nature portfolio

Peer Review File

Symmetry-breaking dynamics of a photoionized carbon dioxide dimer

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

Please see attachment for review report.

Reviewer #2 (Remarks to the Author):

The article reports on EUV pump-EUV probe Coulomb explosion imaging experiments performed on carbon dioxide dimers. Combining experimental results and ab-initio calculations, the authors show that molecular ionization leads to an evolution from the neutral dimer to an ionic structure that differs substantially from its expected stable geometry. This geometry is characterized by a charge asymmetry that is created upon direct vertical ionization. In the ground electronic state the cation forms a T-shape that is more compact than the initial neutral dimer. This is monitored by measuring the increase of the kinetic energy of the measured coulomb exploded fragment. Similarly, the process is also observed in the electronic excited state that forms a metastable dication dimer characterized by a C03 carbonate moiety.

Neither the experimental approach nor the theoretical methods are new but they are applied to a very interesting case. Although not new, these type of experiments remains challenging. Beyond the experimental challenge, I found the article well written and the analysis and reasoning very well thought. As a consequence I consider the article suited for nature comms.

I have several suggestions that the authors might want to consider:

1) I found some of the figure captions confusing:

In Figure 1, "Figure 1 Comparing the KER spectra of (CO 2) 2 Coulomb explosion events"
… it should be something like : KER spectra of coincident pairs of CO2+ ions (indicating exactly what the signal is)?

In Figure 3, "Snapshots of the ionization induced dynamics in the CO 2 dimer, comparing typical trajectory calculations using either DFT/BNL or CASPT2 ground-state potentials"
It could be indicated that these are snapshots of "molecular dynamics calculations"? DFT/BL dynamics and CASPT2 dynamics seems misleading to me as these methods refer to electronic structure calculations.

2) Because the pump and the probe are identical pulses, I assume that the signal in the positive and negative delays are symmetric. Is it indeed the case or the negative delay signal has not been recorded?

3) It would be useful to explicitly show what the distances taken to compute the KER are. A schematic showing explicitly the chosen distance between the monomers (and therefore how it is defined) would be useful. A graph showing how this distance evolves with time would also be useful to get an idea of the changes that the molecule experiences.

4) Mind the Typos such as in the ref:
Ref 29 "Vaidhyanathan, R. et al. Direct Observation and Quantification of CO 2 Binding Within an Amine-Functionalized Nanoporous Solid. Science (80-.). 330, 650–653 (2010)"

Overall, the results are interesting and the article well thought. I support the publication.

Reviewer #3 (Remarks to the Author):

File Edit Options Buffers Tools Text Help
The authors have performed a combined experimental and theoretical investigation
of dynamics induced by ionization of the carbondioxide dimer, $(CO_2)_2$, with the triggered dynamics monitored in time delays by Coulomb explosion imaging (CEI).
The conclude that the system undergoes non-trivial dynamics towards a T-shaped dimer structure and formation of a CO_3 moiety.
Furthermore, AIMD simulations are performed in the 2nd excited state of the ionized dimer and of the doubly ionized system.

The presentation is clear and I have no remarks on the experimental part of the study.
However, I find the discussion of the delocalized and localized valence-ionized states unclear, and I fear that the theoretical framework of the treatment of (nearly) degenerate states in the dynamics
in simply inadequate and the differences between the BNL DFT and XMS-CASPT2 simulations possibly misleading.
Hence, I recommend rejection or possibly major revision of the paper.

Detailed comments are given below, describing my concerns:

1) Please, motivate choice and evaluate quality of BNL functional for this system.

2) In the XMS-CASPT2 calculations presented in Figure 2, I would have expected to have also a set of states
with ionization of the CO_2 molecule that lacks amplitude in the our lowest-energy many-body eigenstates
within the SA4-XMS-CASPT2(7e6o)/aug-cc-pvdz theory.
Please discuss this aspect.
Why are these states not appearing or presented?

3) Given that the authors confirm that each XMS-CASPT2 state in Figure 2 actually corresponds to two degenerate states,
I ask myself if the localization(symmetry-breaking or delocalization(symmetry adapted) Dyson orbitals
carry any meaning in isolation. If they are degenerate, any linear combination of the states is an equally valid representation.
As I understand it the ground state of the ionized CO_2 dimer is degenerate and BOMD is not applicable.

4) It is natural that the Born-Oppenheimer dynamics is strongly affected by whether the ionization is localized or delocalized,
but I question whether the proper quantum dynamics, involving a wavefunction propagating involving the degenerate ionized states
would be well represented by Born-Oppenheimer dynamics on a single surface. Hence, I question whether the theoretical framework
for the simulations is appropriate and realistic. Naturally, the DFT/BNL and CASPT2 based simulations produce very different trajectories,
but that does not mean any of them are based on a firm theoretical basis.
This problem should affect how the ground state dynamics of the ionized CO_2 dimer and the excited state dynamics,
since in both cases there is degeneracy, whereas for the dicationic CO_2 dimer, I imagine that the ground state is non-degenerate in its spin manifold.

Reviewer #1 (Attachment):

In their manuscript, Livshits *et.al* describe a combined experimental and theoretical study of symmetry breaking dynamics in EUV ionized carbon dioxide dimers. They perform a time-resolved EUV pump – EUV probe coulomb explosion experiment of CO_2 dimers. The pump pulse creates $(CO_2)_2^+$ ions and the probe EUV pulse double ionizes these dimers resulting in coulomb explosion which is measured with ion-ion coincidence. Using the measured kinetic energy release spectra at different pump-probe time delays, combined with detailed theoretical calculations, the authors find that a rearrangement from the slipped parallel geometry in neutral dimers to a T-shaped structure occurs at 100 fs after the ionization. Furthermore, they find that higher excited states of the ionized dimer are populated and exhibit a CO_3 moiety in the $C_2O_4^+$ complex that persists after the second ionization step which results in a metastable dication.

Overall, this is an interesting and detailed study of structural rearrangements of CO_2 dimers caused by ionization. Though the interpretation and conclusions heavily rely on theoretical calculations, the calculations are rigorous with two different approaches compared to the experimental data. The manuscript is well written, and the work is clearly presented which makes it accessible to a broad audience. Based on the important insight obtained from this study which has implications in astrophysical phenomena combined with the unique experimental measurements and rigorous theoretical modeling, I find this manuscript suitable for publication in Nature Communications in its present form. I have some minor comments below that may help improve the manuscript:

1. It will help the reader if the authors avoid very long sentences. For example, the last sentence on page 7 – "While a full calculation …".

2. It is not clear what the authors are trying to say in the following statement in the Discussion section – "This finding may affect the interpretation of experimental studies of cationic CO_2 clusters, which nature can potentially depend on their formation mechanism."

3. The following statement in the Discussion section needs a reference – "Such a metastable asymmetric dication, featuring a CO_3 carbonate moiety, was previously proposed as an asymmetric intermediate in CO_2^{2+} + CO_2 collisions."

We would like to thank all the reviewers for their comments that helped us improve our manuscript. In the following we describe our response to the reviewers comments and the revisions made to improve our manuscript.

We thank reviewer 1 for supporting the publication of our work in nature communications. Revisions made following reviewer #1 comments:

1. The reviewers comment was: It will help the reader if the authors avoid very long sentences. For example, the last sentence on page 7 – "While a full calculation ...".

   Long sentence on pg.7 was revised and now reads:

   "While a full calculation including the excited states cannot be performed using DFT/BNL potentials, ground-state simulations indicate that the C_{2h} conserving dynamics can be expected to exhibit a distinctively faster response. High KER events would onset already at ~50 fs and low KER events at time-delays as early as 150 fs, see figure 3 and SM for typical examples."

2. The reviewers comment was: It is not clear what the authors are trying to say in the following statement in the Discussion section – "This finding may affect the interpretation of experimental studies of cationic CO2 clusters, which nature can potentially depend on their formation mechanism."

   We thank the reviewer for pointing out that the statement was not clear. The revised text reads:

   "This finding may affect the interpretation of experimental studies of cationic CO_2 clusters, which can potentially form T-shaped or slipped parallel structures depending on their formation mechanism. Indeed, different local minima on the electronic ground-state may form by bottom-up association of neutral monomers to a charged monomer ion, or by top-down ionization of a parent neutral cluster."

3. The reviewer noticed a missing citation. ref #11 that was added to support our discussion of an earlier proposal for CO3 moiety formation in a C2O4^2+ collision complex.

We thank reviewer #2 for supporting the publication of our work in nature communications. We made the following revisions based on the suggestions of reviewer #2:

1. Reviewer #2's comment was that some of the figure captions are confusing:

   In Figure 1, "Figure 1 Comparing the KER spectra of (CO 2) 2 Coulomb explosion events" … it should be something like : KER spectra of coincident pairs of CO2+ ions (indicating exactly what the signal is)?

   In Figure 3, "Snapshots of the ionization induced dynamics in the CO2 dimer, comparing typical trajectory calculations using either DFT/BNL or CASPT2 ground-

state potentials" It could be indicated that these are snapshots of "molecular dynamics calculations"? DFT/BL dynamics and CASPT2 dynamics seems misleading to me as these methods refer to electronic structure calculations.

We thank the reviewer for pointing out the confusing captions, which we revised and improved:

Figure 1 caption was revised adopting the reviewer suggestion to clearly begin with: "KER spectra of coincident $CO_2^+ pairs, \ldots.$"

The revised caption Figure #3: now begins with:

"Snapshots of calculated molecular dynamics following ionization of the CO_2 dimer,…"

2. The reviewers comment was: Because the pump and the probe are identical pulses, I assume that the signal in the positive and negative delays are symmetric. Is it indeed the case or the negative delay signal has not been recorded?

   We thank the reviewer for pointing out the potential confusion. The simulated KER are not derived from a distance, it is directly calculated by propagating AIMD trajectories on the dication state: see for example the supplementary movies #4 and #5.
   The text describing the KER estimates (on pg. 5) was revised to avoid an understandable confusion that the KER was estimated based on the distance.

   "To demonstrate that CEI can be used for differentiating between the two dynamical scenarios, we performed ab initio molecular dynamics simulations on the dication state to estimate the KER after a time-delayed second ionization."

   This point is also stated in Figure 3 and 4 captions: "The values in parenthesis indicate the time-resolved KER, calculated for a 2nd ionization of each of the geometries and ab initio simulation of the Coulombic explosion on the dication ground-state"

3. The reviewer wrote: Because the pump and the probe are identical pulses, I assume that the signal in the positive and negative delays are symmetric. Is it indeed the case or the negative delay signal has not been recorded?

   The reviewer is correct, the equal intensity of the "pump" and "probe" pulses results in a symmetric response for positive and negative time delays. As the reviewer suggested, we added to the SM a section, titled "Systematic test of the symmetric response to positive and negative time delays". It describes Figure S6 that shows the symmetric response recorded for positive and negative time delays, as expected by the reviewer.

4. The reviewer pointed to typo's in the references – we screened the reference list and hopefully found and revised all the typos.

Reviewer #3 comments focused on the discussion of our results. The reviewer wrote :

I find the discussion of the delocalized and localized valence-ionized states unclear, and I fear that the theoretical framework of the treatment of (nearly) degenerate states in the dynamics in simply inadequate and the differences between the BNL DFT and XMS-CASPT2 simulations possibly misleading.

We thank the reviewer for the comments that helped us clarify and improve the manuscript

Here are our point-by-point responses to the reviewer's detailed comments and description of the revisions we made to improve the manuscript and make it suitable for publication:

1. Reviewer #3 wrote: 1) "Please, motivate choice and evaluate quality of BNL functional for this system."

We chose the BNL functional for the calculation of (I) The dication AIMD simulations of the CO_2 dimer dication (formed with the probe pulse) that allowed to evaluate the KER for different time delays between the pump and probe pulses. And (II), the singly ionized dimer ground-state dynamics.

(I) The reviewer correctly expresses concern about the quality of the BNL functional for the dication CO_2 dimer. We share the reviewer's concern and therefore describe in the last part of the first paragraph "Theoretical Methods" section:

"The DFT/BNL dynamics for the dication were validated by performing simulations also on the XMS-CASPT2/(8e,9o) level for 21 representative configurations initiated on the triplet dication ground-state and for 80 configurations initiated on the singlet dication (see SM for more details). Unfortunately, due to near-degeneracy, DFT/BNL could not simulate dynamics on the singlet dication."

In the supplementary section, we discuss the details of the BNL benchmarking relative to XMS-CASPT2/(8e,9o) level dynamics. See for example the comparison made for a typical trajectory in figure S3.

(II) As for the singly ionized dimer dynamics, the conclusions of our manuscript clearly justify the concerns of the reviewer. Indeed, we found that BNL/DFT and other DFT functionals (such as B3LYP) are not good for describing the dynamics of the cation dimer. In view of the reviewer's comment, we improved the discussion of this aspect.

"It is interesting to note that although DFT/BNL and CASPT2 methods exhibit the same consistent electronic structure, the near degeneracy of the low-lying states results in

remarkably different molecular dynamics of the nuclei, when calculated classically on the ab-initio potentials. This conclusion is not limited to the BNL functional and is just as valid for other DFT functionals such as B3LYP, which we found to exhibit similar dynamics. This finding should serve as an important warning to always check the DFT-based dynamics when near degeneracies appear in other molecular and cluster systems."

2. The reviewer wrote: "In the XMS-CASPT2 calculations presented in Figure 2, I would have expected to have also a set of states with ionization of the CO2 molecule that lacks amplitude in the our lowest-energy many-body eigenstates within the SA4-XMS-CASPT2(7e6o)/aug-cc-pvdz theory.
   Please discuss this aspect.
   Why are these states not appearing or presented?"

As we explain in the beginning of pg. 4: "The four-state averaging constraint results in four orbitals that break the C_{2h} symmetry and in the localization of the hole on one of the CO_2 monomers." We thank the reviewer for this comment that helped improve the description of how this comes about. The following text was added at the end of pg. 4:

"Indeed, in Figure 2, the localized CASPT2 Dyson state looks very similar to the sum of the degenerate delocalized Dyson states in the BNL/DFT calculation. In the SM we show that extending the CAS to enable six state-averaging does not qualitatively alter the electronic structure but reveals two of the four missing sibling states, corresponding to the difference of the delocalized states.

It is noteworthy that the DFT/BNL states do not break symmetry, even though the pairs of orbitals are nearly degenerate as well. Furthermore, the fact that CASPT2 breaks symmetry is particular to the Franck-Condon geometry: in the SM we show that symmetry breaking does not happen in the global minimum geometry of the ionized dimer explaining why the global minimum is dynamically inaccessible by symmetry-breaking dynamics starting in the FC geometry."

Furthermore, a new section titled "Symmetry-Breaking at the Franck-Condon point of the cation CO_2 dimer" was added to the revised SM, in which we discuss this issue at some length and show that the states with a localized hole on the second monomer can be recovered by increasing the active space and the number of states in the averaging from 4 to 6, a level that unfortunately is not suitable for AIMD purposes. Nevertheless, as can be seen in Table S1 in the SM, the higher-level calculation validates the symmetry breaking and the states observed in the four-state mixing CAS calculations used for the NA-AIMD simulations.

3. Reviewer #3 wrote: "Given that the authors confirm that each XMS-CASPT2 state in Figure 2 actually corresponds to two degenerate states, I ask myself if the localization (symmetry-breaking or delocalization(symmetry adapted) Dyson orbitals
   carry any meaning in isolation. If they are degenerate, any linear combination of the states is an equally valid representation. As I understand it the ground state of the ionized CO2 dimer is degenerate and BOMD is not applicable."

We fully agree with the referee that if the Dyson orbitals are degenerate, any linear combination of the degenerate set is an equally valid representation. Indeed, it is impossible to determine at the present level of theory how to start the BO dynamics at the FC point from this degeneracy. In fact, this is the main point of our paper. We argue that there are two choices for the BO dynamics: One is to assume hole delocalization (use a non-localized Dyson orbital), which is what we see in the molecular dynamics based on DFT. The other is to assume hole localization (on one of the monomers), as in the CASPT2-based molecular dynamics. The two scenarios lead to very different dynamics. The hole-delocalized dynamics preserve the symmetry of the dimer while the hole-localized one breaks it. Our experiments indicate that the latter dynamics prevail, which is the main novelty of this work.

To emphasized this point to the readers, the end of the discussion section was revised, and now includes the following text:

"One can question the validity of NA-AIMD in systems which have degenerate adiabatic states. However, this problem arises only within the degeneracy itself: If nuclei quickly move to break symmetry, degeneracy is eradicated, and the NA-AIMD picture can subsequently be used. Still, at time zero, it is impossible to decide a priori whether one should localize the hole (as in CASPT2) or not (as in BNL/DFT). A posteriori, it turns out that only the hole-localized CASPT2 dynamics is consistent with our experimental results."

4. The reviewer continued the line of thought presented in comment 3 and wrote: " It is natural that the Born-Oppenheimer dynamics is strongly affected by whether the ionization is localized or delocalized, but I question whether the proper quantum dynamics, involving a wavefunction propagating involving the degenerate ionized states would be well represented by Born-Oppenheimer dynamics on a single surface. Hence, I question whether the theoretical framework for the simulations is appropriate and realistic. Naturally, the DFT/BNL and CASPT2 based simulations produce very different trajectories, but that does not mean any of them are based on a firm theoretical basis.
   This problem should affect how the ground state dynamics of the ionized CO2 dimer and the excited state dynamics, since in both cases there is degeneracy, whereas for the dicationic CO2 dimer, I imagine that the ground state is non-degenerate in its spin manifold."

We fully agree with the referee that the BO dynamics are affected by the hole localization (see also our response to the referee comment no. 3). We also agree that under electronic degenerate states, it is not evident if the molecular dynamics would be well represented by Born-Oppenheimer dynamics. To convey this point to the readers we revised the end of the discussion section, as described above in our response to comment no. 3.

To conclude, we believe that the revised manuscript addresses all the concerns raised by the reviewers and is now suitable for publication.

REVIEWER COMMENTS

Reviewer #2 (Remarks to the Author):

The authors have answered my comments.
The article contains substantial new scientific results that are very well discussed.
I found the article suitable for publication in nature communications as it is.

Reviewer #3 (Remarks to the Author):

In the revision, the authors have discuss and in most details addressed the remarks of the reviewers.

However, even though the impression from the rebuttal is that the authors have confirm my concerns about the limitations on an adiabatic simulation of degenerate or nearly degenerate state, the description and discussion is still not clear.

1) The authors write that TDDFT is not suitable because non-adiabatic transitions should be taken into account, and therefore CASPT2 is used. But although CASPT2 is a superior method, also TDDFT can be used with simple models of the non-adiabatic couplings. The essential question I raised is whether BOMD is performed or NA-AIMD.

2)Whether the methods at symmetric geometries giev degenerate states with localized or delocalized orbitals should not matter if the non-adiabatic couplings are treated correctly, as I understand it. Hence, I would recommend removing the emphasis on the delocalized DFT and localized CASPT2 difference.

2) How are the non-adiabatic couplings calculated, and please present the surface hopping population transfer.

Hence, I recommend revision to clarify this aspect of the study.
The reader is given the impression that localized or delocalized oritals give different dynamics, whereas as I understood the study, BOMD on DFT and NA-AIMD on CASPT2 give different dynamics,
which are very different conclusions. This needs to be clarified, possibly by performing NA-AIMD on DFT and BOMD on CASPT2, to complement the misaligned comparison. If I have misunderstood something about their simulations, I apologize and the required response would of course be different.

Dear reviewers and editor,

We would like to thank all the reviewers and editorial staff that help us improve our manuscript.

We were happy that reviewer 2 was content and had agreed with the first reviewer's recommendation to publish the paper. He even stated that the
article contains substantial new scientific results that are very well discussed.

Reviewer 3 still had some questions, which we have answered below.

Reviewer #3 wrote:
In the revision, the authors have discuss and in most details addressed the remarks of the reviewers. However, even though the impression from the rebuttal is that the authors have confirm my concerns about the limitations on an adiabatic simulation of degenerate or nearly degenerate state, the description and discussion is still not clear.

We thank the reviewer for his help in improving the clarity of our manuscript. In the following, we describe point-by-point our responses and revisions made toward improving the clarity of our text:

1) The reviewer wrote: The authors write that TDDFT is not suitable because non-adiabatic transitions should be taken into account, and therefore CASPT2 is used. But although CASPT2 is a superior method, also TDDFT can be used with simple models of the non-adiabatic couplings. The essential question I raised is whether BOMD is performed or NA-AIMD.

We thank the reviewer for pointing out that our description might not be sufficiently clear, as in the earlier version we wrote:

"Unfortunately, TDDFT/BNL is unsuitable for studying non-adiabatic dynamics on the excited states of the cation because of the incorrect description of the ground-state and the first excited state conical intersection as discussed in the literature.[28] "

We understand from the reviewer's comments that this paragraph may be misunderstood as if the non-adiabatic transitions could not be simulated in TDDFT. The actual reason is that the TDDFT calculations we attempted to perform in order to simulate the excited state dynamics simply crash (also when using alternative functionals). This is a well-known phenomenon in this type of calculations, occurring in the vicinity of conical intersections as was discussed for the example in reference 28.

In order to improve the clarity of this point in our manuscript, we revised the text on the 4th line from the bottom of pg 5 that now reads:

"Unfortunately, TDDFT/BNL and TDDFT/B3LYP were found unsuitable for studying dynamics on the excited states of the cation because of the incorrect description of the ground-state and the first excited state conical intersection, as discussed in the literature.[28]"

And added also the following sentence to the discussion:

"TDDFT could perhaps allow access to the symmetry-breaking states, though such a calculation was not possible in this system."

2) The reviewer wrote: Whether the methods at symmetric geometries giev degenerate states with localized or delocalized orbitals should not matter if the non-adiabatic couplings are treated correctly, as I understand it. Hence, I would recommend removing the emphasis on the delocalized DFT and localized CASPT2 difference.

In principle, the reviewer is correct in claiming that the set of wavefunctions used should not affect the outcome of the calculation. This is indeed strictly true if one computes the nuclear wavepacket dynamics, in which the nuclei can be simultaneously in a superposition of two electronic states. However, even when we include non-adiabatic effects in the NA-AIMD simulation, the nuclear motion is still classical. In fact, as we state in our discussion of the CASPT2 dynamics:

"we performed NA-AIMD simulations on the four low-lying adiabatic potential energy surfaces of the $(CO_2)_2^+$ cation and found low surface hopping rates, so the dynamics is essentially adiabatic in nature."

Regarding this point, the reviewer also asks:
3) How are the non-adiabatic couplings calculated, and please present the surface hopping population transfer.

In view of the 2nd and 3rd comments, we decided to improve the clarity of this statement on pg. 6 line 2 that now reads:

"we performed NA-AIMD using the fewest switches surface-hopping (FSSH) method[29] on the four low-lying adiabatic potential energy surfaces of the $(CO_2)_2^+$ cation and found low surface hopping rates. In two trajectories out of 80, we observed a temporary transition from the first excited state to the ground state at about 300 and 400 fs. In both trajectories, the system "hopped" back to the excited state shortly afterward. We conclude that the dynamics is essentially adiabatic."

We hope that the method we used to incorporate non adiabatic effects is now clear, as well as our conclusion that the simulated dynamics are essentially adiabatic.

4) The reviewer continues and writes:

The reader is given the impression that localized or delocalized oritals give different dynamics, whereas as I understood the study, BOMD on DFT and NA-AIMD on CASPT2 give different dynamics, which are very different conclusions. This needs to be clarified, possibly by performing NA-AIMD on DFT and BOMD on CASPT2, to complement the misaligned comparison. If I have misunderstood something about their simulations, I apologize and the required response would of course be different.

Indeed, the reviewer's impression that the difference between the two calculations is due to Born-Openheimer molecular dynamics vs NA-AIMD dynamics is a misunderstanding. We hope our revisions clarified this point, as the CASPT2 dynamics are essentially adiabatic. Specifically, the direct comparison in Fig. 3 shows the molecular dynamics trajectory on the DFT ground state potential with the molecular dynamics trajectory on the CASPT2 ground state potential, in which there were no "hopping" events within the FSSH method.

The difference between the two simulations lies in symmetry breaking: The DFT ground state exhibits a hole with a B_u symmetry, resulting in a classical force field that must conserve the C2h symmetry. In contrast, the CASPT2 ground state is a linear combination of degenerate B_g and A_u symmetry states that breaks the C_{2h} symmetry and exhibits charge localization that drives the observed dynamics.

To further clarify this point we improved the text on pg. 5 line 1 that now reads:

"The DFT/BNL dynamics, with the delocalized hole and a B_u symmetry, essentially preserve the "slipped parallel" (C_{2h}) geometry. In contrast, the CASPT2 ground state is a linear combination of degenerate B_g and A_u symmetry states with a localized hole that breaks the C_{2h} symmetry, resulting in a T-shaped geometry that emerges when the neutral monomer rotates with respect to the ionized one.

This rotation is driven by the torque developed as the charged monomer induces a dipole in the neutral one.”

We believe that the revisions described above have clarified our work and made the manuscript suitable for publication.

Roi Baer and Daniel Strasser, on behalf of all the authors.

REVIEWER COMMENTS

Reviewer #3 (Remarks to the Author):

The authors have a made an adequate attempt for clarify the theoretical details, as requested in the previous comments,
and I recommend publication of the manuscript.

I still feel that a rigorous approach would be to try to investigate the difference between a delocalized and localized orbital set within one and the same methods, but I do not have any ideas how to perform that in practice, and at least the description in now a bit more clear.

Reviewer #3 wrote:

- “The authors have a made an adequate attempt for clarify the theoretical details, as requested in the previous comments,
  and I recommend publication of the manuscript.”

We are grateful for the reviewers comments that helped us improve our manuscript.

- “I still feel that a rigorous approach would be to try to investigate the difference between a delocalized and localized orbital set within one and the same methods, but I do not have any ideas how to perform that in practice, and at least the description in now a bit more clear.”

A full quantum dynamics calculation of both electron and nuclei degrees of freedom would in principle allow such comparison. To the best of our knowledge, for this type of system it is currently beyond the state-of-the-art.