Polarizability and aqueous solvation of sulfate dianion

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Abstract

Polarizability of sulfate dianion solvated in water clusters and in an extended water slab is investigated by a combination of *ab initio* calculations and classical and Car-Parrinello molecular dynamics. Quantum chemistry calculations at the MP2/aug-cc-pvdz level are performed for structures obtained from molecular dynamics simulations replacing water oxygens and hydrogens by fractional point charges. Sulfate polarizability in bulk water amounts to roughly 7 Å^3. Despite this large value sulfate clearly prefers interior over surface solvation, in accord with previous experimental evidence for large aqueous clusters.

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I. INTRODUCTION

Sulfate dianion belongs to the most ubiquitous components of aerosol particles and, together with several additional ionic species, its role in the chemistry of the troposphere both in polluted and in remote areas can hardly be overestimated [1,2]. Among other atmospherically relevant anions one can list monovalent ions such as nitrate, bisulfate, chloride, and bromide as prominent examples. It has been predicted recently that, in liquid aerosols polarizable anions such as chloride can be found both in the bulk and at the air/water interface [3]. Moreover, the location of the anion has a profound effect on tropospheric chemistry, which can take different routes if surface processes are involved, compared to reactions in the aqueous bulk [4].

Recently, hydration of sulfate dianion in clusters with 4–40 water molecules has been investigated by means of photoelectron spectroscopy and hybrid density functional (B3LYP) calculations [5–7]. These studies addressed the question of sequential solvation and stabilization of SO_4^{2-} by water molecules. They also helped to resume and old controversy concerning the stability of gas phase sulfate dianion. Both from the recent experiment and calculations it follows that isolated SO_4^{2-} is unstable with respect to spontaneous electron autodetachment, and that a minimal number of three water molecules is necessary to stabilize the dianion [5]. The experiments also indicate that in water clusters sulfate dianion prefers interior over surface solvation. The first solvation shell around SO_4^{2-} closes at around twelve water molecules, with the first four waters being most strongly bound [5,6].

Within a recent computational study of a series of four aqueous sodium halides we have shown that the propensity of the anion for the vacuum/water interface directly correlates with the value of its polarizability [8]. Consequently, we have concluded that for a quantitative modeling of interfacial processes it is crucial to employ reliable values of ion polarizabilities, which can actually change upon moving the ion from the gas phase into aqueous clusters or bulk solutions [9]. The present study focuses on two aspects of the aqueous solvation of the sulfate dianion. First, we aim at evaluating the polarizability of SO_4^{2-}

in different aqueous environments. Following our recent study of the chloride anion [9] we employ *ab initio* quantum chemical calculations for system geometries obtained from molecular dynamics (MD) simulations, replacing water molecules by fractional point charges. Methodologically, however, sulfate dianion differs from chloride in two aspects: in the gas phase it is unstable with respect to electron autodetachment, and it is a molecular rather than atomic ion. In the following section we describe in detail how we construct a parameterization for a polarizable sulfate dianion, based on an older non-polarizable potential model [10]. The second aim of the present work is to address questions concerning surface vs. interior solvation of aqueous sulfate dianion. We achieve this goal by performing MD simulations of SO_4^{2-} in an aqueous slab employing a polarizable potential model, and by relating the results to experimental observations.

II. SYSTEMS AND COMPUTATIONAL METHODS

The employed computational strategy represents a pragmatic combination of *ab initio* quantum chemistry for small systems, Car–Parrinello Molecular Dynamics (CPMD) for moderate size clusters, and classical MD with a polarizable force field for extended systems. Since the gas phase sulfate dianion is not stable with respect to electron autodetachment, already the smallest model systems have to contain a certain minimal number of water molecules. The first four waters form a very tight sub–shell around the dianion [5], therefore, we have adopted the $SO_4^{2-}(H_2O)_4$ cluster as the starting model for *ab initio* calculations of the polarizability of the anion. As in our previous study of the aqueous chloride anion [9], we have replaced the water molecules by point charges of -0.82 e on oxygens and +0.41 e on hydrogens, and evaluated the dianion polarizability at the MP2/aug-cc-pvdz level. In addition, vertical ionization potentials have been evaluated both for explicit water molecules and for the point charge solvent model. As a check of method and basis set convergence we have also performed B3LYP calculations with up to aug-cc-pvtz basis set. The *ab initio* calculations of the polarizability were performed using the Gaussian98 program package [11].

As a next step, we have performed CPMD simulations for a cluster containing 13 water molecules forming a complete first solvation shell around the sulfate dianion. A 4 ps Car-Parrinello *ab initio* MD trajectory was generated at 250 K with a timestep of 0.121 fs using a fictitious electron mass of 800 au [12]. The electronic structure was computed within the Kohn-Sham forumulation of density functional theory [13] with the BLYP exchange-correlation functional [14,15]. Only the valence electrons were treated explicitly, with norm-conserving pseudopotentials representing the valence-core interactions [16]. The Kohn-Sham orbitals were expanded in a plane wave basis set to an energy cutoff of 70 Ry in a cubic box with edge length 32 au, and cluster boundary conditions [17] were applied. For the subsequent *ab initio* evaluation of sulfate polarizability, we have, for cluster configurations generated in the CPMD simulations, employed both the point charge solvent model described above as well as water charge distributions based on the centers of the maximally localized Wannier functions [18,19]. The Wannier charge model for water is defined by a +6 e charge at the oxygen nucleus, +1 e charges at the hydrogen nuclei, and -2 e at each of the four Wannier function centers corresponding to the two bonding and two lone pairs of oxygen [20]. The *ab initio* MD simulation and Wannier orbital analysis were performed using the CPMD program [21].

Finally, we have performed classical MD simulations using polarizable potentials with the SO_4^{2-} anion placed initially at the surface of an extended water slab. Since the charge distribution of the sulfate dianion corresponds roughly to a full negative charge on each of the oxygens and two positive charges on sulfur, we can assume that the latter is hard and non-polarizable. Therefore, for the MD simulation, which works with atomic polarizabilities, we have distributed the almost isotropic polarizability of the sulfate dianion obtained from *ab initio* calculations by placing one quarter of its value on each of the four oxygens of the dianion. A 1 ns constant temperature (300 K) classical MD simulation with a timestep of 1 fs was generated using the Amber6 program package [22]. The system contained 556 polarizable water molecules and a single polarizable sulfate dianion. Periodic boundary conditions were applied, with one of the box lengths extended to 100 Å to generate a slab geometry with two open interfaces [23]. The SPC/POL force-field for water was used [24]. For the sulfate dianion, the polarizability model has been developed within the present study. The rest of the sulfate parameters were taken from a previous non-polarizable Model 2 in Ref. [10], except for a slight (by 0.16 Å) increase of the van der Waals radii of the four oxygen atoms, which reflected the use of a polarizable model and also improved the stability of the polarization calculations. A cutoff for intermolecular interactions was set at 12 Å. Long range electrostatic interactions were treated using the smooth particle mesh Ewald sum [25]. In the MD run, we have used the value of polarizability obtained from calculations of the $SO_4^{2-}(H_2O)_4$ cluster. As a consistency check we have then re-evaluated at the MP2/aug-cc-pvdz level the SO_4^{2-} polarizability using a series of snapshots from this simulation, replacing again water molecules with fractional point charges.

III. RESULTS AND DISCUSSION

Sulfate dianion in the gas phase is unstable with respect to electron autodetachment, and at least three water molecules are needed to stabilize it [5]. Obviously, it is, therefore, impossible to evaluate the polarizability of the isolated ion. This is one of the principle differences from our previous study on polarizability and aqueous solvation of the chloride anion [9], which is a stable isolated species in the gas phase. Since the first four water molecules, which have the strongest stabilization effect, form a very compact sub–shell around sulfate dianion [5], we have adopted for our study the $SO_4^{2-}(H_2O)_4$ cluster as the entry level system. The MP2/aug-cc-pvdz optimized geometry of this cluster, which is very similar to that obtained earlier using the B3LYP density functional [5], is depicted in Fig. 1. We see that each of the water molecules makes a bridge between two oxygens of the dianion. These eight hydrogen bonds stabilize the extra electron density of SO_4^{2-}. Replacing the four water molecules with fractional point charges has only a minor effect of the vertical electron detachment energy, changing it from 1.6 to 1.4 eV. As in our previous study [9] we can, therefore, use this replacement for a straightforward evaluation of the SO_4^{2-} polarizability. In the D_{2d} symmetric

$SO_4^{2-}(H_2O)_4$ cluster the sulfate dianion polarizability is almost isotropic (with anisotropies smaller than 3 %) and its mean value reads 7.10 Å^3. In order to check the convergence of the value of the polarizability with basis set size, we have compared B3LYP calculations using the aug-cc-pvdz and aug-cc-pvtz basis sets. With the smaller basis the B3LYP method yields a mean polarizability of 7.15 Å^3, which is almost identical to the value obtained at the MP2/aug-cc-pvdz level. With the aug-cc-pvtz basis the B3LYP polarizability reads 7.39 Å^3, which demonstrates very good convergence with the basis set size.

An *ab initio* MD simulation of the sulfate anion in a 13 water cluster was carried out to see whether the ion remains well solvated in the interior of the cluster, or prefers to establish a location on the surface of the cluster (like the heavier halogen anions). Before presenting results from this simulation, we provide an indication of the performance of the density functional method used in the *ab initio* simulation by comparing MP2 and BLYP results for the geometrical parameters of the minimum energy configuration of $SO_4^{2-}(H_2O)_4$ in Table I. Overall, the agreement between the two electronic structure methods appears to be very good. The sulfate bond lengths and sulfate O–water H distances are within 0.006 Å, the sulfate bond angle is within 0.5°. The deviations in the water internal geometrical parameters are slightly larger: 0.014 Å in the bond length, and 1.3° in the angle.

The time evolution of the overall cluster structure during the *ab initio* simulation is depicted by the snapshots shown in Fig. 2. It is evident that, while the hydration shell rapidly expands, the sulfate dianion remains well-solvated in the interior of the cluster for the duration of the simulation. Quantitative details on the changes in the size and shape of the cluster, and the location of the anion, are given in Fig. 3. Fig. 3a shows that the radius of gyration of the cluster increases by about 10%, and the eccentricity (a measure of deviation from a spherical shape) increases by a factor of 2.5, during the first ps of the simulation, within which the systems relaxes from the initial structure corresponding to a local minimum. Fig. 3b shows that the position of the sulfate dianion remains close to the cluster center of mass, with deviations from the center of mass oscillating between 10% and

25% of the radius of gyration.

Ab initio MD simulations naturally include electronic polarization effects as the electronic structure fluctuates in response to motion of the nuclear degrees of freedom. In our cluster simulation, individual water molecules experience varying degrees of polarization depending on their location in the cluster. The electronic structure of individual water molecules is conveniently described in terms of the Wannier function centers (WFCs) [20]. We have use the position of the nuclei and WFCs to calculate the dipole moments of the individual water molecules. A histogram of water dipole moments computed during the last ps of the simulation is plotted in Fig. 4. The values span a wide range, with the majority between 2 D to 3 D, which are close to the water dimer and bulk dipole moments, respectively [20]. The higher (lower) values correspond to water molecules that are closest (farthest) to, and hence more (less) polarized by the anion.

MP2/aug-cc-pvdz polarizabilities evaluated along the CPMD trajectory are given in Table II. We see that for water represented by three point charges the sulfate polarizability (which is again almost perfectly isotropic) oscillates with variations smaller than 0.1 Å^3 around 7 Å^3. Employing the Wannier charges for water, which account for the polarization of the water molecules, leads to a systematic but small (by 0.25 Å^3) decrease of the sulfate polarizability, as in our previous calculations for chloride anion [9]. We conclude that within the variations of the CPMD geometries sulfate polarizability in a cluster of 13 water molecules coincides with that in water tetramer.

Using the above value of 7.1 Å^3 for the the polarizability of SO_4^{2-} in water tetramer, evenly distributed on the four oxygens of the dianion, we have performed a long MD calculation, placing SO_4^{2-} initially at the surface of the water slab. The most important qualitative result is that the dianion almost immediately leaves the interfacial region and "dives" into the interior of the slab. Quantitatively, the situation is depicted in Fig. 5, which shows the time evolution of the vertical distance of the center of mass of SO_4^{2-} from the center of the (horizontally placed) slab. One clearly sees that during the 1 ns simulation the dianion explores the whole interior of the slab, never, however, returning into the interfacial layer. This is in perfect agreement with the recent experimental study of sulfate dianion with up to 60 water molecules, which directly indicates interior solvation in large aqueous clusters [6,7]. It is also interesting to compare this behavior of sulfate dianion to that of monoanions with a similarly large polarizability, such as iodide. While iodide acts as a surfactant with a significant propensity for the interface [8,26], sulfate dianion strongly prefers interior solvation. The interior vs. surface solvation results from a subtle balance between electrostatic and polarization forces [23]. Apparently, for the dianion the balance is shifted towards electrostatic interactions, which favor bulk solvation.

Finally, to evaluate the effect of the bulk solution environment on the polarizability of the sulfate anion, we have sampled 20 uncorrelated geometries, separated by 50 ps, from the above 1 ns MD run. For all these geometries, we have re–evaluated at the MP2/aug-cc-pvdz level the SO_4^{2-} polarizability, replacing each water molecule in the slab with three point charges. This procedure gives a value of the mean sulfate polarizability of 6.9 +/- 0.2 Å^3 (with anisotropies again smaller than 3 %). Note that the distribution of the values corresponding to different water geometries is relatively narrow, indicating that employing a single averaged value of polarizability for bulk MD simulations is well justified. Moreover, within the fluctuations along the MD trajectories, the sulfate polarizability in bulk water is the same as that in small water clusters. In conclusion, for modeling of aqueous solvation of sulfate dianion both in clusters and in the bulk it is appropriate to employ a value of polarizability around 7 Å^3.

IV. CONCLUSIONS

Polarizability and aqueous solvation of sulfate dianion have been investigated by a combination of computational techniques including *ab initio* quantum chemistry, Car–Parrinello molecular dynamics, and classical MD simulations with a polarizable force field. An averaged value of 7 Å^3 has been obtained for the polarizability of SO_4^{2-} both in clusters and in bulk aqueous solution. The present approach, based on replacing water molecules by point charges, is likely to give an upper bound to the value of polarizability [9]. Nevertheless, the present value is not sufficient to bring the sulfate dianion to the vacuum/water interface of a water slab. MD simulations show that SO_4^{2-} clearly prefers bulk solvation, which is in accord with photoelectron spectroscopy experiments on sulfate dianion in large water clusters [5–7].

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FIGURE CAPTIONS

Figure 1:

Optimized structure of $SO_4^{2-}(H_2O)_4$ at the MP2/aug-cc-pvdz level displayed with realistic atomic radii.

Figure 2:

Snapshots of $SO_4^{2-}(H_2O)_{13}$ at ps intervals during the 4 ps Car-Parrinello MD simulation.

Figure 3:

Time evolution of the geometric parameters during the Car-Parrinello MD simulation of $SO_4^{2-}(H_2O)_{13}$. a) The cluster radius of gyration. Inset: time evolution of the cluster eccentricity, defined as $1 - I_{min}/I_{avg}$, where I_{min} and I_{avg} are the minimum and average principal moments of inertia, respectively. b) The distance between the sulfur atom and the cluster center of mass.

Figure 4:

Histogram of individual water dipole moments during the last ps of the Car-Parrinello MD simulation of $SO_4^{2-}(H_2O)_{13}$.

Figure 5:

Time evolution of the vertical distance of the center of mass of the sulfate dianion in the center of the horizontal aqueous slab. The dianion was initially placed at the vacuum/water interface, marked by the space between the thin dotted lines.

TABLES

TABLE I. Geometric parameters for energy minimum structures of $SO_4^{2-}(H_2O)_4$.

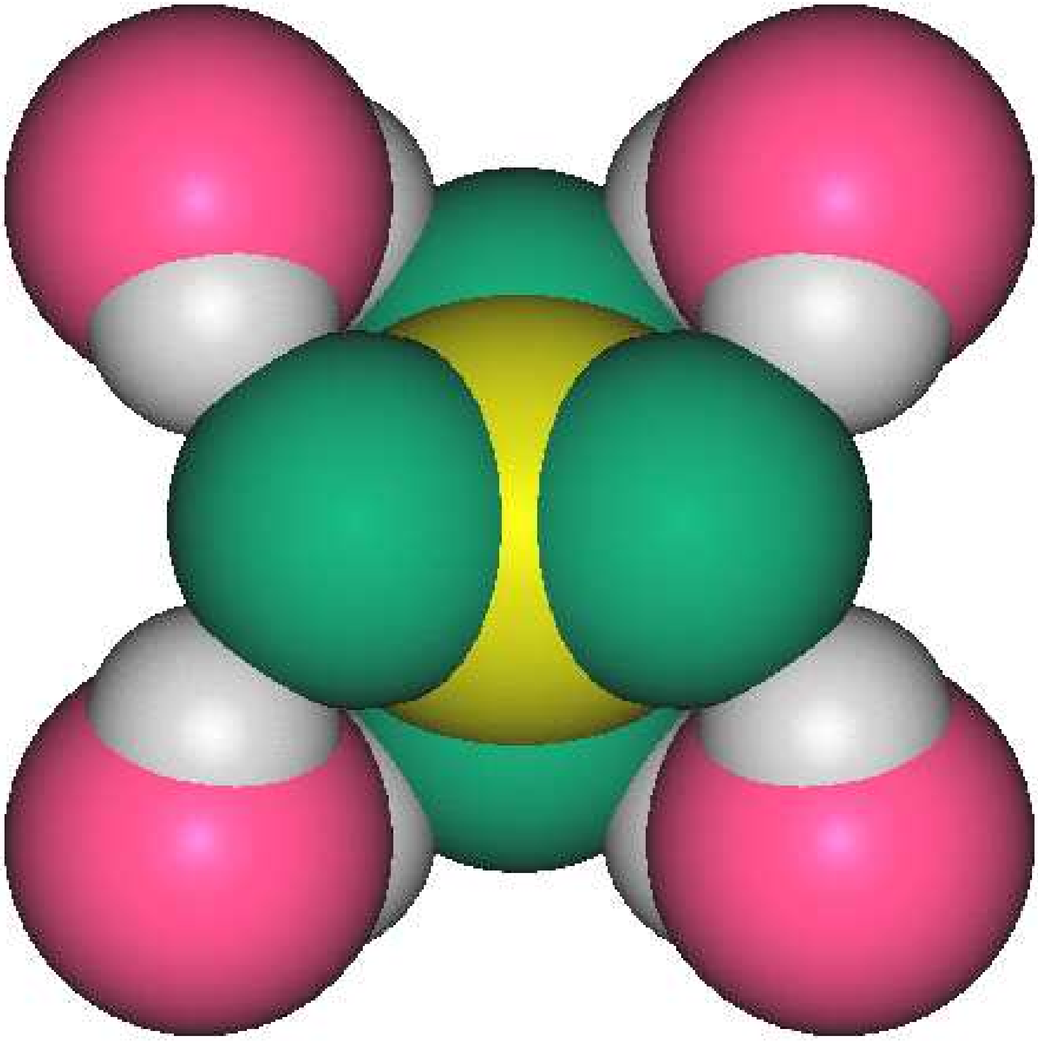
Parameter[†]	MP2/aug-cc-pvdz	DFT-BLYP/plane waves
S–O (Å)	1.525	1.519
O–S–O (°)	109.0	109.5
O–H_w (Å)	1.991	1.996
O_w–H_w (Å)	0.985	0.999
H_w–O_w–H_w (°)	96.3	95.0

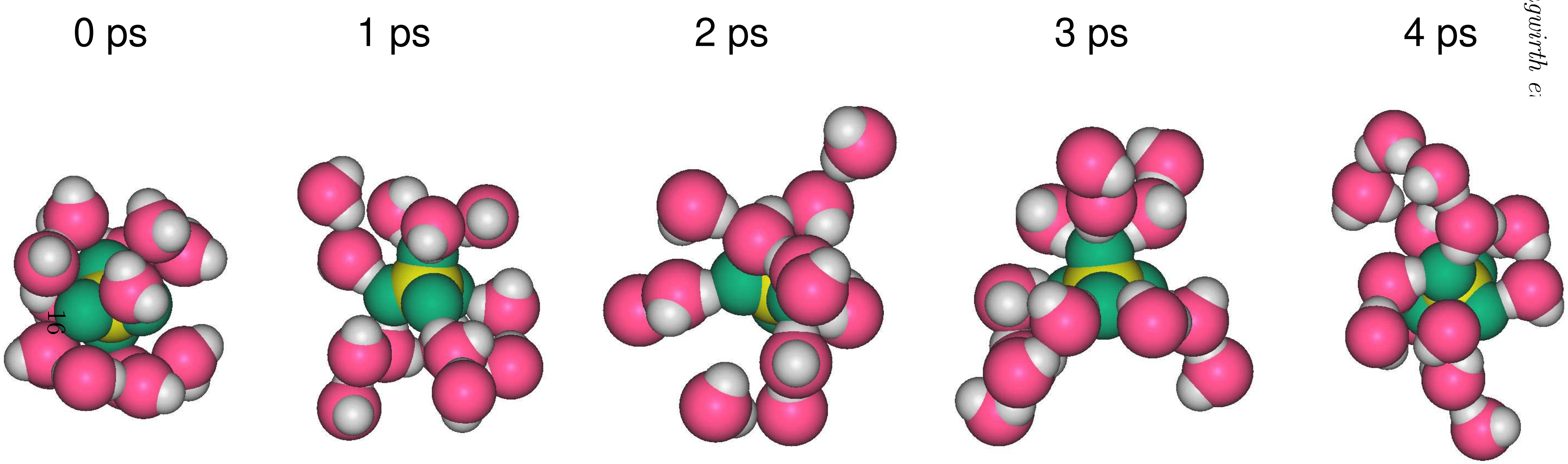
[†] Water atoms are denoted by the subscript w.

TABLE II. Polarizability (in Å^3) of sulfate dianion in 13 water molecules for four snapshots separated by 1 ps taken from a Car-Parrinello MD simulation.

Time (ps)	Charge Model	Polarizability
1	SPCE	7.13
1	Wannier	6.85
2	SPCE	7.01
2	Wannier	6.78
3	SPCE	7.10
3	Wannier	6.82
4	SPCE	6.85
4	Wannier	6.56

Figure 1, Jungwirth et al.





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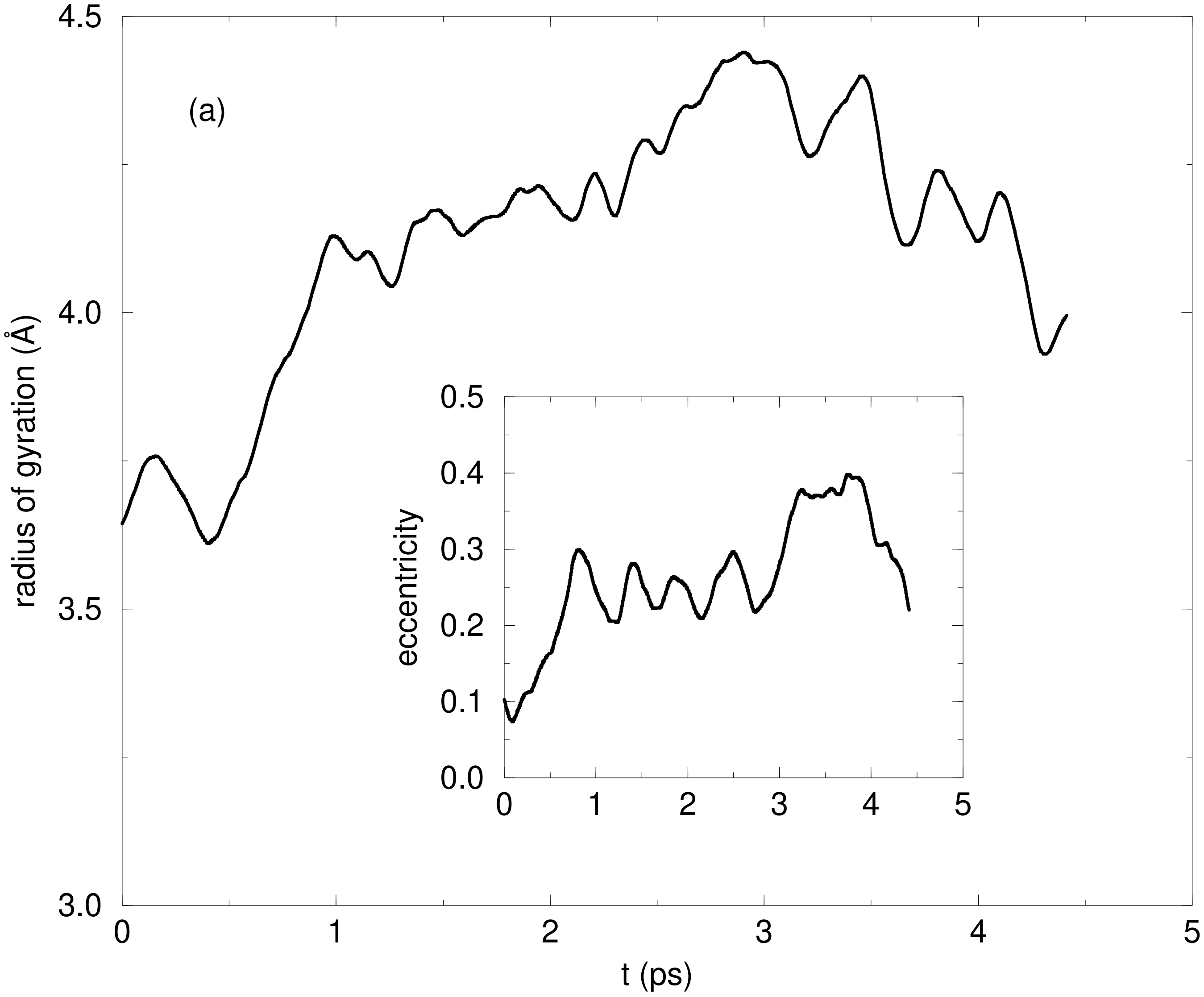

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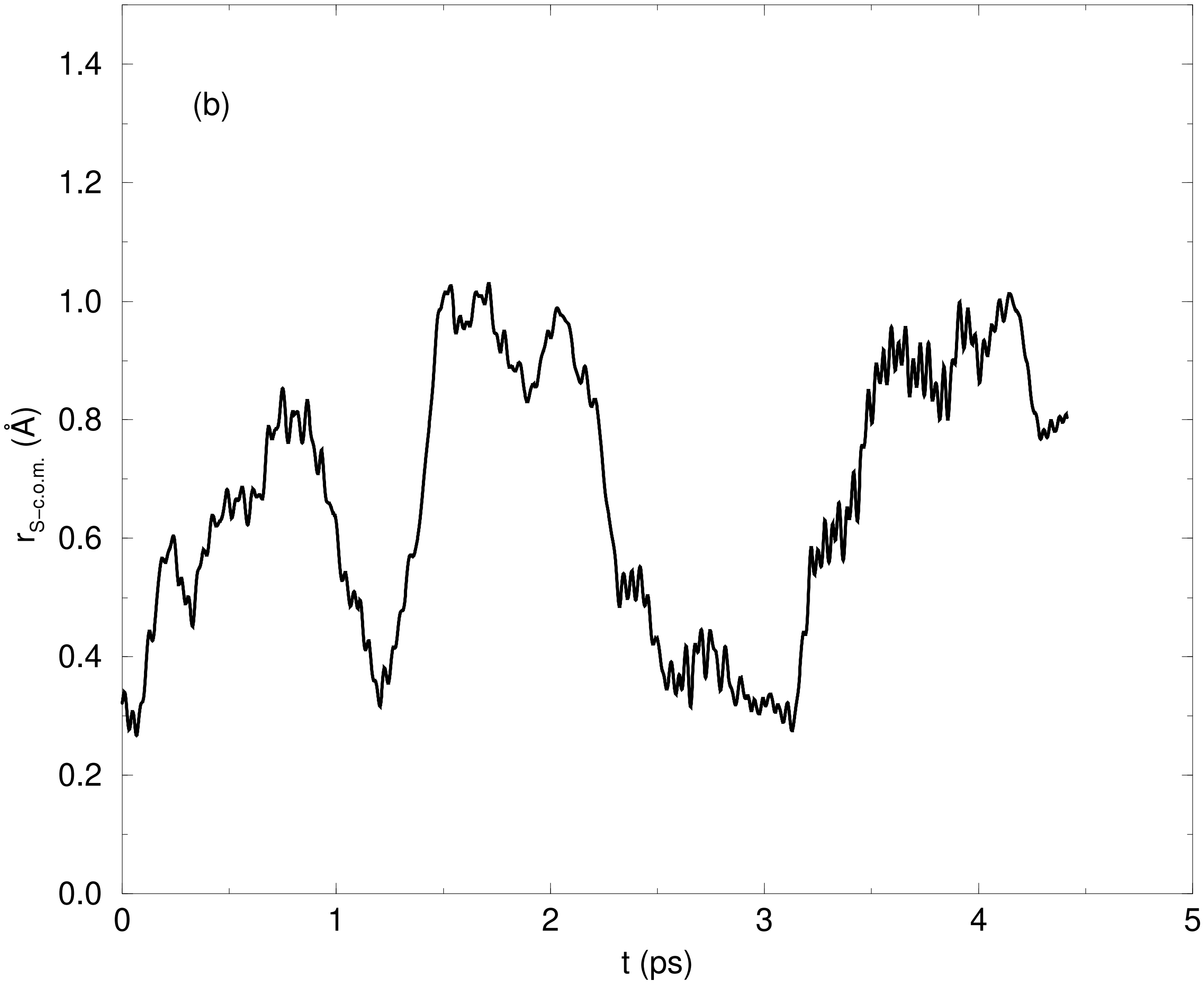

Figure 3b, Jungwirth et al.

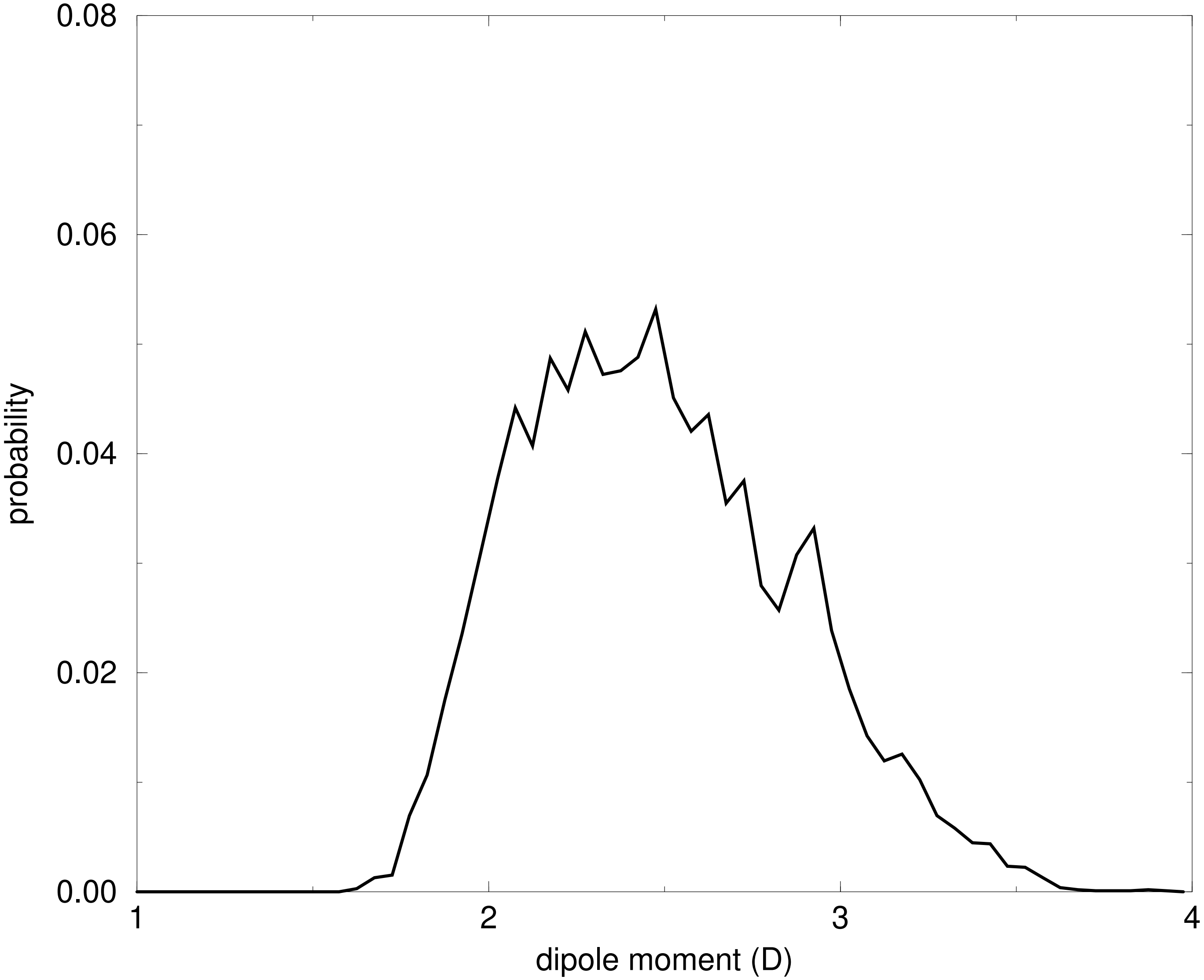

Figure 4, Jungwirth et al.

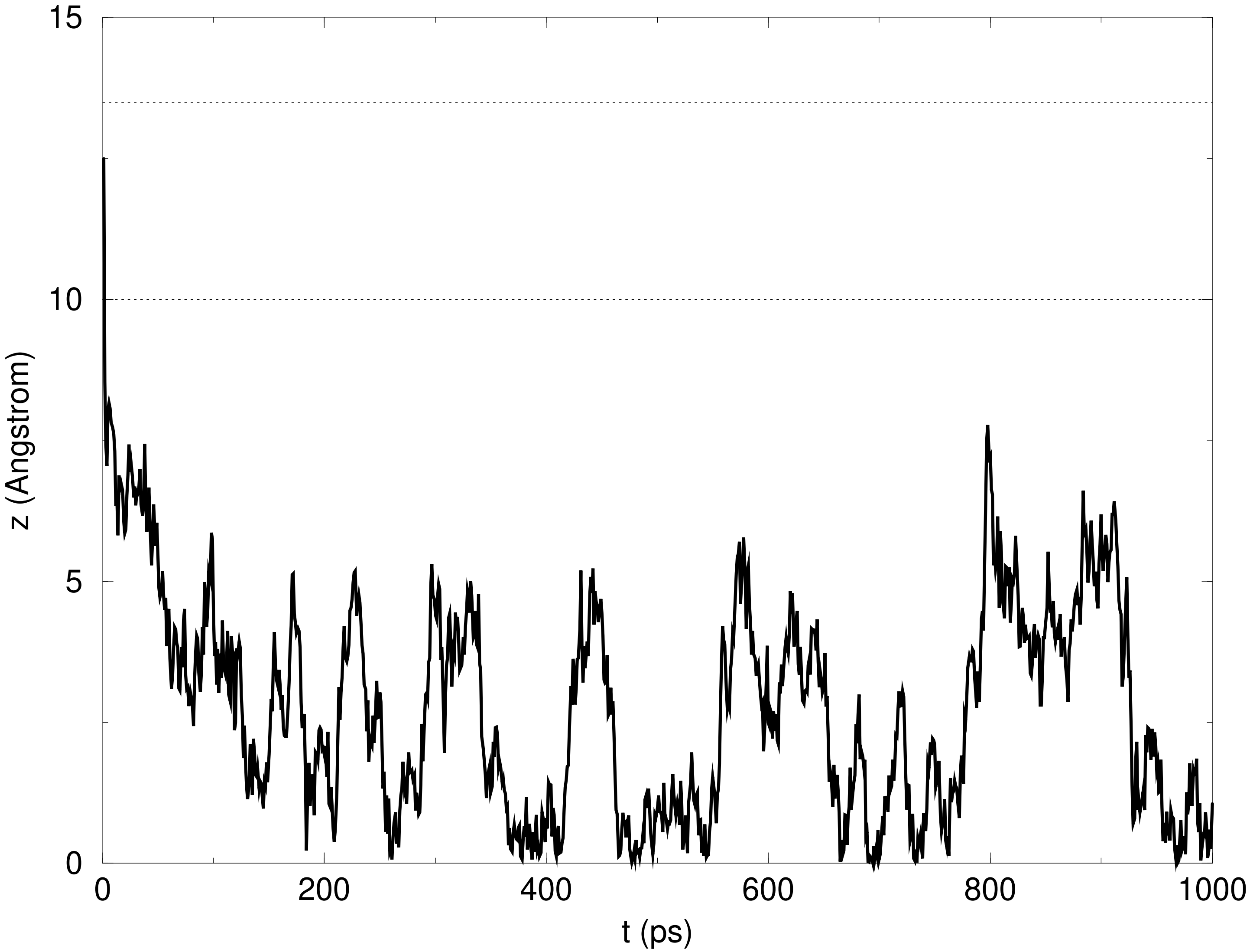

Figure 5, Jungwirth et al.