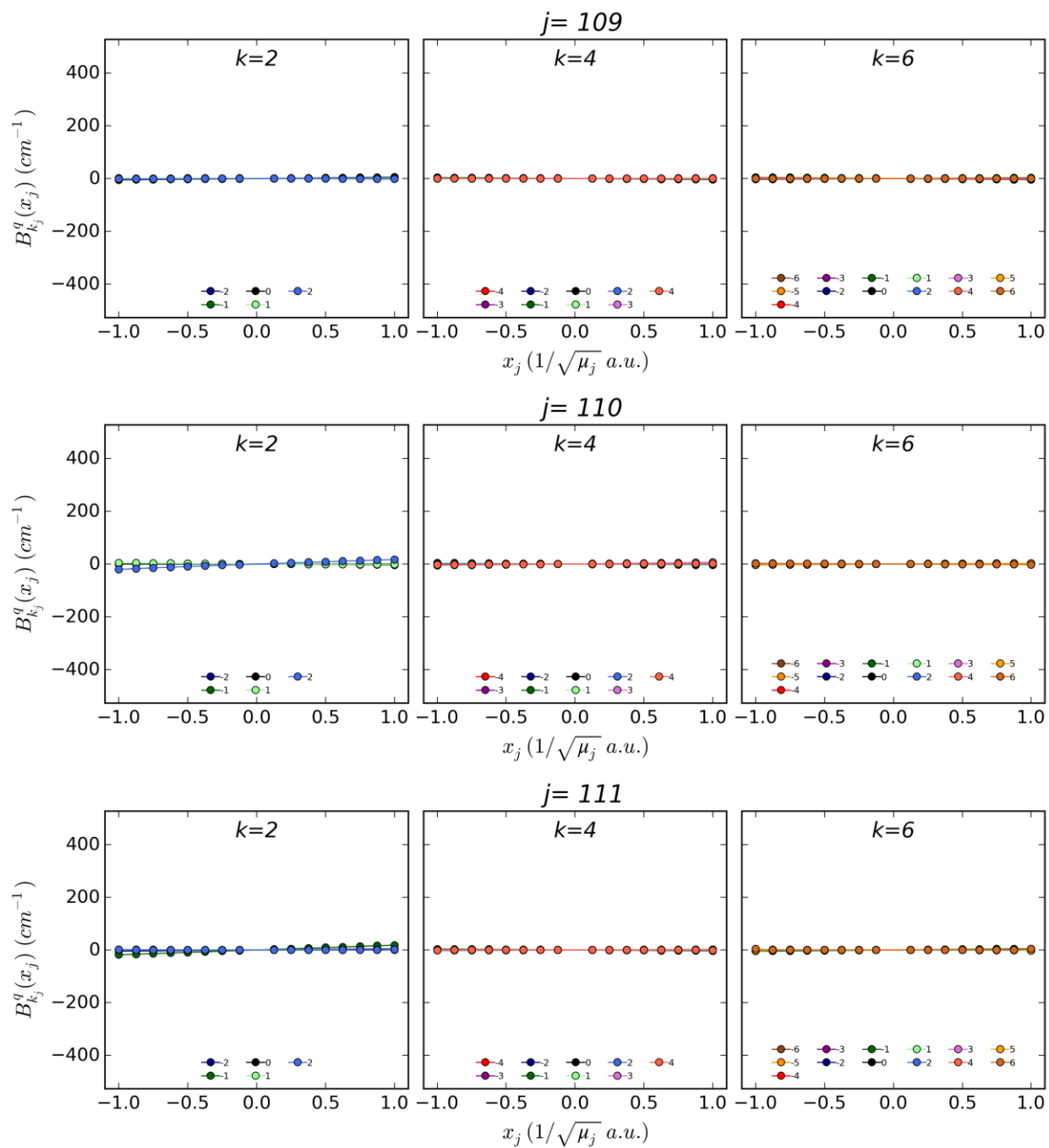


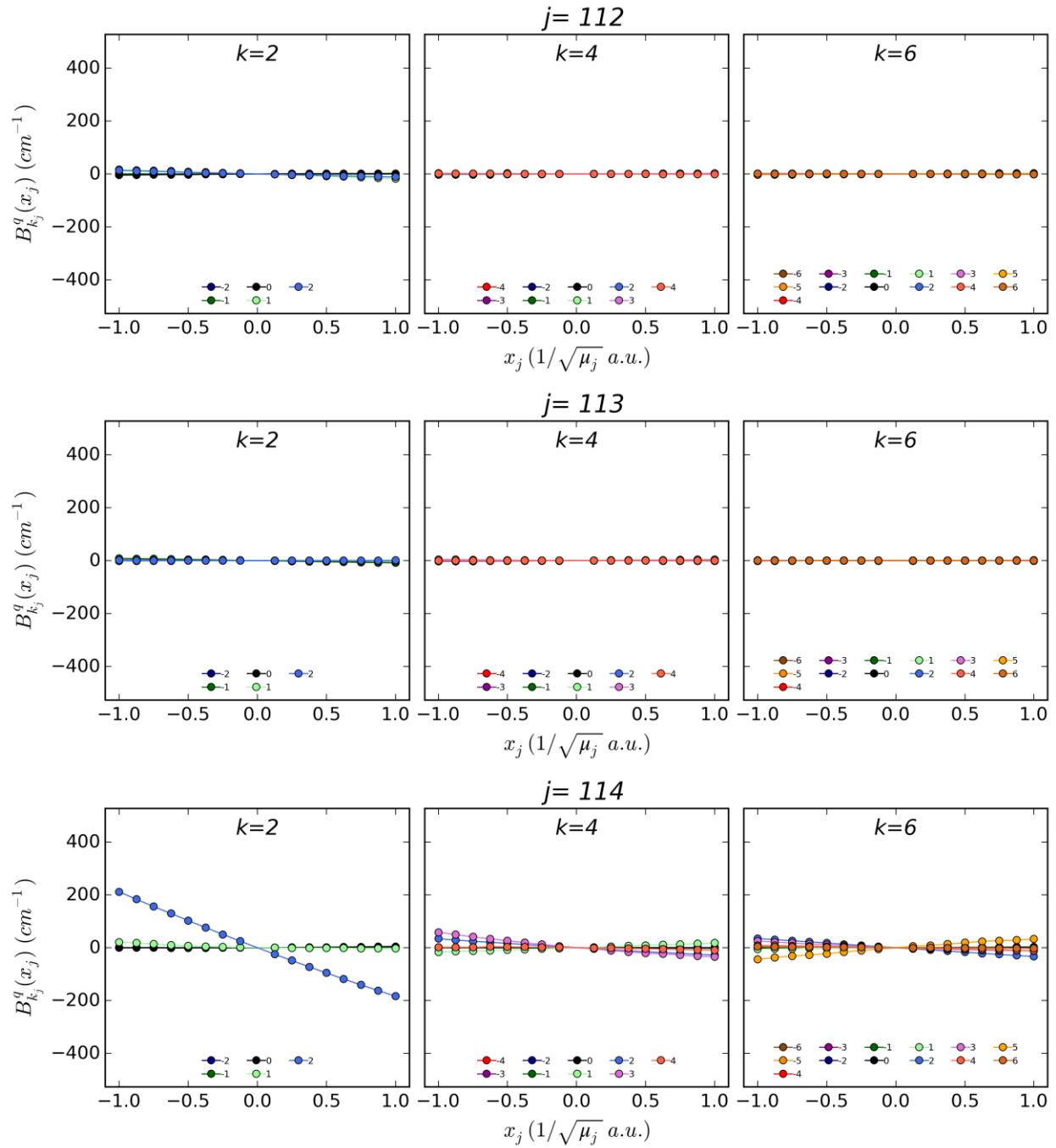


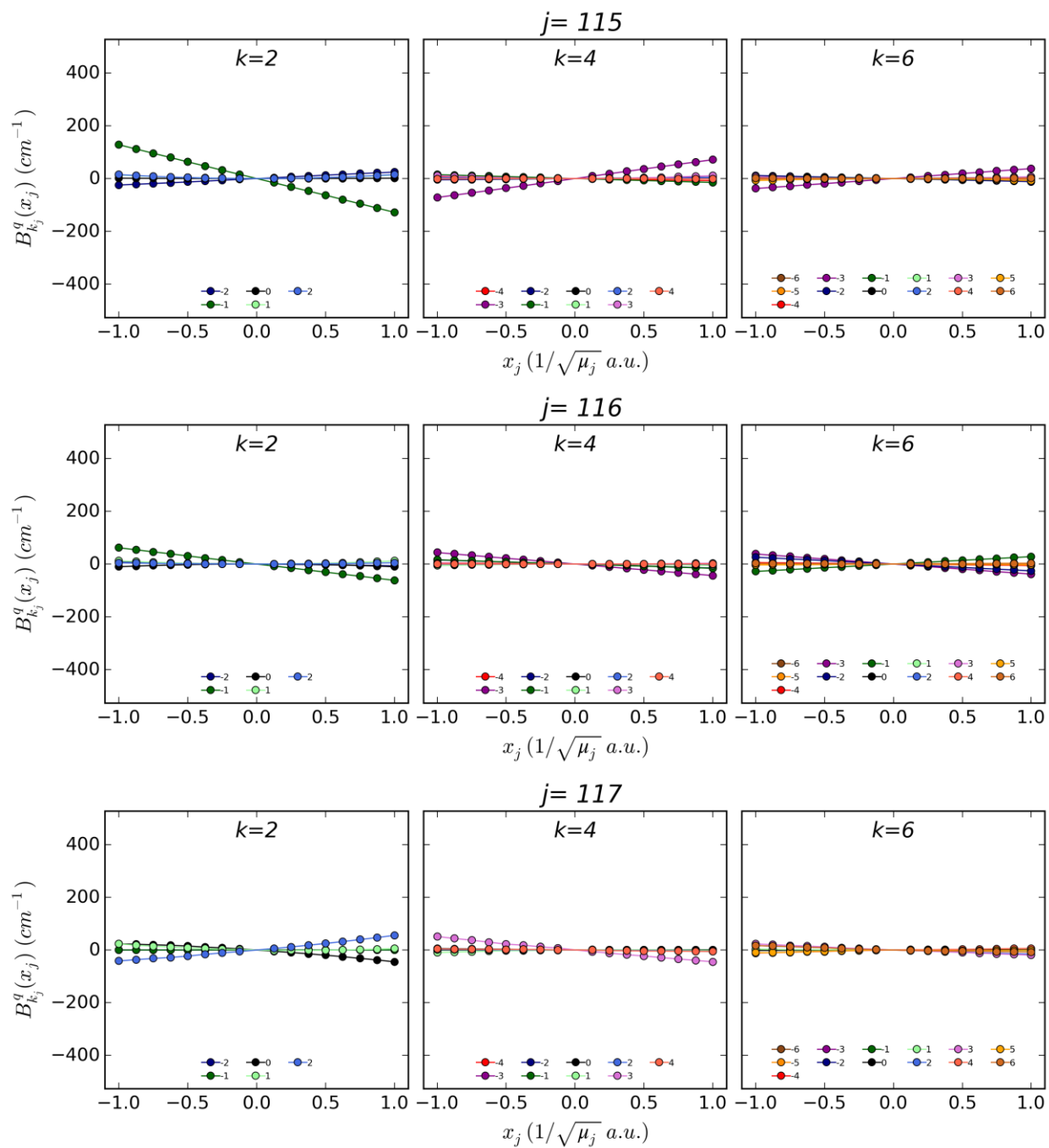


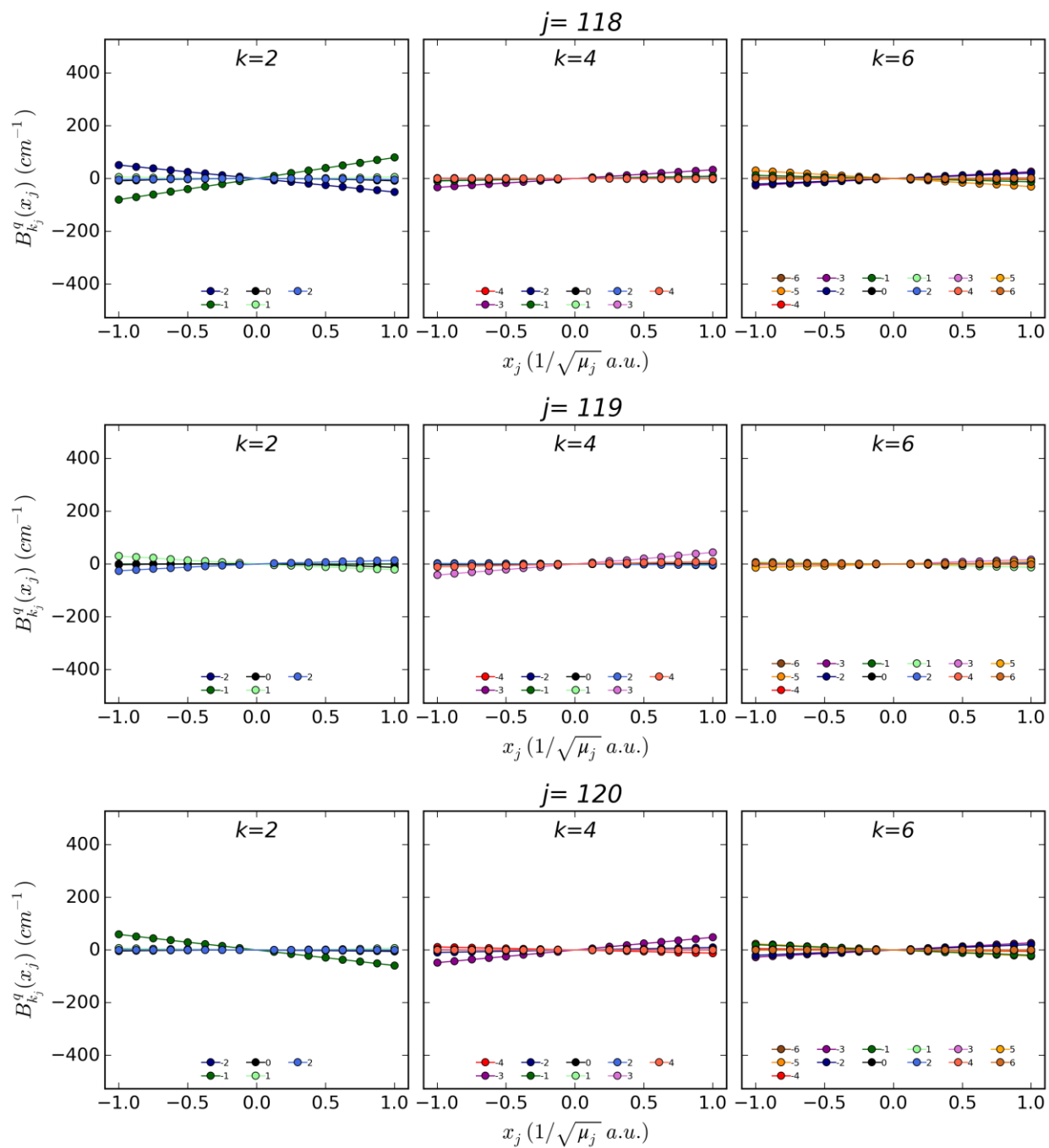


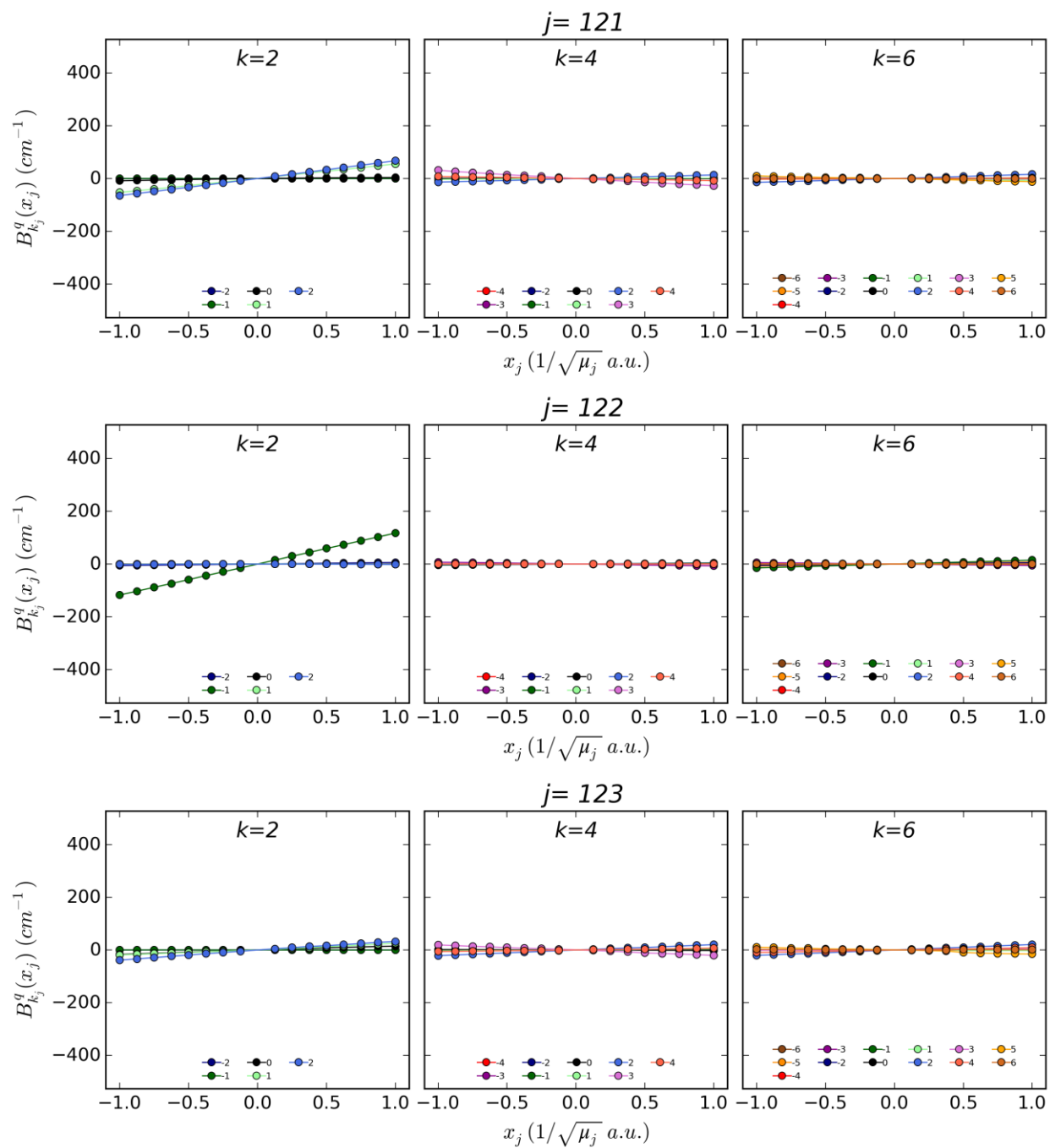


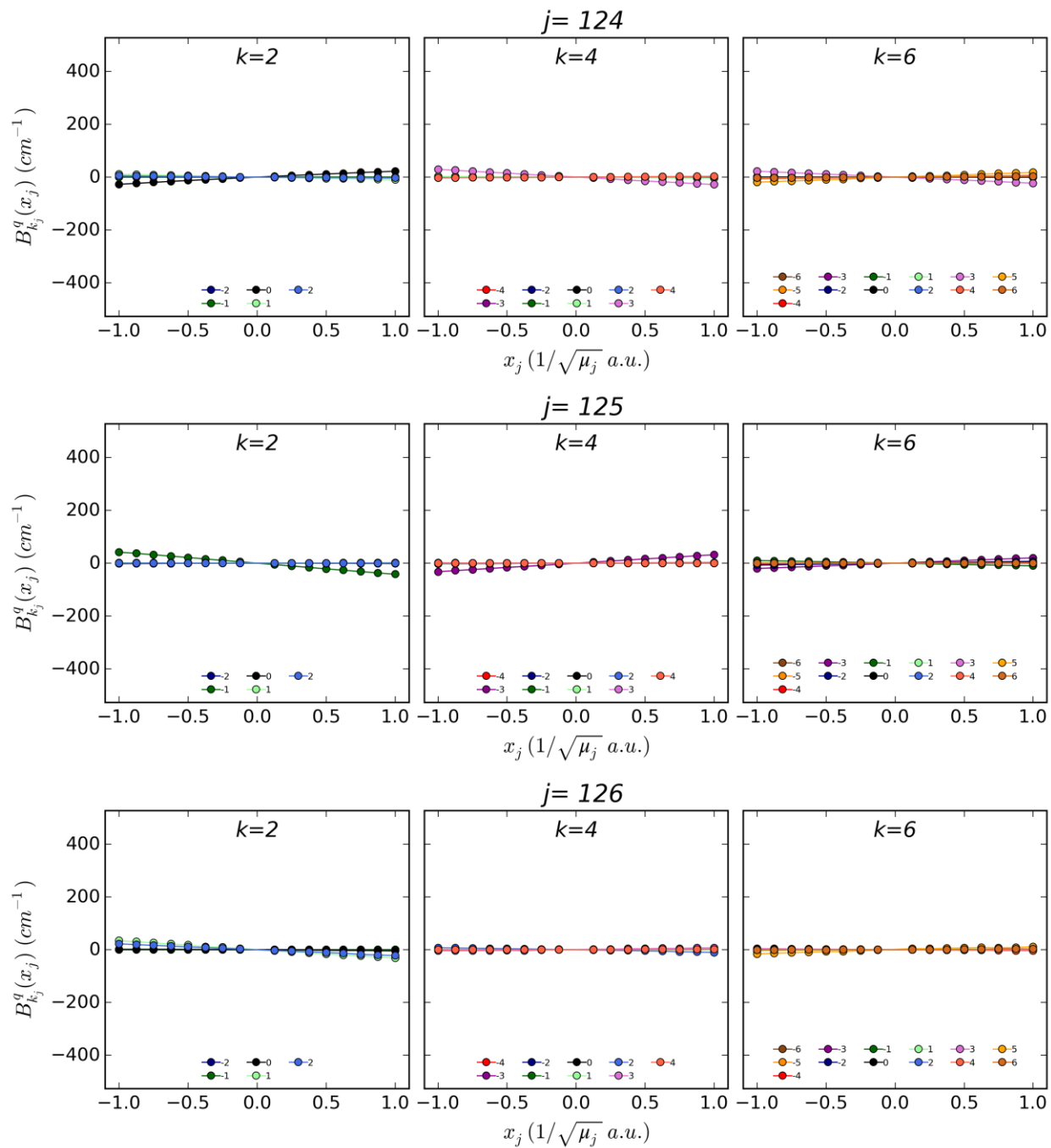


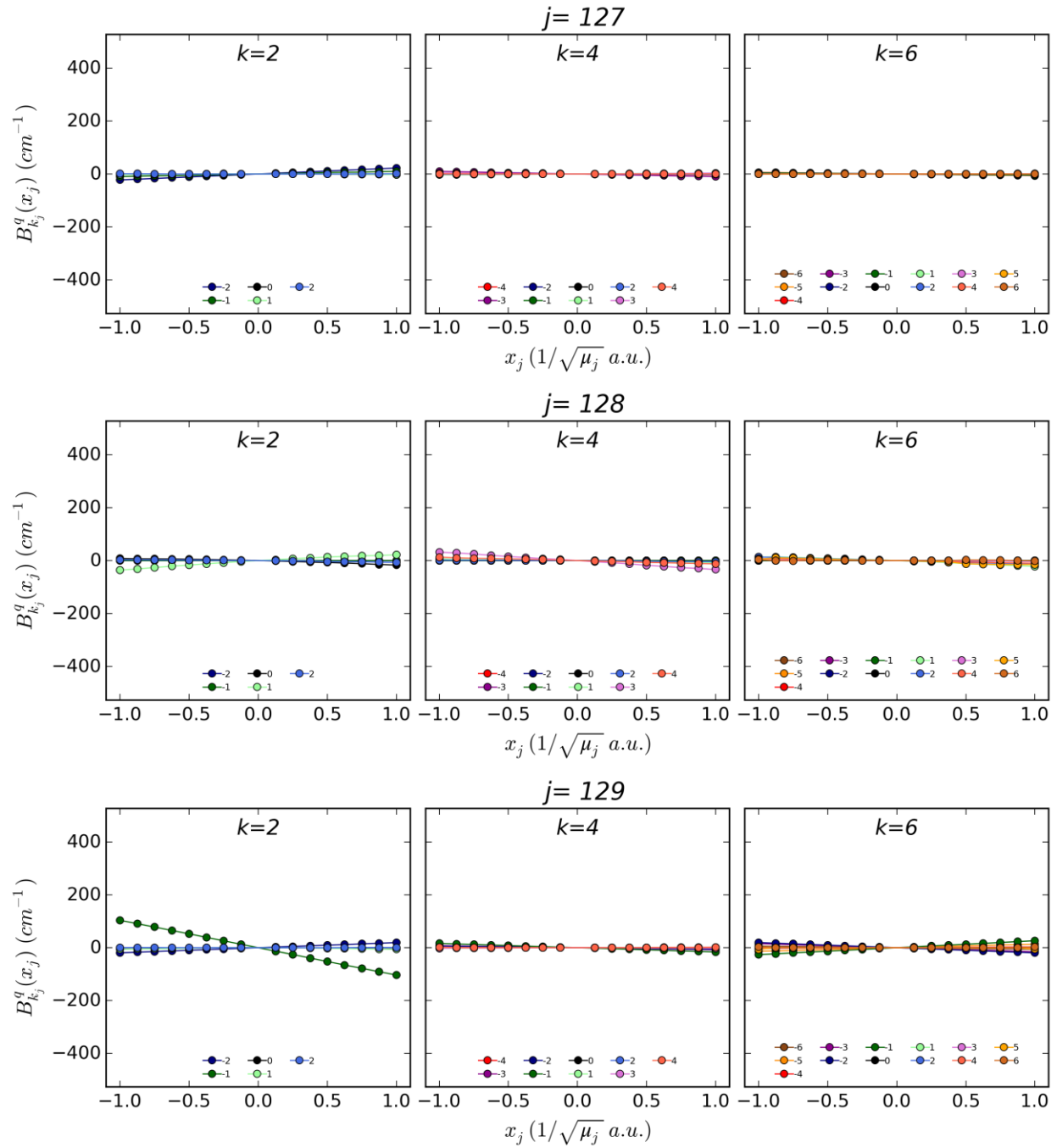


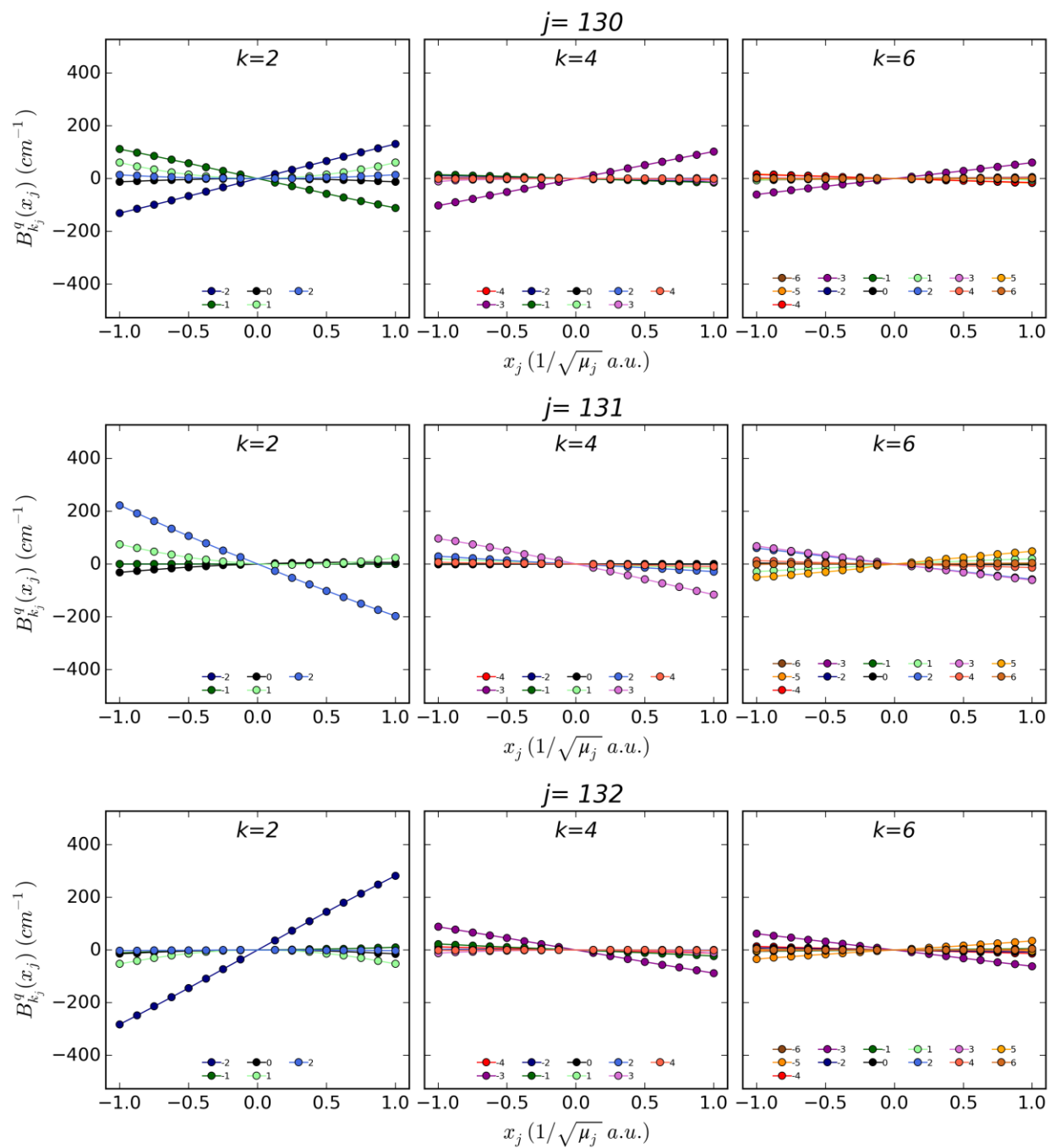




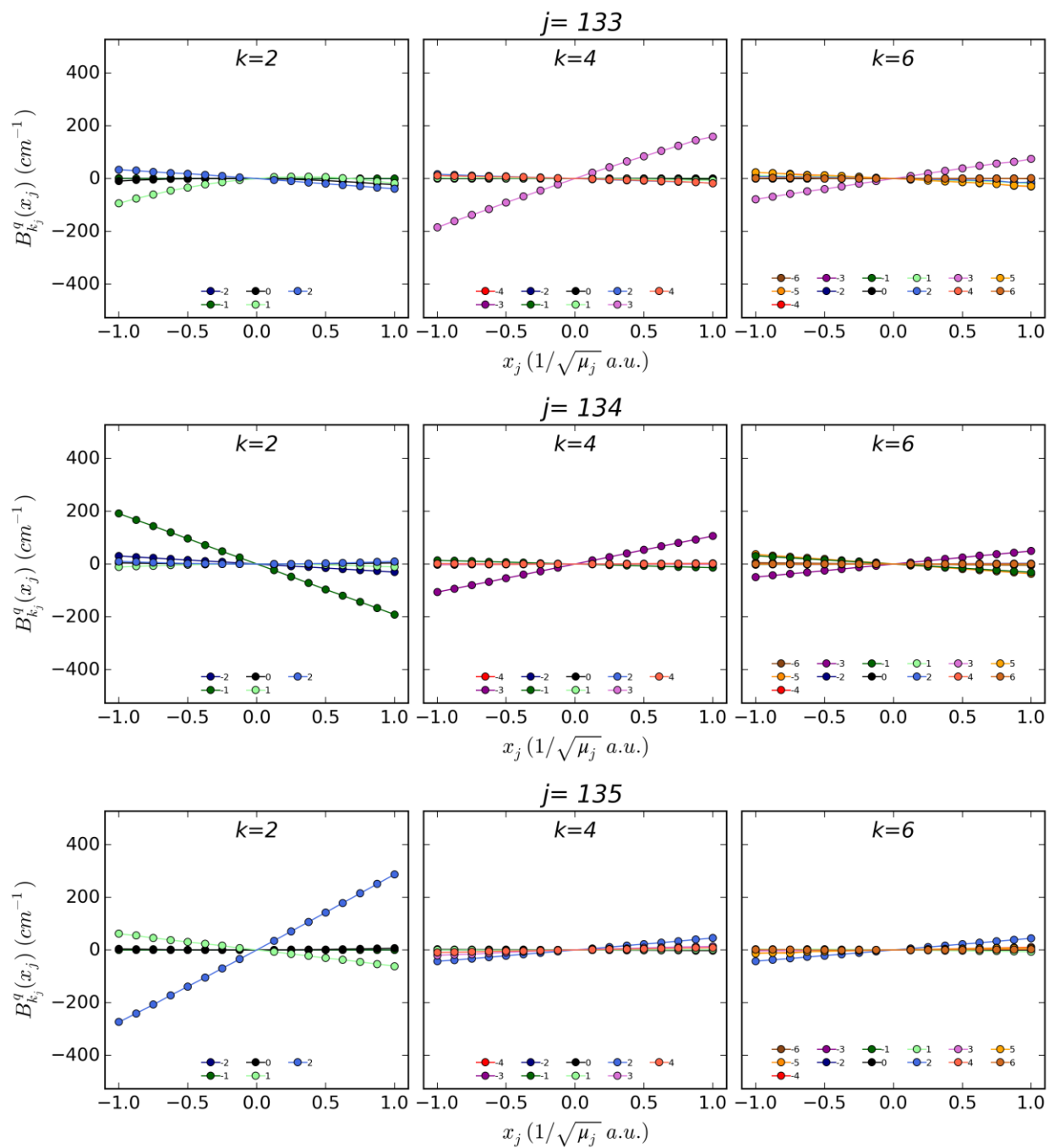


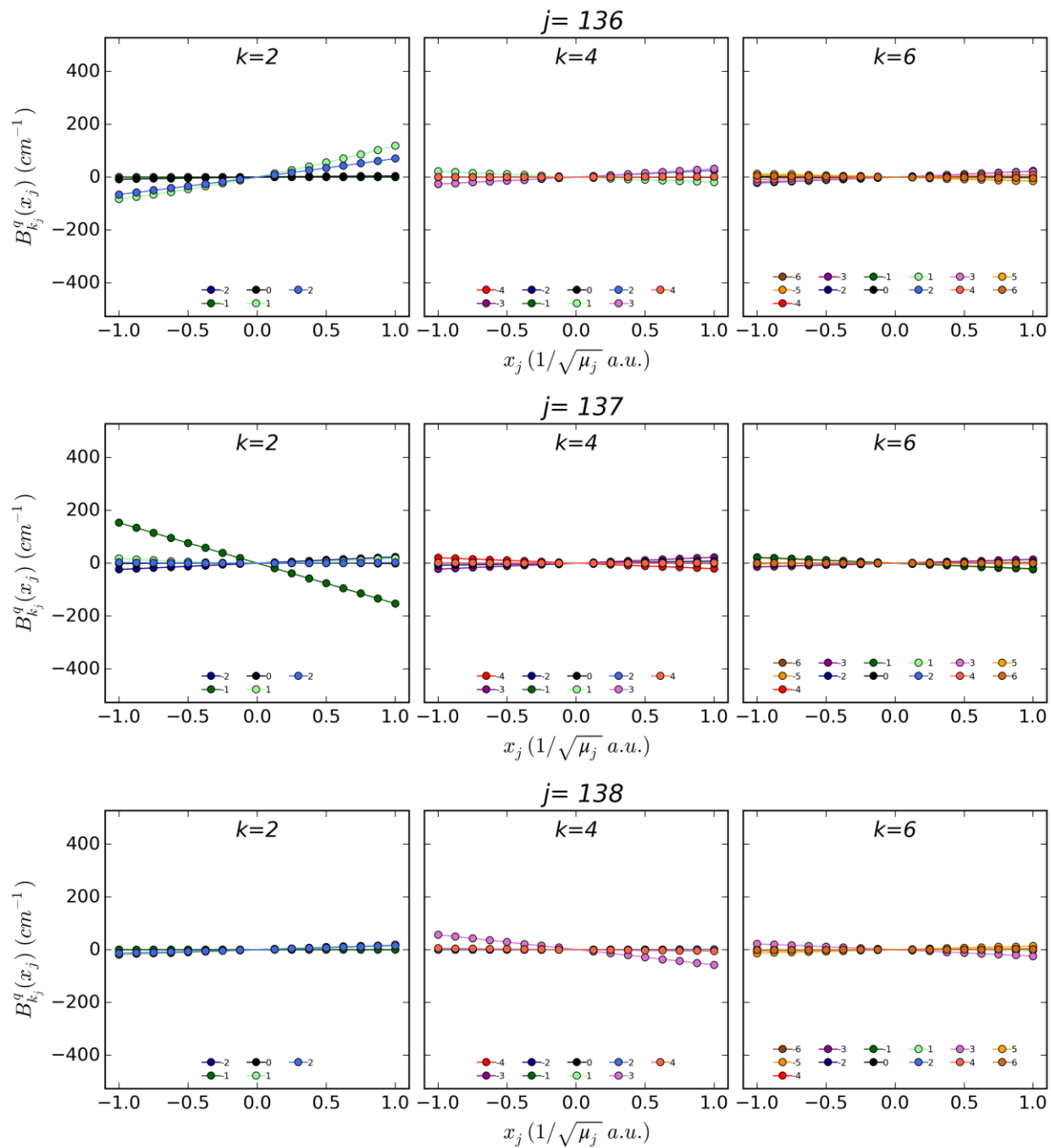


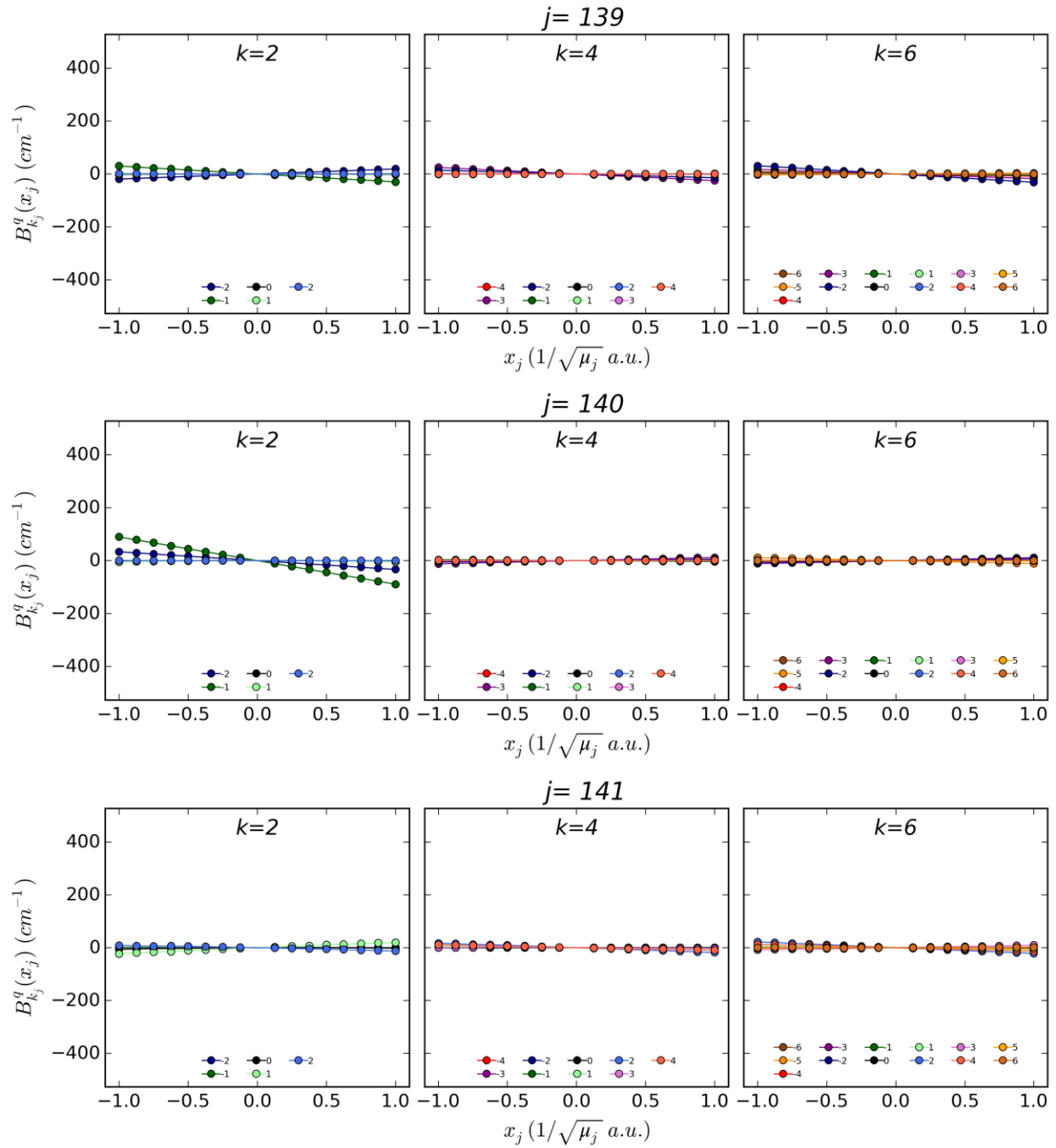


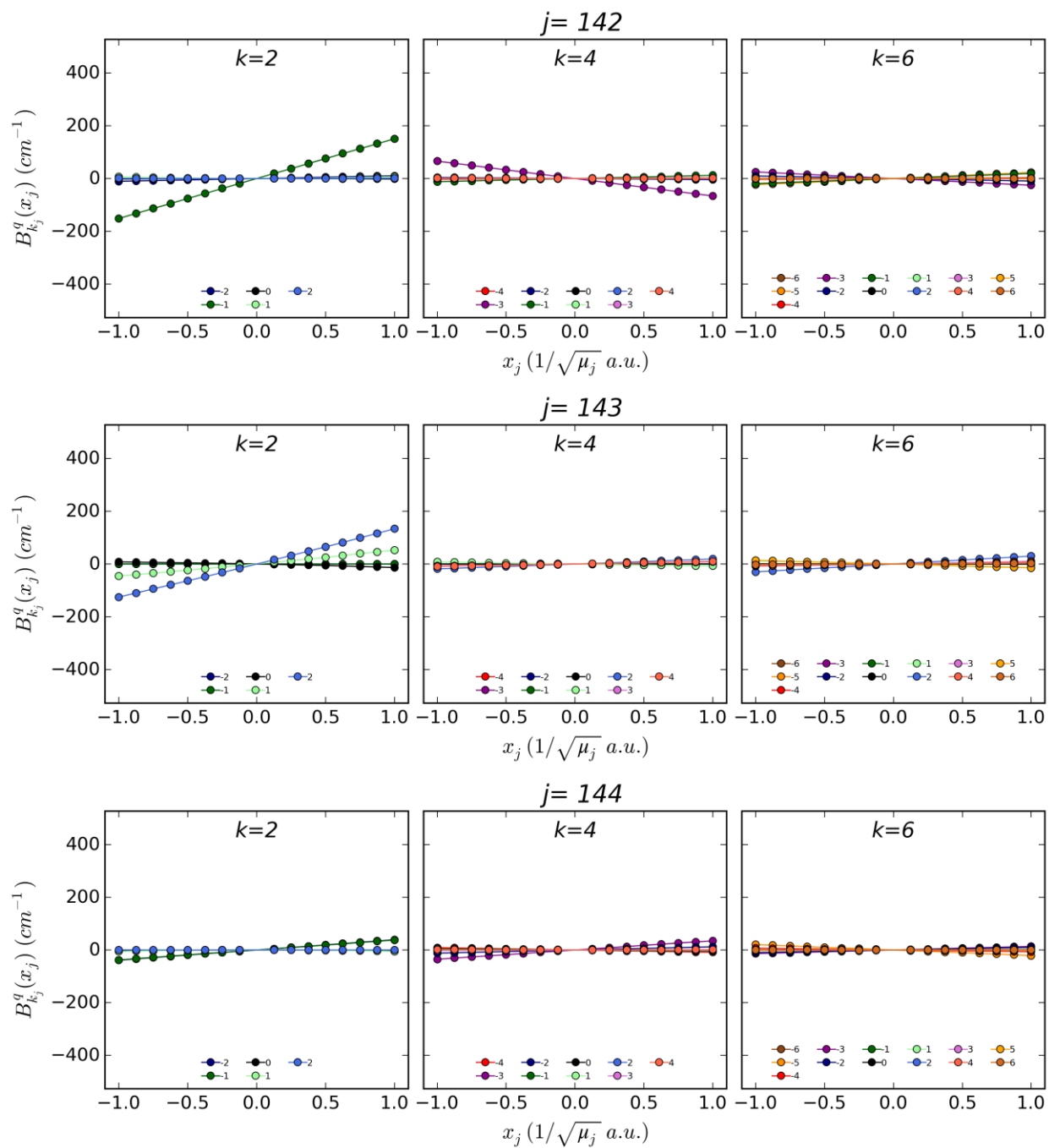


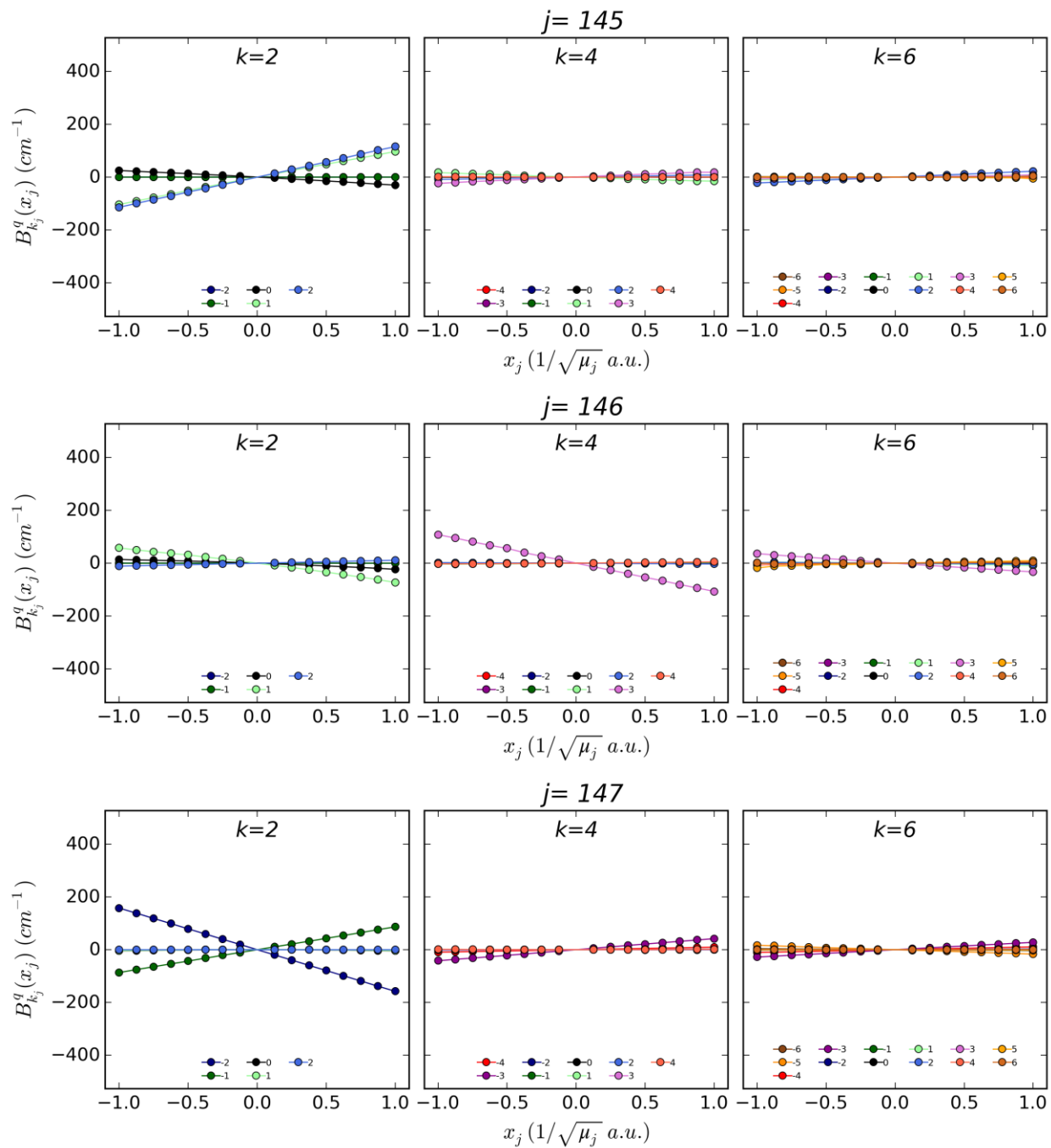


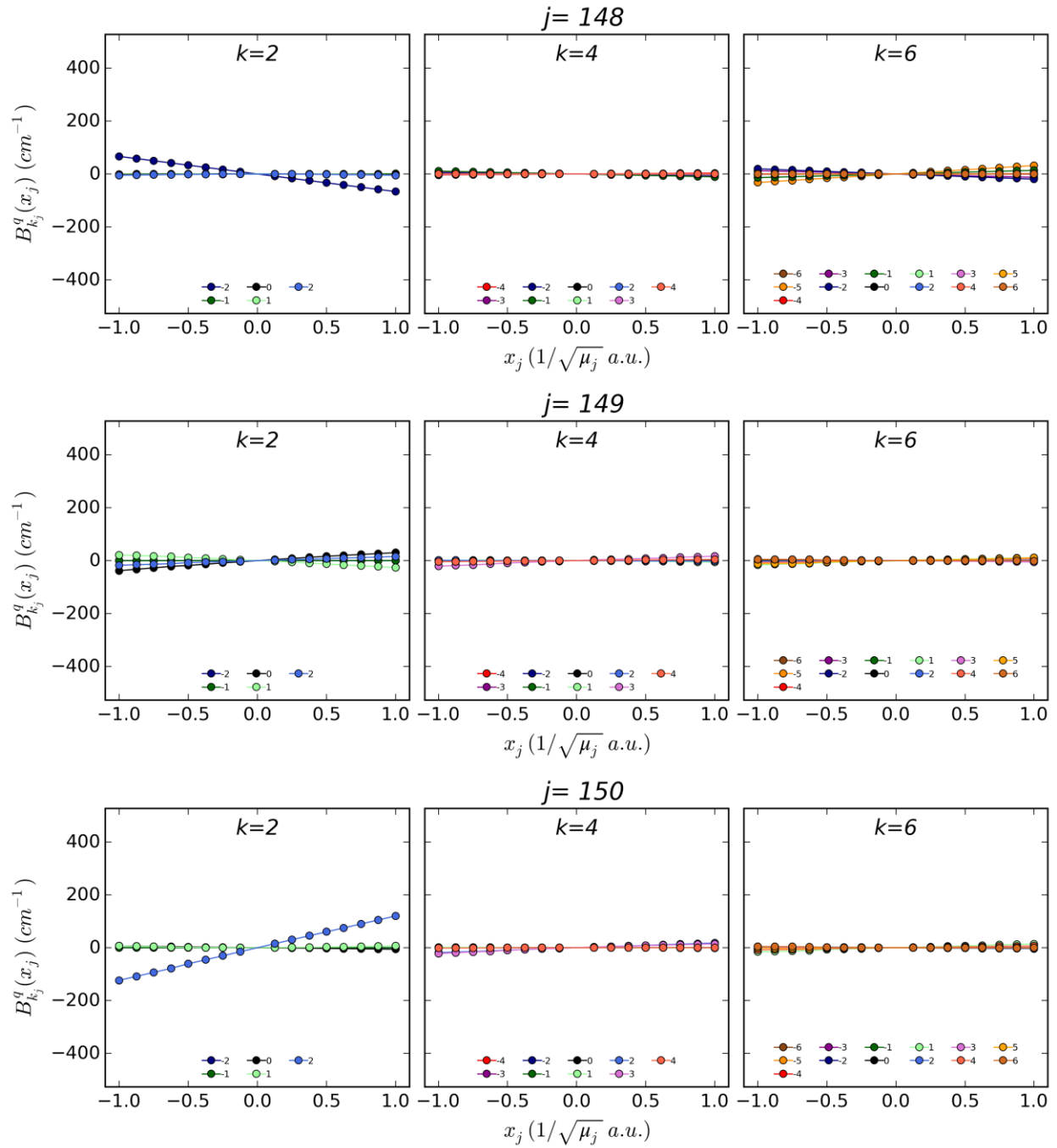


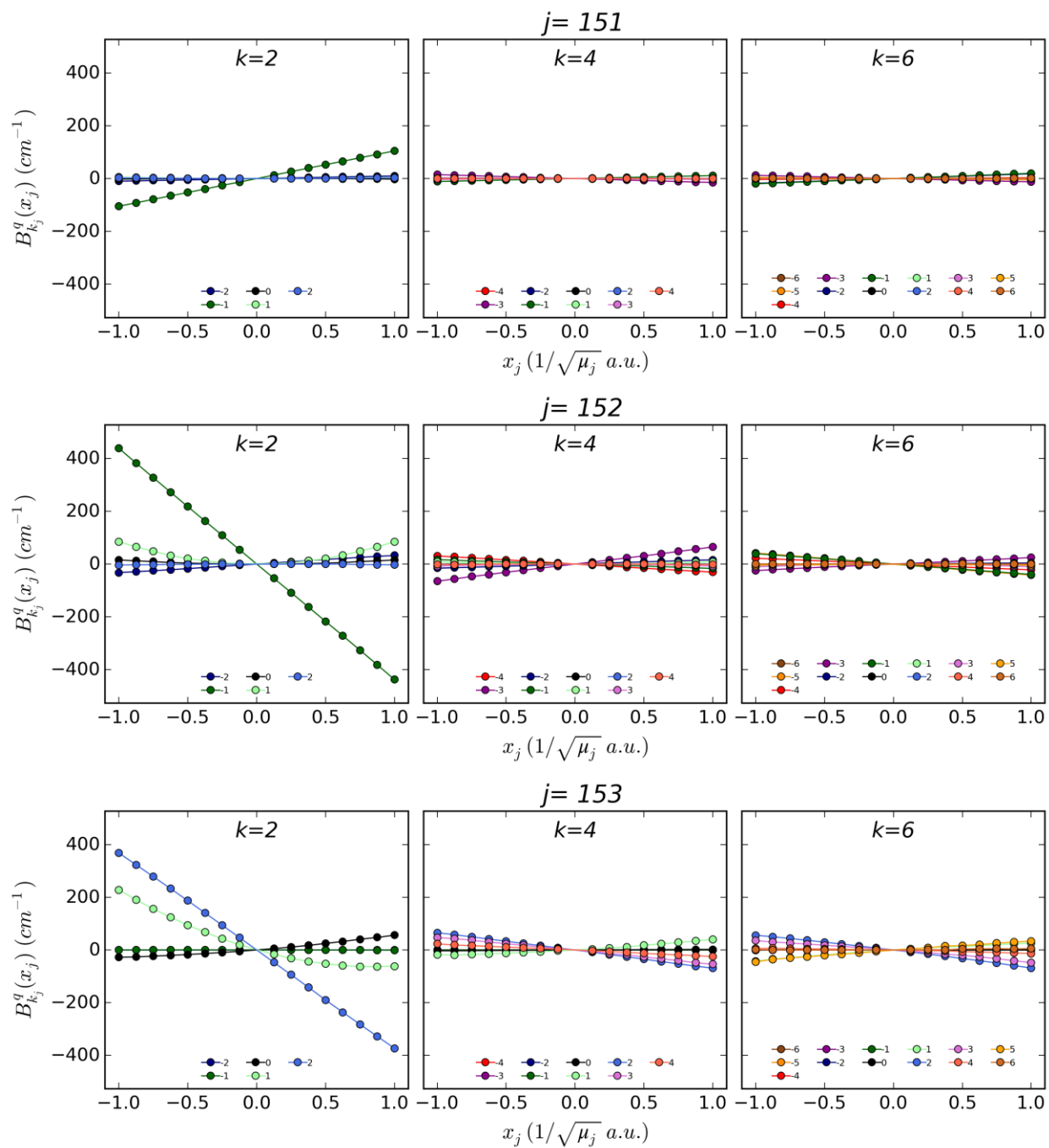


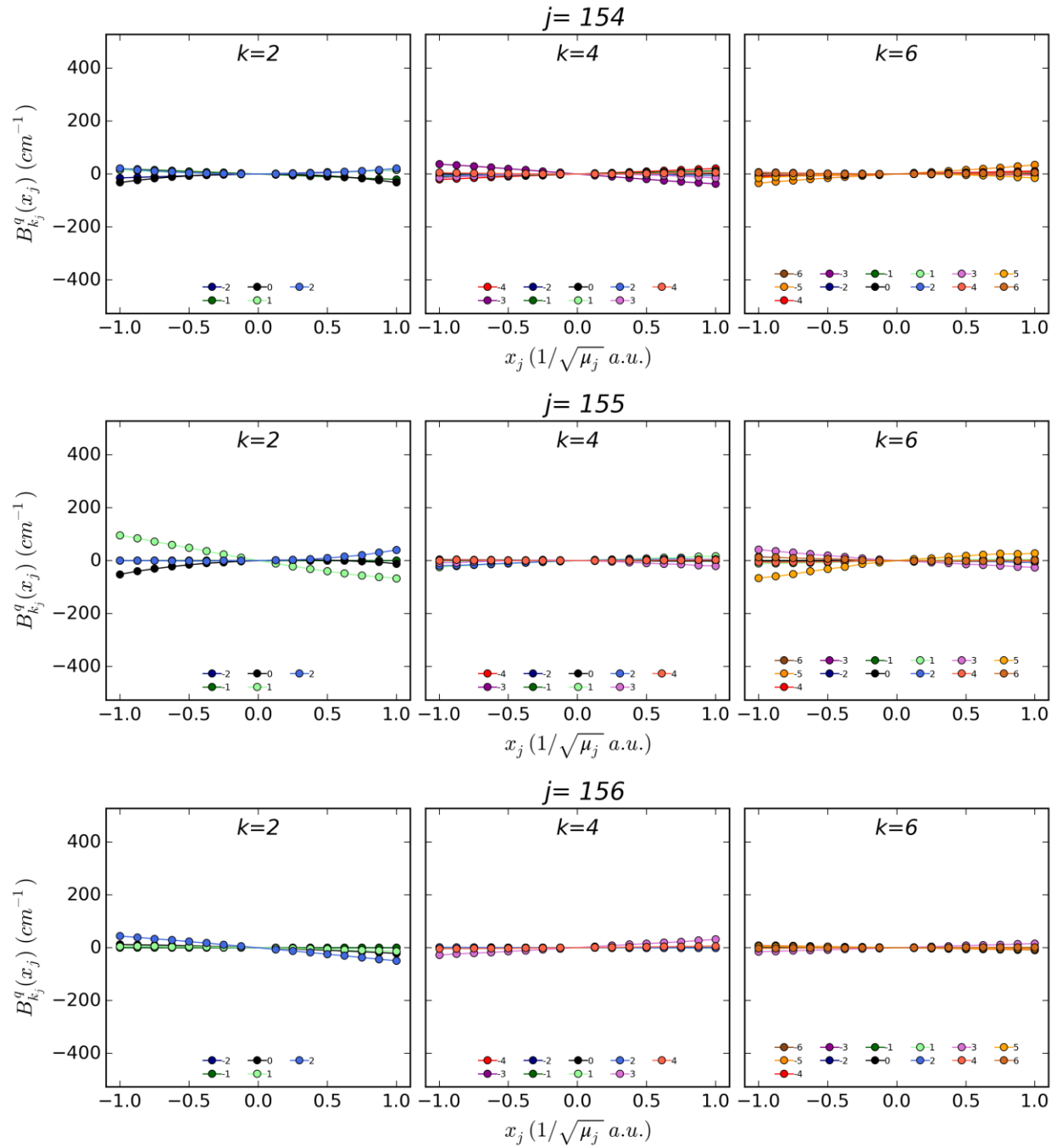




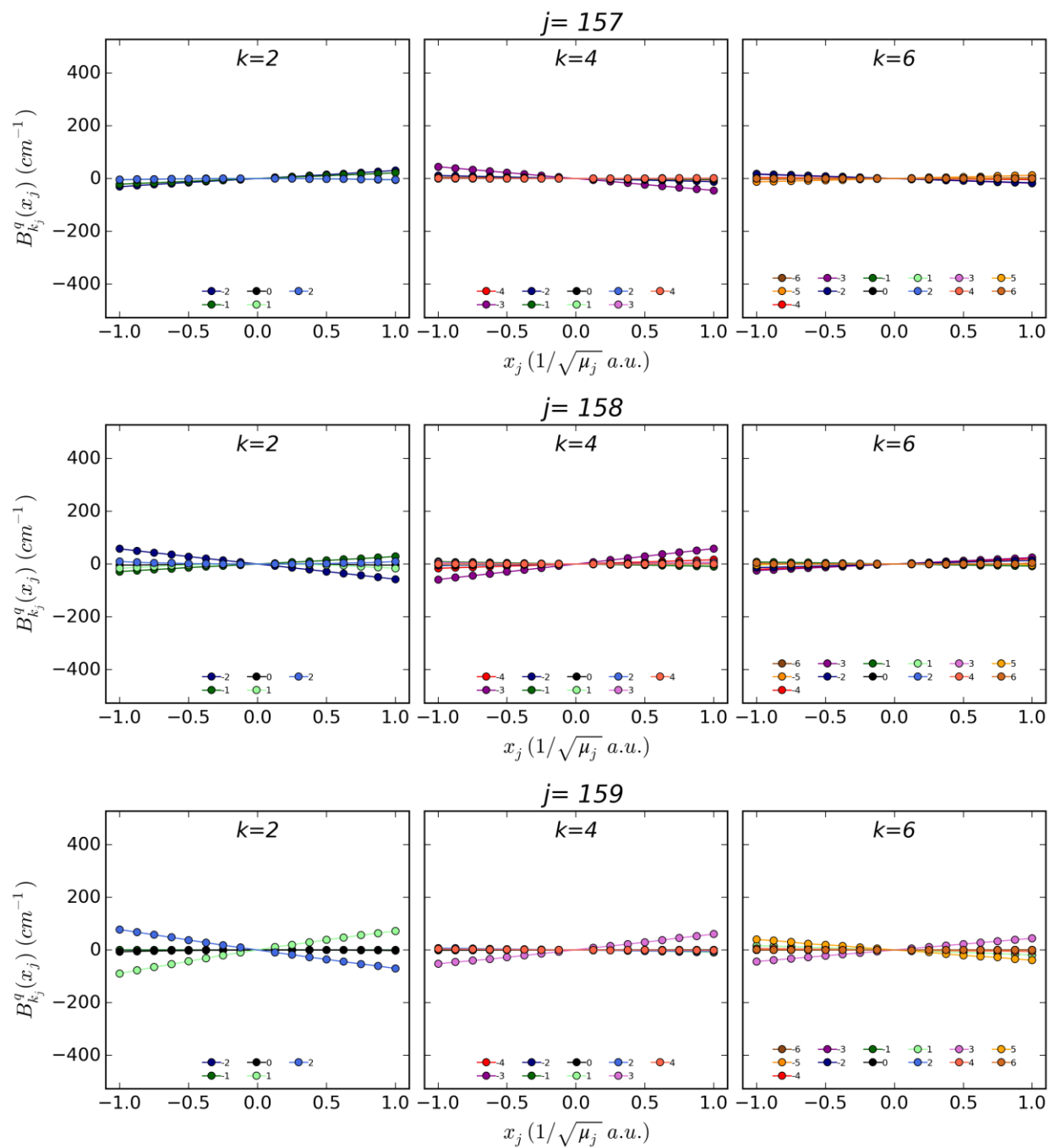


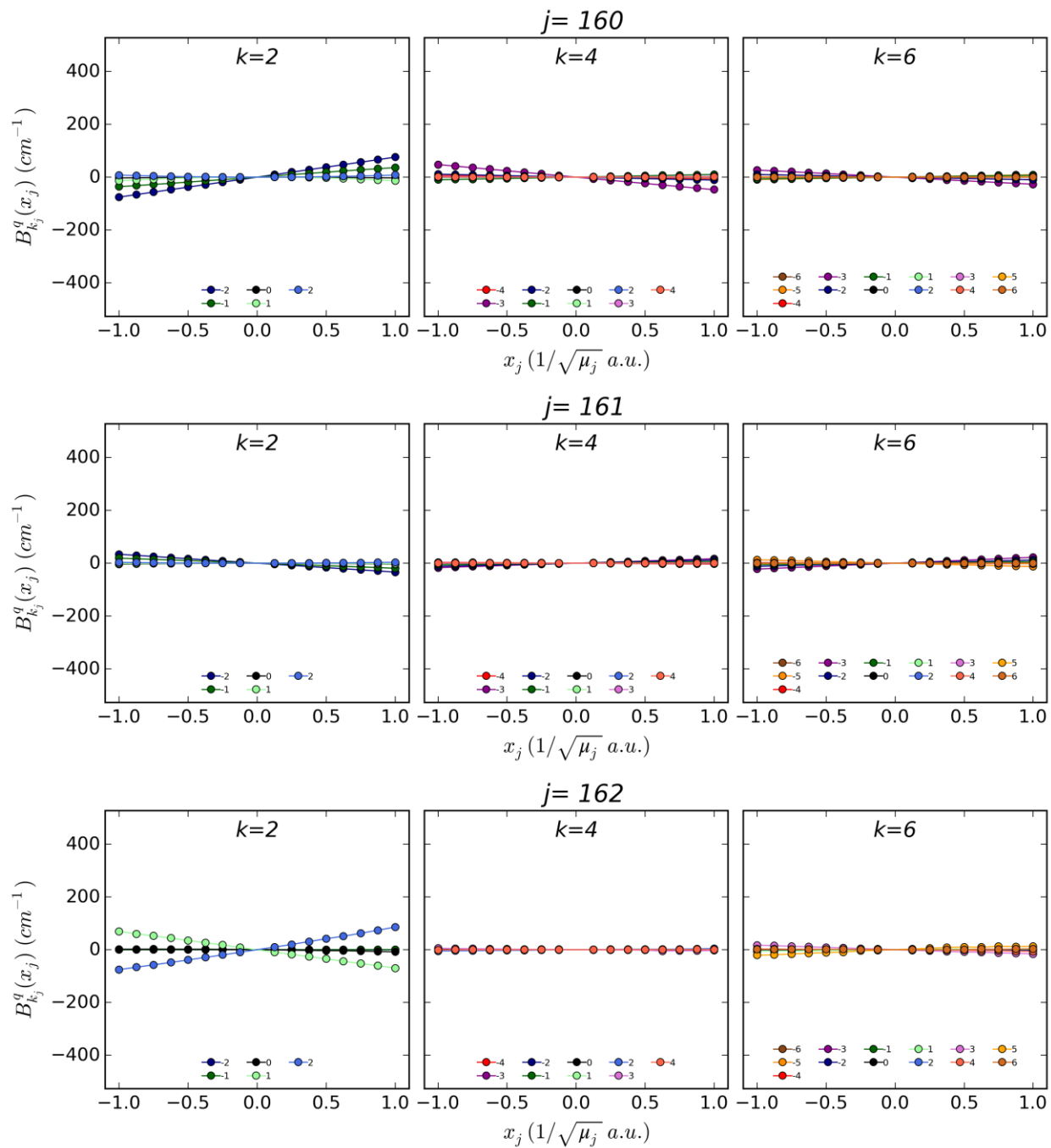


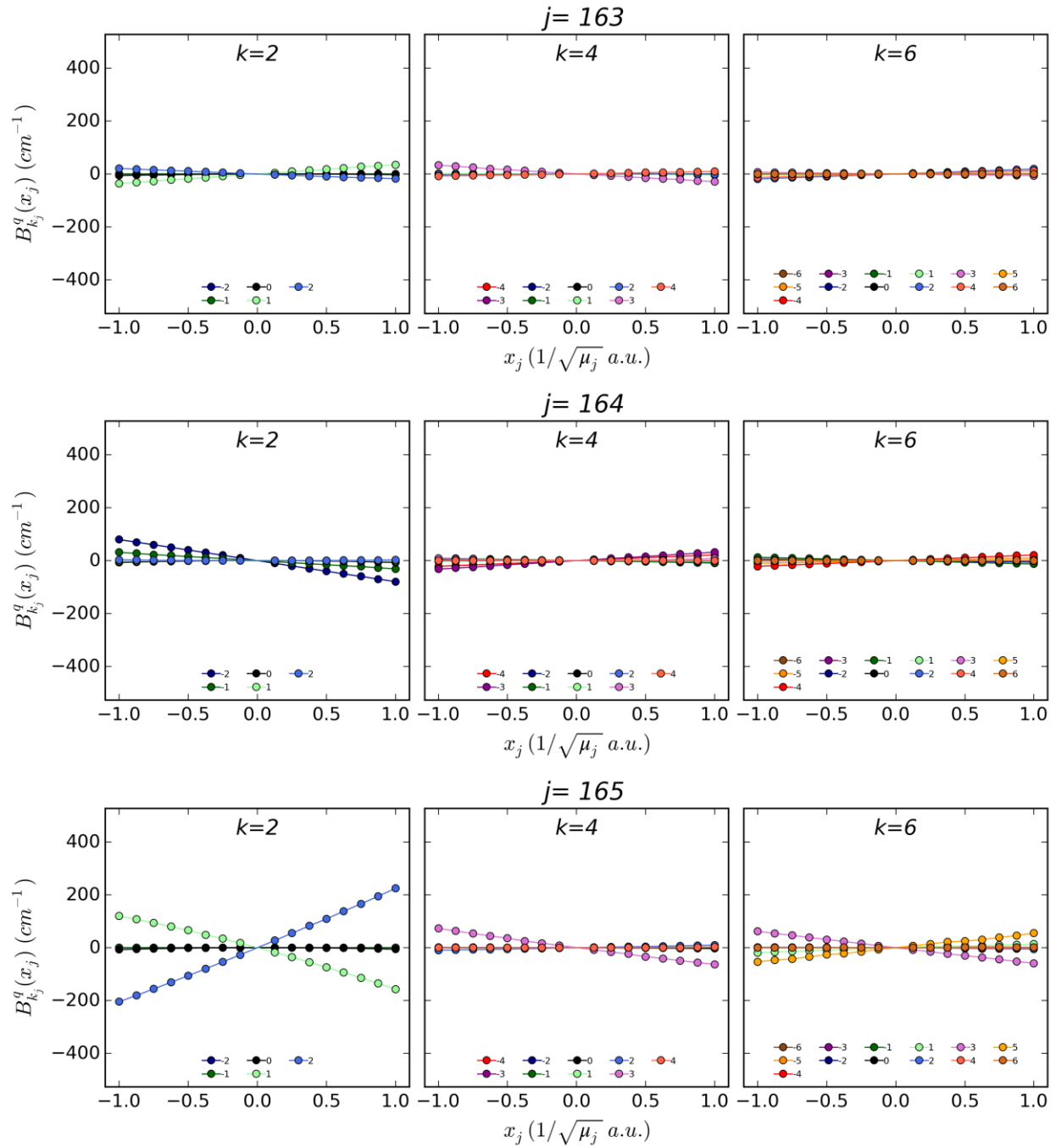


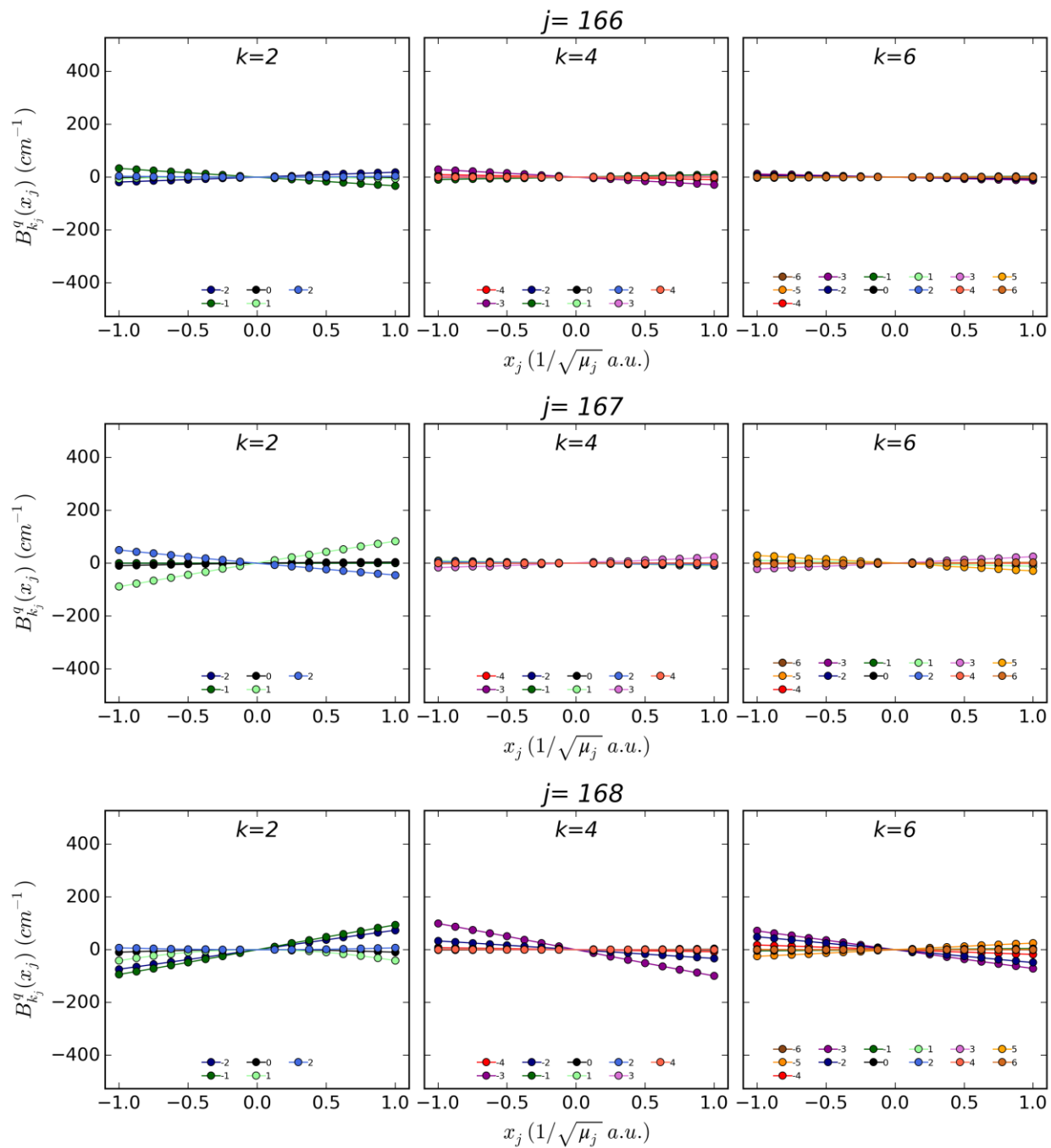


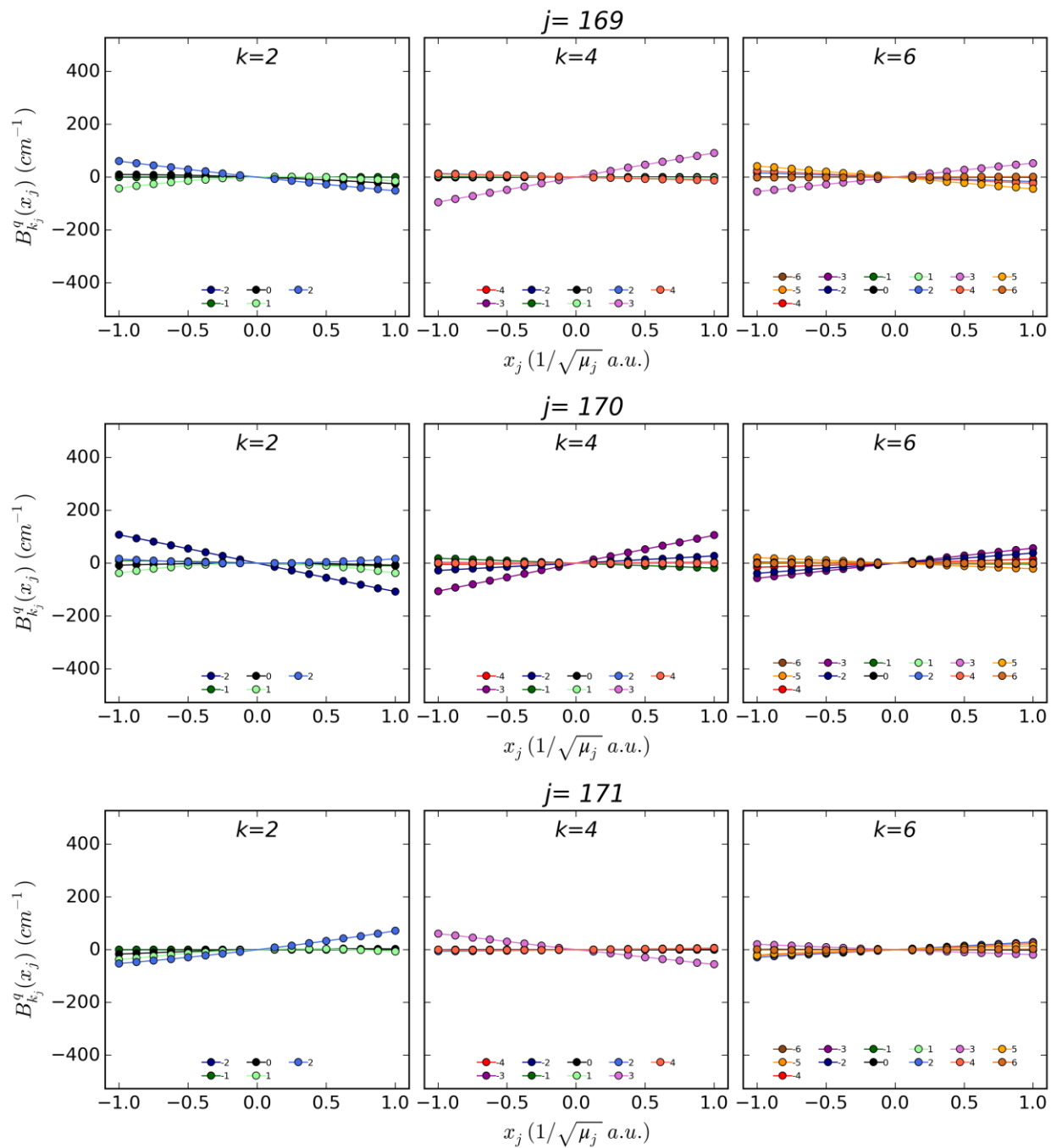


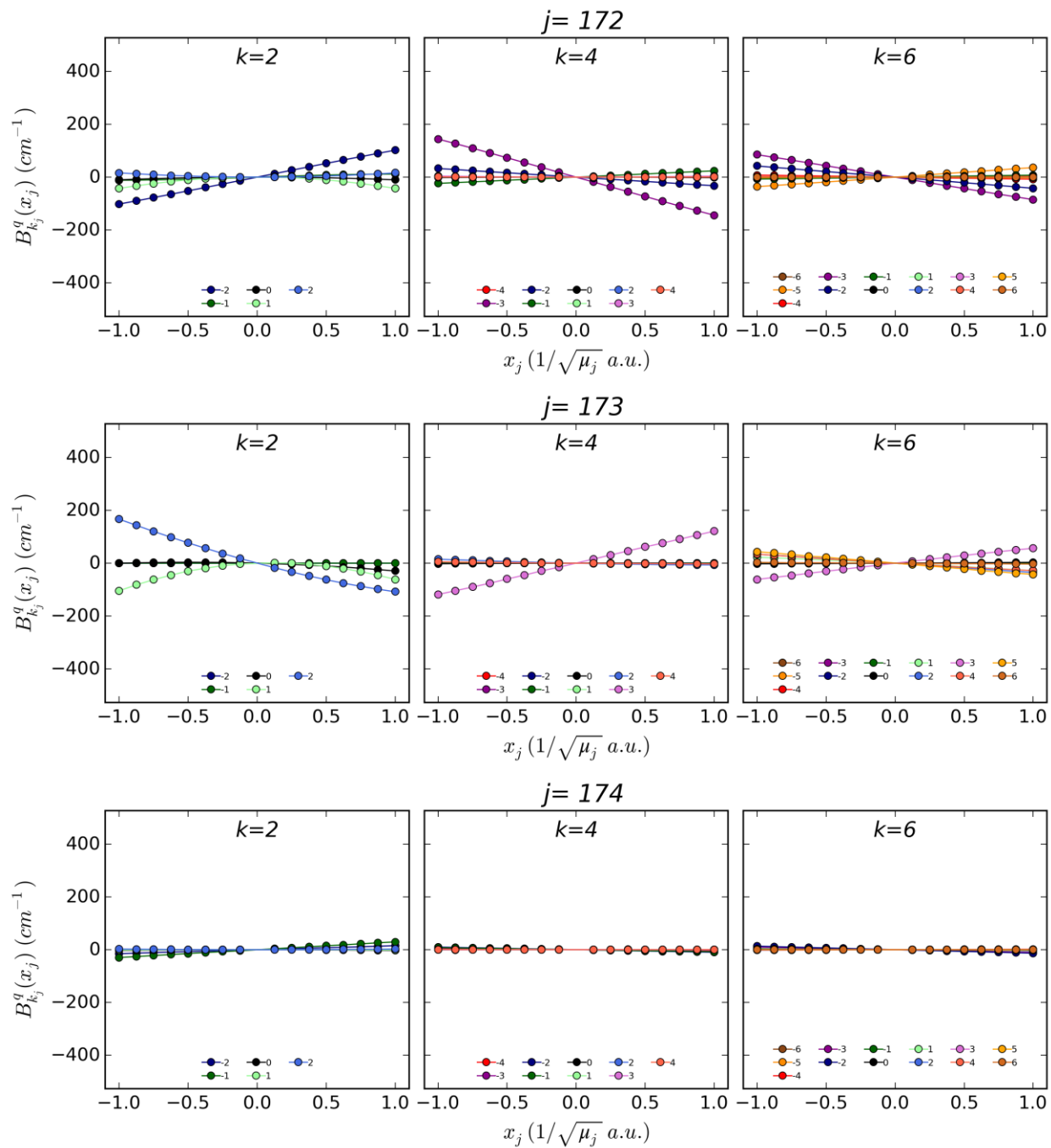


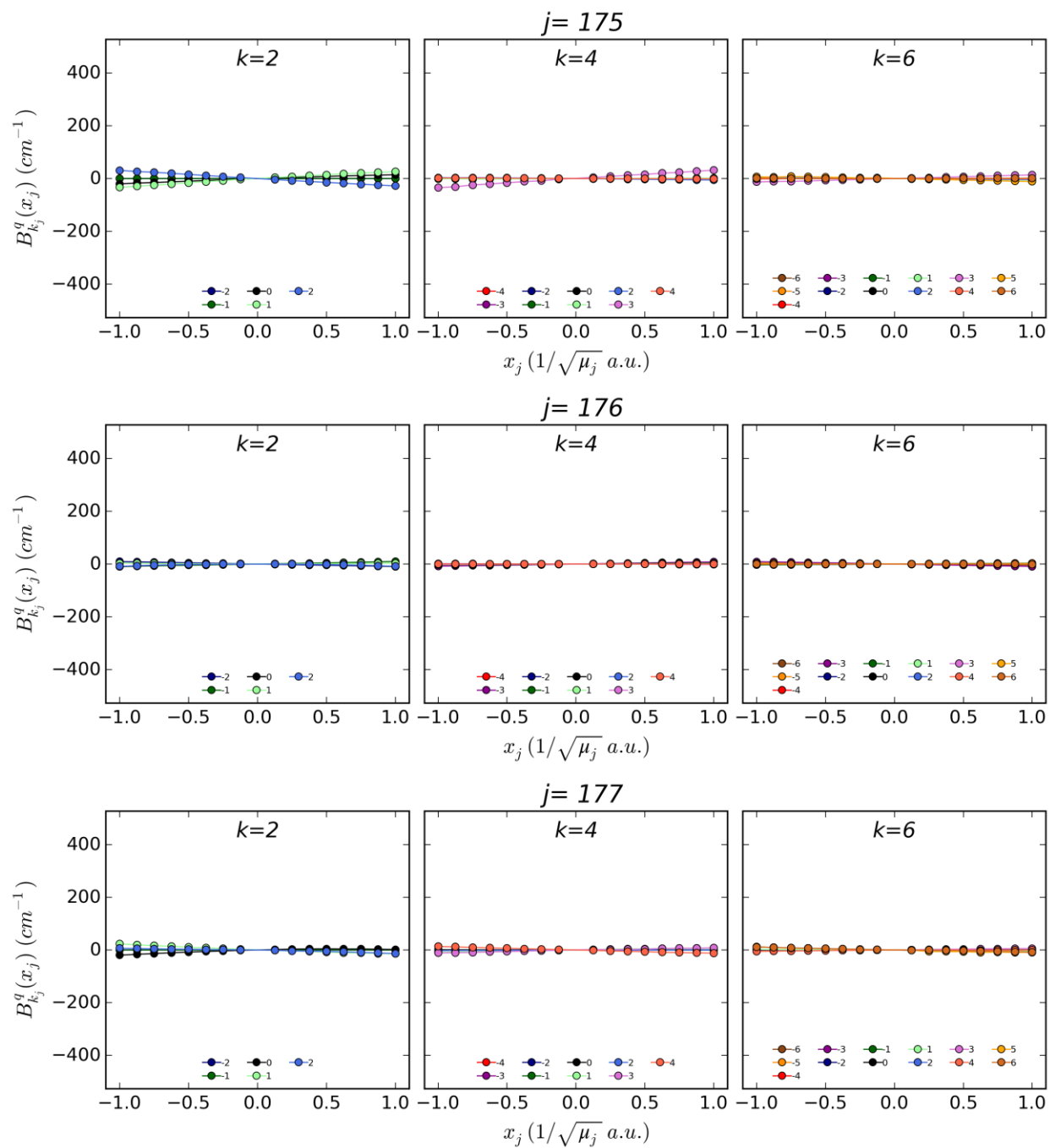


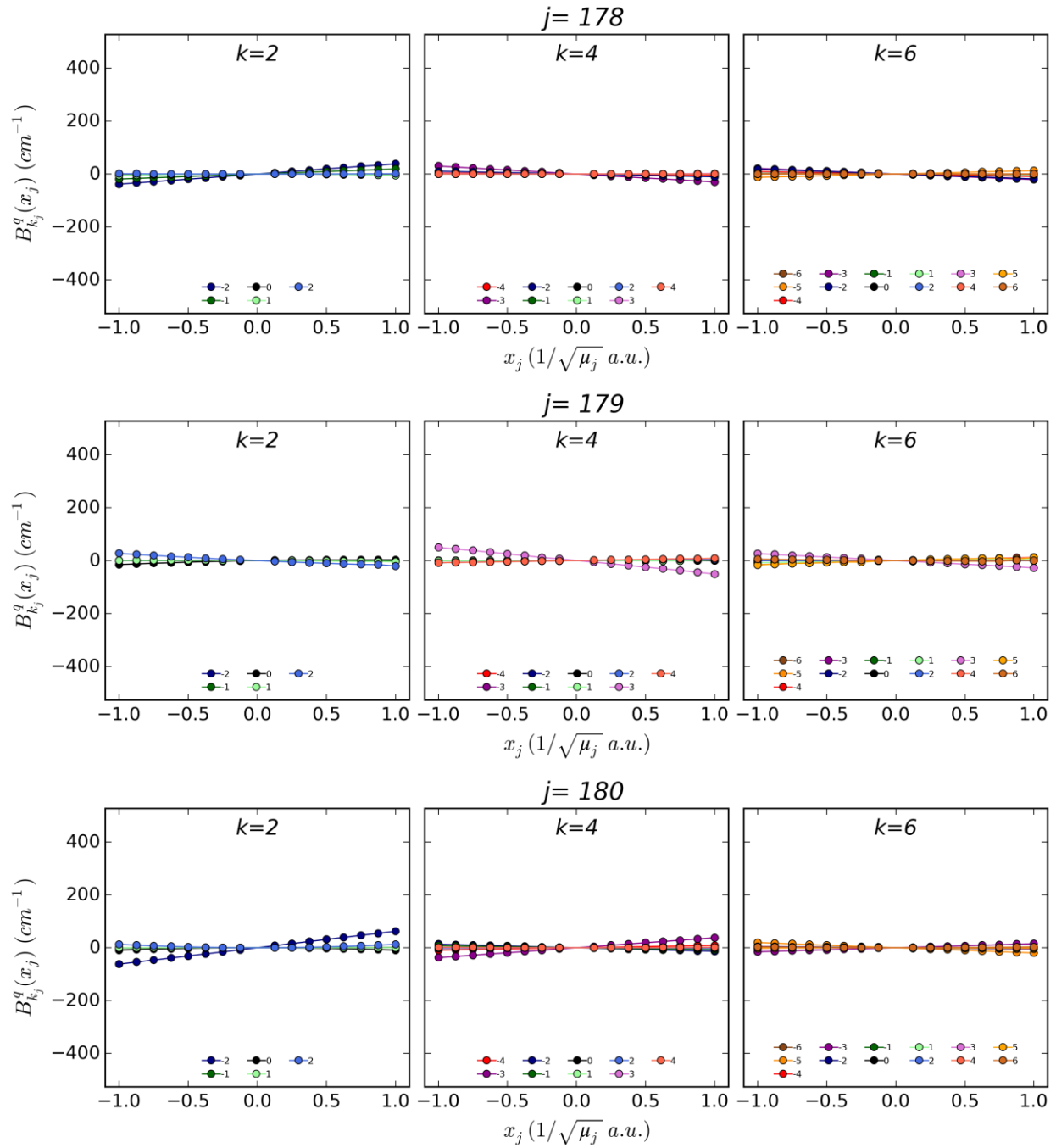




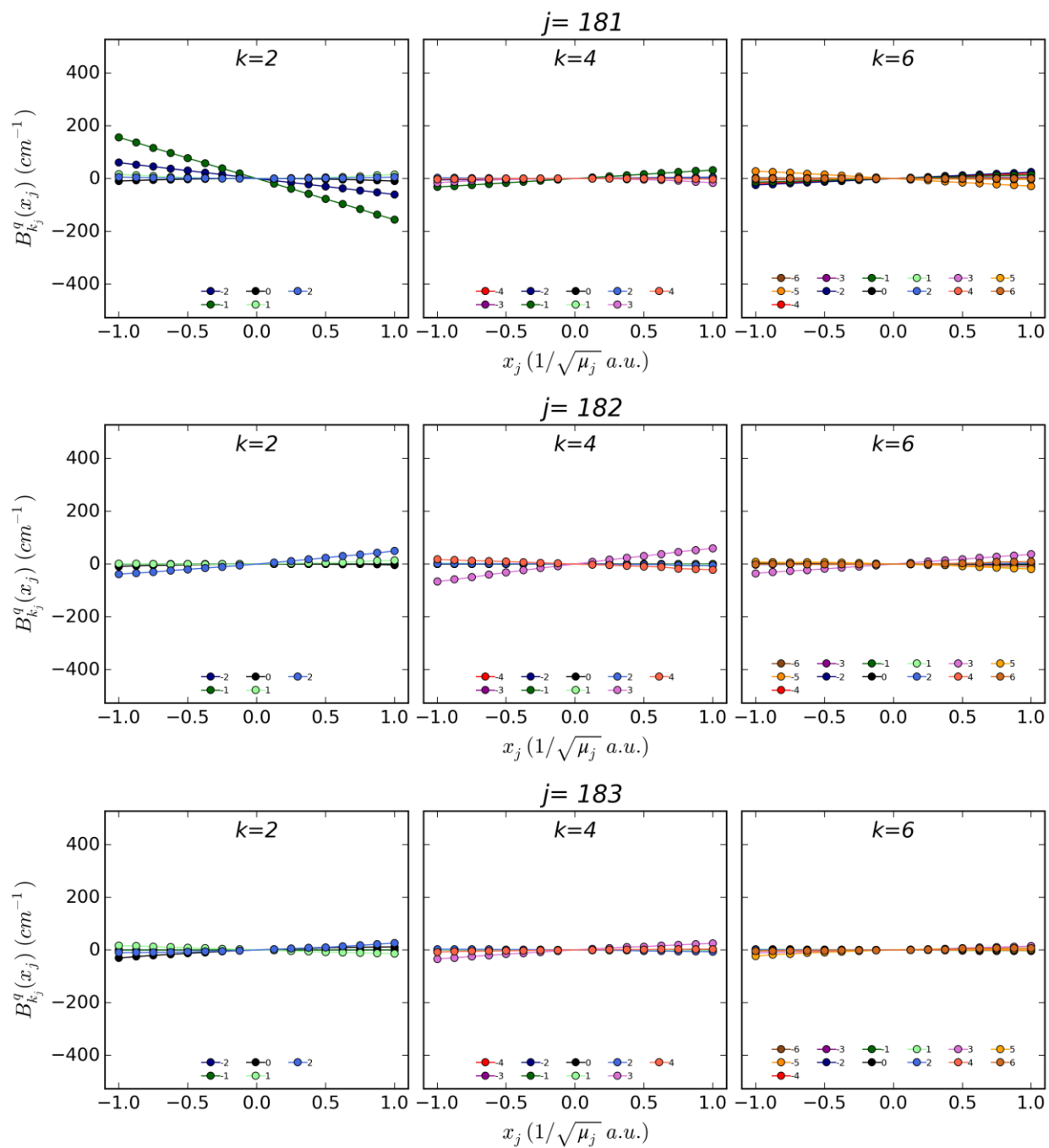


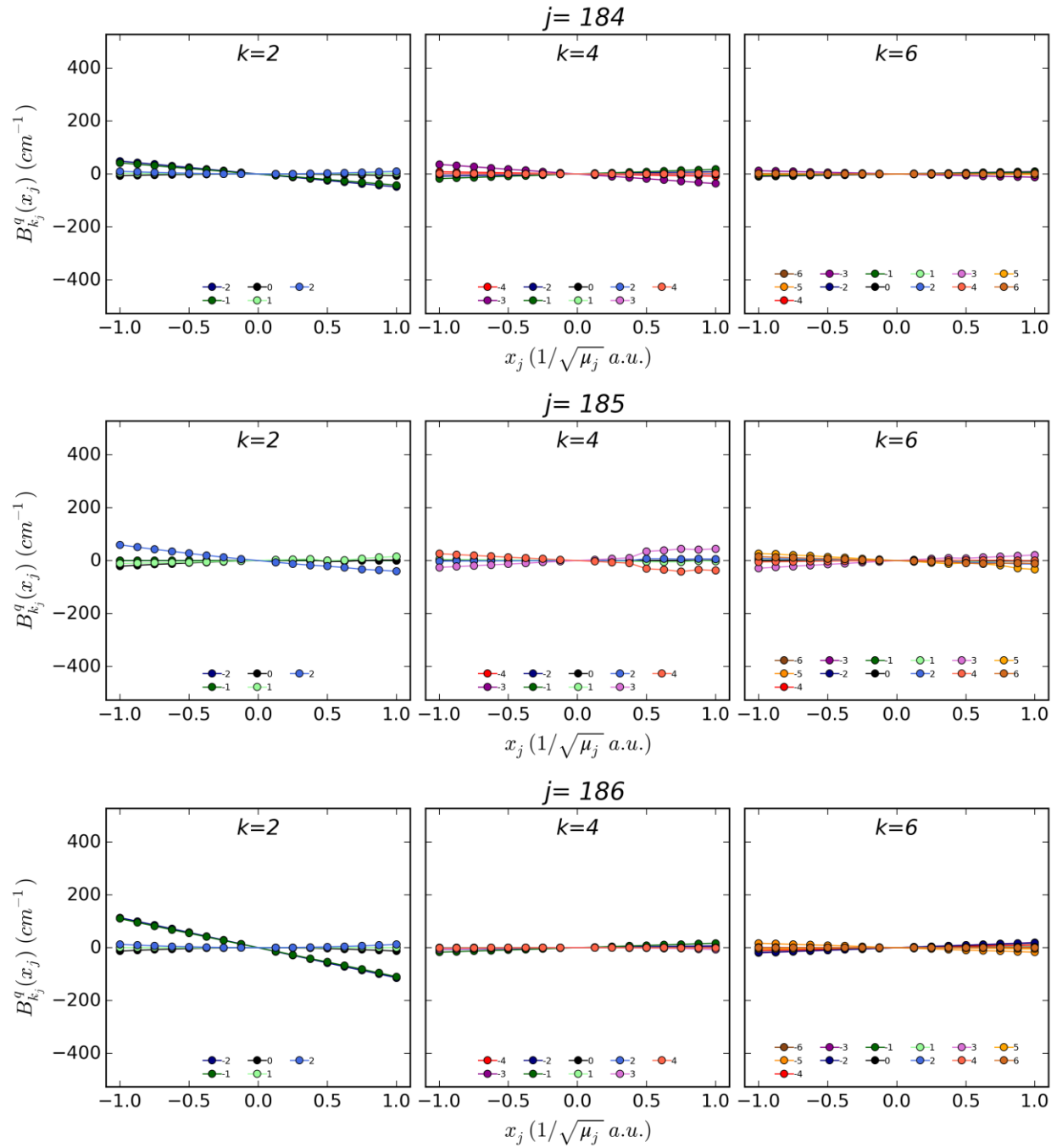


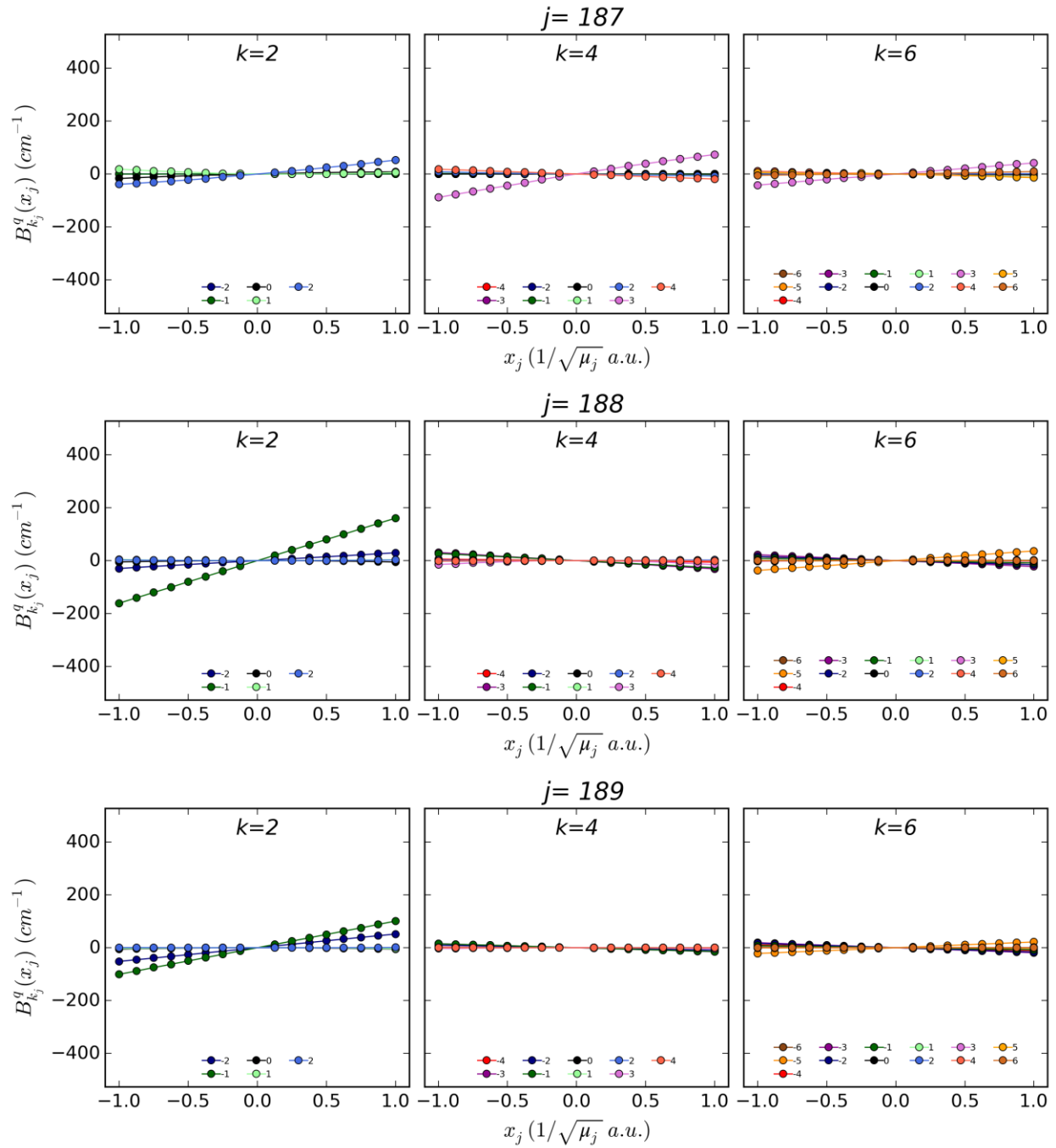


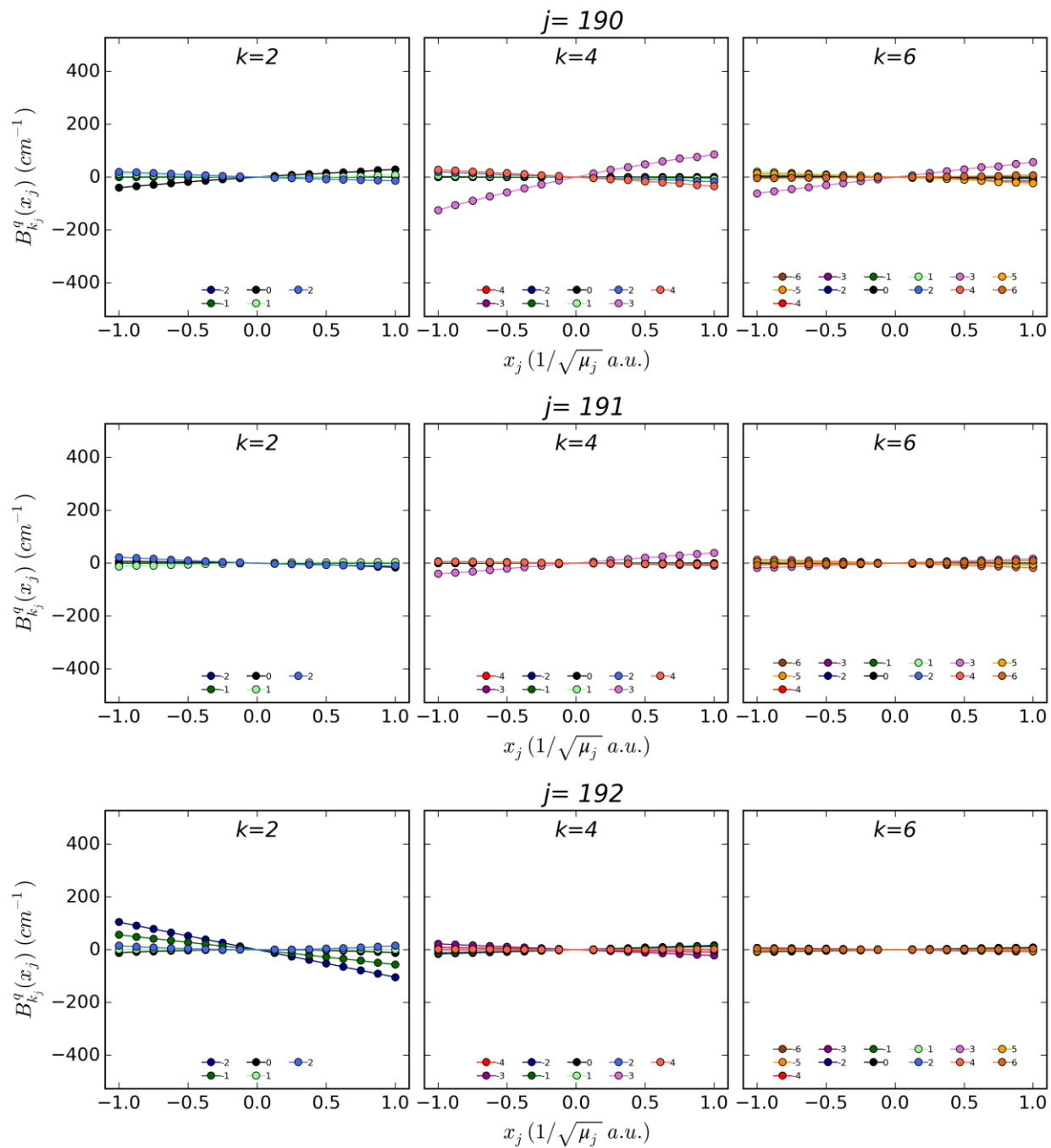


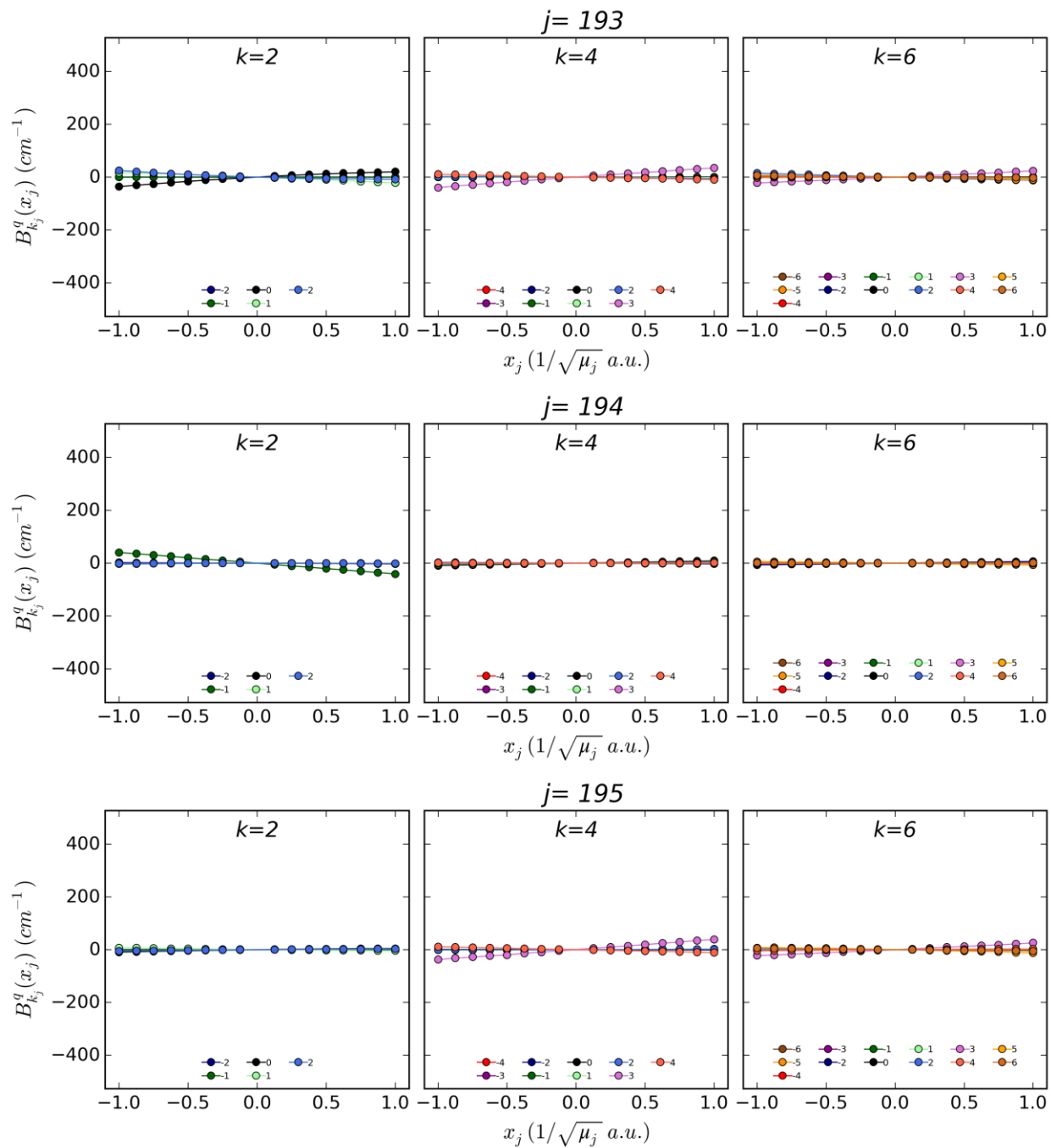


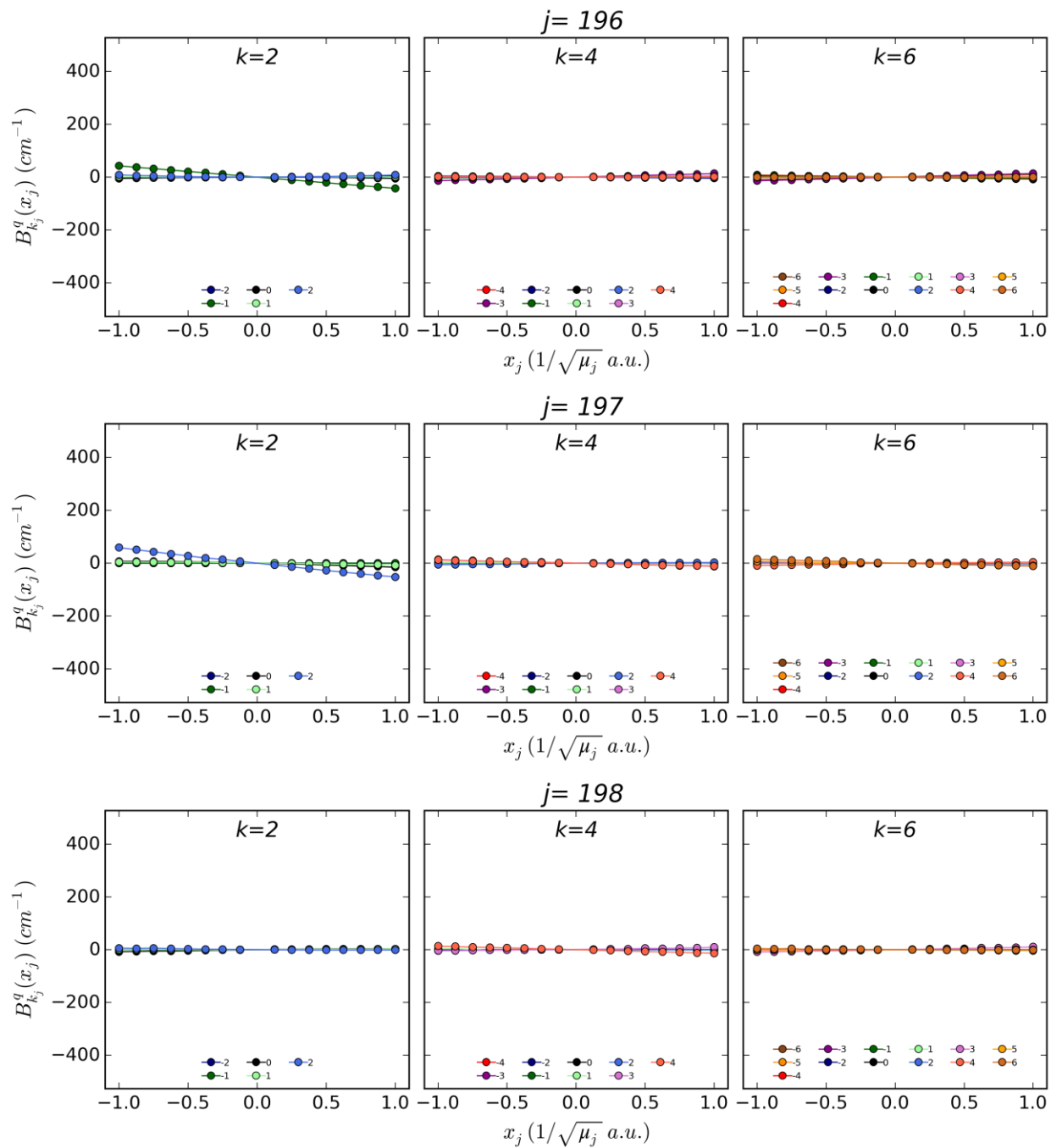


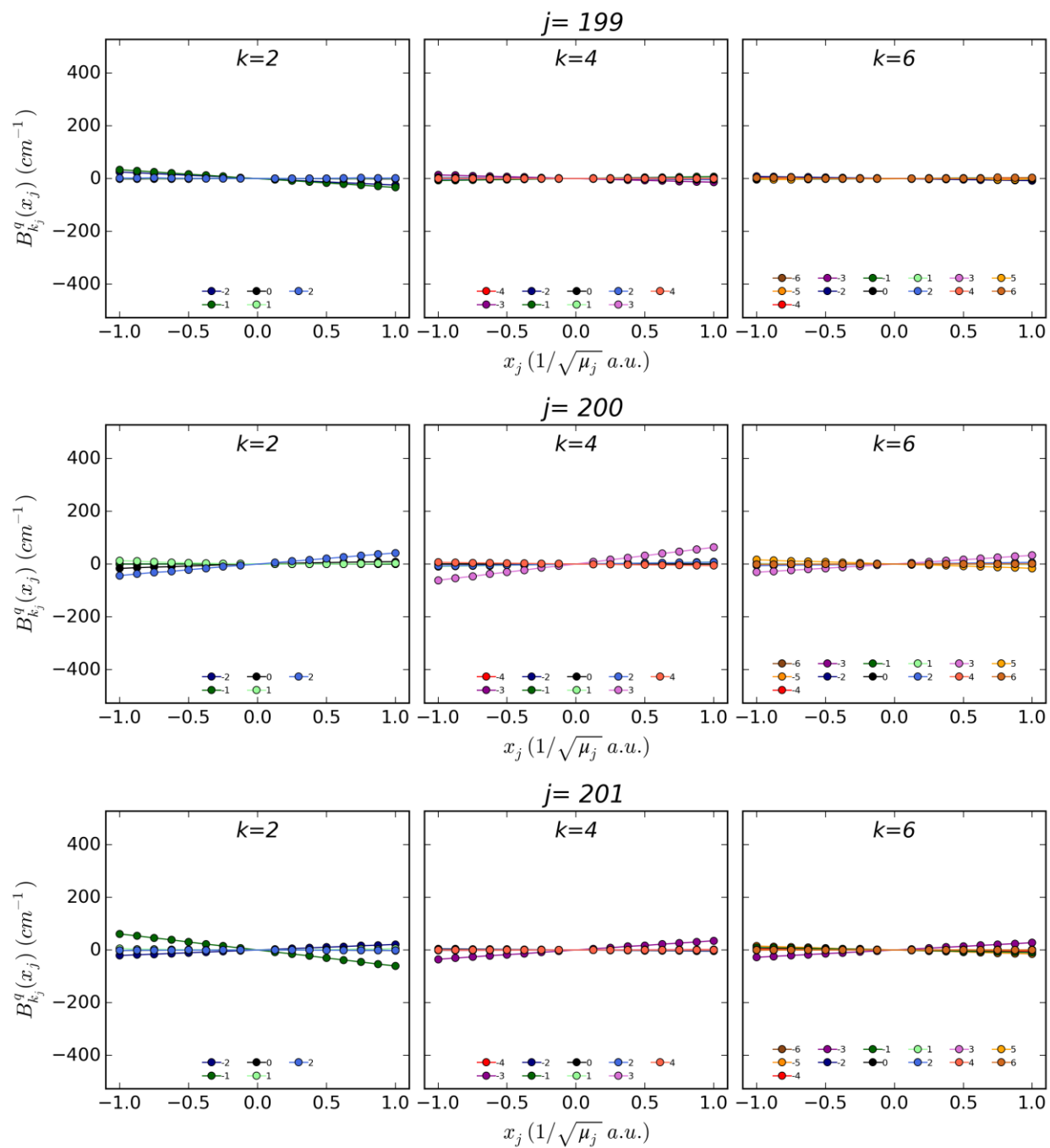


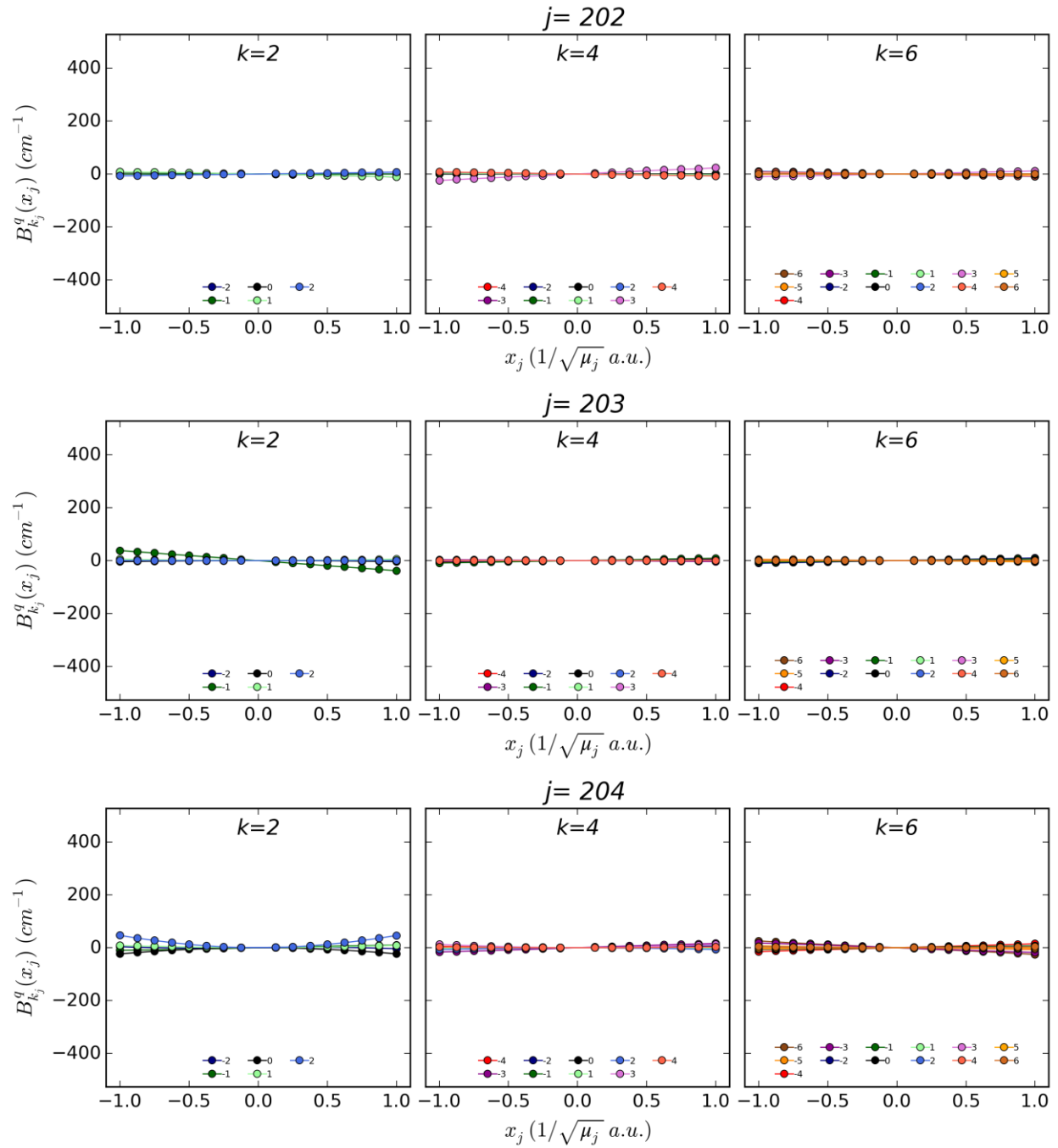




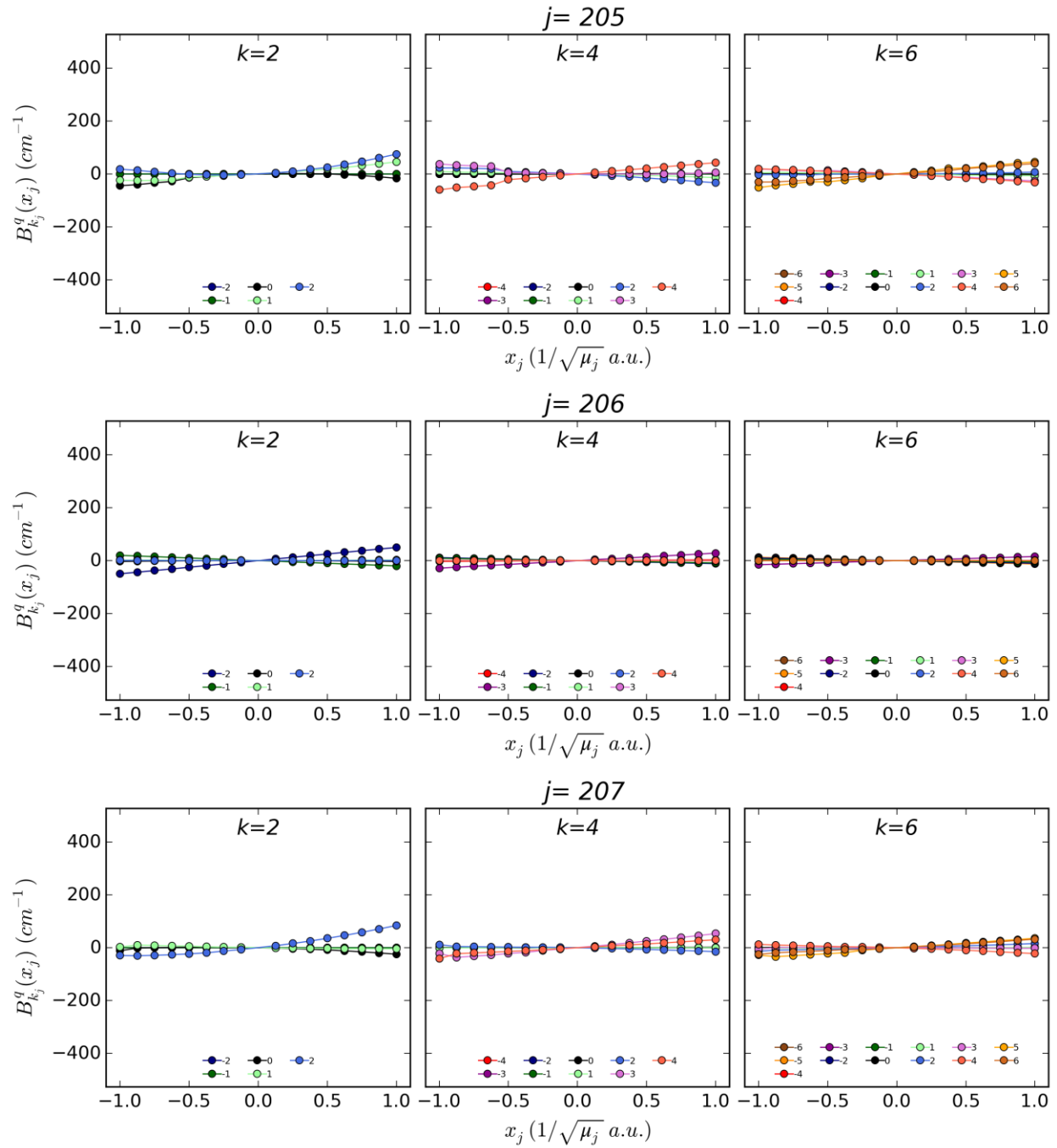


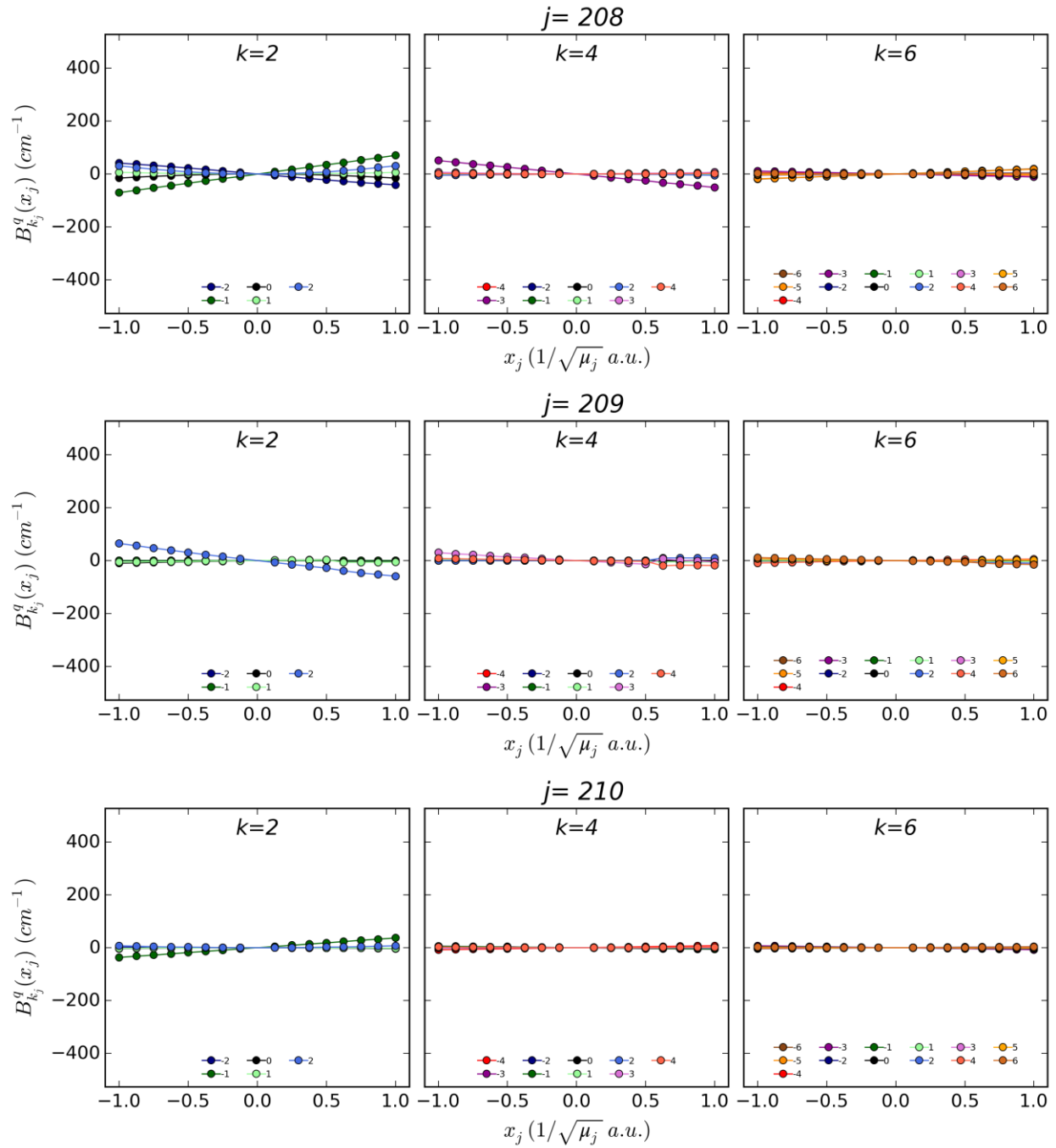


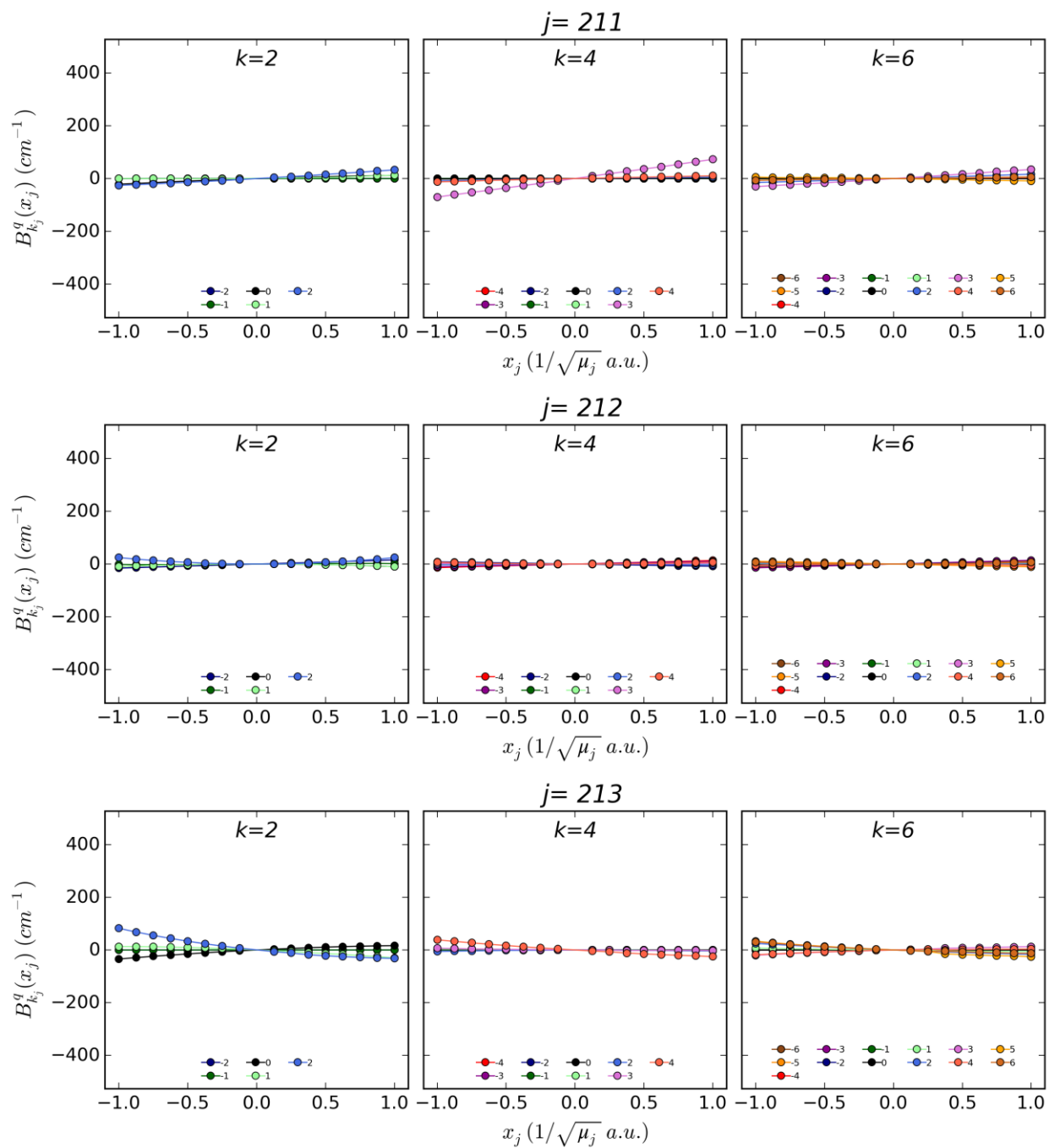


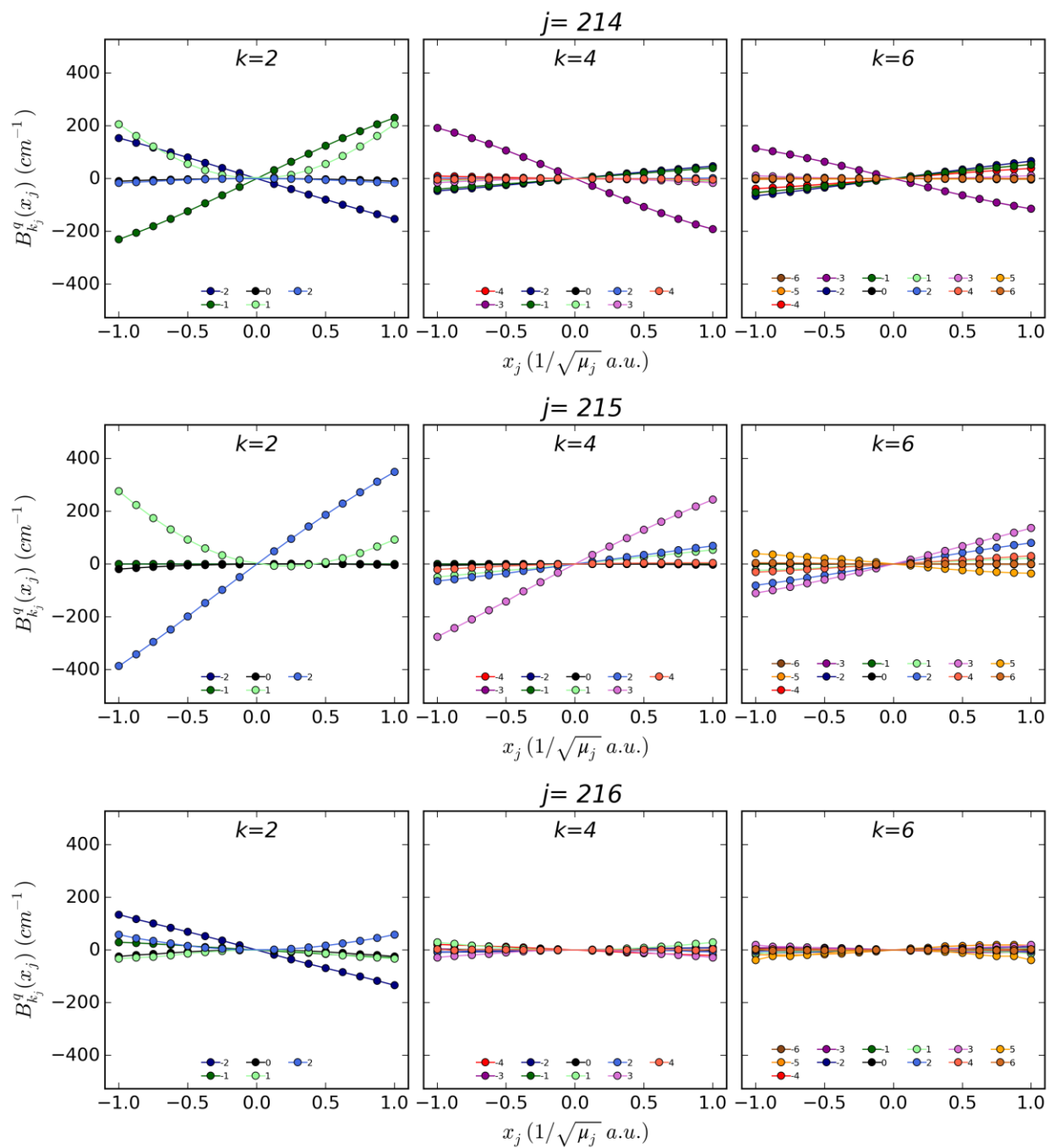


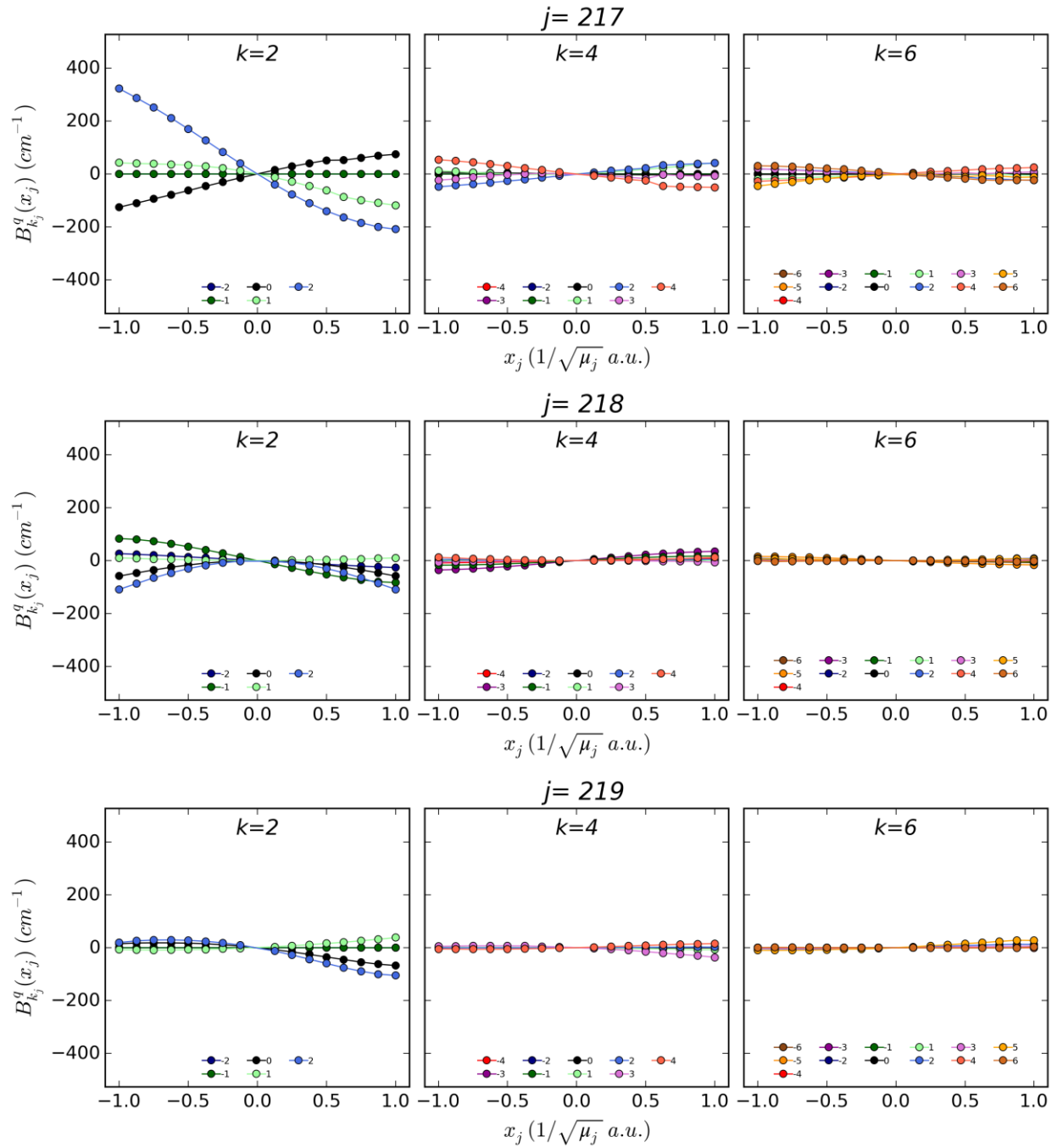


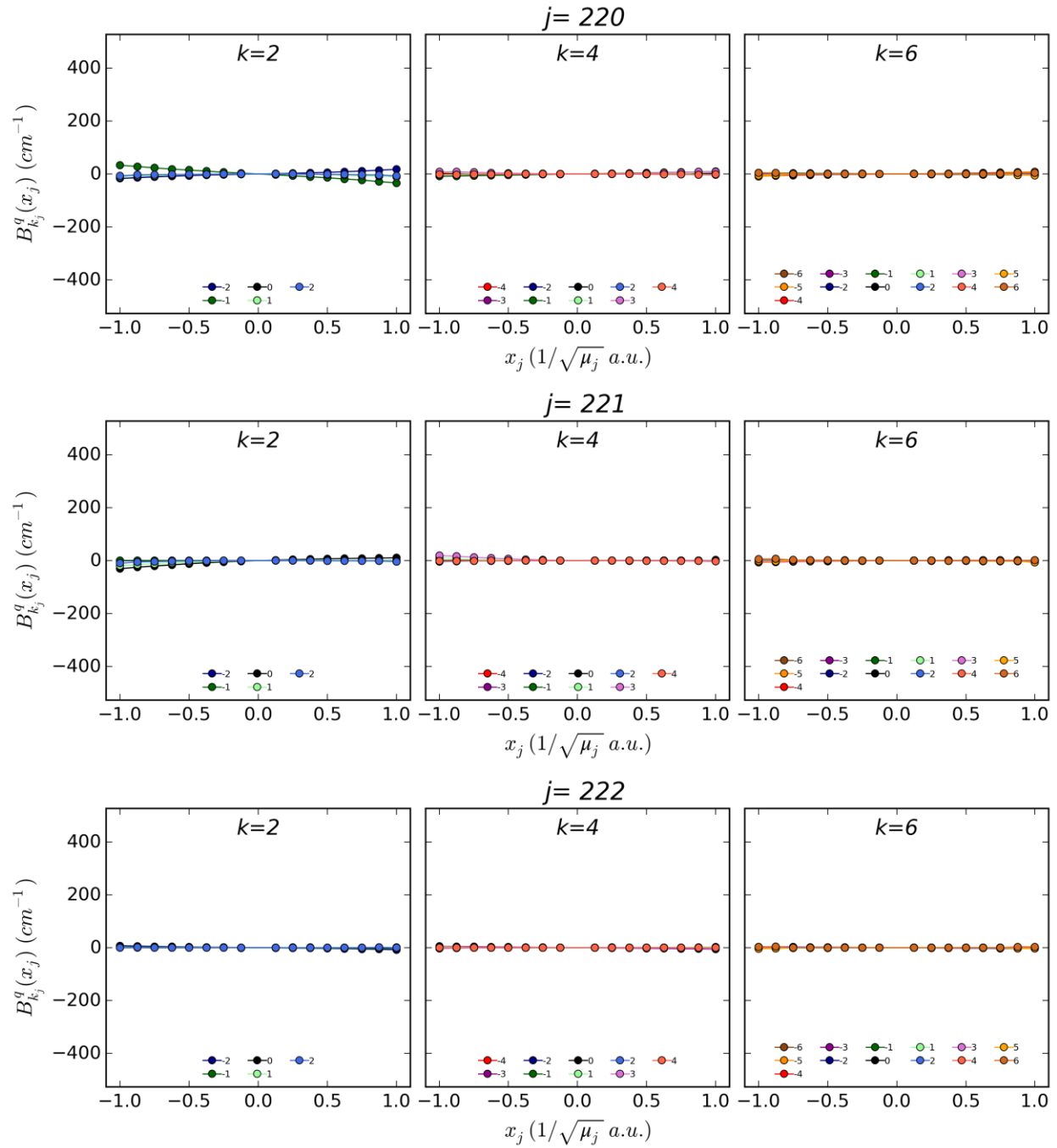


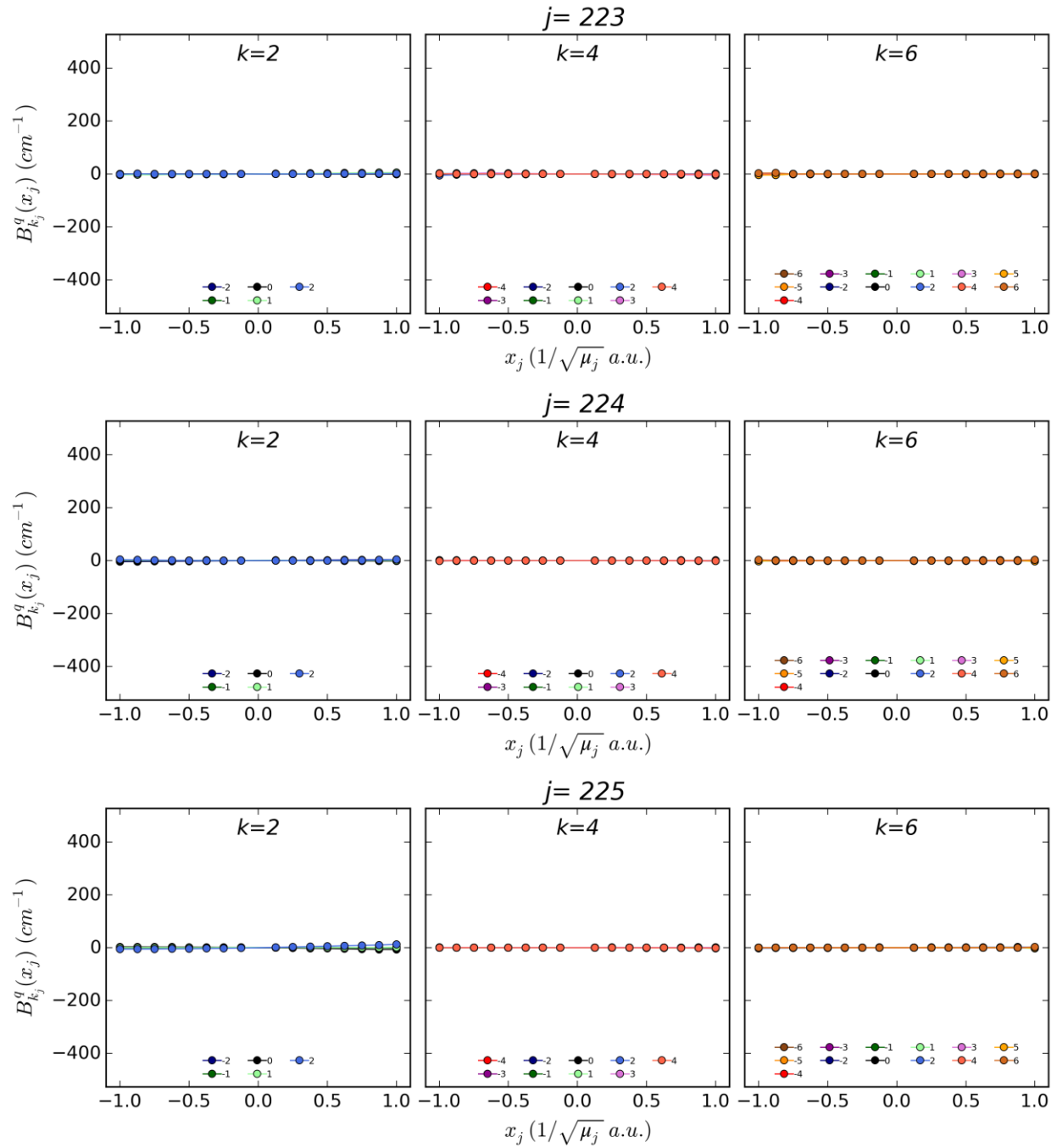


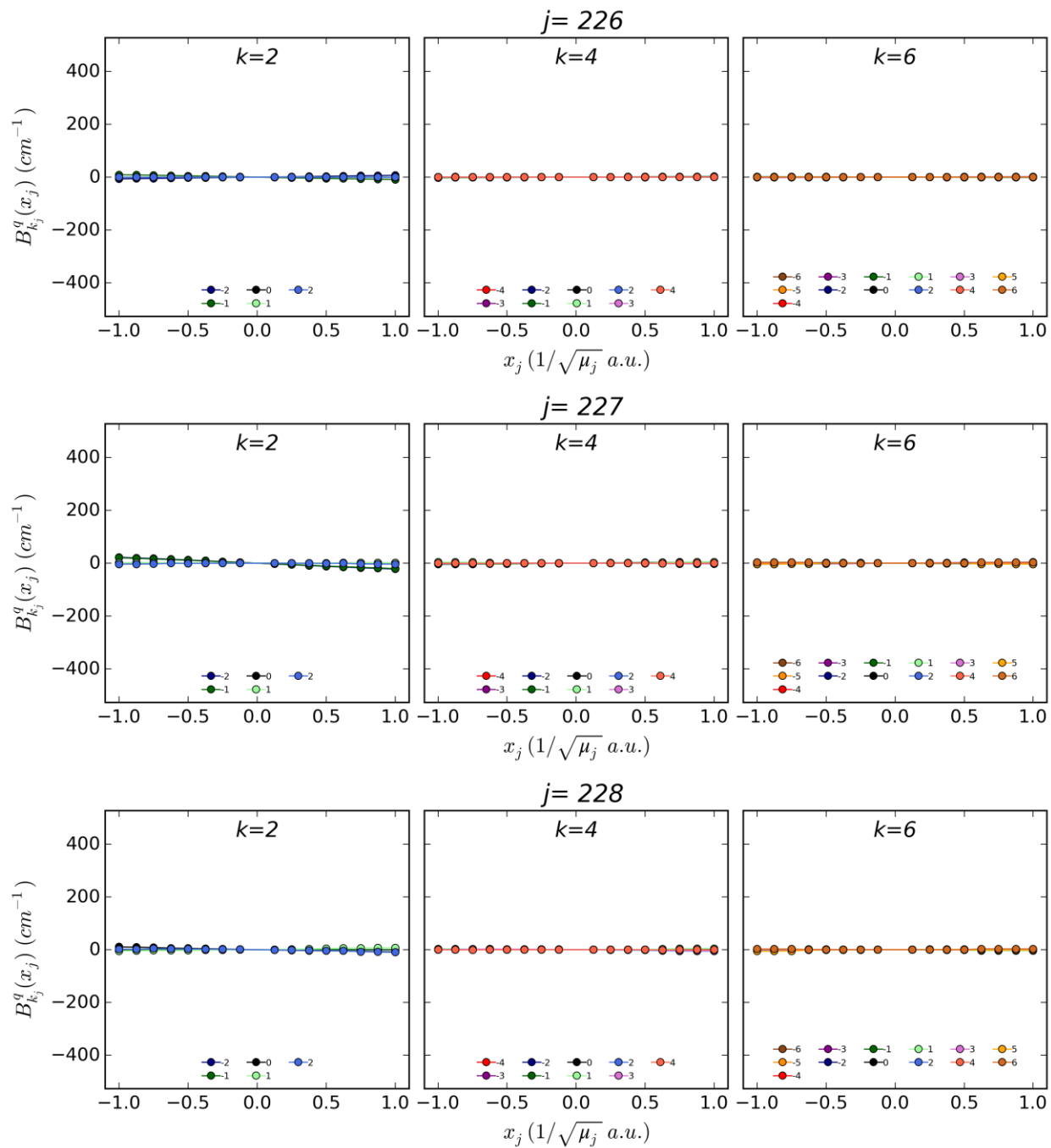




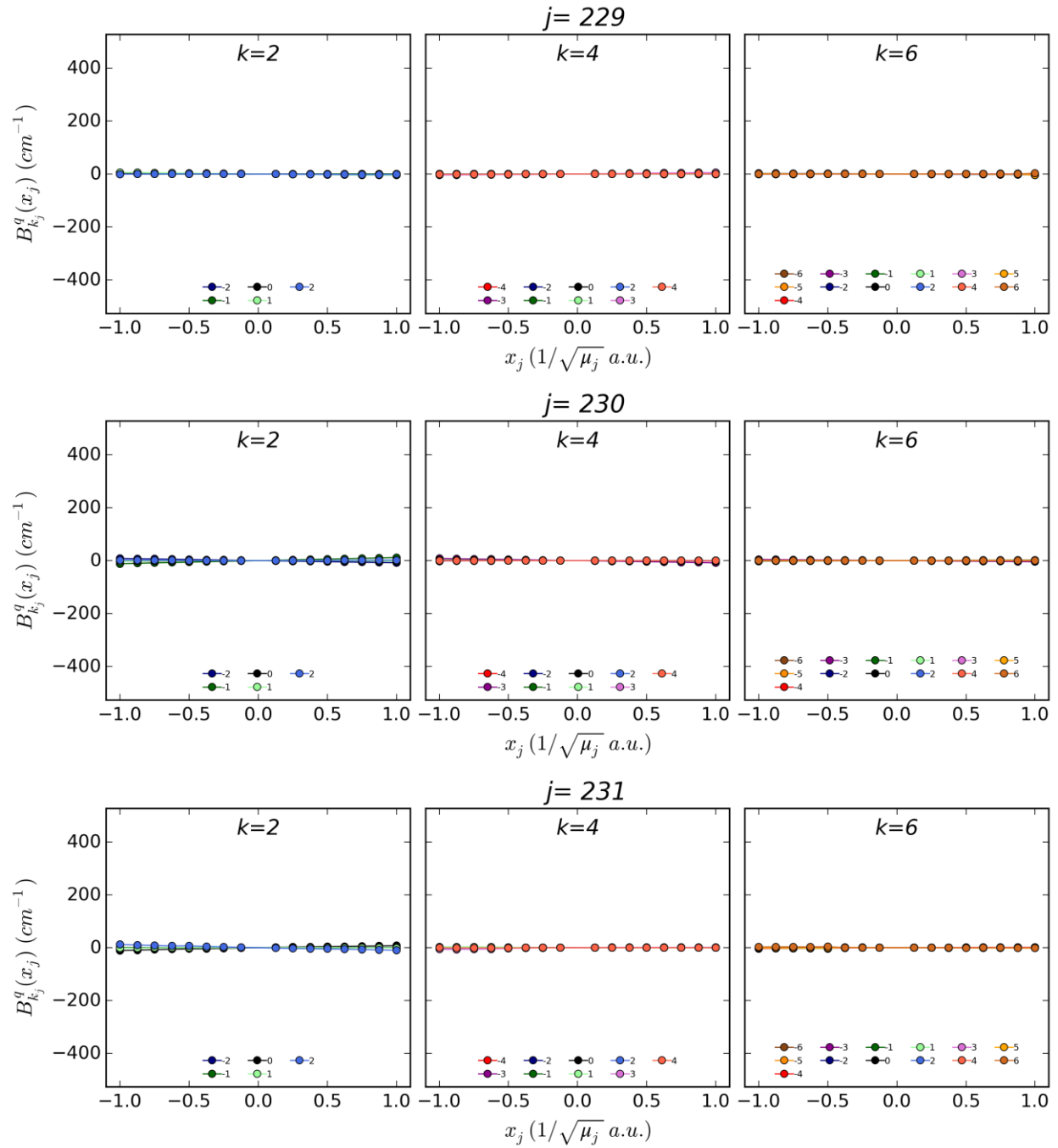


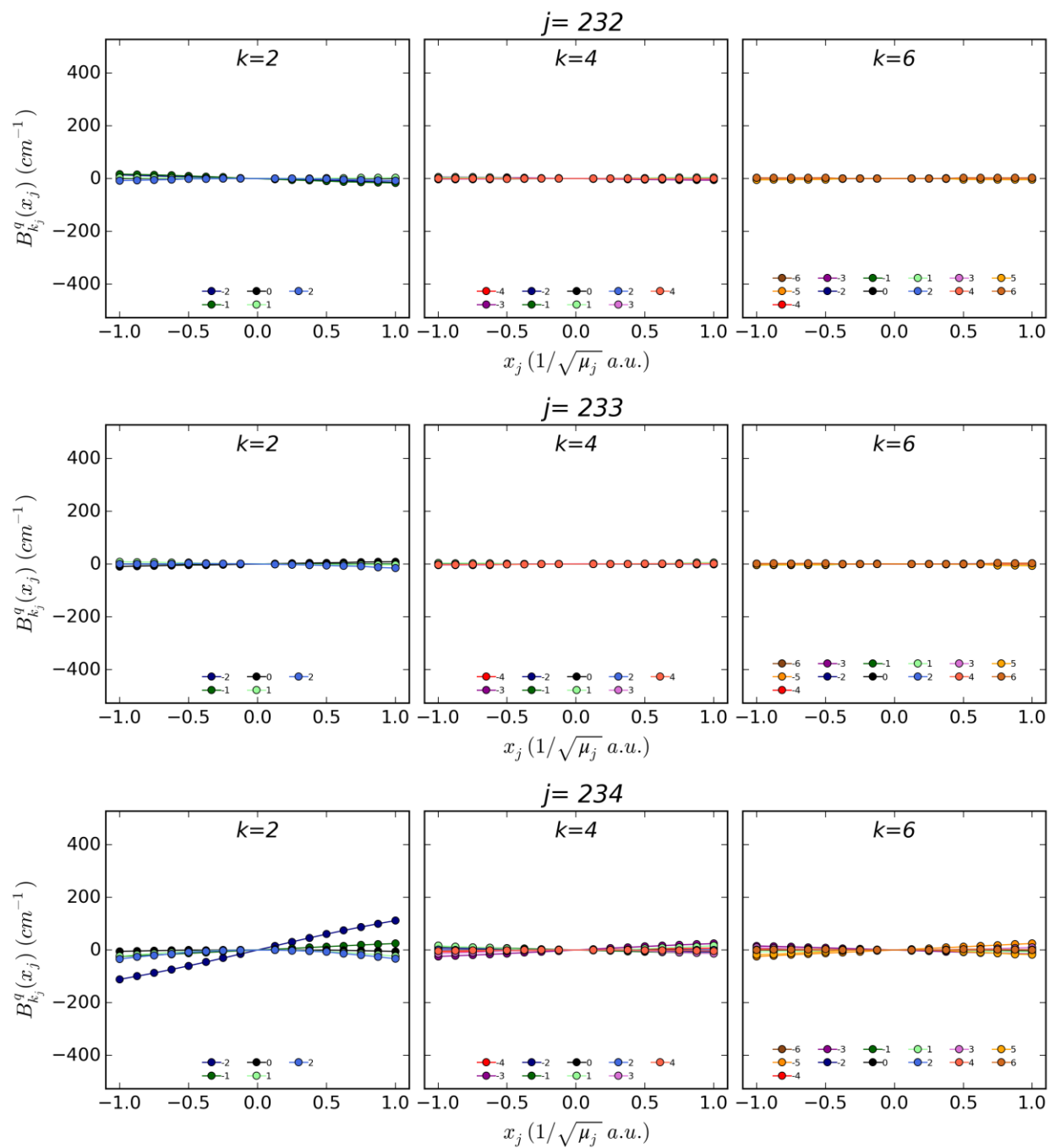


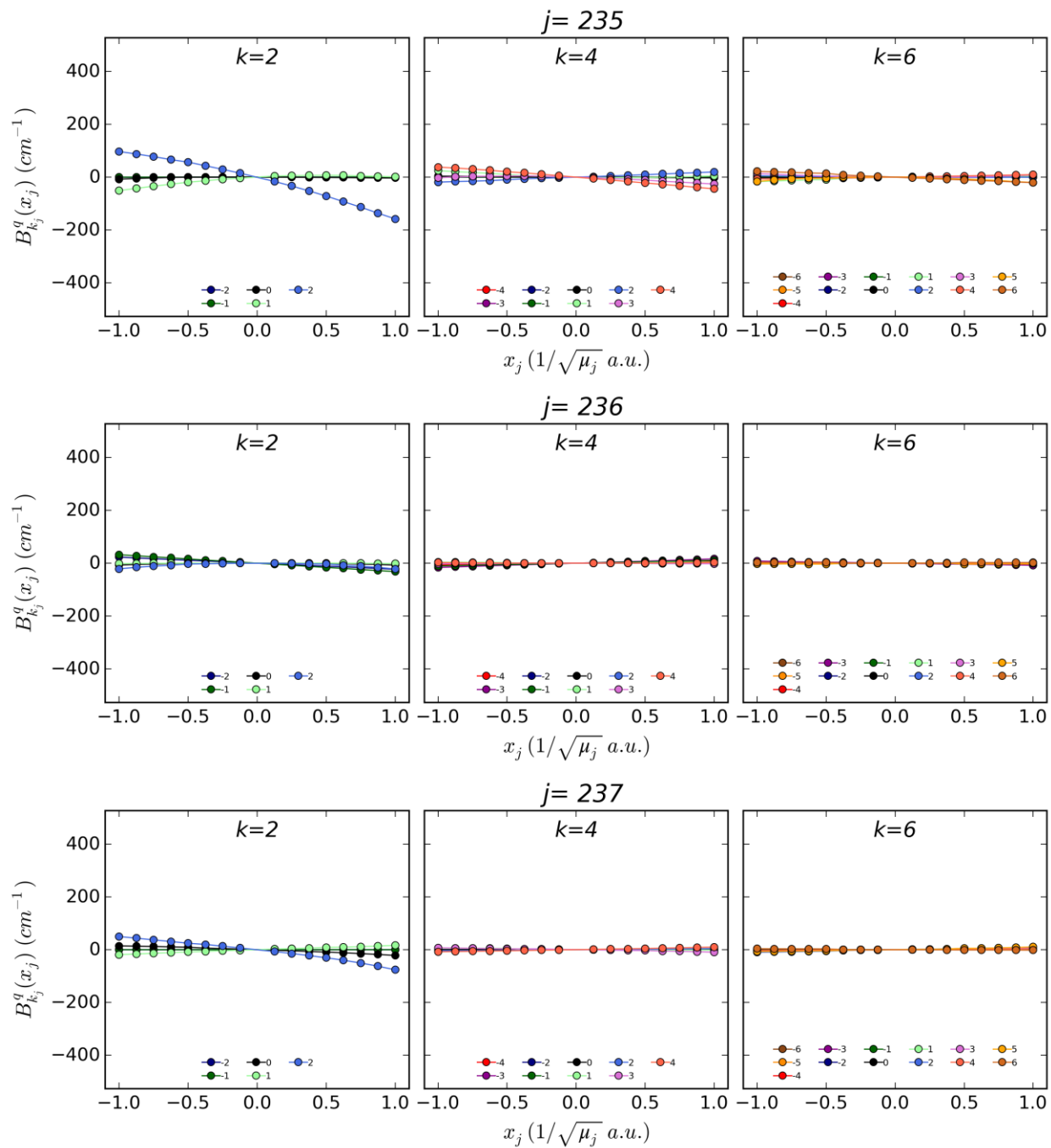


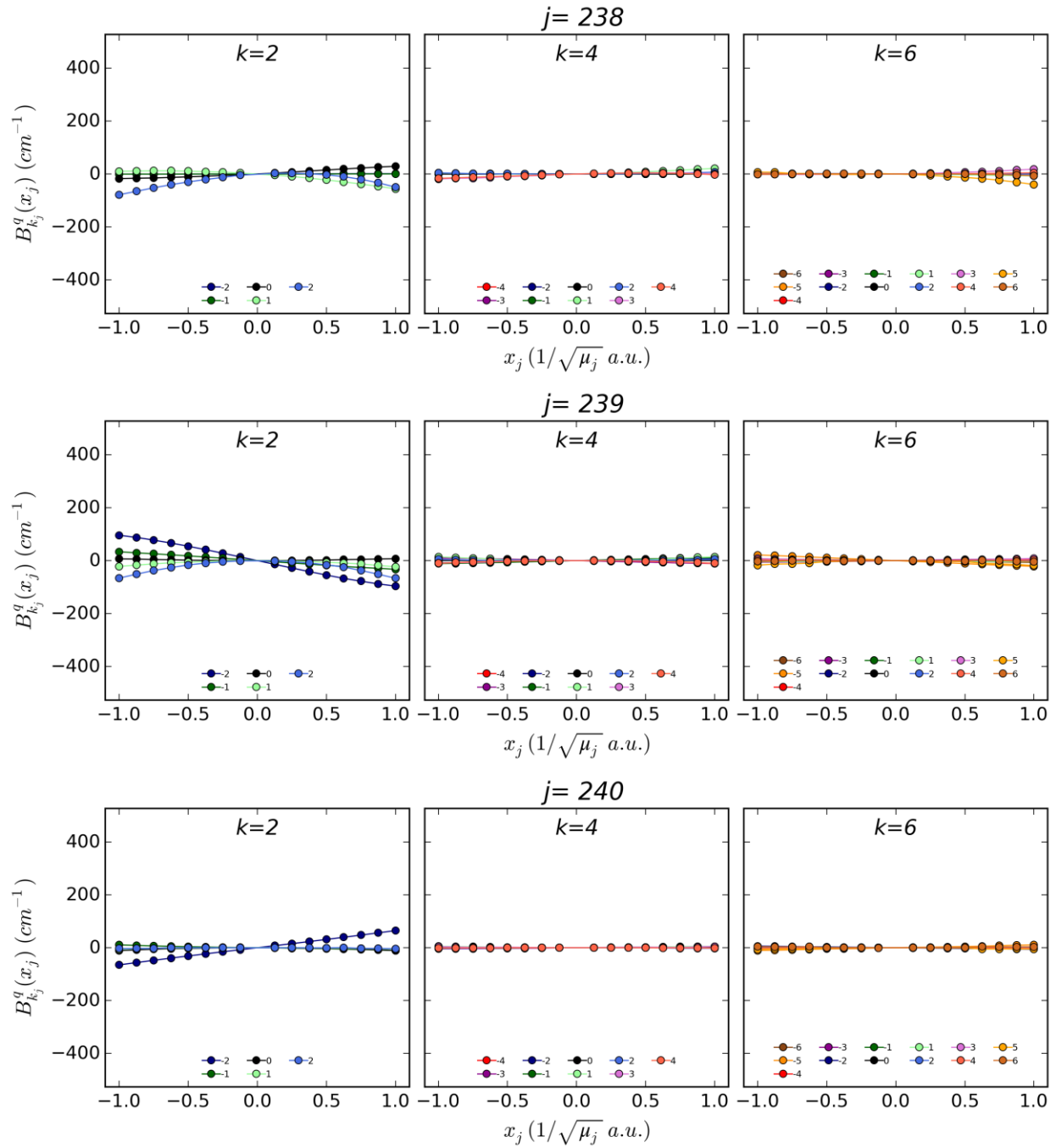


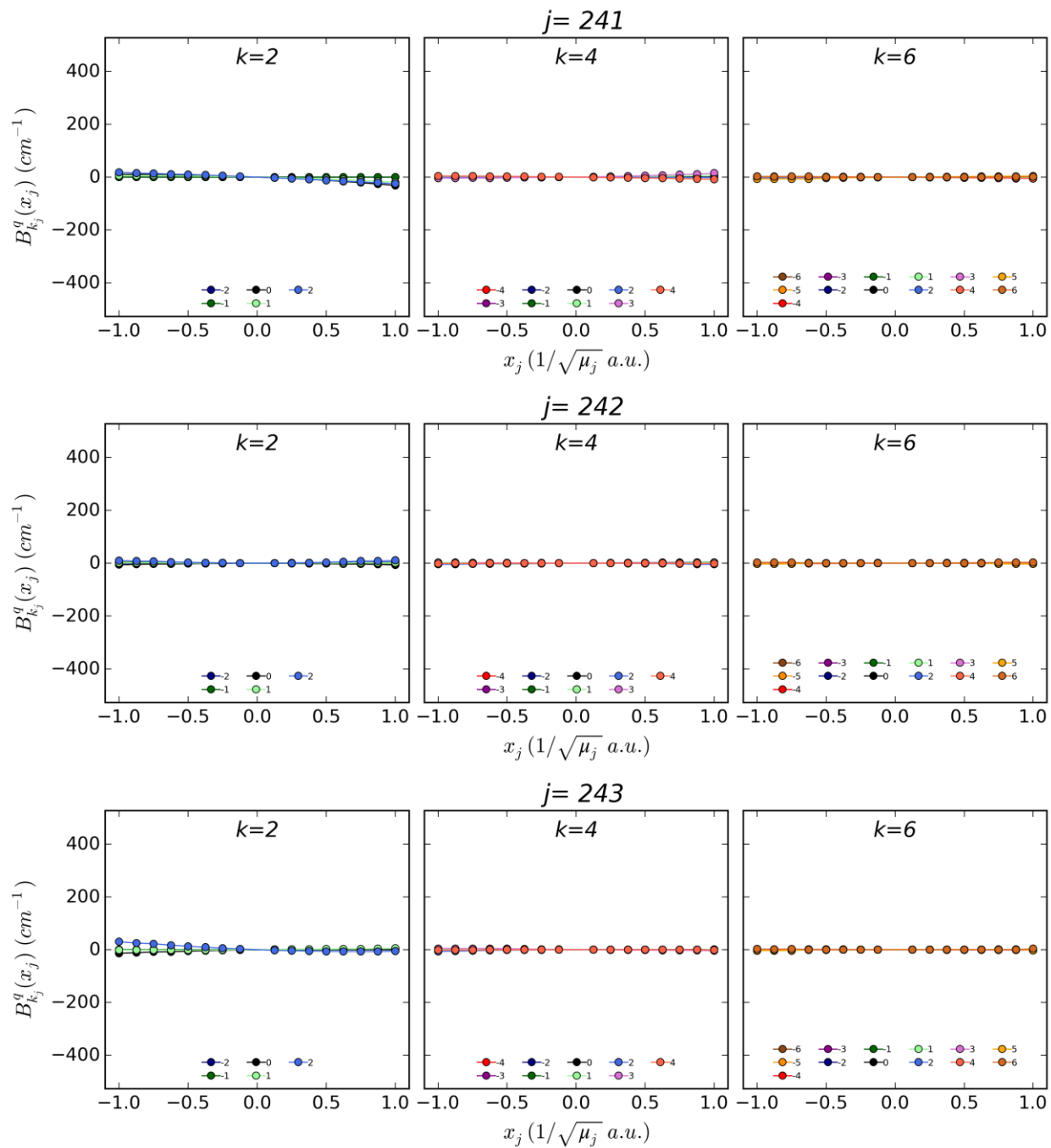


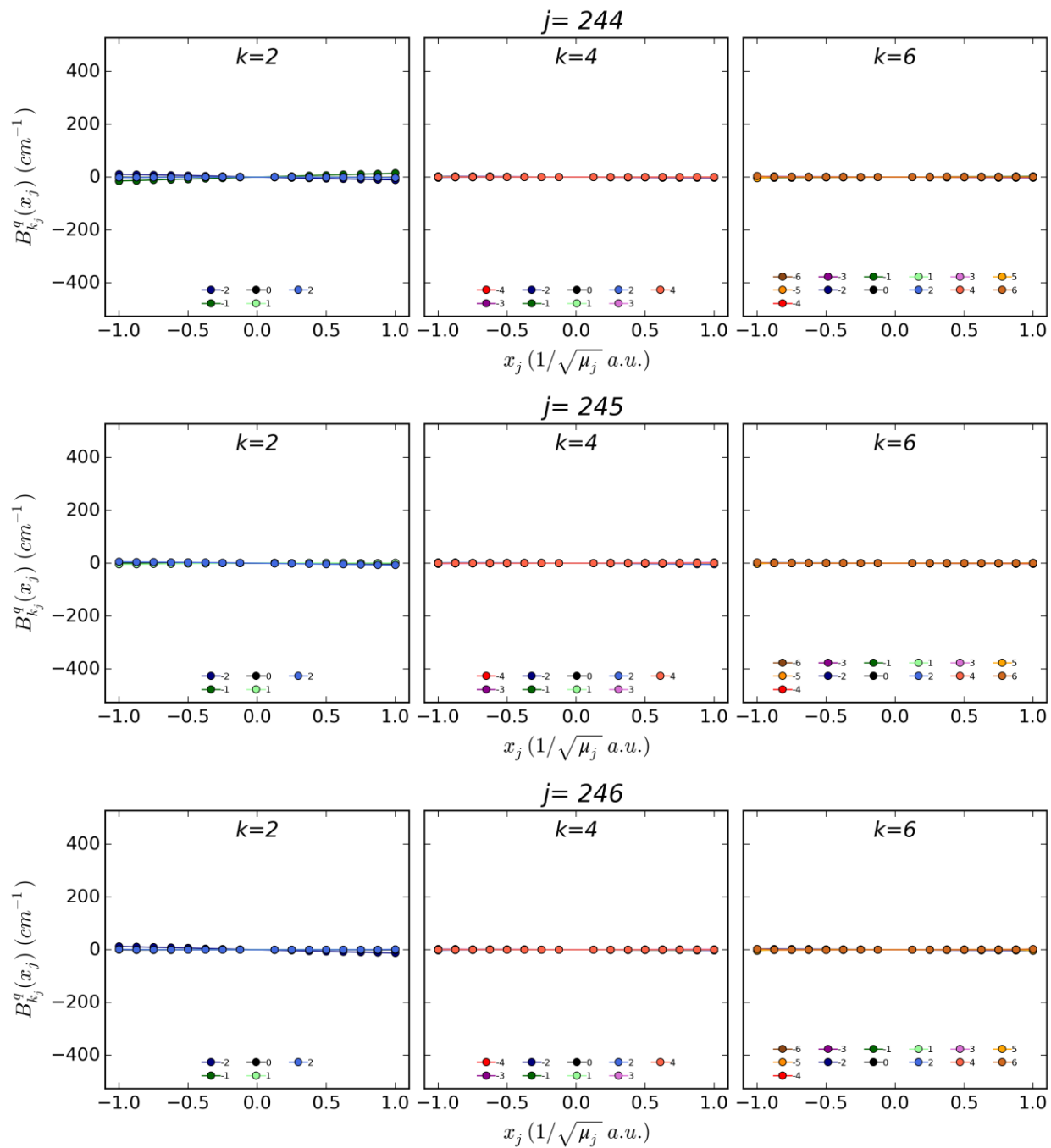


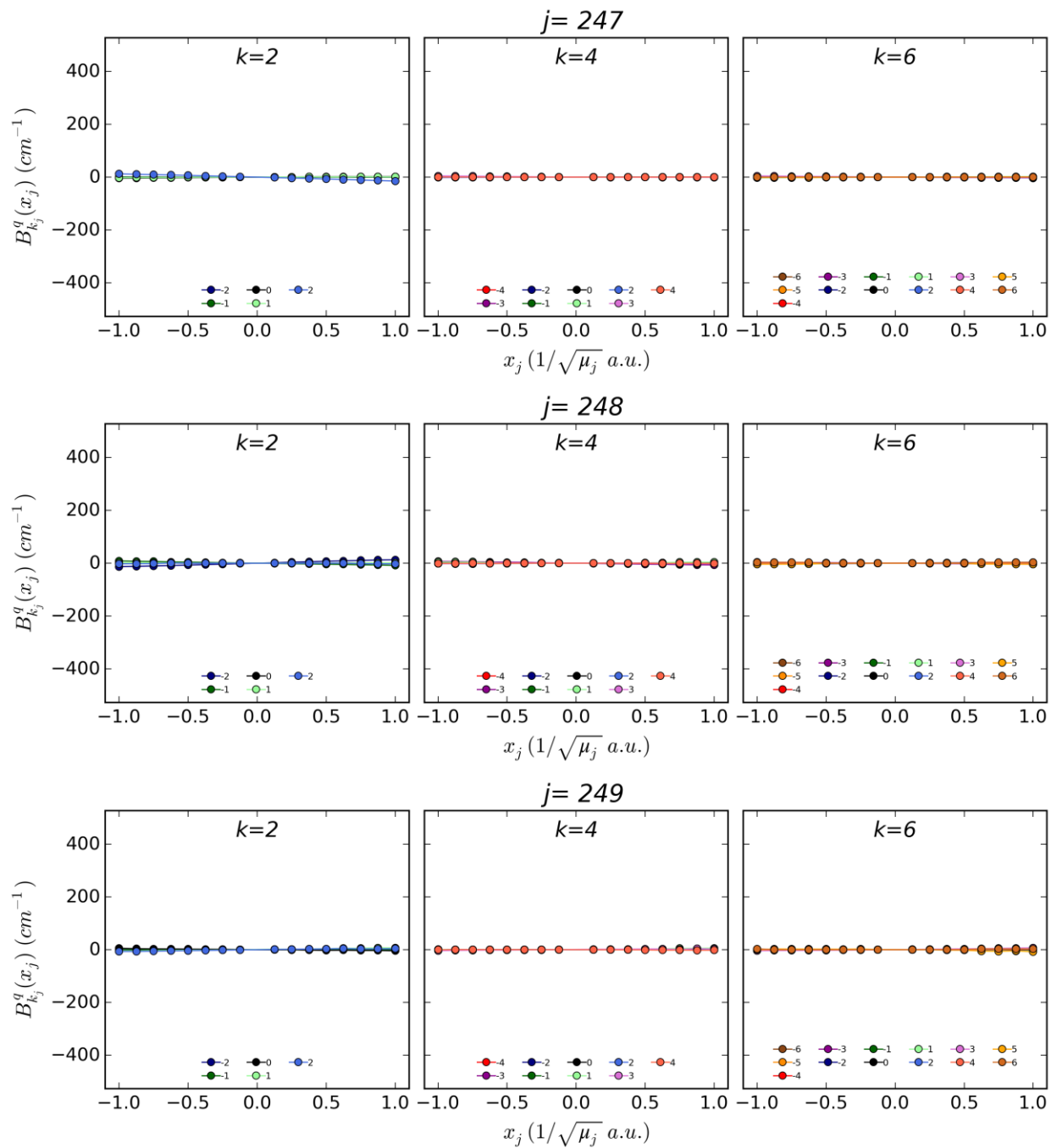


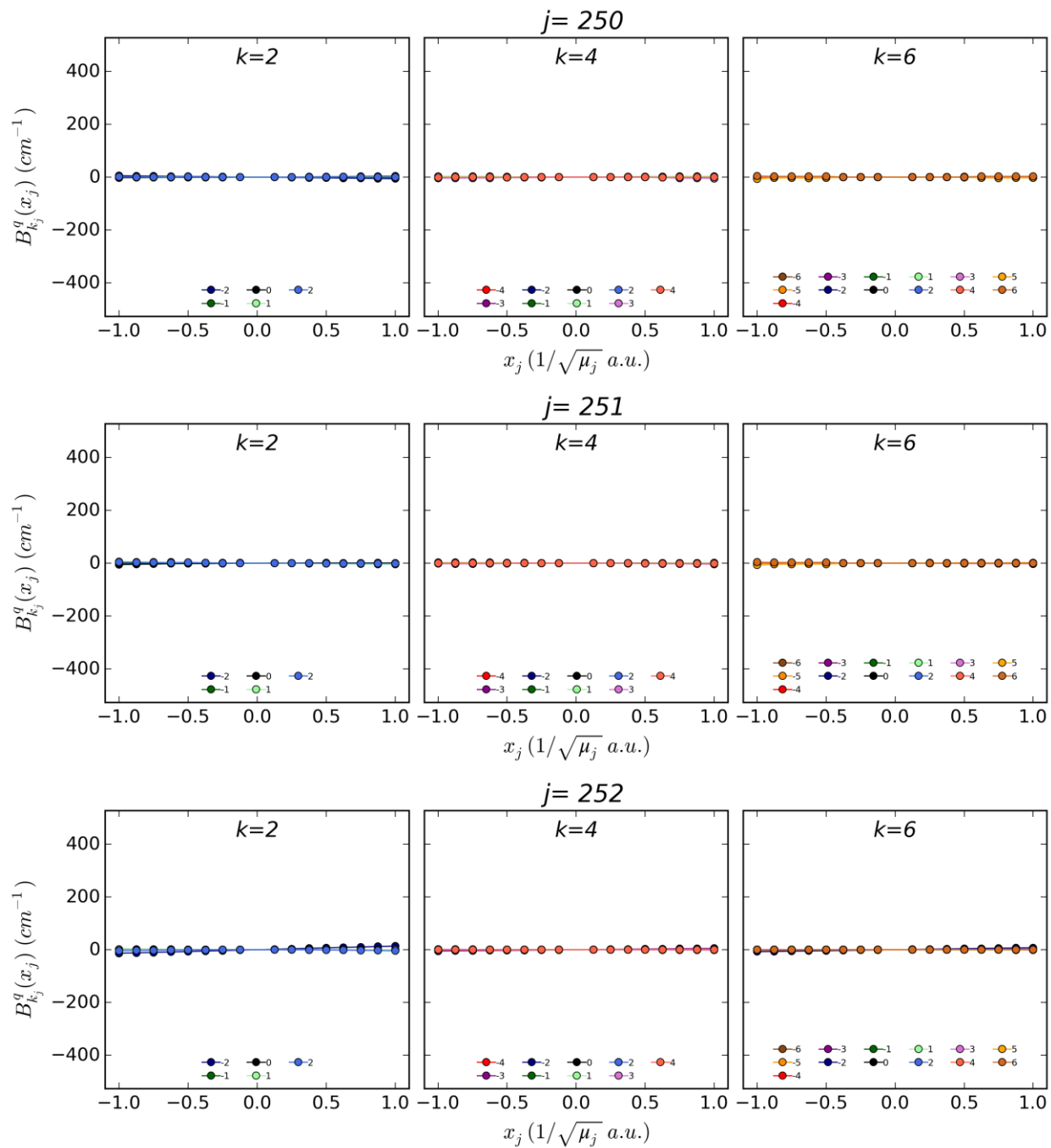




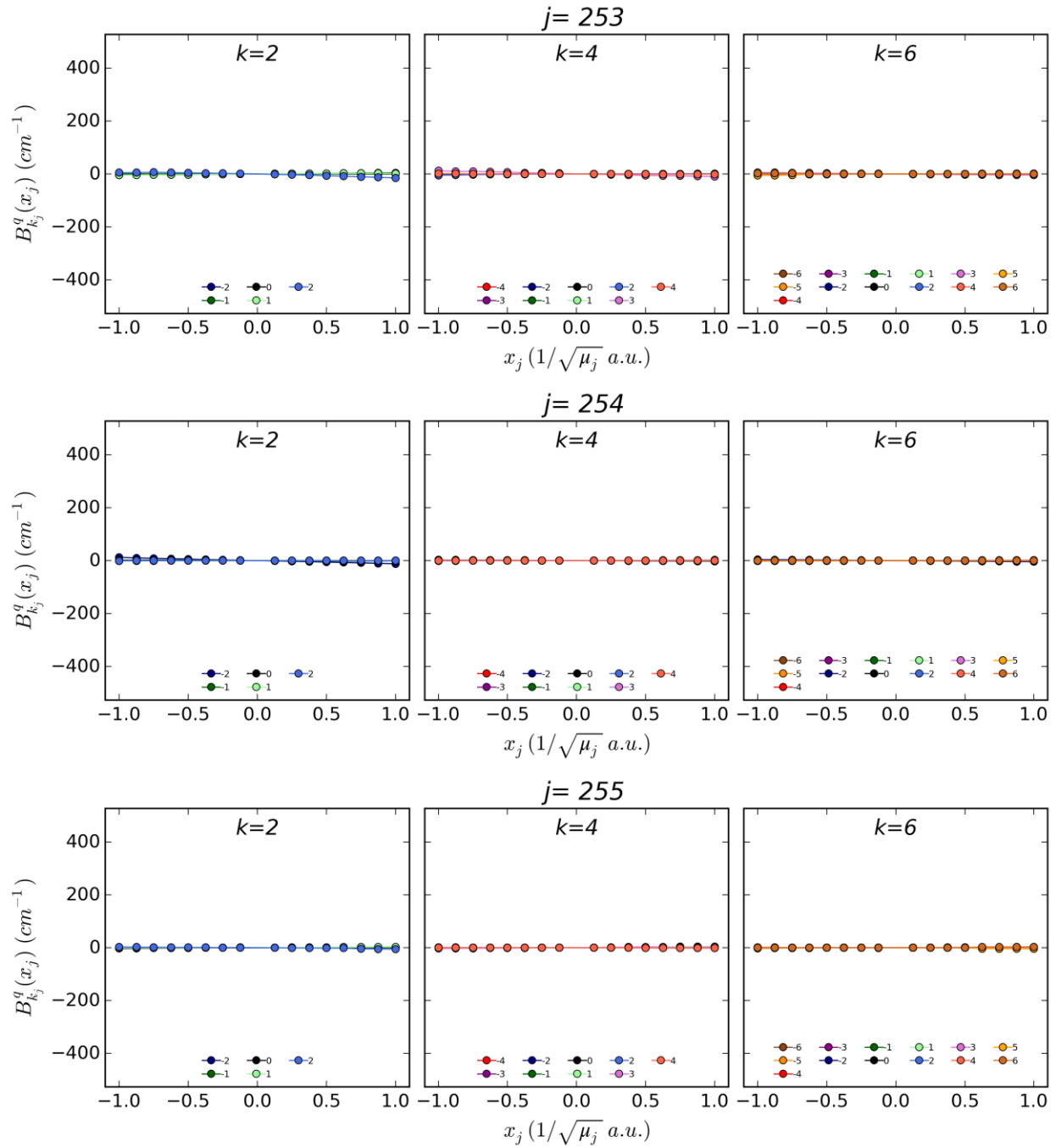


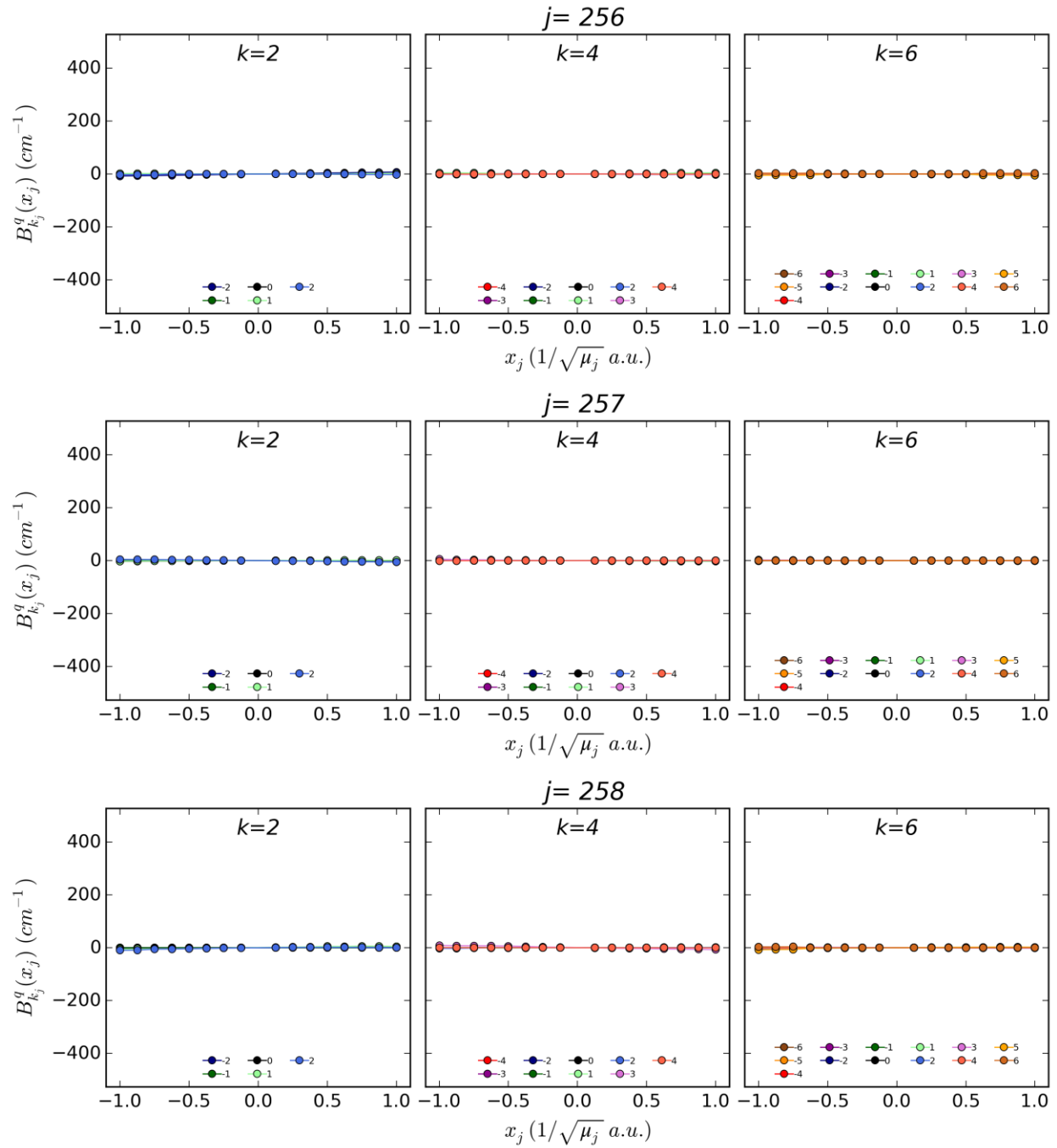


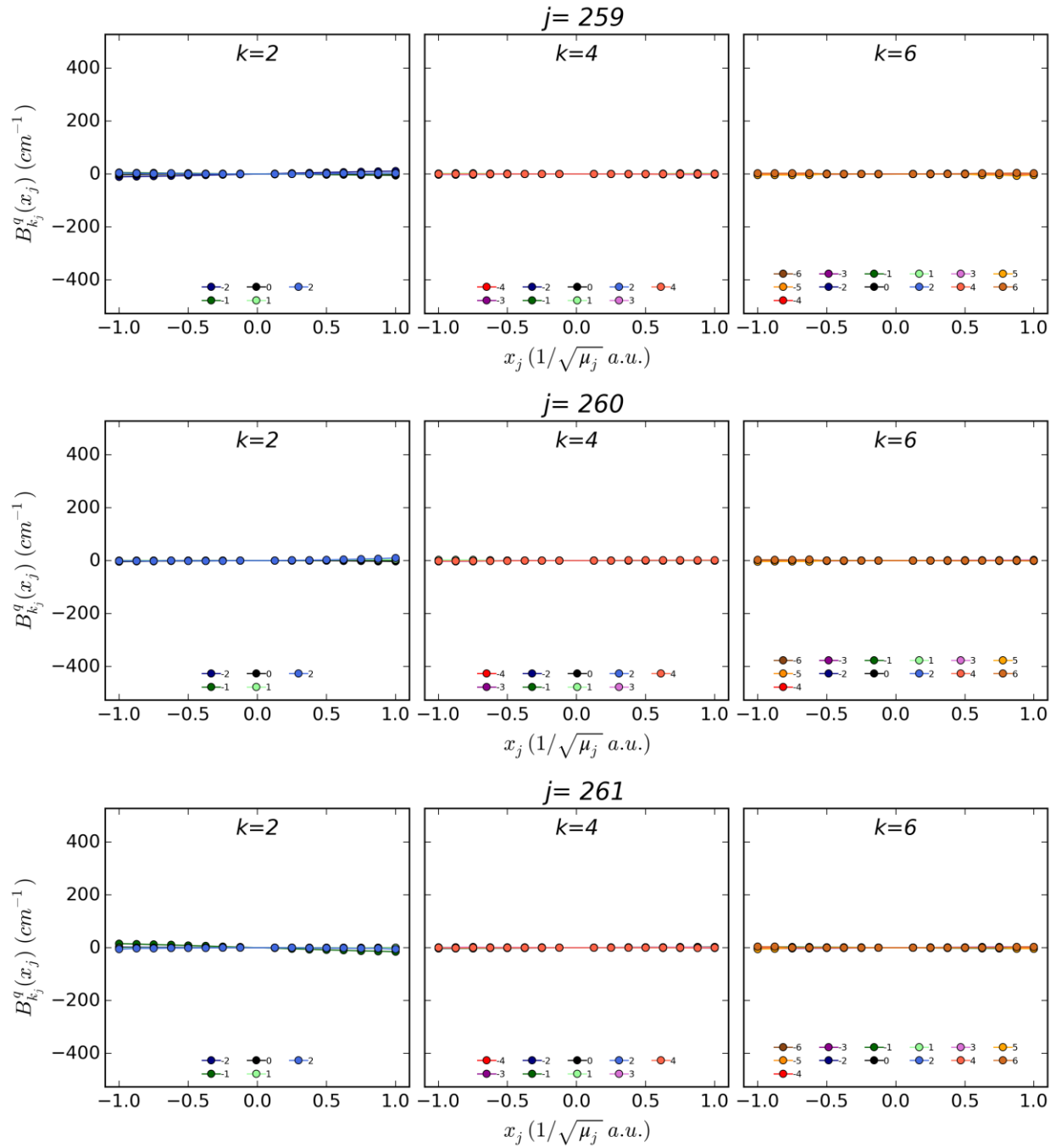


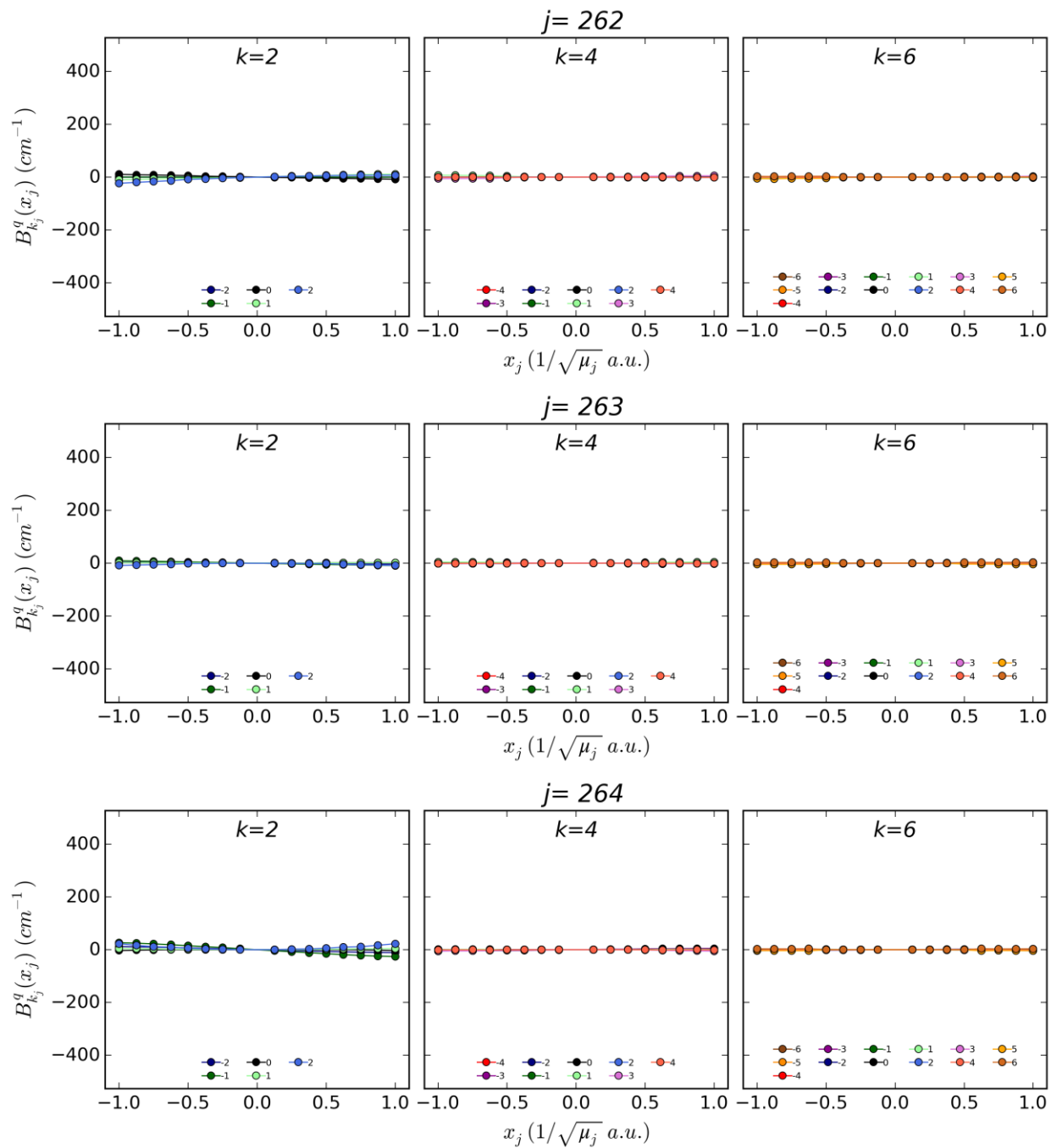


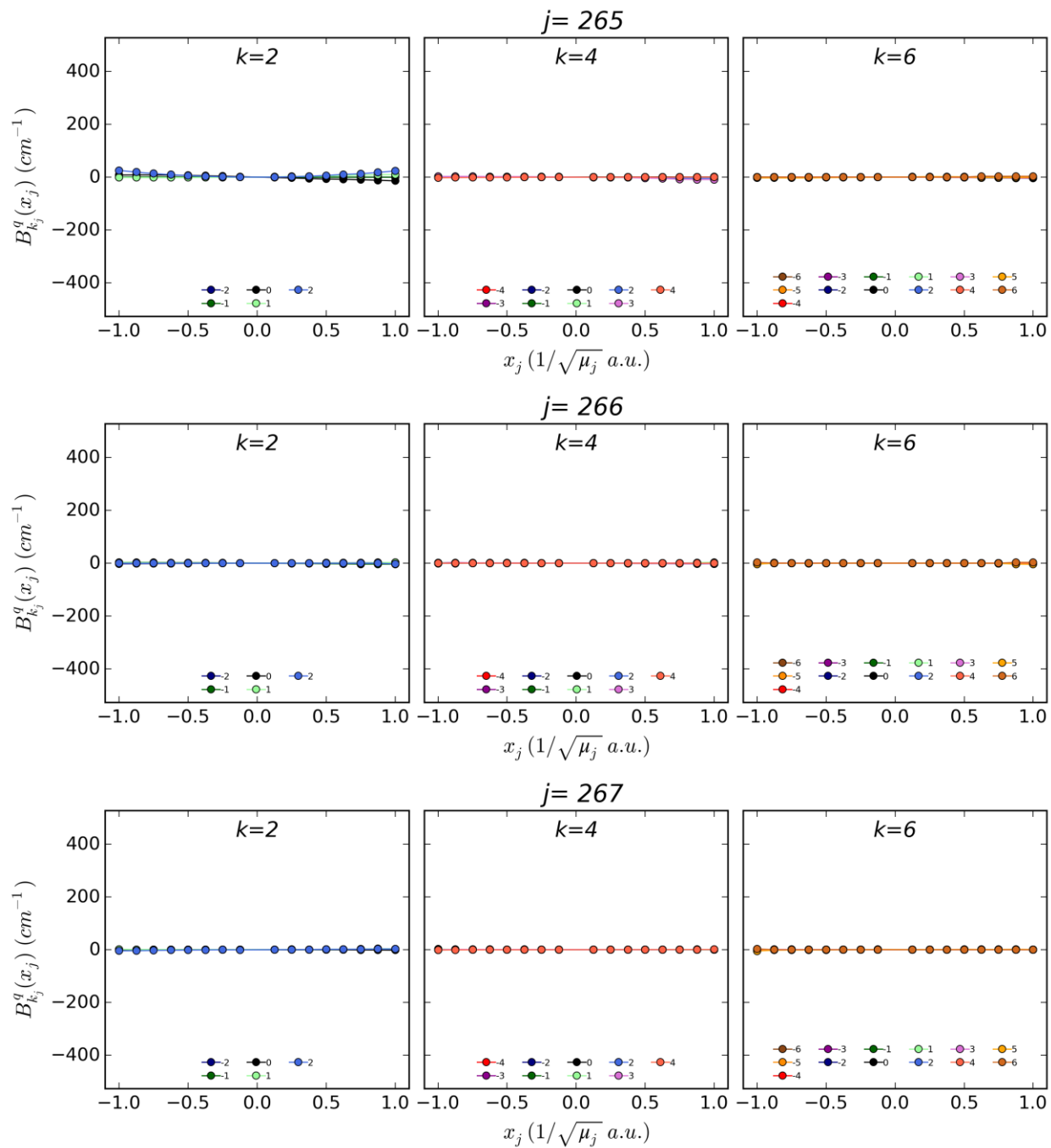


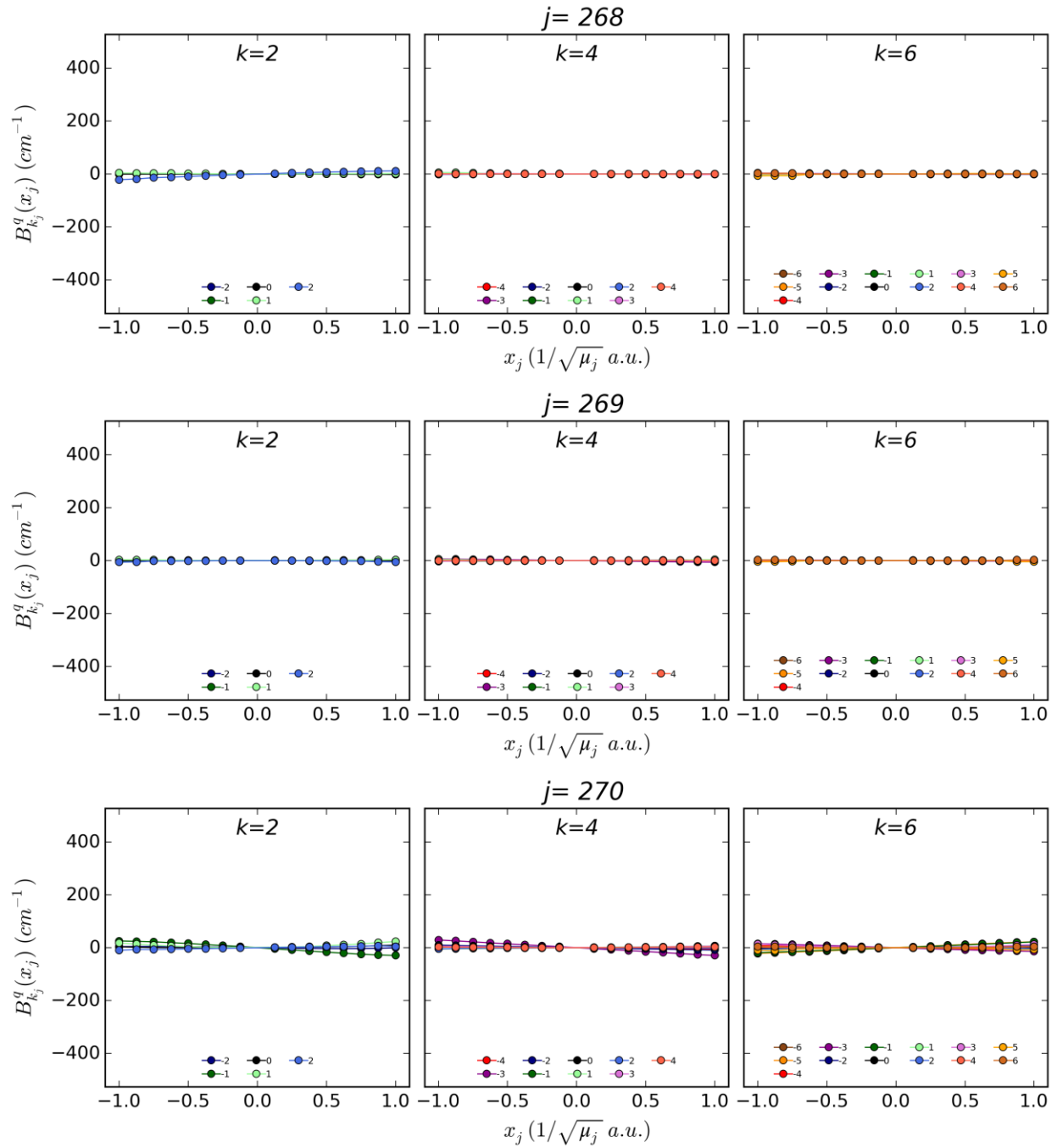


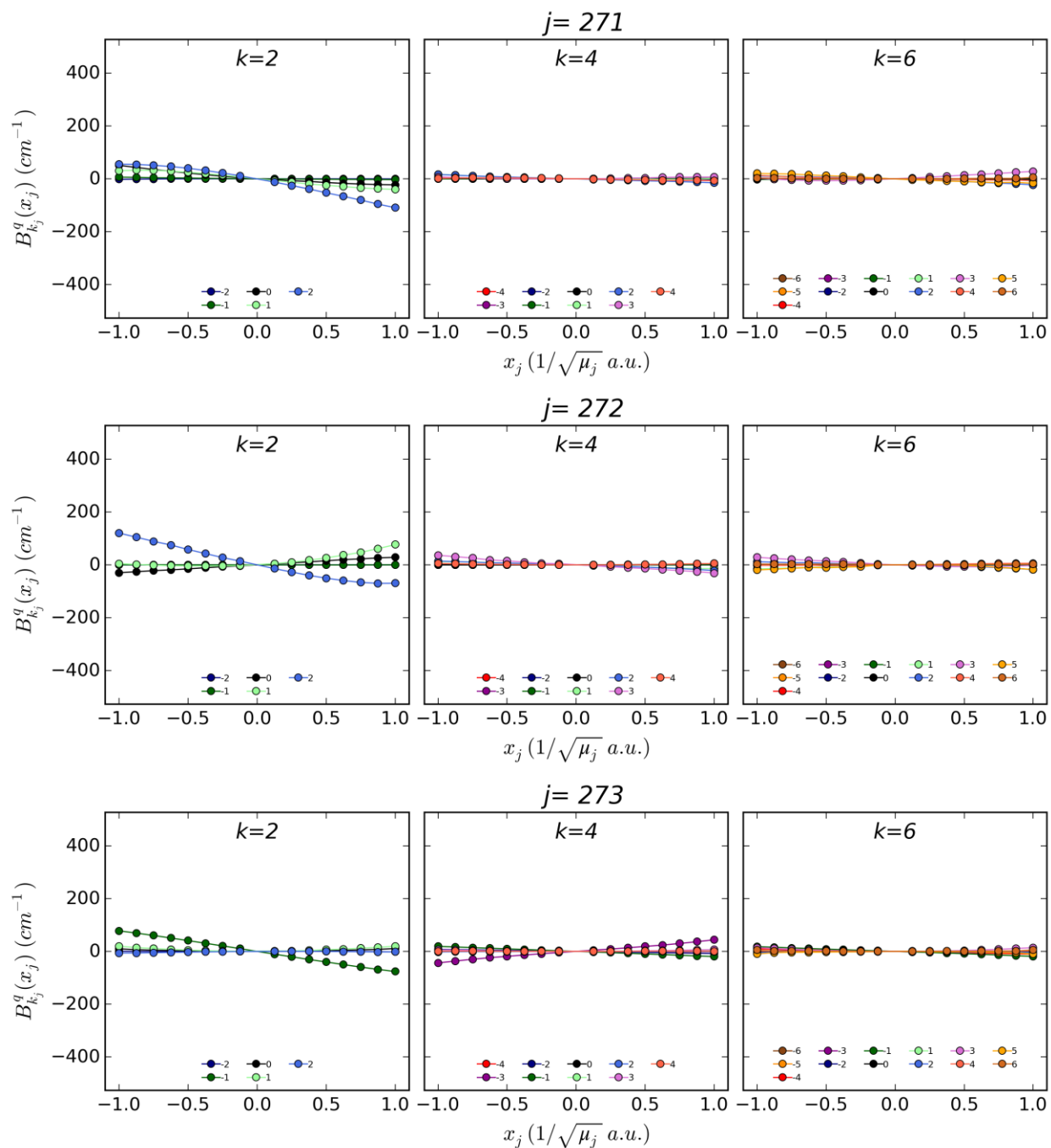












**Fig. S64.** Crystal field parameters as a function of displacement for all 273 vibrational modes.

Once all transition rates are determined, we construct the Master matrix  $\Gamma$  whose elements are  $\gamma_{fi}$ , with the diagonal elements defined as below<sup>42</sup>. This definition ensures that the columns of  $\Gamma$  add to zero which is required to maintain constant population during time evolution.

$$\gamma_{ii} = \sum_{f \neq i} -\gamma_{fi}$$

While this matrix is not symmetric (Table S22), it can be shown to have real eigenvalues and eigenvectors<sup>18,42</sup>. Thus, by numerical diagonalisation we find the sixteen eigenvalues  $-\frac{1}{t_k}$ , which are the negative relaxation rates of the system. One of these is equal to zero by definition, which corresponds to the solution of the Master equation in equilibrium. Calculation of this matrix and its diagonalisation as a function of variable temperature (under the assumption of temperature-independent  $\langle i|\hat{H}_j|f\rangle$  coupling elements) gives the relaxation rates (Table S23). We note that due to limitations of double-point floating precision arithmetic, the minimal eigenvalue is not zero and thus determines the noise floor of the calculation (Table S23, Rate 1); therefore we are only able to calculate rates down to 50 K in this instance. From these results we see that fourteen rates are extremely fast (Table S23, Rates 3 – 16), while only one is very slow (Table S23, Rate 2). This is in agreement with analogous calculations described for  $\text{Mn}_{12}$ <sup>18</sup>, where the fast rates correspond to spin motion on either side of the barrier and the slow rate corresponds to Orbach relaxation over the barrier. In order to determine the overall magnetic relaxation rate under the action of all sixteen relaxation rates, we directly calculate the populations of each state and the total magnetisation as a function of time. Here,  $\varphi_{i,k}$  are the eigenvectors of  $\Gamma$ ,  $\lambda_k$  are determined by solution of the system of linear equations based on the initial values  $p_1(0) = 1$  with all  $p_{i \neq 1}(0) = 0$ , and we employ the Hellman-Feynman theorem to determine the magnetisation of each state  $M_i$ . We then fit the calculated magnetisation decay curve using a single exponential function (see Magnetisation) to extract the overall magnetic

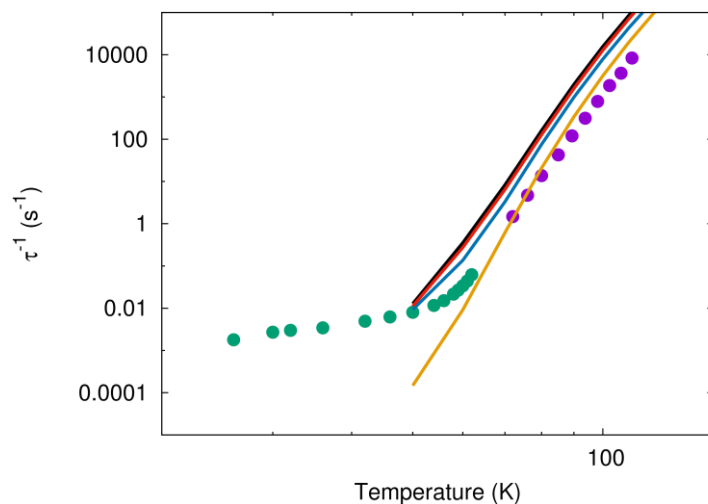


relaxation time. Following this protocol, we find that only the slowest relaxation rate (Table S23, Rate 2) contributes to the overall dynamics (Figs. 4a and S65).

$$p_i(t) = \sum_k \lambda_k \varphi_{i,k} e^{-\frac{t}{\tau_k}}$$

$$M(t) = \sum_i p_i(t) M_i$$

We are obliged to introduce a Gaussian linewidth to each vibrational mode in order to satisfy conservation of energy. Performing simulations of the magnetic relaxation as a function of this linewidth parameter,  $\sigma$ , we find that if  $\sigma < 0.1 \text{ cm}^{-1}$  we observe no relaxation: this corresponds to the limiting case where the Gaussian function approximates a delta function. Using larger values of  $\sigma$  from 0.1 to  $100 \text{ cm}^{-1}$  we find slight changes in the relaxation rates (Fig. S65); the slope of the temperature dependence remains the same, indicating the effective  $U_{\text{eff}}$  value of the Orbach mechanism is unchanged, however there is a shift towards faster relaxation with increasing  $\sigma$ , which results in a change in the effective  $\tau_0^{-1}$  prefactor of the Orbach mechanism. Setting  $\sigma = 10 \text{ cm}^{-1}$  as derived from the IR and Raman spectral linewidth, we find good agreement with the experimental data (Fig. 4a).



**Fig. S65.** Temperature dependence of the magnetic relaxation rate. Solid purple points are the relaxation rates extracted from AC susceptibility data (Table S5) and solid green points from DC magnetisation decay data (Table S8). Solid lines give the *ab initio* calculated Orbach relaxation rate for different choices of  $\sigma$ :  $\sigma = 0.1$  (orange), 1 (blue), 10 (black) and 100  $\text{cm}^{-1}$  (red).

To get an insight into the nature of the Orbach relaxation pathway for **1**, we re-cast the matrix  $\Gamma$  (Table S22) by only considering transitions that increase magnetic moment commencing with unit population in the  $|-15/2\rangle$  state (Fig. 4b, Table S24)<sup>30,47</sup>. We see that the most probable pathway for Orbach relaxation is  $|\pm 15/2\rangle \rightarrow |\pm 13/2\rangle \rightarrow |\pm 11/2\rangle \rightarrow |\pm 9/2\rangle \rightarrow |\pm 5/2\rangle \rightarrow |\mp 3/2\rangle \rightarrow |\mp 7/2\rangle \rightarrow |\mp 11/2\rangle \rightarrow |\mp 13/2\rangle \rightarrow |\mp 15/2\rangle$ , which involves excitations to ca. 1300  $\text{cm}^{-1}$ ; we observe a  $U_{\text{eff}}$  barrier of ca. 1200  $\text{cm}^{-1}$  and thus we propose that the effective barrier is reduced due to less-favourable lower energy pathways. We were then interested to know which vibrational mode(s) permit(s) the first step in this pathway ( $|\pm 15/2\rangle \rightarrow |\pm 13/2\rangle$ ); examining the contributions from each vibrational mode to  $\gamma_{3,1} = \gamma_{4,2}$ , we find that only four modes have appreciable contributions (Table S25), and in all cases the displacements mainly involve motion of the two C–H groups on each  $\text{Cp}^{\text{ttt}}$  ring (Fig. S66). Modes 64 and 65 involve a

rocking-like deformation of the  $\text{Cp}^{\text{III}}$  ring where one C-H group moves away from Dy while the (C)-H atom on the other side of the ring moves towards Dy; for mode 64 this motion is asymmetric about the metal centre, while for mode 65 it is symmetric. Modes 66 and 67 involve both C-H groups on the  $\text{Cp}^{\text{III}}$  ring moving away from Dy; for mode 66 this motion is symmetric about the metal centre and for mode 67 it is asymmetric. Therefore, we can identify that substitution of the H atoms on the  $\text{Cp}^{\text{III}}$  rings for other elements or R-groups should significantly change the vibrational modes that permit magnetic relaxation over the barrier, and therefore possibly lead to slower relaxation and magnetic hysteresis at higher temperatures.

**Table S22.** Master matrix  $\Gamma$  for single spin-phonon transitions at 150 K with  $\sigma = 10 \text{ cm}^{-1}$ . Columns 1 – 8, in units of  $\text{s}^{-1}$ .

|                      | $ + 15/2\rangle$ | $ - 15/2\rangle$ | $ + 13/2\rangle$ | $ - 13/2\rangle$ | $ - 11/2\rangle$ | $ + 11/2\rangle$ | $ + 9/2\rangle$ | $ - 9/2\rangle$ |
|----------------------|------------------|------------------|------------------|------------------|------------------|------------------|-----------------|-----------------|
| $ + 15/2\rangle$     | -5.71282E+10     | 0.00000E+00      | 4.83652E+12      | 8.56233E+02      | 4.88396E+05      | 1.77528E+12      | 8.57064E+08     | 1.23850E+03     |
| $ - 15/2\rangle$     | 0.00000E+00      | -5.71282E+10     | 8.56233E+02      | 4.83652E+12      | 1.77528E+12      | 4.88396E+05      | 1.23850E+03     | 8.57064E+08     |
| $ + 13/2\rangle$     | 5.53758E+10      | 9.80345E+00      | -5.26865E+12     | 0.00000E+00      | 1.35373E+06      | 4.85296E+12      | 8.36758E+11     | 1.34433E+06     |
| $ - 13/2\rangle$     | 9.80345E+00      | 5.53758E+10      | 0.00000E+00      | -5.26865E+12     | 4.85296E+12      | 1.35373E+06      | 1.34433E+06     | 8.36758E+11     |
| $ - 11/2\rangle$     | 4.82014E+02      | 1.75208E+09      | 1.16690E+05      | 4.18319E+11      | -6.79826E+12     | 0.00000E+00      | 1.00459E+07     | 6.07323E+11     |
| $ + 11/2\rangle$     | 1.75208E+09      | 4.82014E+02      | 4.18319E+11      | 1.16690E+05      | 0.00000E+00      | -6.79826E+12     | 6.07323E+11     | 1.00459E+07     |
| $ + 9/2\rangle$      | 1.54420E+05      | 2.23145E-01      | 1.31675E+10      | 2.11549E+04      | 1.83398E+06      | 1.10872E+11      | -1.76494E+12    | 1.26870E-38     |
| $ - 9/2\rangle$      | 2.23145E-01      | 1.54420E+05      | 2.11549E+04      | 1.31675E+10      | 1.10872E+11      | 1.83398E+06      | 1.26870E-38     | -1.76494E+12    |
| $ - 7/2\rangle$      | 1.19097E-01      | 5.92221E+04      | 3.91427E+04      | 5.81589E+08      | 5.85919E+10      | 1.41352E+06      | 1.11639E+07     | 3.26913E+10     |
| $ + 7/2\rangle$      | 5.92221E+04      | 1.19097E-01      | 5.81589E+08      | 3.91427E+04      | 1.41352E+06      | 5.85919E+10      | 3.26913E+10     | 1.11639E+07     |
| $ - 5/2\rangle$      | 4.03896E+01      | 4.52276E+04      | 1.27491E+05      | 4.94204E+07      | 3.06926E+08      | 1.31045E+06      | 4.59540E+08     | 2.82533E+11     |
| $ + 5/2\rangle$      | 4.52276E+04      | 4.03896E+01      | 4.94204E+07      | 1.27491E+05      | 1.31045E+06      | 3.06926E+08      | 2.82533E+11     | 4.59540E+08     |
| <b>73% + 3/2&gt;</b> | 6.15038E+03      | 4.70579E+02      | 7.21995E+06      | 1.12458E+06      | 8.72868E+06      | 1.14923E+08      | 3.38635E+09     | 4.01902E+08     |
| <b>73% - 3/2&gt;</b> | 4.70579E+02      | 6.15038E+03      | 1.12458E+06      | 7.21995E+06      | 1.14923E+08      | 8.72868E+06      | 4.01902E+08     | 3.38635E+09     |
| <b>89% - 1/2&gt;</b> | 6.71721E+02      | 1.64665E+02      | 2.95195E+05      | 7.05848E+05      | 9.88785E+07      | 1.56882E+07      | 2.06801E+08     | 2.99208E+08     |
| <b>89% + 1/2&gt;</b> | 1.64665E+02      | 6.71721E+02      | 7.05848E+05      | 2.95195E+05      | 1.56882E+07      | 9.88785E+07      | 2.99208E+08     | 2.06801E+08     |

**Table S22 cont.** Master matrix  $\Gamma$  for single spin-phonon transitions at 150 K with  $\sigma = 10 \text{ cm}^{-1}$ . Columns 9 – 16, in units of  $\text{s}^{-1}$ .

|                    | $ -7/2\rangle$ | $ +7/2\rangle$ | $ -5/2\rangle$ | $ +5/2\rangle$ | $73\% +3/2\rangle$ | $73\% -3/2\rangle$ | $89\% -1/2\rangle$ | $89\% +1/2\rangle$ |
|--------------------|----------------|----------------|----------------|----------------|--------------------|--------------------|--------------------|--------------------|
| $ +15/2\rangle$    | 3.14790E+03    | 1.56532E+09    | 4.49394E+06    | 5.03223E+09    | 2.02845E+09        | 1.55201E+08        | 4.62999E+08        | 1.13499E+08        |
| $ -15/2\rangle$    | 1.56532E+09    | 3.14790E+03    | 5.03223E+09    | 4.49394E+06    | 1.55201E+08        | 2.02845E+09        | 1.13499E+08        | 4.62999E+08        |
| $ +13/2\rangle$    | 1.18456E+07    | 1.76004E+11    | 1.62414E+08    | 6.29579E+10    | 2.72637E+10        | 4.24658E+09        | 2.32963E+09        | 5.57043E+09        |
| $ -13/2\rangle$    | 1.76004E+11    | 1.18456E+07    | 6.29579E+10    | 1.62414E+08    | 4.24658E+09        | 2.72637E+10        | 5.57043E+09        | 2.32963E+09        |
| $ -11/2\rangle$    | 1.52843E+12    | 3.68731E+07    | 3.37037E+10    | 1.43902E+08    | 2.84118E+09        | 3.74075E+10        | 6.72636E+10        | 1.06722E+10        |
| $ +11/2\rangle$    | 3.68731E+07    | 1.52843E+12    | 1.43902E+08    | 3.37037E+10    | 3.74075E+10        | 2.84118E+09        | 1.06722E+10        | 6.72636E+10        |
| $ +9/2\rangle$     | 5.31653E+07    | 1.55684E+11    | 9.21239E+09    | 5.66392E+12    | 2.01227E+11        | 2.38823E+10        | 2.56824E+10        | 3.71583E+10        |
| $ -9/2\rangle$     | 1.55684E+11    | 5.31653E+07    | 5.66392E+12    | 9.21239E+09    | 2.38823E+10        | 2.01227E+11        | 3.71583E+10        | 2.56824E+10        |
| $ -7/2\rangle$     | -2.14031E+12   | 0.00000E+00    | 2.00531E+11    | 1.08641E+10    | 2.11765E+11        | 2.47068E+12        | 1.38834E+11        | 2.08816E+11        |
| $ +7/2\rangle$     | 0.00000E+00    | -2.14031E+12   | 1.08641E+10    | 2.00531E+11    | 2.47068E+12        | 2.11765E+11        | 2.08816E+11        | 1.38834E+11        |
| $ -5/2\rangle$     | 4.76370E+10    | 2.58081E+09    | -6.22190E+12   | 0.00000E+00    | 4.44570E+11        | 1.75875E+11        | 9.86946E+10        | 6.27177E+10        |
| $ +5/2\rangle$     | 2.58081E+09    | 4.76370E+10    | 0.00000E+00    | -6.22190E+12   | 1.75875E+11        | 4.44570E+11        | 6.27177E+10        | 9.86946E+10        |
| $73\% +3/2\rangle$ | 1.69712E+10    | 1.98003E+11    | 1.49980E+11    | 5.93332E+10    | -3.99552E+12       | 0.00000E+00        | 2.68680E+11        | 5.53869E+11        |
| $73\% -3/2\rangle$ | 1.98003E+11    | 1.69712E+10    | 5.93332E+10    | 1.49980E+11    | 0.00000E+00        | -3.99552E+12       | 5.53869E+11        | 2.68680E+11        |
| $89\% -1/2\rangle$ | 5.32385E+09    | 8.00743E+09    | 1.59316E+10    | 1.01241E+10    | 1.28560E+11        | 2.65021E+11        | -1.48086E+12       | 0.00000E+00        |
| $89\% +1/2\rangle$ | 8.00743E+09    | 5.32385E+09    | 1.01241E+10    | 1.59316E+10    | 2.65021E+11        | 1.28560E+11        | 0.00000E+00        | -1.48086E+12       |

**Table S23.** Relaxation rates for single spin-phonon transitions with  $\sigma = 10 \text{ cm}^{-1}$ .

| Temperature (K) | Rate 1 (s <sup>-1</sup> ) | Rate 2 (s <sup>-1</sup> ) | Rate 3 (s <sup>-1</sup> ) | Rate 4 (s <sup>-1</sup> ) | Rate 5 (s <sup>-1</sup> ) | Rate 6 (s <sup>-1</sup> ) | Rate 7 (s <sup>-1</sup> ) | Rate 8 (s <sup>-1</sup> ) |
|-----------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 200             | 9.69324E-04               | 1.82547E+08               | 1.09648E+12               | 1.34807E+12               | 1.43078E+12               | 1.46142E+12               | 1.99303E+12               | 2.06784E+12               |
| 190             | 3.00259E-03               | 1.12305E+08               | 1.12003E+12               | 1.35581E+12               | 1.43080E+12               | 1.46193E+12               | 1.98411E+12               | 2.05137E+12               |
| 180             | 3.07169E-03               | 6.53008E+07               | 1.14469E+12               | 1.36414E+12               | 1.43113E+12               | 1.46249E+12               | 1.97489E+12               | 2.03446E+12               |
| 170             | 1.91565E-03               | 3.55359E+07               | 1.17035E+12               | 1.37297E+12               | 1.43177E+12               | 1.46311E+12               | 1.96537E+12               | 2.01716E+12               |
| 160             | 2.94623E-03               | 1.78787E+07               | 1.19684E+12               | 1.38217E+12               | 1.43271E+12               | 1.46378E+12               | 1.95558E+12               | 1.99958E+12               |
| 150             | 8.21209E-05               | 8.18893E+06               | 1.22396E+12               | 1.39155E+12               | 1.43391E+12               | 1.46451E+12               | 1.94557E+12               | 1.98186E+12               |
| 140             | 5.49531E-04               | 3.34799E+06               | 1.25140E+12               | 1.40092E+12               | 1.43534E+12               | 1.46531E+12               | 1.93541E+12               | 1.96423E+12               |
| 130             | 1.47920E-03               | 1.19096E+06               | 1.27881E+12               | 1.41003E+12               | 1.43694E+12               | 1.46617E+12               | 1.92522E+12               | 1.94695E+12               |
| 120             | 7.47322E-04               | 3.56386E+05               | 1.30572E+12               | 1.41860E+12               | 1.43864E+12               | 1.46712E+12               | 1.91514E+12               | 1.93037E+12               |
| 110             | 1.97619E-04               | 8.57527E+04               | 1.33162E+12               | 1.42634E+12               | 1.44035E+12               | 1.46816E+12               | 1.90535E+12               | 1.91493E+12               |
| 100             | 3.25621E-03               | 1.56113E+04               | 1.35596E+12               | 1.43295E+12               | 1.44198E+12               | 1.46930E+12               | 1.89608E+12               | 1.90108E+12               |
| 90              | 1.36081E-03               | 1.98454E+03               | 1.37827E+12               | 1.43817E+12               | 1.44342E+12               | 1.47056E+12               | 1.88755E+12               | 1.88927E+12               |
| 80              | 3.32740E-04               | 1.61138E+02               | 1.39829E+12               | 1.44187E+12               | 1.44455E+12               | 1.47196E+12               | 1.87982E+12               | 1.88001E+12               |
| 70              | 4.87790E-04               | 8.29709E+00               | 1.41610E+12               | 1.44409E+12               | 1.44526E+12               | 1.47349E+12               | 1.87276E+12               | 1.87365E+12               |
| 60              | 2.50423E-03               | 3.54599E-01               | 1.43219E+12               | 1.44506E+12               | 1.44555E+12               | 1.47513E+12               | 1.86787E+12               | 1.86863E+12               |
| 50              | 6.53460E-04               | 1.29686E-02               | 1.44494E+12               | 1.44523E+12               | 1.44773E+12               | 1.47684E+12               | 1.86468E+12               | 1.86503E+12               |

**Table S23 cont.** Relaxation rates for single spin-phonon transitions with  $\sigma = 10 \text{ cm}^{-1}$ .

| Temperature (K) | Rate 9 (s <sup>-1</sup> ) | Rate 10 (s <sup>-1</sup> ) | Rate 11 (s <sup>-1</sup> ) | Rate 12 (s <sup>-1</sup> ) | Rate 13 (s <sup>-1</sup> ) | Rate 14 (s <sup>-1</sup> ) | Rate 15 (s <sup>-1</sup> ) | Rate 16 (s <sup>-1</sup> ) |
|-----------------|---------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| 200             | 4.36131E+12               | 4.37971E+12                | 4.53815E+12                | 4.69209E+12                | 7.01018E+12                | 7.04559E+12                | 8.37807E+12                | 8.37822E+12                |
| 190             | 4.34064E+12               | 4.37436E+12                | 4.50595E+12                | 4.63648E+12                | 6.91982E+12                | 6.95548E+12                | 8.24201E+12                | 8.24217E+12                |
| 180             | 4.31346E+12               | 4.36952E+12                | 4.48465E+12                | 4.58430E+12                | 6.82975E+12                | 6.86550E+12                | 8.10312E+12                | 8.10328E+12                |
| 170             | 4.27831E+12               | 4.36082E+12                | 4.47628E+12                | 4.54052E+12                | 6.74050E+12                | 6.77612E+12                | 7.96179E+12                | 7.96195E+12                |
| 160             | 4.23646E+12               | 4.34023E+12                | 4.48013E+12                | 4.51369E+12                | 6.65268E+12                | 6.68790E+12                | 7.81858E+12                | 7.81872E+12                |
| 150             | 4.19012E+12               | 4.30258E+12                | 4.49442E+12                | 4.50949E+12                | 6.56701E+12                | 6.60152E+12                | 7.67425E+12                | 7.67438E+12                |
| 140             | 4.14106E+12               | 4.25202E+12                | 4.51769E+12                | 4.52410E+12                | 6.48430E+12                | 6.51772E+12                | 7.52989E+12                | 7.53000E+12                |
| 130             | 4.09044E+12               | 4.19471E+12                | 4.54881E+12                | 4.55145E+12                | 6.40545E+12                | 6.43736E+12                | 7.38695E+12                | 7.38703E+12                |
| 120             | 4.03904E+12               | 4.13428E+12                | 4.58659E+12                | 4.58762E+12                | 6.33146E+12                | 6.36138E+12                | 7.24739E+12                | 7.24745E+12                |
| 110             | 3.98743E+12               | 4.07263E+12                | 4.62948E+12                | 4.62985E+12                | 6.26331E+12                | 6.29073E+12                | 7.11382E+12                | 7.11386E+12                |
| 100             | 3.93608E+12               | 4.01087E+12                | 4.67524E+12                | 4.67535E+12                | 6.20195E+12                | 6.22636E+12                | 6.98956E+12                | 6.98958E+12                |
| 90              | 3.88540E+12               | 3.94978E+12                | 4.72079E+12                | 4.72082E+12                | 6.14818E+12                | 6.16910E+12                | 6.87868E+12                | 6.87869E+12                |
| 80              | 3.83573E+12               | 3.88989E+12                | 4.76234E+12                | 4.76234E+12                | 6.10250E+12                | 6.11954E+12                | 6.78562E+12                | 6.78562E+12                |
| 70              | 3.78739E+12               | 3.83156E+12                | 4.79599E+12                | 4.79599E+12                | 6.06504E+12                | 6.07796E+12                | 6.71433E+12                | 6.71433E+12                |
| 60              | 3.74069E+12               | 3.77506E+12                | 4.81901E+12                | 4.81901E+12                | 6.03547E+12                | 6.04430E+12                | 6.66670E+12                | 6.66670E+12                |
| 50              | 3.69628E+12               | 3.72089E+12                | 4.83127E+12                | 4.83127E+12                | 6.01323E+12                | 6.01837E+12                | 6.64086E+12                | 6.64086E+12                |

**Table S24.** Normalised transition probabilities for single spin-phonon transitions at 150 K with  $\sigma = 10 \text{ cm}^{-1}$ , commencing with unit population in  $|-15/2\rangle$  and only including transitions that increase the magnetic moment, rounded to the nearest percent. Columns 1 – 8.

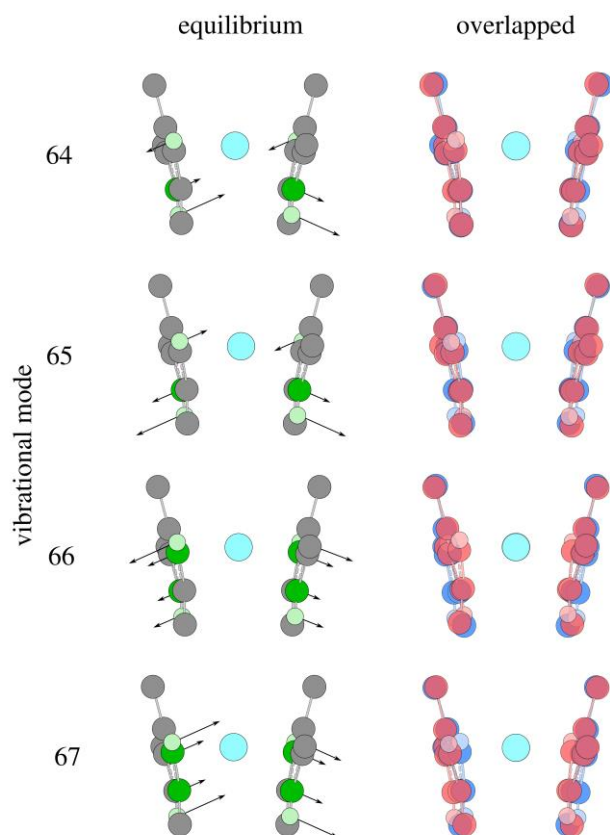
|                                     | $ +15/2\rangle$ | $ -15/2\rangle$ | $ +13/2\rangle$ | $ -13/2\rangle$ | $ -11/2\rangle$ | $ +11/2\rangle$ | $ +9/2\rangle$ | $ -9/2\rangle$ |
|-------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|----------------|
| $ +15/2\rangle$                     | 0               | 0               | 81              | 0               | 0               | 19              | 0              | 0              |
| $ -15/2\rangle$                     | 0               | 0               | 0               | 0               | 0               | 0               | 0              | 0              |
| $ +13/2\rangle$                     | 0               | 0               | 0               | 0               | 0               | 52              | 21             | 0              |
| $ -13/2\rangle$                     | 0               | 97              | 0               | 0               | 0               | 0               | 0              | 0              |
| $ -11/2\rangle$                     | 0               | 3               | 0               | 94              | 0               | 0               | 0              | 0              |
| $ +11/2\rangle$                     | 0               | 0               | 0               | 0               | 0               | 0               | 16             | 0              |
| $ +9/2\rangle$                      | 0               | 0               | 0               | 0               | 0               | 0               | 0              | 0              |
| $ -9/2\rangle$                      | 0               | 0               | 0               | 3               | 63              | 0               | 0              | 0              |
| $ -7/2\rangle$                      | 0               | 0               | 0               | 0               | 33              | 0               | 0              | 7              |
| $ +7/2\rangle$                      | 0               | 0               | 0               | 0               | 0               | 0               | 0              | 0              |
| $ -5/2\rangle$                      | 0               | 0               | 0               | 0               | 0               | 0               | 0              | 58             |
| $ +5/2\rangle$                      | 0               | 0               | 0               | 0               | 0               | 0               | 0              | 0              |
| <b>73%<math> +3/2\rangle</math></b> | 0               | 0               | 0               | 0               | 0               | 0               | 0              | 0              |
| <b>73%<math> -3/2\rangle</math></b> | 0               | 0               | 0               | 0               | 0               | 0               | 0              | 1              |
| <b>89%<math> -1/2\rangle</math></b> | 0               | 0               | 0               | 0               | 0               | 0               | 0              | 0              |
| <b>89%<math> +1/2\rangle</math></b> | 0               | 0               | 0               | 0               | 0               | 0               | 0              | 0              |



**Table S24 cont.** Normalised transition probabilities for single spin-phonon transitions at 150 K with  $\sigma = 10 \text{ cm}^{-1}$ , commencing with unit population in  $|-15/2\rangle$  and only including transitions that increase the magnetic moment, rounded to the nearest percent.

Columns 9 – 16.

|                  | $ -7/2\rangle$ | $ +7/2\rangle$ | $ -5/2\rangle$ | $ +5/2\rangle$ | $\% +3/2\rangle$ | $\% -3/2\rangle$ | $\% -1/2\rangle$ | $\% +1/2\rangle$ |
|------------------|----------------|----------------|----------------|----------------|------------------|------------------|------------------|------------------|
| $ +15/2\rangle$  | 0              | 0              | 0              | 0              | 0                | 0                | 0                | 0                |
| $ -15/2\rangle$  | 0              | 0              | 0              | 0              | 0                | 0                | 0                | 0                |
| $ +13/2\rangle$  | 0              | 6              | 0              | 0              | 1                | 0                | 0                | 0                |
| $ -13/2\rangle$  | 0              | 0              | 0              | 0              | 0                | 0                | 0                | 0                |
| $ -11/2\rangle$  | 0              | 0              | 0              | 0              | 0                | 0                | 0                | 0                |
| $ +11/2\rangle$  | 0              | 54             | 0              | 0              | 1                | 0                | 0                | 1                |
| $ +9/2\rangle$   | 0              | 5              | 2              | 24             | 4                | 1                | 1                | 0                |
| $ -9/2\rangle$   | 0              | 0              | 0              | 0              | 0                | 0                | 0                | 0                |
| $ -7/2\rangle$   | 0              | 0              | 0              | 0              | 0                | 0                | 0                | 0                |
| $ +7/2\rangle$   | 0              | 0              | 3              | 1              | 46               | 9                | 6                | 1                |
| $ -5/2\rangle$   | 7              | 0              | 0              | 0              | 0                | 0                | 0                | 0                |
| $ +5/2\rangle$   | 0              | 0              | 0              | 0              | 3                | 18               | 2                | 1                |
| $\% +3/2\rangle$ | 2              | 0              | 38             | 0              | 0                | 0                | 7                | 6                |
| $\% -3/2\rangle$ | 29             | 0              | 15             | 0              | 0                | 0                | 0                | 0                |
| $\% -1/2\rangle$ | 1              | 0              | 4              | 0              | 0                | 11               | 0                | 0                |
| $\% +1/2\rangle$ | 1              | 0              | 3              | 0              | 0                | 5                | 0                | 0                |



**Fig. S66.** Main atomic displacements involved in vibrational modes 64, 65, 66 and 67. Atoms represented by circles: cyan circles = Dy, larger ligand circles = C, smaller and lighter coloured ligand circles = H, <sup>t</sup>Bu groups omitted for clarity. Green (grey) circles represent atoms with significant (negligible) displacements; red (blue) overlapped structure shows negative (positive) displacement.

**Table S25.** Vibrational contributions (single-phonon) to at 150 K with  $\sigma = 10 \text{ cm}^{-1}$ .

| Vibrational Mode | Transition rate ( $\text{s}^{-1}$ ) |
|------------------|-------------------------------------|
| 64               | 9.82106E+09                         |
| 65               | 7.00002E+09                         |
| 66               | 1.30154E+10                         |
| 67               | 2.55100E+10                         |

We have also investigated the possibility of two-phonon processes by calculating the transition rates due to the second-order Raman process<sup>43</sup>. The second-order Raman process employs two phonons (labelled  $j$  and  $k$ ), the first mixing the initial electronic state (labelled  $i$ ) with an intermediate state (labelled  $c$ ) and the second mixing the intermediate state with the final electronic state (labelled  $f$ ) and thus effecting a transition. Orbach provided the formalism for this contribution to the transition rate<sup>43</sup>, and under the approximation  $E_f \approx E_i \ll E_c$  the denominator is  $E_c - E_i$ . However, we include all possible combinations of vibrations and intermediate states and thus the detailed balance criterion is not satisfied using this denominator (because we do not impose a requirement that  $|E_c - E_i| \approx |E_c - E_f|$ ). Hence, we adopt a denominator accounting for both energy differences. By employing the Boltzmann expressions for the probability of excited vibrational state populations as described above, and substituting the energy differences between electronic states in order to satisfy the delta function, we define the transition rates of the two-phonon second-order Raman process as:

*Two phonons absorbed:*

$$\gamma_{fi} = \frac{2\pi}{\hbar} \sum_j \sum_k \sum_c \left[ \frac{|\langle c | \hat{H}_j | i \rangle \langle f | \hat{H}_k | c \rangle|^2}{|E_c - E_i| \times |E_f - E_c|} e^{-|E_c - E_i|/k_B T} e^{-|E_f - E_c|/k_B T} \rho_j(E_c - E_i) \rho_k(E_f - E_c) \right]$$

*Phonon  $j$  absorbed,  $k$  emitted:*

$$\gamma_{fi} = \frac{2\pi}{\hbar} \sum_j \sum_k \sum_c \left[ \frac{|\langle c | \hat{H}_j | i \rangle \langle f | \hat{H}_k | c \rangle|^2}{|E_c - E_i| \times |E_f - E_c|} e^{-|E_c - E_i|/k_B T} \rho_j(E_c - E_i) \rho_k(E_f - E_c) \right]$$

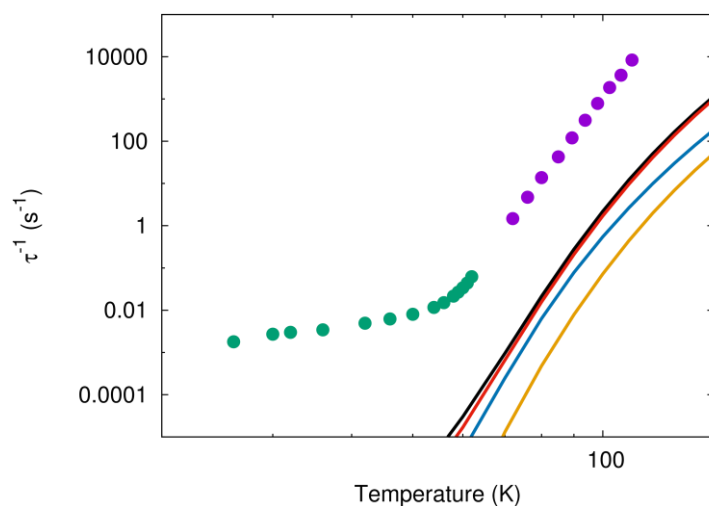
*Phonon  $j$  emitted,  $k$  absorbed:*

$$\gamma_{fi} = \frac{2\pi}{\hbar} \sum_j \sum_k \sum_c \left[ \frac{|\langle c | \hat{H}_j | i \rangle \langle f | \hat{H}_k | c \rangle|^2}{|E_c - E_i| \times |E_f - E_c|} e^{-|E_f - E_c|/k_B T} \rho_j(E_c - E_i) \rho_k(E_f - E_c) \right]$$

*Two phonons emitted:*

$$\gamma_{fi} = \frac{2\pi}{\hbar} \sum_j \sum_k \sum_c \left[ \frac{|\langle c | \hat{H}_j | i \rangle \langle f | \hat{H}_k | c \rangle|^2}{|E_c - E_i| |E_f - E_c|} \rho_j(E_c - E_i) \rho_k(E_f - E_c) \right]$$

We calculate the electronic part of the spin-phonon elements in exactly the same way as described above (Table S26). Calculation of  $\Gamma$  and its diagonalisation as a function of variable temperature (again under the assumption of temperature-independent  $\langle i | \hat{H}_j | f \rangle$  coupling elements) gives the spin-two-phonon relaxation rates (Table S27). From these results we see that twelve rates are extremely fast (Table S27, Rates 5 – 16), while two are in an intermediate range (Table S27, Rates 3 and 4) and one is very slow (Table S27, Rate 2). Again we calculate and fit the magnetisation decay as described above and find that only the slowest Raman relaxation rate (Table S27, Rate 2) contributes to the overall dynamics. Altering the value of  $\sigma$  shifts the relaxation rates in a similar manner to the single-phonon case (Figs. 4a and S66).



**Fig. S67.** Temperature dependence of the magnetic relaxation rate. Solid purple points are the relaxation rates extracted from AC susceptibility data (Table S5) and solid green points from DC magnetisation decay data (Table S8). Solid lines give the *ab initio* calculated Raman relaxation rate for different choices of  $\sigma$ :  $\sigma = 0.1$  (orange), 1 (blue), 10 (black) and  $100 \text{ cm}^{-1}$  (red).

**Table S26.** Master matrix  $\Gamma$  for spin-two-phonon transitions at 150 K with  $\sigma = 10 \text{ cm}^{-1}$ . Columns 1 – 8, in units of  $\text{s}^{-1}$ .

|                  | $ +15/2\rangle$ | $ -15/2\rangle$ | $ +13/2\rangle$ | $ -13/2\rangle$ | $ -11/2\rangle$ | $ +11/2\rangle$ | $ +9/2\rangle$ | $ -9/2\rangle$ |
|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|----------------|
| $ +15/2\rangle$  | -2.08125E+05    | 3.14767E-03     | 3.40310E+06     | 1.88923E+00     | 4.65907E+01     | 1.66538E+08     | 2.40765E+07    | 1.57265E+02    |
| $ -15/2\rangle$  | 3.14767E-03     | -2.08125E+05    | 1.88923E+00     | 3.40310E+06     | 1.66538E+08     | 4.65907E+01     | 1.57265E+02    | 2.40765E+07    |
| $ +13/2\rangle$  | 3.89639E+04     | 2.16308E-02     | -4.65269E+06    | 1.49451E+01     | 2.44505E+01     | 1.31149E+06     | 5.50771E+07    | 1.27818E+03    |
| $ -13/2\rangle$  | 2.16308E-02     | 3.89639E+04     | 1.49451E+01     | -4.65269E+06    | 1.31149E+06     | 2.44505E+01     | 1.27818E+03    | 5.50771E+07    |
| $ -11/2\rangle$  | 4.59819E-02     | 1.64362E+05     | 2.10760E+00     | 1.13049E+05     | -1.69274E+08    | 1.11791E+02     | 7.17236E+02    | 3.48993E+06    |
| $ +11/2\rangle$  | 1.64362E+05     | 4.59819E-02     | 1.13049E+05     | 2.10760E+00     | 1.11791E+02     | -1.69274E+08    | 3.48993E+06    | 7.17236E+02    |
| $ +9/2\rangle$   | 4.33795E+03     | 2.83351E-02     | 8.66714E+05     | 2.01139E+01     | 1.30938E+02     | 6.37118E+05     | -8.61618E+07   | 4.59960E+04    |
| $ -9/2\rangle$   | 2.83351E-02     | 4.33795E+03     | 2.01139E+01     | 8.66714E+05     | 6.37118E+05     | 1.30938E+02     | 4.59960E+04    | -8.61618E+07   |
| $ -7/2\rangle$   | 2.37617E-02     | 4.51704E+02     | 2.84502E+01     | 2.43650E+05     | 1.24114E+05     | 4.08256E+02     | 7.03979E+04    | 1.58657E+06    |
| $ +7/2\rangle$   | 4.51704E+02     | 2.37617E-02     | 2.43650E+05     | 2.84502E+01     | 4.08256E+02     | 1.24114E+05     | 1.58657E+06    | 7.03979E+04    |
| $ -5/2\rangle$   | 3.97905E-02     | 8.09585E+00     | 8.57013E+01     | 2.43786E+04     | 5.25298E+05     | 3.99749E+03     | 3.09016E+04    | 6.98231E+04    |
| $ +5/2\rangle$   | 8.09585E+00     | 3.97905E-02     | 2.43786E+04     | 8.57013E+01     | 3.99749E+03     | 5.25298E+05     | 6.98231E+04    | 3.09016E+04    |
| $\% +3/2\rangle$ | 1.29044E+00     | 2.09405E-01     | 1.12390E+03     | 1.75925E+02     | 1.11848E+04     | 1.15129E+05     | 5.34803E+05    | 1.02709E+06    |
| $\% -3/2\rangle$ | 2.09405E-01     | 1.29044E+00     | 1.75925E+02     | 1.12390E+03     | 1.15129E+05     | 1.11848E+04     | 1.02709E+06    | 5.34803E+05    |
| $\% -1/2\rangle$ | 8.94645E-02     | 3.91586E-01     | 8.06178E+01     | 2.60394E+02     | 3.22670E+03     | 3.99149E+03     | 5.88275E+04    | 9.16475E+04    |
| $\% +1/2\rangle$ | 3.91586E-01     | 8.94645E-02     | 2.60394E+02     | 8.06178E+01     | 3.99149E+03     | 3.22670E+03     | 9.16475E+04    | 5.88275E+04    |

**Table S26 cont.** Master matrix  $\Gamma$  for spin-two-phonon transitions at 150 K with  $\sigma = 10 \text{ cm}^{-1}$ . Columns 9 – 16, in units of  $\text{s}^{-1}$ .

|                  | $ -7/2\rangle$ | $ +7/2\rangle$ | $ -5/2\rangle$ | $ +5/2\rangle$ | $\% +3/2\rangle$ | $\% -3/2\rangle$ | $\% -1/2\rangle$ | $\% +1/2\rangle$ |
|------------------|----------------|----------------|----------------|----------------|------------------|------------------|------------------|------------------|
| $ +15/2\rangle$  | 6.28055E+02    | 1.19392E+07    | 4.42727E+03    | 9.00782E+05    | 4.25598E+05      | 6.90637E+04      | 6.16654E+04      | 2.69909E+05      |
| $ -15/2\rangle$  | 1.19392E+07    | 6.28055E+02    | 9.00782E+05    | 4.42727E+03    | 6.90637E+04      | 4.25598E+05      | 2.69909E+05      | 6.16654E+04      |
| $ +13/2\rangle$  | 8.60979E+03    | 7.37349E+07    | 1.09177E+05    | 3.10565E+07    | 4.24404E+06      | 6.64321E+05      | 6.36222E+05      | 2.05499E+06      |
| $ -13/2\rangle$  | 7.37349E+07    | 8.60979E+03    | 3.10565E+07    | 1.09177E+05    | 6.64321E+05      | 4.24404E+06      | 2.05499E+06      | 6.36222E+05      |
| $ -11/2\rangle$  | 3.23764E+06    | 1.06498E+04    | 5.76833E+07    | 4.38967E+05    | 3.64066E+06      | 3.74743E+07      | 2.19501E+06      | 2.71527E+06      |
| $ +11/2\rangle$  | 1.06498E+04    | 3.23764E+06    | 4.38967E+05    | 5.76833E+07    | 3.74743E+07      | 3.64066E+06      | 2.71527E+06      | 2.19501E+06      |
| $ +9/2\rangle$   | 3.35252E+05    | 7.55565E+06    | 6.19483E+05    | 1.39974E+06    | 3.17796E+07      | 6.10326E+07      | 7.30571E+06      | 1.13816E+07      |
| $ -9/2\rangle$   | 7.55565E+06    | 3.35252E+05    | 1.39974E+06    | 6.19483E+05    | 6.10326E+07      | 3.17796E+07      | 1.13816E+07      | 7.30571E+06      |
| $ -7/2\rangle$   | -1.06906E+08   | 1.07866E+06    | 8.19808E+06    | 1.09272E+07    | 6.90934E+06      | 4.14305E+06      | 6.01885E+07      | 3.30529E+07      |
| $ +7/2\rangle$   | 1.07866E+06    | -1.06906E+08   | 1.09272E+07    | 8.19808E+06    | 4.14305E+06      | 6.90934E+06      | 3.30529E+07      | 6.01885E+07      |
| $ -5/2\rangle$   | 1.94749E+06    | 2.59580E+06    | -1.25349E+08   | 3.60401E+06    | 2.09107E+06      | 4.87339E+06      | 2.12221E+07      | 2.86940E+07      |
| $ +5/2\rangle$   | 2.59580E+06    | 1.94749E+06    | 3.60401E+06    | -1.25349E+08   | 4.87339E+06      | 2.09107E+06      | 2.86940E+07      | 2.12221E+07      |
| $\% +3/2\rangle$ | 5.53724E+05    | 3.32030E+05    | 7.05445E+05    | 1.64409E+06    | -1.83191E+08     | 2.48720E+07      | 1.13978E+06      | 8.92350E+05      |
| $\% -3/2\rangle$ | 3.32030E+05    | 5.53724E+05    | 1.64409E+06    | 7.05445E+05    | 2.48720E+07      | -1.83191E+08     | 8.92350E+05      | 1.13978E+06      |
| $\% -1/2\rangle$ | 2.30804E+06    | 1.26747E+06    | 3.42574E+06    | 4.63189E+06    | 5.45374E+05      | 4.26980E+05      | -1.92248E+08     | 2.04376E+07      |
| $\% +1/2\rangle$ | 1.26747E+06    | 2.30804E+06    | 4.63189E+06    | 3.42574E+06    | 4.26980E+05      | 5.45374E+05      | 2.04376E+07      | -1.92248E+08     |

**Table S27.** Relaxation rates for spin-two-phonon transitions with  $\sigma = 10 \text{ cm}^{-1}$ .

| Temperature (K) | Rate 1 (s <sup>-1</sup> ) | Rate 2 (s <sup>-1</sup> ) | Rate 3 (s <sup>-1</sup> ) | Rate 4 (s <sup>-1</sup> ) | Rate 5 (s <sup>-1</sup> ) | Rate 6 (s <sup>-1</sup> ) | Rate 7 (s <sup>-1</sup> ) | Rate 8 (s <sup>-1</sup> ) |
|-----------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 200             | 5.84244E-08               | 2.52549E+04               | 7.88786E+06               | 8.16207E+06               | 8.41963E+07               | 9.47294E+07               | 9.93387E+07               | 1.24381E+08               |
| 190             | 7.86942E-08               | 1.56268E+04               | 7.01940E+06               | 7.21941E+06               | 8.40636E+07               | 9.28639E+07               | 9.82659E+07               | 1.21084E+08               |
| 180             | 1.20641E-07               | 9.13709E+03               | 6.18002E+06               | 6.32065E+06               | 8.38874E+07               | 9.10686E+07               | 9.72551E+07               | 1.17795E+08               |
| 170             | 6.32579E-08               | 4.99837E+03               | 5.37351E+06               | 5.46821E+06               | 8.36531E+07               | 8.93565E+07               | 9.63204E+07               | 1.14536E+08               |
| 160             | 6.00855E-08               | 2.52663E+03               | 4.60399E+06               | 4.66458E+06               | 8.33500E+07               | 8.77414E+07               | 9.54718E+07               | 1.11330E+08               |
| 150             | 1.79568E-08               | 1.16189E+03               | 3.87597E+06               | 3.91242E+06               | 8.29736E+07               | 8.62373E+07               | 9.47119E+07               | 1.08203E+08               |
| 140             | 1.07758E-08               | 4.76479E+02               | 3.19438E+06               | 3.21474E+06               | 8.25288E+07               | 8.48579E+07               | 9.40336E+07               | 1.05187E+08               |
| 130             | 5.25585E-08               | 1.69800E+02               | 2.56468E+06               | 2.57507E+06               | 8.20306E+07               | 8.36159E+07               | 9.34189E+07               | 1.02317E+08               |
| 120             | 5.23586E-08               | 5.08167E+01               | 1.99283E+06               | 1.99756E+06               | 8.15025E+07               | 8.25223E+07               | 9.28421E+07               | 9.96296E+07               |
| 110             | 6.49953E-08               | 1.21977E+01               | 1.48519E+06               | 1.48706E+06               | 8.09730E+07               | 8.15850E+07               | 9.22742E+07               | 9.71659E+07               |
| 100             | 5.90292E-08               | 2.20534E+00               | 1.04824E+06               | 1.04887E+06               | 8.04720E+07               | 8.08084E+07               | 9.16896E+07               | 9.49659E+07               |
| 90              | 2.56949E-08               | 2.75657E-01               | 6.87906E+05               | 6.88070E+05               | 8.00269E+07               | 8.01917E+07               | 9.10746E+07               | 9.30667E+07               |
| 80              | 5.07175E-08               | 2.13820E-02               | 4.08292E+05               | 4.08325E+05               | 7.96596E+07               | 7.97286E+07               | 9.04348E+07               | 9.14975E+07               |
| 70              | 1.31275E-08               | 9.57942E-04               | 2.09834E+05               | 2.09840E+05               | 7.93831E+07               | 7.94062E+07               | 8.98020E+07               | 9.02744E+07               |
| 60              | 2.42049E-08               | 3.01781E-05               | 8.68290E+04               | 8.68300E+04               | 7.91989E+07               | 7.92046E+07               | 8.92327E+07               | 8.93942E+07               |
| 50              | 5.24865E-08               | 7.41004E-07               | 2.53732E+04               | 2.53734E+04               | 7.90958E+07               | 7.90966E+07               | 8.87931E+07               | 8.88306E+07               |



**Table S27 cont.** Relaxation rates for spin-two-phonon transitions with  $\sigma = 10 \text{ cm}^{-1}$ .

| Temperature (K) | Rate 9 (s <sup>-1</sup> ) | Rate 10 (s <sup>-1</sup> ) | Rate 11 (s <sup>-1</sup> ) | Rate 12 (s <sup>-1</sup> ) | Rate 13 (s <sup>-1</sup> ) | Rate 14 (s <sup>-1</sup> ) | Rate 15 (s <sup>-1</sup> ) | Rate 16 (s <sup>-1</sup> ) |
|-----------------|---------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| 200             | 1.41637E+08               | 1.41779E+08                | 1.68209E+08                | 1.76789E+08                | 1.77082E+08                | 1.91742E+08                | 2.23178E+08                | 2.25431E+08                |
| 190             | 1.38353E+08               | 1.39438E+08                | 1.66550E+08                | 1.75160E+08                | 1.75343E+08                | 1.89726E+08                | 2.21390E+08                | 2.22353E+08                |
| 180             | 1.34930E+08               | 1.36917E+08                | 1.64951E+08                | 1.73667E+08                | 1.73769E+08                | 1.87716E+08                | 2.19085E+08                | 2.19526E+08                |
| 170             | 1.31389E+08               | 1.34205E+08                | 1.63400E+08                | 1.72322E+08                | 1.72371E+08                | 1.85720E+08                | 2.15689E+08                | 2.17499E+08                |
| 160             | 1.27756E+08               | 1.31298E+08                | 1.61883E+08                | 1.71136E+08                | 1.71153E+08                | 1.83751E+08                | 2.12096E+08                | 2.15352E+08                |
| 150             | 1.24062E+08               | 1.28199E+08                | 1.60391E+08                | 1.70113E+08                | 1.70114E+08                | 1.81825E+08                | 2.08304E+08                | 2.13058E+08                |
| 140             | 1.20338E+08               | 1.24918E+08                | 1.58919E+08                | 1.69247E+08                | 1.69254E+08                | 1.79958E+08                | 2.04295E+08                | 2.10603E+08                |
| 130             | 1.16624E+08               | 1.21472E+08                | 1.57468E+08                | 1.68542E+08                | 1.68551E+08                | 1.78172E+08                | 2.00054E+08                | 2.07966E+08                |
| 120             | 1.12963E+08               | 1.17888E+08                | 1.56040E+08                | 1.67982E+08                | 1.67991E+08                | 1.76491E+08                | 1.95564E+08                | 2.05131E+08                |
| 110             | 1.09402E+08               | 1.14202E+08                | 1.54640E+08                | 1.67550E+08                | 1.67557E+08                | 1.74941E+08                | 1.90806E+08                | 2.02076E+08                |
| 100             | 1.05993E+08               | 1.10463E+08                | 1.53270E+08                | 1.67225E+08                | 1.67231E+08                | 1.73550E+08                | 1.85769E+08                | 1.98782E+08                |
| 90              | 1.02794E+08               | 1.06737E+08                | 1.51934E+08                | 1.66988E+08                | 1.66991E+08                | 1.72341E+08                | 1.80445E+08                | 1.95232E+08                |
| 80              | 9.98599E+07               | 1.03112E+08                | 1.50630E+08                | 1.66818E+08                | 1.66820E+08                | 1.71337E+08                | 1.74843E+08                | 1.91420E+08                |
| 70              | 9.72482E+07               | 9.97036E+07                | 1.49361E+08                | 1.66699E+08                | 1.66701E+08                | 1.69003E+08                | 1.70548E+08                | 1.87358E+08                |
| 60              | 9.50164E+07               | 9.66571E+07                | 1.48137E+08                | 1.63023E+08                | 1.66621E+08                | 1.66621E+08                | 1.69974E+08                | 1.83102E+08                |
| 50              | 9.32295E+07               | 9.41465E+07                | 1.46984E+08                | 1.57116E+08                | 1.66572E+08                | 1.66572E+08                | 1.69599E+08                | 1.78793E+08                |

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