Electron binding energies of SO$_2$ at the surface of a water cluster

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ABSTRACT

The electronic properties of SO$_2$ at the surface of a water cluster were investigated by employing a combination of Born–Oppenheimer molecular dynamics and electron propagator theory (EPT). In our work, we utilized a revised version of the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional, which incorporates empirical corrections for dispersion interactions in line with a recent study of the air–water interface conducted by Ohto et al. [J. Phys. Chem. Lett. 10(17), 4914–4919 (2019)]. Polarization effects induce a significant broadening of the electron binding energy distribution, as predicted by EPT. This broadening can result in a substantial increase in electron affinity, impacting the chemical reactivity of SO$_2$ at the air–water interface, a topic of significant and recent research interest. We discuss the relationship between electron binding energies (EBEs) and the specific connections of SO$_2$ to water. The results indicate that configurations involving an O$_2$⋯H bond tend to yield higher electron affinities compared to complex formation through S⋯O$_2$ bonds. Surprisingly, SO$_2$ molecules not bound to water molecules according to a specific criterion may also exhibit higher electron affinities. This feature can be explained by the role played by the polarization field from water molecules. Our best estimate for the HOMO–LUMO (H–L) gap of SO$_2$ at the surface of a water cluster is 11.6 eV. Very similar H–L gaps are predicted for isolated and micro-solvated SO$_2$. Fukui functions for the gas phase, and the micro-solvated SO$_2$–H$_2$O complex supports the view that the LUMO is predominantly localized on the SO$_2$ moiety.

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I. INTRODUCTION

The interactions of SO$_2$ with water molecules in water clouds are of fundamental interest to understand its chemical reactivity and the generation of H$_2$SO$_4$ in atmospheric chemistry.$^1$ Therefore, spectroscopic probes relying on surface harmonic generation (SHG) were important for providing evidence of the existence of surface-adsorbed SO$_2$ in water.$^2$ Binding of SO$_2$ to a water droplet surface can be seen as the first step of a chemical process where a solute–solvent complex is formed without solvent bond breaking.$^1$ In the gas-phase, the formation of SO$_2$–H$_2$O was investigated by several studies.$^{3,4}$ The most stable gas-phase complexes illustrate the competition between sulfur–oxygen S⋯O and hydrogen O$_2$⋯H bond (HB) interactions. Several works have discussed the microhydration of SO$_2$ at the surface of small water clusters.$^{5,6}$ The presence of cyclic hydrogen bond (HB) arrays involving SO$_2$ highlights that HB interactions are reinforced by the collective polarization effects inherent in hydrogen bond networks.$^{5,6}$ It is also noteworthy to highlight the presence of dissolved SO$_2$ reaction products, specifically HSO$_3^-$ and H$^+$ charged species, at the interfacial layer. These species may induce significant spectral changes in the tetrahedrally coordinated modes.$^7$

It was recently found that the reactivity of organic compounds is significantly increased in aqueous suspensions.$^{8,9}$ The acceleration of organic reactions in droplets formed by electrospray ionization was discussed by Wei et al.$^{10,11}$ Other interesting discoveries concerning the acceleration of chemical reactions at the water–air interface are illustrated by the presence of the C$_3$H$_5$N$^-$ anion in water microdroplets.$^{12}$ The proposed explanation, in this case, was that high electric fields at the interface foster electron transfer from OH$^-$ to C$_3$H$_5$N, leading to the formation of C$_3$H$_4$N$^-$ and the OH$^-$ radical.$^{12}$ The comprehension of the molecular mechanisms that underlie the significantly accelerated chemical kinetics at the air–water interface is of paramount importance and
has been recently reviewed. This intriguing phenomenon has garnered attention in recent research endeavors, with several studies dedicated to investigating and understanding its underlying mechanisms. The interaction between SO$_2$ and water has been the focus of numerous studies, including investigations into SO$_2$ at the water/air interface, the structural aspects of SO$_2$–water droplets, and the photochemical behavior of SO$_2$ on water surfaces. However, certain specific properties that are highly relevant for gaining a deeper understanding of the chemical reactivity of SO$_2$ within interacting water droplets, such as electron binding energies, including ionization spectra and electron affinity, require further exploration and will be the primary focus of the present work. Electron binding energies (EBEs) in molecular systems can be accurately determined through electron propagator theory (EPT).

In this study, Born–Oppenheimer Molecular Dynamics (BOMD) was conducted to generate configurations of a SO$_2$–water droplet. The methodology employed in this work follows a similar approach previously utilized by Shomay et al. The BOMD technique allows for the simulation of molecular systems based on the fundamental principles of quantum mechanics, providing detailed information about the dynamics and interactions within the system. In the context of BOMD, density functional theory (DFT) is often employed to calculate the energies and forces within the system. When dealing with interfaces, it is crucial to select a DFT methodology that can adequately capture the density fluctuations present at the interface. This subject has been carefully discussed by Ohto et al. The authors pointed out that interfacial properties are very dependent on the choice of the DFT methodology. After a comprehensive benchmark, the authors concluded that exchange-correlation functionals constrained to satisfy exact functional conditions, such as RevPBE and RevPBE0, along with van der Waals corrections for dispersion, provided a better description of the interfacial properties. In line with this previous work, the present study has adopted the RevPBE functional for the BOMD. By utilizing this functional, the aim is to enhance the accuracy and reliability of the simulations in capturing the interfacial properties of the SO$_2$–water droplet system. It is essential to emphasize the pronounced heterogeneity of the air–water interface in small water microdroplets. This heterogeneity has notable implications for the distribution of the water monomeric dipole moment and results in significant alterations in the organization of the hydrogen bond network. Consequently, it justifies the selection of a theoretical approach capable of accurately describing these specific characteristics. Ionization energies and electron affinities (EBEs) of SO$_2$ at the surface of a water droplet were calculated by applying EPT to a representative set of Born–Oppenheimer molecular dynamics (BOMD) configurations.

II. THEORETICAL CALCULATIONS

A. Computational details

BOMD was carried out in a microcluster with SO$_2$ and 31 water (W) molecules [SO$_2$–W$_{31}$] at $T = 200$ K. The decision to use a relatively small number of water molecules was influenced by both the high computational cost of BOMD and the need for adequate statistical sampling. This temperature is the same as in a previous study. It is expected that at a temperature of 200 K, SO$_2$ will exhibit a relatively stronger binding to the water cluster surface compared to higher temperatures. In line with Zhong et al., SO$_2$–W$_{31}$ was placed in a cubic box with 30 Å sides with periodic boundary conditions, a system large enough to avoid interactions of the central system with adjacent periodic images. A canonical sampling through velocity rescaling (CSVR) thermostat was adopted.

Configurations were generated with the CP2K program, which uses a mixed Gaussian and plane wave (GPW) basis set. Building upon a prior investigation of the air–water interface, we employed the RevPBE exchange-correlation functional in combination with the Grimme D3 empirical correction for the dispersion energy, incorporating Becke–Johnson damping [D3-(BJ)]. This combination is represented by RevPBE-D3(BJ). Goedecker–Teter–Hutter (GTH) pseudopotentials were used for representing core electrons, and a triple-$\zeta$ (TZVP-GTH) basis set was employed for valence electrons. The time step was 0.5 fs. The equilibrium phase corresponds to 10 000 BOMD steps (5 ps). This was followed by an additional 50 000 steps (25 ps) for production.

To further evaluate the accuracy of the RevPBE-D3(BJ) functional, we conducted geometry optimizations for the SO$_2$–H$_2$O complex using high-level $ab$ initio methods, specifically Moller–Plesset second-order perturbation theory (MP2) and coupled cluster with single and double excitations (CCSD). These calculations employed Dunning’s basis sets (cc-pVXZ, with X = T, Q) and were carried out within the all-electron Gaussian and Plane-Wave (GAPW) framework using the CP2K program.

Electron binding energies (EBEs) were computed using electron propagator theory (EPT) within the framework of the outer valence Green’s function approximation (OVGF). To estimate EBEs, we established two distinct systems. In the first system, referred to as NW0, SO$_2$ was embedded within the polarization field generated by the surrounding water molecules, which were represented by point charges. In the second system, we introduced the first closest water in interaction to SO$_2$, while the remainder of the water molecules were approximated by point charges. This system is denoted as NW1.

The embedding charges are Merz–Sing–Kollman (MK) charges calculated at the MP2 level within the Polarizable Continuum Model (PCM) with the dielectric constant of liquid water. The MP2 calculations were performed with Dunning’s aug-cc-pVQZ basis set. The calculated charges (in atomic units) were $qO = -0.786$ and $qH = +0.393$. These charge values are similar to those used in various intermolecular interaction models of liquid water and have been adopted in recent studies to represent the polarizing environment associated with the hydrogen bond network in water. However, it’s important to note that the representation of the electrostatic environment at interfaces by a unique set of point charges should be seen as an approximation due to charge heterogeneities at the Gibbs dividing surface. The EPT calculations were conducted using the Gaussian16 software.

B. Results

1. SO$_2$–H$_2$O complex in the gas-phase

We will first discuss the gas-phase optimized structures of the SO$_2$–H$_2$O complex. These structures are shown in Fig. 1, where the left panel illustrates a complex energetically stabilized through an S···O interaction.
FIG. 1. SO$_2$–H$_2$O optimized structures: (left) S····O interaction [CC]; (right) O····H hydrogen bond interaction [HB]. Distances (in Å) are from RevPBE-D3(BJ)/TZVP-GTH calculations (see Table I for additional data).

There is some discussion on the ability of the oxygen atom to participate in chalcogen–chalcogen [CC] bonds. However, as a simplification, we will name this complex stabilized by a S····O interaction as [CC]. In the top right panel, we show a complex stabilized by an O····H interaction, which will be represented as [HB]. It is reasonable to expect some competition between [CC] and [HB] configurations in condensed phases. Considering that previous works pointed out RevPBE-D3(BJ) as a good choice to study the air–water interface, we have carried out geometry optimizations for SO$_2$–H$_2$O with this functional and also with ab initio methods (MP2 and CCSD). This is important to further assess the reliability of the present adopted DFT method and to compare the energy difference between complex formation via S····O and O····H interactions. The results of these calculations are gathered in Tables I and II. The calculated interaction energies are defined as

$$\Delta E_B = E[H_2O] + E[SO_2] - E[SO_2 - H_2O],\quad (1)$$

where the energies of the fragments are calculated at the geometry of the complex and include counterpoise corrections.

A strong agreement is observed when comparing ab initio and DFT [RevPBE-D3(BJ)] results for geometry and interaction energies. In the case of the CC complex, the S····O distances from CCSD/pVTZ (2.85 Å) and RevPBE-D3(BJ) (2.86 Å) practically coincide. Similarly, for the HB structure, the H····O$_3$ distances also exhibit good concordance between CCSD/pVTZ (2.17 Å) and RevPBE-D3(BJ) (2.24 Å). Electron binding energies obtained from ab initio and DFT calculations with empirical dispersion corrections align well.

For the CC complex, the $\Delta E_B$ value from CCSD/pVTZ (3.66 kcal/mol) and RevPBE-D3(BJ)/TZVP-GTH (3.87 kcal/mol) calculations differs by ~0.2 kcal/mol. It’s worth noting the enhanced interaction energies when moving from RevPBE to RevPBE-D3(BJ).

<table>
<thead>
<tr>
<th>TABLE I. Data for the SO$_2$–H$_2$O structure from ab initio and DFT calculations. Distances in Å. Angles in degrees. TZVP-GTH results in italics.</th>
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<tr>
<td></td>
</tr>
<tr>
<td>[CC]</td>
</tr>
<tr>
<td>S····O</td>
</tr>
<tr>
<td>pVTZ</td>
</tr>
<tr>
<td>pVQZ</td>
</tr>
<tr>
<td>[HB]</td>
</tr>
<tr>
<td>H····O$_3$</td>
</tr>
<tr>
<td>pVTZ</td>
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<tr>
<td>pVQZ</td>
</tr>
<tr>
<td>RevPBE</td>
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<tr>
<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td>[CC]</td>
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<tr>
<td>S····O</td>
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<td>pVTZ</td>
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<td>pVQZ</td>
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<td>TZVP-GTH</td>
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<td>[HB]</td>
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<td>H····O$_3$</td>
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<tr>
<td>pVTZ</td>
</tr>
<tr>
<td>pVQZ</td>
</tr>
<tr>
<td>TZVP-GTH</td>
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</tbody>
</table>

TABLE II. SO$_2$···H$_2$O interaction energies $\Delta E_B$ (kcal/mol) from ab initio and DFT all-electron calculations for CC and HB complexes. TZVP-GTH results in italics.

<table>
<thead>
<tr>
<th></th>
<th>MP2</th>
<th>CCSD</th>
<th>RevPBE</th>
<th>RevPBE-D3(BJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CC</td>
<td>CC</td>
<td>CC</td>
<td>CC</td>
</tr>
<tr>
<td>TZVP-GTH</td>
<td>...</td>
<td>...</td>
<td>2.88 [1.65]</td>
<td>3.87 [2.70]</td>
</tr>
<tr>
<td>Other values</td>
<td>3.58</td>
<td>3.58</td>
<td>3.58</td>
<td>3.58</td>
</tr>
</tbody>
</table>
The difference in $\Delta E_B$ between CC and HB complexes in all-electron calculations is around 1.5 kcal/mol, comparing $ab$ initio with RevPBE-D3(BJ) outcomes. However, this difference is smaller (around 1.2 kcal/mol) in RevPBE-D3(BJ)/TZVP-GTH calculations. The difference between CC and HB $\Delta E_B$ illustrates the competitive nature between these two structures, and it is expected that this will also be important in condensed phases.

2. SO$_2$ at the surface of a water cluster

A relevant aspect concerning the structure of the SO$_2$–water microdroplet is the formation of S···O$_W$ and O$_W$···H bonds in the gas phase and water. The P[S···O$_W$] and P[O$_W$···H] distributions of these distances in the microdroplet are shown in Fig. 2.

The distribution of S···O$_W$ distances between the closest O$_W$ and the SO$_2$ sulfur atom shows a maximum at 2.9 Å. This value is similar to the one observed in the CC optimized geometry of the SO$_2$···H$_2$O complex predicted at the TZVP-GTH level (see Table I). P[O···H] shows a first maximum at 2.3 Å and a second one at ∼4 Å. The first value is very similar to the O···H distance for the HB geometry of the SO$_2$···H$_2$O complex. The position of the second maximum is in very good agreement with the data for the radial distribution function reported by Baer et al. 17 By using the information from the optimized geometry and distribution functions, it will be assumed that there is a CC bond in the microdroplet when the S···O$_W$ distance is less than 2.9 Å. In addition, the hydrogen bond between SO$_2$ and water molecules is defined when the O$_S$···H distance is less than 2.3 Å.

Different criteria for bond formation and different values were proposed. 17,22 Our values can be compared to those proposed by Baer et al., and adopted by Shamay et al., where the S···O$_W$ distance should be less than 3.5 Å and the O$_S$···H distance less than 2.2 Å. Several works discussed the interesting question concerning the fraction of configurations where SO$_2$ is bounded to the droplet surface through S···O$_W$ or O$_S$···H interactions. A few different situations can be identified, and the results with the present defined criteria are gathered in Fig. 3. We adopted a [n1][n2] notation, where [n1] is the number of S···O$_W$ bonds and [n2] is the number of O$_S$···H bonds. Therefore, [0][0] means that for a given configuration, SO$_2$ is not bounded through S···O nor O$_S$···H but remains close to the microdroplet surface. [0][1] describe configurations where SO$_2$ is bounded through a single O$_S$···H to water. S···O$_W$ (or S···O) bounded configurations are denoted by [1][n2], with [n2 = 0, 1, 2]. Consistent with prior studies on clusters of comparable sizes, the proportion of [0][0] configurations is ∼0.57. 17 Our current predictions for the fractions of [0][1] and [0][2] configurations are 0.19 and 0.003, respectively. This aligns with earlier findings that emphasize the negligible presence of [0][2] configurations.

Regarding [1][n2] configurations, which entail binding through [1] S···O$_W$ and [n2] O$_S$···H, we note that the proportions of [1][0] and [1][1] configurations are 0.16 and 0.10, respectively. In contrast, the occurrence of [1][2] configurations lacks notable significance. Recent research has demonstrated that the interaction pattern of SO$_2$ with water microclusters is very dependent on the cluster’s size. 28 Notably, the presence of [0][0] configurations diminishes significantly as the cluster size grows, while the fraction of [1][1] configurations increases. This shift can be attributed to the increasing availability of water molecules to form bonds with individual SO$_2$ molecules. More precisely, the water–air interface in water clusters is characterized by the prominent presence of single-donor and single-acceptor (da) water molecules. 29 In this context, our primary objective is to explore the connection between various SO$_2$ connectivities and their corresponding electronic properties. For the purposes of our discussion, we will assume that even a relatively small cluster offers insights into this relationship.
3. Electronic properties

Before discussing electron binding energies (EBEs) for SO$_2$ at the water cluster’s surface using electron propagator theory, it is important to evaluate the method’s predictions for the EBEs of SO$_2$ and H$_2$O. These predictions are documented in Table III, where data from experiments and other theoretical calculations have been compiled. We note that EBEs for SO$_2$–H$_2$O complexes do not seem to have been extensively investigated, despite some discussion on the difference between the LUMO energies for the CC and HB configurations of SO$_2$–H$_2$O. For SO$_2$, a good agreement between the present results and data from the literature is observed. However, for H$_2$O, a 0.3 eV difference in the first vertical ionization energy is observed between our result (12.93 eV) and the experiment (12.64 eV). Comparing the EBEs for CC and HB complexes reveals that both the ionization energy and electron affinity of the HB complex are increased compared to the EBEs of the CC complex.

The HOMO–LUMO (HL) gap for the CC complex is 11.45 eV, which differs by ~0.4 eV compared to the value for the HB complex. Table III also presents the EBEs based on DFT-B3LYP calculations. In this case, the HL gap for CC and HB is 5.55 and 4.04 eV, respectively. These results reflect the well-known underestimation of the HL gap by DFT calculations and underscore the importance of conducting EPT calculations for accurate predictions of frontier orbital energies. The stabilization of LUMO energies when comparing CC and HB complexes is 0.71 eV, which is 0.3 eV below the value predicted by B3LYP (~1.0 eV).

It should be expected that the energies and the localized/non-localized nature of the frontier orbitals of SO$_2$ will be dependent on the number of closely interacting water molecules, whereas the remaining ones will mainly play the role of a polarizing background. Additionally, exploring the correlation between EBEs and the connectivity pattern of SO$_2$ at the water microdroplet’s surface is of paramount importance. The frontier orbitals of SO$_2$–W$_2$ for a snapshot of a [1][1] configuration from BOMD are depicted in Fig. 4. Notably, while the HOMO is associated with the H$_2$O orbitals, the LUMO is predominantly characterized by the SO$_2$ moiety, with some contribution from the water molecule bound by an S ⋅ ⋅ ⋅ O$_2$ interaction.

Therefore, it should be expected that the LUMO for SO$_2$–water at the surface of a water cluster should be mainly localized on SO$_2$, whereas its energy will exhibit some (weak) dependence on the number of water molecules in the microdroplet, basically reflecting the strength of the electrostatic polarizing field from water. However, in line with what is observed in water clusters, the HOMO energy and the associated electronic density delocalization should be more dependent on the microdroplet size.

In an initial approach, we will present the density of states (DOS) for the HOMO and LUMO energies of SO$_2$ within the electrostatic embedding of the water molecules represented by point charges. A total of 4000 configurations from BOMD were collected for these calculations, and the resulting DOS are illustrated in Fig. 5, including both embedding and non-embedding outcomes.

It is important to emphasize that the non-embedding results correspond to the identical configurations as those used in the embedding scenario. Consequently, these outcomes capture the

![FIG. 4. HOMO (left) and LUMO (right) for a [1][1] configuration of SO$_2$–W$_2$. The isodensity is 0.01 e/(a$_0$)$^3$.](image)

![FIG. 5. Dependence of the IE, EA, and HOMO–LUMO gap on the electrostatic embedding. Results for a system including explicitly one water molecule (SO$_2$–W$_2$+EMB) are also shown.](image)
interactions between SO$_2$ and the droplet and should not be mistaken for gas-phase calculations.

The DOS exhibits well-fitted Gaussian or stretched Gaussian distributions. When considering the distribution of ionization energies [P(IE)] for SO$_2$ with incorporated polarization charges, the main difference lies in the broadening of P(IE) in the embedding situation. The explicit inclusion of a water molecule red-shifts the maximum of P(IE) by $\sim$0.2 eV relative to the position with embedding only, where it exhibits a peak at 12.6 eV.

For P(EA), a comparison between SO$_2$ and SO$_2$+EMB reveals that electrostatic embedding red-shifts the electron affinities. Furthermore, the explicit inclusion of a water molecule does not result in significant changes relative to SO$_2$+EMB, supporting the view that the LUMO is primarily localized on the SO$_2$ moiety.

The right panel of Fig. 5 illustrates the distribution of the HOMO–LUMO (HL) gap, denoted as P(E$_{\text{Gap}}$). Interestingly, these distributions appear quite similar, with only a minor blue shift (less than 0.1 eV) observed in the presence of polarizing charges compared to the non-embedded scenario. However, the explicit inclusion of a water molecule leads to a distribution quite similar to what is observed in the non-embedding case. Therefore, our results indicate that the HL gap for SO$_2$ at the surface of a water cluster is only slightly modified relative to the predicted value of 11.5 eV for isolated SO$_2$ (see Table III). This is in line with the results for the electronic absorption spectrum of SO$_2$ in the gas phase and at the air–water interface (Martins–Costa et al., 2018). Their work predicts a moderate blue shift (3 nm) in the UV–Vis spectrum for SO$_2$ at the interface relative to the gas-phase situation.

Performing high-level ab initio electron propagator theory (EPT) calculations with a larger number of water molecules becomes prohibitively expensive. However, considering the strong localization of the LUMO at the SO$_2$ moiety, the electron affinity (EA) of the SO$_2$–water system is expected to exhibit a weak dependence on the number of water molecules (NWs). This is in contrast to the EA of isolated water clusters, which does depend on the cluster size. Moreover, considering the delocalization of the HOMO in water as the number of water molecules (NWs) increases, the ionization energy (IE) of the system is expected to decrease and approach the IE of larger water clusters, as shown in previous research (do Couto et al., 2006).

Exploring how the distribution of electron binding energies (EBEs) is influenced by the connectivity of SO$_2$ to water molecules is an interesting subject. Our particular focus will be on the...
dependence of electron affinities (EAs), which holds fundamental significance in chemical reactivity, particularly for the formation of anionic SO₂ species. It is worth noting that our analysis has a semi-quantitative nature, acknowledging the inherent statistical limitations stemming from the relatively small fractions associated with specific connectivities.

Figure 6 displays the distribution of EBEs for different connectivities. A comparison between P(IE) for [0][0] and [1][0] shows that while the two distributions peak at nearly the same value (around 12.6 eV), [1][0] exhibits a red shift relative to [0][0] for higher and lower ionization energies, which is consistent with the results for the SO₂–H₂O complex (see Table III). P(EA) for [1][0] is also red-shifted relative to [0][0]. The [0][0] and [0][1] distributions show the highest values of EAs, illustrating again that, although O···H bonding stabilizes the LUMO energies, higher EAs are also associated with [0][0] configurations.

These findings are consistent with the dependence of the LUMO energy on the O···H distance, as observed in prior work by Zhong et al. These authors compared LUMO positions when O···H and S···O W interactions were formed, concluding that HB formation results in a LUMO energy ~1.0 eV lower than the chalcogen–chalcogen S···O W formation, which aligns perfectly with the results reported in Table III. Our findings support and reinforce these observations, highlighting an increase in electron affinity (indicated by the minus-signed LUMO energy) when O···H bonding occurs. Nevertheless, it is important to emphasize that our results also suggest that higher electron affinities are associated with unbound [0][0] configurations, as illustrated in Fig. 6.

Further insight into electron attachment localization can be obtained through the calculation of Fukui functions. Figure 7 presents the Fukui f⁺ function, which is defined using a finite difference approximation as \( f^+(r) = \rho_{N+1}(r) - \rho_N(r) \), where \( \rho_{N+1}(r) \) and \( \rho_N(r) \) are the electron densities for systems with \( N+1 \) and \( N \) electrons, respectively. The Fukui \( f^+(r) \) function describes the electronic density reorganization upon electron attachment. A large \( f^+(r) \) is indicative of increased electronic affinity in a specific region. The electron attachment process occurs at the same geometry as the neutral system. As demonstrated in Fig. 7, the electronic density reorganization during vertical electron attachment is localized on the SO₂ moiety. This characteristic is observed in both the isolated SO₂–H₂O complex and the complex at the surface of the water cluster subject to the polarization field of the water environment. This aligns with the earlier discussion regarding LUMO localization on SO₂ (see Fig. 4). In the case of SO₂–H₂O at the water cluster, negative \( f^+(r) \) values are observed in regions that suggest atomic charge transfer from equatorial (in the direction of the SO bond) to polar (perpendicular to the SO bond) regions.

III. CONCLUSIONS

By combining Born–Oppenheimer Molecular Dynamics (BOMD) with electron propagator theory, electron binding energies (EBEs) for SO₂ at the air–water interface of a water droplet have been determined.

One of the main conclusions drawn from this study is the significant impact of polarization effects arising from the water environment on the electron binding energies (EBEs) of SO₂. These effects lead to a notable broadening of EBEs when compared to isolated SO₂. The research also investigated the dependence of EBEs on the connectivity of SO₂ to water molecules. It was observed that [0][1] configurations, which correspond to the formation of an O···H bond, result in higher electron affinity (EA) values compared to [1][0] configurations, where an S···O W bond is formed. Additionally, higher EAs are also observed for [0][0] unbound configurations, further emphasizing the role of polarization effects. The HOMO–LUMO (H–L) gap is nearly the same when comparing SO₂ in the gas phase to SO₂ at the surface of a water cluster.

To investigate the dependence of the results on cluster size or the explicit inclusion of a larger number of water molecules, alternative methodologies may be necessary. These alternatives could include the parametrization of density functional theory (DFT) to accurately reproduce electron binding energies from electron propagator theory (EPT), as previously proposed, or the development of effective DFT methods using machine learning techniques.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

João B. L. Martins: Conceptualization (supporting); Data curation (equal); Formal analysis (equal); Writing – review & editing (equal). Benedito J. C. Cabral: Conceptualization (lead); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (lead); Resources (equal); Software (equal); Supervision (lead); Validation (equal); Visualization (equal); Writing – original draft (lead); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES


