

Supporting Information

Acid–base properties of monomethylgermanium(IV) in aqueous solutions

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I. NMR Titration Studies

1. Calibration procedure of the glass electrode

Reagents. Double-deionized ultra-pure water (18.2 M Ω cm) was obtained from a PURELAB[®] Chorus I Analytical (Elga) cartridge system. KCl (ACS reagent >99%, Sigma-Aldrich) was used as received. The 0.1001 mol L⁻¹ HCl and 0.1006 mol L⁻¹ carbonate-free KOH solutions were prepared from Merck concentrates (Titrisol[®]) by dilution with boiled and argon-saturated ultrapure water. They were standardized by titration against oven-dried (120 °C for 2 h) Tris buffer (Aldrich-Sigma, 99.9%) and potassium hydrogen phthalate (Aldrich-Sigma, 99.99%), respectively. The concentration of the standardized solutions corresponded to the average of at least five replicates and was known with a relative precision better than 0.15%. They were stored under purified argon using Ascarite II (Acros, 20–30 mesh) scrubbers in order to prevent absorption of carbon dioxide. Standardizations of the acid and base solutions were carried out with a Titrand 904 (Metrohm) automatic titration setup equipped with a 5 mL piston burette. Delivered volumes were corrected according to a linear calibration function obtained by weighing for each glass burette known quantities of water and by taking into account the buoyancy effect.

Equipment. p[H] values of NMR samples were measured with a PHM 240 ionometer (Radiometer) fitted with a combined semi-micro high-alkalinity glass electrode (ref. 60234110, Metrohm). The Ag/AgCl reference compartment was filled with a saturated AgCl/KCl solution. The potential differences (ΔE_{mes}) were measured at a ± 0.1 mV resolution. The water-jacketed titration vessel was connected to a Lauda RE106 circulator. Magnetically stirred solutions were kept at a constant temperature of 298.2(2) K and maintained under an argon stream to exclude CO₂ from the laboratory atmosphere.

Glass electrode calibration and data treatment. The cell was calibrated in two steps as a hydronium ion concentration probe ($p[H] = -\log([H^+] + [D^+])$) for an ionic strength of $I = 1$ mol L⁻¹ over a p[H] range spanning from 1 to 12.8 by performing HCl/KOH titrations. Considering the low amount of D₂O (5%) added for locking the spectrometer frequency, no corrections for the isotopic effect has been applied as the expected contribution (less than +0.02 p[H] unit as compared to pure H₂O) [1] remains within experimental error. First, 2 mL of the standardized 0.0963 mol L⁻¹ HCl solution containing 0.9 mol L⁻¹ KCl were titrated with 1.62 mL of 0.0964 mol L⁻¹ KOH containing also 0.9 mol L⁻¹ KOH in 60 μ L increments (28 points) delivered with a GS-1200-A micrometer burette-style dispenser (Gilmont). In the second step, 29 data points in the basic range were collected in the same way simply by switching the reagents contained in the vessel (KOH) and in the burette (HCl). The proton concentration for each of the 57 considered HCl–KOH titration points was calculated by the mass balance equations, assuming a water autoprotolysis constant of $K_w = 10^{-13.79}$ ($I = 1$ mol L⁻¹ KCl, $T = 298.15$ K). [2] Accordingly, the actual ionic strength varied slightly from 1.00 to 0.95 mol L⁻¹ for each individual titration. Both datasets ($1.017 \leq p[H] \leq 1.998$ and $11.717 \leq p[H] \leq 12.774$; Figure S1) were merged and processed by unweighted nonlinear least-squares using the OriginPro 2018 package. The standard deviation (σ) for each refined parameter returned by the minimization routine is reported in parentheses.

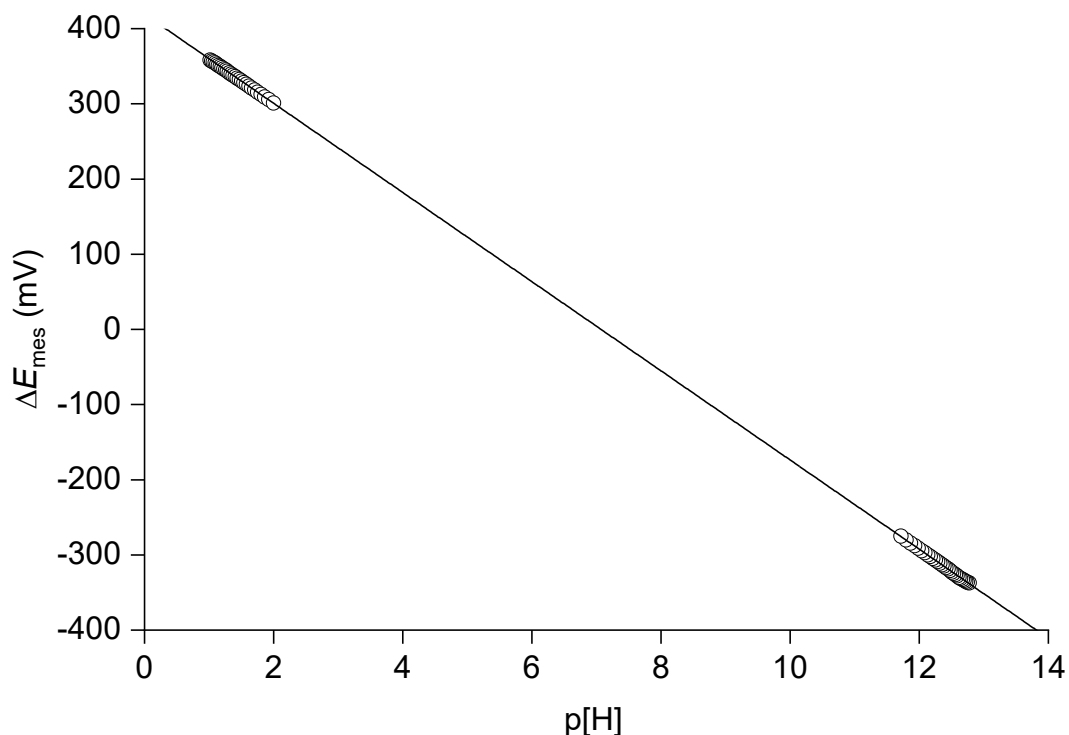


Figure S1. Calibration data of the glass electrode used for the NMR titration of $(\text{CH}_3)\text{Ge}(\text{OH})_3$ (samples 1–17). The black line corresponds to Eq. (1) with the following refined parameters: $\Delta E^\circ = 419.30(8) \text{ mV}$, $S = 59.30(1) \text{ mV}$, $J_a = 0 \text{ mV mol}^{-1} \text{ L}$, and $J_b = 0 \text{ mV mol}^{-1} \text{ L}$.

The fitting function was the four-parameter extended Nernst equation (Eq. (1); black line in Figure S1), which takes into account the standard potential ($\Delta E^\circ = 419.30(8) \text{ mV}$), the slope ($S = 59.30(1) \text{ mV}$), and the correction terms accounting for the changes in liquid junction potential in the acidic ($E_{ja} = J_a [\text{H}^+]$ with $J_a = 0 \text{ mV mol}^{-1} \text{ L}$) and alkaline ($E_{jb} = J_b [\text{OH}^-]$ with $J_b = 0 \text{ mV mol}^{-1} \text{ L}$) regions.[3] The adjusted slope is close to the expected value of 59.16 mV at 298.15 K and within the accepted tolerance of $\pm 0.5\%$.

$$\Delta E_{\text{cal}} = \Delta E^\circ + S \log [\text{H}^+] + J_a [\text{H}^+] + J_b K_w [\text{H}^+]^{-1} \quad (1)$$

ΔE_{mes} readings collected during the NMR titration were converted into $p[\text{H}]$ values with the help of a Microsoft excel spreadsheet by solving iteratively Eq. (1).

$$p[\text{H}] = \frac{\Delta E^\circ - \Delta E_{\text{mes}} + J_a [\text{H}^+] + J_b K_w [\text{H}^+]^{-1}}{S} \quad (2)$$

2. NMR samples

Table S1. Composition of NMR samples,^a measured potentials, and corresponding p[H] values.

N ^o	V_{Ge} (μL)	V_{KCl} (μL)	$V_{\text{D}_2\text{O}}$ (μL)	V_{KOH}^b (μL)	$[\text{Ge}]_{\text{Tot}}$ (mmol L^{-1})	$[\text{K}]_{\text{Tot}}$ (mol L^{-1})	$[\text{Cl}]_{\text{Tot}}$ (mol L^{-1})	ΔE_{mes} (mV)	p[H] _{mes}
1	75	165	25	0	5.97	0.990	0.990	315.9	1.74 ^c
2	75	165	25	6	5.97	0.996	0.990	308.1	1.88 ^c
3	75	165	25	12	5.97	1.002	0.990	294.4	2.11 ^c
4	75	165	25	18	5.97	1.008	0.990	259.3	2.70 ^c
5	75	165	25	46	5.97	1.009	0.990	258.6	2.71 ^c
6	75	165	25	47	5.97	1.009	0.990	252.5	2.81 ^c
7	75	165	25	48	5.97	1.009	0.990	241.9	2.99 ^c
8	75	165	25	49	5.97	1.010	0.990	228.5	3.22 ^c
9	75	165	25	51	5.97	1.011	0.990	78.4	5.75 ^c
10	75	165	25	53	5.97	1.011	0.990	−131.5	9.29 ^c
11	75	164	25	56	5.97	1.007	0.984	−165.9	9.87 ^c
12	75	164	25	60	5.97	1.008	0.984	−202.5	10.49 ^c
13	75	164	25	65	5.97	1.010	0.984	−225.3	10.87 ^c
14	75	163	25	75	5.97	1.008	0.978	−247.9	11.25 ^c
15	75	163	25	85	5.97	1.012	0.978	−262.0	11.49 ^c
16	75	162	25	100	5.97	1.012	0.972	−279.6	11.79 ^c
17	75	160	25	120	5.97	1.008	0.960	−295.6	12.06 ^c
18		500 ^d		15	5.79	1.006	0.948	−296.7	12.10 ^e
19		500 ^d		30	5.63	1.002	0.921	−316.8	12.44 ^e
20		500 ^d		70	5.23	0.993	0.856	−333.1	12.72 ^e
21		500 ^d		110	4.89	0.985	0.800	−345.0	12.92 ^e
22		500 ^d		150	4.59	0.978	0.751	−351.5	13.03 ^e

^a Samples 1–17: 5 μL of dioxane and $(395 - V_{\text{KCl}} - V_{\text{KOH}})$ μL were added to the mixture to reach a total volume of 500 μL . ^b Composition of the added KOH solution: $[\text{KOH}] = 0.871 \text{ mol L}^{-1}$ (figures in red), $[\text{KOH}] = 0.50 \text{ mol L}^{-1}$ (figures in black), $[\text{KOH}] = 0.20 \text{ mol L}^{-1}$ (figures in blue). ^c $\Delta E^\circ = 419.30 \text{ mV}$, $S = 59.30 \text{ mV}$, $J_a = 0 \text{ mV mol}^{-1} \text{ L}$, $J_b = 0 \text{ mV mol}^{-1} \text{ L}$. ^d Mixture resulting from the combination of samples 12–17. ^e $\Delta E^\circ = 420.16 \text{ mV}$, $S = 59.23 \text{ mV}$, $J_a = -61.9 \text{ mV mol}^{-1} \text{ L}$, $J_b = 99.3 \text{ mV mol}^{-1} \text{ L}$.

3. ^1H NMR titration data

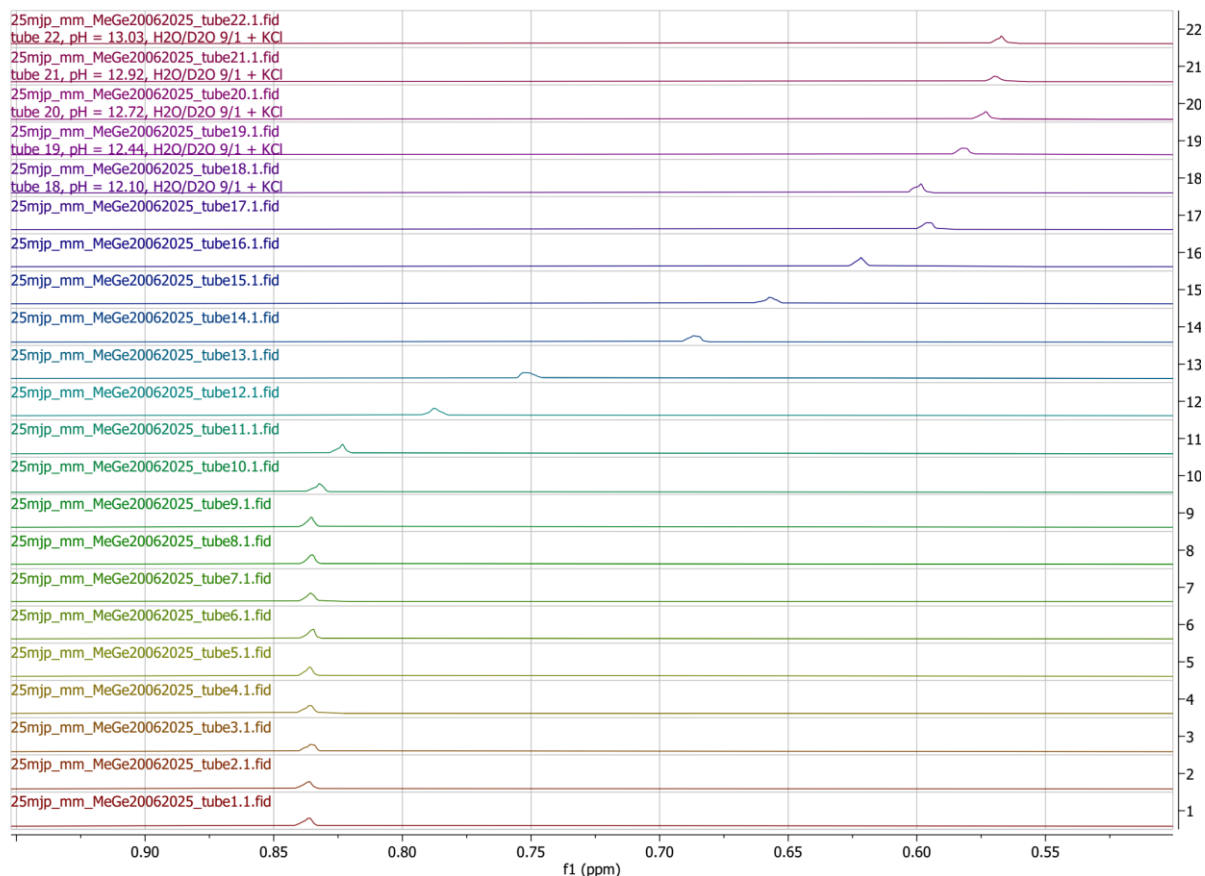


Figure S2. ^1H NMR spectra (600.33 MHz) of $(\text{CH}_3)\text{Ge}(\text{OH})_3$ in $\text{H}_2\text{O}/\text{D}_2\text{O}$ 95/5 v/v as a function of $\text{p}[\text{H}]$. $I = 1 \text{ mol L}^{-1} \text{ K}(\text{Cl}/\text{OH})$, $T = 298 \text{ K}$. $\text{p}[\text{H}]$ values are reported in Table S1.

4. ^{13}C NMR titration data

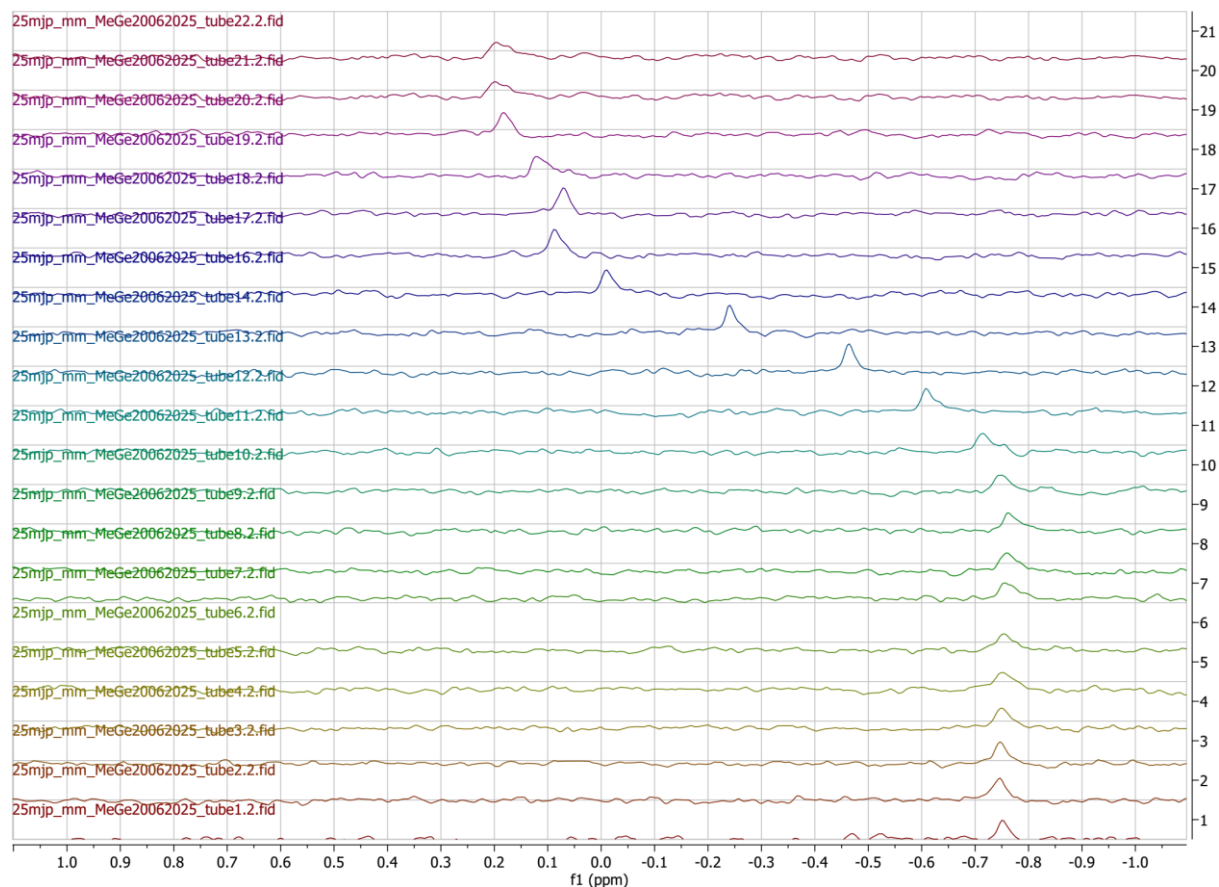


Figure S3. ^{13}C NMR spectra (150.95 MHz) of $(\text{CH}_3)\text{Ge}(\text{OH})_3$ in $\text{H}_2\text{O}/\text{D}_2\text{O}$ 95/5 v/v as a function of $\text{p}[\text{H}]$. $I = 1 \text{ mol L}^{-1} \text{ K}(\text{Cl}/\text{OH})$, $T = 298 \text{ K}$. $\text{p}[\text{H}]$ values are reported in Table S1.

II. SIT analysis of the pK_a of $(CH_3)Ge(OH)_3$

According to the Specific Ion interaction Theory (SIT), the activity coefficient γ_i of a given ion i of charge z_i is given by Eq. (3), where m_j is the molality of the counter ion j . [4-5] The SIT treatment is based on the assumption that the specific ion interaction coefficients $\varepsilon(i,j)$ between a cation i and an anion j are not or are only weakly dependent on the ionic strength I_m expressed in the molal scale ($mol\ kg^{-1}$). Therefore, molar concentrations were converted into molalities by using the conversion factors ζ tabulated by Grenthe *et al.*, [5] which are based on solution densities compiled by Söhlneel and Novotny.[6]

$$\log \gamma_i = -z_i^2 D + \sum_{j=1}^N \varepsilon(i, j) m_j \quad \text{with } D = \frac{0.509 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} \quad (3)$$

Conditional molal equilibrium constants pK_a^m were derived from the measured values expressed in the molar scale by applying relation (4), where ν_i stands for the stoichiometric coefficient. For the considered protolysis equilibrium, $\Delta \nu = 1$.

$$pK_a^m = pK_a - \Delta \nu \log \xi \quad \text{with } \Delta \nu = \sum_{\text{products}} \nu_i - \sum_{\text{reagents}} \nu_i \quad (4)$$

For the first protolysis equilibrium of $(CH_3)Ge(OH)_3$, the SIT equation is given by Eq. (5), with $\Delta \varepsilon = \varepsilon((CH_3)Ge(OH)_3, NaCl) - \varepsilon(Na^+, [(CH_3)Ge(OH)_2O]^-) - \varepsilon(H^+, Cl^-)$. Details on its derivation can be found in any open-access volume of the *Chemical Thermodynamics Series* published by the OECD Nuclear Energy Agency Thermochemical Data Base Project (NEA-TDB; https://www.oecd-nea.org/jcms/pl_22166/thermochemical-database-tdb-project).

$$pK_a^m + 2D = pK_a^0 - \Delta \varepsilon I_m \quad (5)$$

By plotting $pK_a^m + 2D$ as a function of I_m a straight line with the slope $\Delta \varepsilon$ and the ordinate at the origin pK_a^0 is obtained. Following NEA-TDB, we selected a weighted linear regression procedure. A peculiarity of their approach is that the uncertainties of $pK_a^m + 2D$ are not only used for the weighting of the data but also for the calculation of the uncertainties of both adjusted parameters (pK_a^0 and $\Delta \varepsilon$). Thus, the uncertainties of intercept and slope do not depend on the dispersion of the data points around the regression line, but rather directly on the uncertainties of the data themselves. This also has the consequence that if the uncertainties of the datapoints represent the 95% confidence level, the uncertainties of intercept and slope will also do so.

III. Bibliography

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