Chloride anion on aqueous clusters, at the air-water interface, and in liquid water: Solvent effects on Cl^- polarizability

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Abstract

The effect of asymmetric aqueous solvation on the polarizability of the chloride anion is investigated by accurate *ab initio* calculations on structures obtained from classical molecular dynamics and Car-Parrinello molecular dynamics simulations. It is shown that water environment significantly reduces the halide polarizability, on clusters, at interfaces, and in the bulk. In the relatively rigid cluster environment, the amount of this reduction strongly depends on the particular geometry of the complex, while in more disordered, extended liquid systems the geometric effect is much weaker. Therefore, a single effective value around 4 Å^3 may be employed for the chloride anion polarizability in aqueous environments.

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I. INTRODUCTION

The behavior of halogen anions in various aqueous environments, such as small and large clusters [1-9], air-water interfaces [10-12], and bulk solutions [13-16], has attracted considerable attention recently. Many of these studies have been aimed at understanding, at a detailed molecular level, the process of salt solvation not only at infinite dilution in the bulk [13], but also at higher solute concentrations [14-16] and in finite size systems, where surface effects play an important role [11-12,17-19]. Interestingly, these basic physical chemistry questions are also of direct relevance to atmospheric research. Indeed, it has been discovered recently that airborne aqueous sea-salt aerosols serve as a global source of molecular chlorine and bromine, both in the polluted and in the remote lower marine troposphere [11,20-21].

One of the most exciting and somehow counterintuitive results of recent studies of halogen anions in aqueous systems with a large surface to bulk ratio is that, except for fluoride, all heavier halogen anions can be found at the air-water interface. In large water clusters, this effect is dramatic, and both simulations [7,17] and photoelectron experiments [1] show, that the heavier halogen anion resides solely at the surface. However, even for extended systems possessing an air-water interfaces, molecular dynamics (MD) simulations of aqueous slabs with solvated salts predict the presence of heavier halogen anions at the surface [11-12], which is supported by most recent scanning electron microscopy (SEM) experiments on bromide doped NaCl crystals exposed to water vapor [22]. These observations are in striking contrast to the behavior of the alkali cations, which are strongly repelled from the aqueous surface [11-12,17], in accord with classical theories of electrolytes [23].

A detailed analysis of the MD simulations reveals that the most important factor that makes it possible for the heavier halogen anions to reside at the surface is the large value of the anion polarizability [11,17]. This has been qualitatively rationalized in terms of an additional energy gain due to an induced shift of the polarizable electron cloud of the anion in the asymmetric electric field created by the sum of water dipoles at the interface

[24]. Further evidence of the major role of polarizability in stabilizing large "soft" ions at the surface stems from preliminary simulations of a mixed NaCl/NaBr doped aqueous slab showing an enhanced concentration of bromide with respect to chloride at the interface [25], in perfect agreement with the SEM experiment [22]. Understandably, the non-polarizable sodium cations or fluoride anions cannot achieve this extra stabilization at the interface and are, therefore, repelled from the interface by the electrostatic image force [11-12,17,23].

In the view of the prominent role of polarizabilities of halogen anions for the properties of the surfaces of aqueous salt solutions, and given the importance of the air-water interface for the atmospheric reactivity of sea-salt aerosols with gaseous pollutants [11], it is crucial that the corresponding MD simulations account for the the effect of polarizability as accurately as possible. Indeed, calculations employing a non-polarizable force field did not show any or only very minor presence of heavier halogens at the surface, and a significant anionic surface concentration builds up only upon inclusion of polarizabilities into the model [11,17,26].

In this respect, it is very satisfactory that qualitative predictions of polarizable force field MD simulations for chloride on small water clusters have been verified by recent Car-Parrinello *ab initio* MD calculations [9]. However, for accurate quantitative predictions it is important to employ appropriate values of halogen ion polarizabilities in the force fields. This is a rather subtle and difficult issue for several reasons. First, strictly speaking, polarizability is an overall and generally non-additive property of the whole system. Luckily, however, for non-covalently interacting particles, the total polarizability can be to a very good approximation separated into molecular (and ionic in the present case) contributions [27]. Second, it is a well known fact that halogen anion polarizabilities in solutions or in ionic crystals are significantly reduced with respect to the corresponding gas phase values [28-29]. Unfortunately, there are no direct measurements of halogen ion polarizabilities in aqueous solutions, and the available data are extrapolations from ionic crystals and salt solutions [28-29]. On the other hand, very accurate *ab initio* calculations have been performed for halogen anions in the gas phase [30] and an attempt to account for the effect of a bulk solvent has been undertaken recently [31].

The principal aim of the present paper is to investigate computationally the effect of aqueous environment, ranging from clusters to the interface and bulk of a solution, on the polarizability of the chloride anion, with special emphasis on the difference between interior and surface solvation. To achieve this goal, we employ a combined approach based on accurate *ab initio* quantum chemical calculations on structures obtained from classical and Car-Parinello MD simulations. The main issue to address is the transferability of halogen ion polarizability between different aqueous environments and estimation of its optimal value for simulations in extended system.

II. COMPUTATIONAL METHODS

In the first step of our computational approach, we have established the least numerically demanding *ab initio* scheme that gives a converged value of the gas phase polarizability of the chloride anion of 5.5 Å^3, which is is the MP2/t-aug-cc-pvtz method [32]. We stress, that while it is sufficient to truncate the perturbative treatment of correlation effects at the second order, it is crucial to employ an extended set of diffuse functions in order to converge the value of the chloride polarizability.

In the next step, we have generated, using the above mentioned method, and employing the standard 6-31^{++}G* basis set for water, optimized geometries for clusters containing a chloride anion and three or six water molecules. For the $Cl^-(H_2O)_3$ cluster we have reached the global minimum with all three waters on one side of the anion (see Fig. 1a), while for the $Cl^-(H_2O)_6$ complex we have located both the global minimum, corresponding to a surface anion (see Fig. 1b) and waters in the 4+2 arrangement [8], and a low-lying stationary point of C_{3v} symmetry, representing an embedded structure with three waters on each side of the chloride anion (see Fig. 1c). Additionally, for the system with six waters, we have also employed geometries corresponding to five snapshots from our previous Car-Parrinello MD simulation [9], separated by a time interval of 1 ps from each other.

Next we generated, using Car-Parrinello MD of Cl^- with 48 water molecules and employing periodic boundary conditions, a set of geometries corresponding to a liquid bulk situation. For *ab initio* evaluation of polarizabilities we extracted successive structures separated by 0.2 ps. Finally, we have simulated the effect of the air-water interface using a classical MD simulation with a polarizable force field. More precisely, we initially placed the chloride anion at the surface of a water slab and followed its trajectory toward the bulk. For *ab initio* analysis successive structures separated by 10 ps were stored.

For evaluating Cl^- polarizabilities in the cluster, bulk, and slab environments, we have replaced the oxygen and hydrogen atoms of the water molecules by point charges of -0.82 e and +0.41 e, respectively. These are the charges used in the popular SPCE water model [33] The replacement of explicit water molecules by point charges leads to a computationally simple and efficient *ab initio* scheme of evaluation of solute polarizability in a solvent of an arbitrary size and geometry. For the clusters under investigation, we have verified that this approach is accurate in the sense that it reproduces the respective values of Cl^- ionization potentials following from all atom calculations (see the next section). In addition to placing point charges at the positions of the nuclei, for the cluster and bulk solution configurations generated in the Car-Parrinello molecular dynamics (CPMD) simulations, we have employed more realistic water charge distributions by using the centers of two electron localized orbitals for the valence electrons. Specifically, we used the maximally localized Wannier functions, which are appropriate for electronic structure calculations employing periodic boundary conditions and plane wave basis sets [34-35]. 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 corresopnding to the two bonding and two lone pairs [36]. A snapshot from the CPMD simulation of the $Cl^-(H_2O)_6$, including the Wannier function centers, is shown in Fig. 1d.

All of the *ab initio* calculations were performed using the Gaussian98 program [37]. The 500 ps constant temperature classical MD simulation was carried out using the Amber6 program package [38]. The system contained 556 polarizable water molecules and a single polarizable chloride anion, replicated in three dimensions by periodic boundary conditions, with one of the box lengths extended to 100 Å to generate two open interfaces. We used the same polarizable force-field as in our previous studies [11-12], and treated the electrostatic interactions using the smooth particle mesh Ewald sum [39]. The Car-Parrinello *ab initio* MD simulations were performed using the CPMD program [40]. The electronic structure was computed using density functional theory and the generalized gradient approximation, treating only the valence electrons explicitly, with pseudopotentials and a plane wave basis set, as described in [9]. Our previous CPMD simulation of $Cl^-(H_2O)_6$ at 250 K employed cluster boundary conditions [41]. The present CPMD simulation of the bulk solution at 300 K contained one chloride anion and 48 water molecules in a cubic box of length 12 Å, replicated using three dimensional periodic boundary conditions.

III. RESULTS AND DISCUSSION

Results of the present MP2 calculations for chloride-water clusters with three and six water molecules (for geometries see Fig. 1) are summarized together with the values for the bare anion in Table 1. We present here only the mean value of the chloride polarizability, since in all aqueous environments under study its asymmetry has been smaller than 10 %. This is rather important in the connection with MD simulations, since polarizable force fields employ a single scalar value for the atomic (ionic) polarizability. In addition, we also show in Table 1 values of vertical ionization potentials (IP), calculated as the energy difference between the anionic system and the lowest state of the corresponding neutral system at the geometry of the anion/water system. For all of the clusters in Table I, we present IPs calculated both with explicit water molecules and with all water atoms replaced by fractional point charges.

First, we note that our calculation for the bare anion presented in Table I reproduces both the converged value of 5.5 $Å^3$ of the chloride polarizability [30] and its vertical IP (the experimental value being 3.61 eV). Second, we see that, for the cluster systems, replacing explicit water molecules by point charges practically does not change the value of the corresponding IP. This justifies the present procedure for calculating chloride polarizability in various aqueous environments, which is straightforward and much simpler than schemes treating waters explicitely [31], and, for asymmetric solvation, might be the only practical possibility. An important conclusion emerging from Table I is that already small water clusters reduce the gas phase polarizability of chloride anion significantly, this effect being strongly isomer dependent. Indeed, for surface isomers with three or six waters the value of Cl^- polarizability is reduced by some 20 %, while for the embedded isomer of $Cl^-(H_2O)_6$ this reduction reaches 34 %.

In order to estimate the effect of thermal fluctuations in the cluster systems, we have evaluated the polarizability and the vertical IP of Cl^- in the $Cl^-(H_2O)_6$ complex, employing five snapshots separated by 1 ps from our previous Car-Parrinello *ab initio* molecular dynamics simulation [9] at 250 K. The results, summarized in Table II, indicate several interesting trends. All the structures from the Car-Parrinello simulation at ambient temperature correspond to a surface location of the chloride anion, albeit the exact geometry can be quite different from the optimal structure discussed above [9]. Nevertheless, the corresponding polarizabilities and IPs are close to those of the optimal structure, with fluctuations of about 5 % (see Table II). In other words, for the cluster under study, the temperature effect is rather small. Another fact worth mentioning is the inverse correlation between the chloride polarizability in a particular geometry and its vertical IP. Qualitatively, the more the anion is bound due to the presence of suitably oriented surrounding water molecules, the more compressed and, hence, less polarizable, its electron cloud becomes.

Investigations of the chloride polarizability in an extended aqueous liquid environment have been based on geometries generated by Car-Parrinello and classical MD simulations. Results for five snapshots of a CP run separated by 0.2 ps are presented in Table II for *ab initio* calculations using either the standard SPCE water charges or charges obtained from the Wannier centers of the localized CP wavefunction. Although the duration of the simulation is relatively short, we see significant fluctuations in both observables under investigation. The chloride polarizability oscillates around 4.1 Å^3 for the SPCE charges, while the use of Wannier charges reduces this value by about 0.3 Å^3. The mean IP value is 7.1 eV for the former and to 8.0 eV for the latter charge model, which is slightly below the experimental value of 8.77 eV.

Finally, we have evaluated the Cl^- polarizabilities and vertical IPs along a classical MD trajectory for an aqueous slab of a thickness of approximately 26 Å. Initially, we have placed the chloride anion at the air-water interface and we have followed the subsequent 500 ps dynamics at ambient temperature. Fig. 2a depicts the distance of the chloride anion from the center of the slab as a function of time. It can be seen that, during this particular trajectory, Cl^- initially remains more or less at the surface, while at 290 ps it 'dives' into the bulk. Thus, by *ab initio* evaluation Cl^- polarizabilities and IPs along the trajectory we can explore the influence of the position of the chloride anion in the slab on these properties.

Fig. 2b depicts the Cl^- polarizabilities and Fig. 2c vertical IPs for 50 subsequent MD geometries displaced from each other by 10 ps. We see that both observables exhibit relatively large fluctuations around mean values of 4.1 Å^3 for the polarizability and 8.2 eV for the vertical IP. Note that the calculated IP is in satisfactory agreement with the experimental value of 8.77 eV, indicating both that the *ab initio* method employed is adequate and that the point charges account for most of the aqueous stabilization of the chloride anion. Interestingly, there is only a weak correlation between the position of the anion in the slab (surface vs. interior) and the corresponding polarizability or IP. This is different from the situation in small clusters, where surface structures have a significantly larger polarizability than the interior geometries, and this lack of strong correlation is clearly due to the liquid disorder at separations smaller than the mean screening distance of Coulomb interactions. However, upon closer inspection one still discovers a negative correlation between the value of the Cl^- polarizability and the IP, as in the cluster systems, showing again that these are two mutually coupled electronic properties of the solute. The present results indicate that the use of a single value of anion polarizability for MD simulations is justified, although one should realize that the chloride anion polarizability can fluctuate by as much as 10%. We note that the present mean value around 4 Å^3 (which represents a reduction of 30% compared to the gas phase) is slightly larger than values between 3.25 and 3.76 Å^3, appearing in the current literature [7,11-13].

In our previous MD studies, we have shown that the somewhat surprising appearance of chloride anions at the air-water interface is primarily due to the large value of the Cl^- polarizability [11,12]. From this perspective, it is encouraging that the actual value of the aqueous chloride anion polarizability is most likely slightly larger than the value we have employed in our earlier studies. Therefore, in reality the propensity of the chloride anion for the interface of an aqueous solution is likely to be even stronger than predicted previously [11,12].

IV. CONCLUSIONS

With the use of accurate *ab initio* calculations based on geometries obtained from classical or Car-Parrinello MD simulations, we have shown in this Letter that aqueous environment significantly reduces the polarizability of the chloride anion. In clusters, this effect is more pronounced for interior than for surface ionic solvation. In the extended liquid, the difference between chloride polarizabilities in the bulk and at the air-water interface is less pronounced, and a single value around 4 Å^3 can be employed.

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FIGURE CAPTIONS

Figure 1:

Geometries of the clusters under investigation. (a) Optimal geometry of $Cl^-(H_2O)_3$, (b) surface isomer of $Cl^-(H_2O)_6$, (c) embedded isomer of $Cl^-(H_2O)_6$, and (d) a snapshot of the $Cl^-(H_2O)_6$ cluster from a CP simulation (small spheres represent the positions of the Wannier charges).

Figure 2:

Correlation between the position of the chloride anion in the aqueous slab (a) with its polarizability (b) and vertical ionization potential (c). Dashed line in (b) and (c) represents a linear fit to the data.

TABLES

TABLE I. Polarizability (in Å^3) and vertical ionization potential (in eV) of bare Cl^- and chloride on/in water clusters with waters treated as point charges or explicitly.

System	Polarizability	Ionization Potential
Cl^-	5.49	3.64
$Cl^-(H_2O)_3$(point charges)	4.54	5.65
$Cl^-(H_2O)_3$ (explicit waters)	—	5.34
$Cl^-(H_2O)_6$ (point charges, surface isomer)	4.30	6.39
$Cl^-(H_2O)_6$ (explicit waters, surface isomer)	—	6.33
$Cl^-(H_2O)_6$ (point charges, embedded isomer)	3.63	6.64
$Cl^-(H_2O)_6$ (explicit waters, embedded isomer)	—	6.65

TABLE II. Polarizability (in Å^3) and vertical ionization potential (in eV) of Cl^- on water hexamer for five snapshots separated by 1 ps taken from a Car-Parrinello MD run.

Time (ps)	Charge Model	Polarizability	Ionization Potential
1	SPCE	4.29	6.27
1	Wannier	3.95	7.19
2	SPCE	4.31	6.22
2	Wannier	3.98	7.17
3	SPCE	4.48	5.97
3	Wannier	4.22	6.80
4	SPCE	4.33	6.61
4	Wannier	3.98	7.38
5	SPCE	4.52	6.09
5	Wannier	4.29	7.01

TABLE III. Polarizability (in Å^3) and vertical ionization potential (in eV) of Cl^- in liquid water for five snapshots separated by 0.2 ps taken from a Car-Parrinello MD run.

Time (ps)	Charge Model	Polarizability	Ionization Potential
0.3	SPCE	4.07	7.02
0.3	Wannier	3.72	7.87
0.5	SPCE	4.15	7.18
0.5	Wannier	3.89	8.03
0.7	SPCE	4.22	7.84
0.7	Wannier	4.01	8.85
0.9	SPCE	4.12	6.93
0.9	Wannier	3.80	7.98
1.1	SPCE	4.26	6.51
1.1	Wannier	3.96	7.30

Figure 1, Jungwirth and Tobias

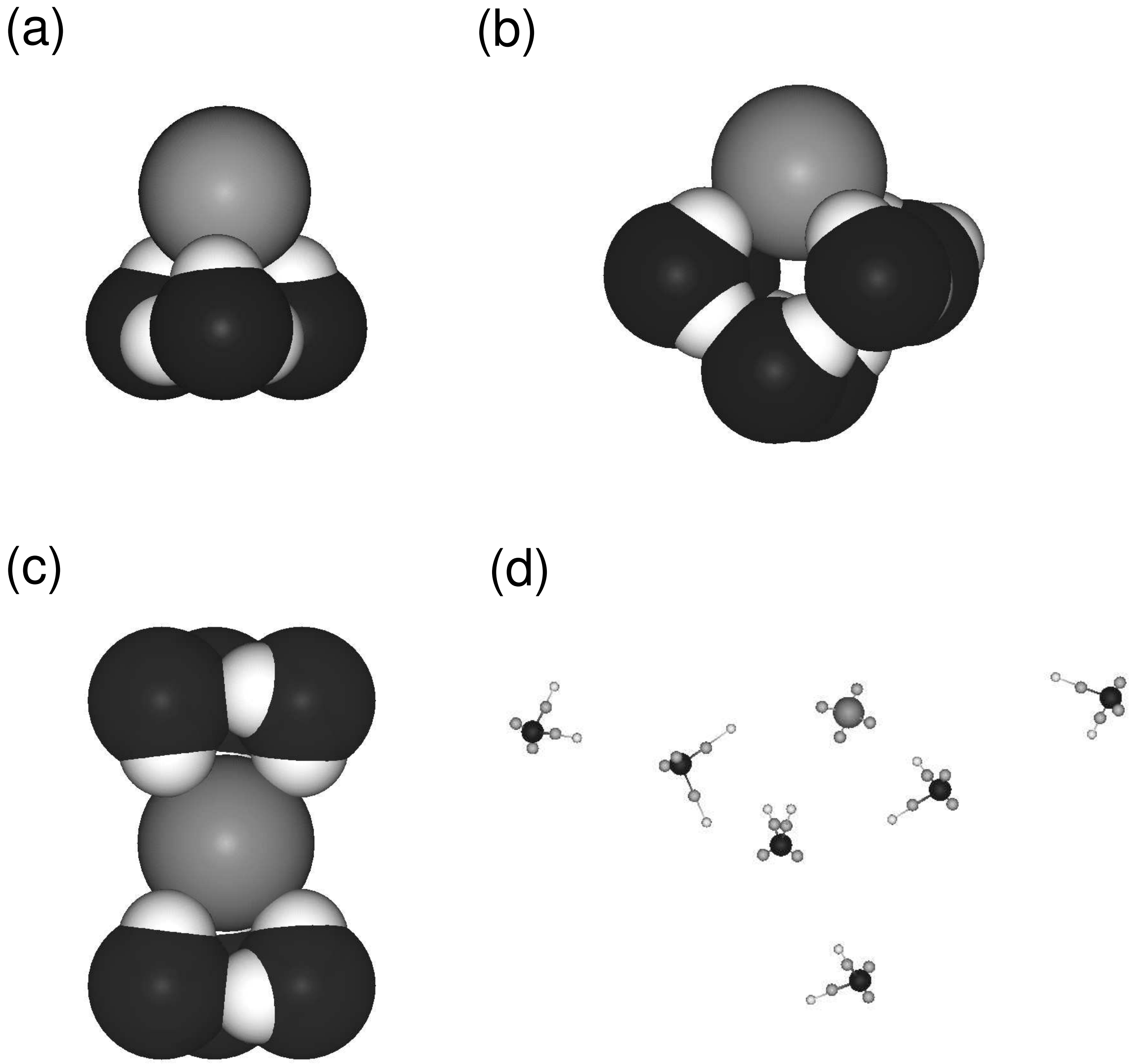
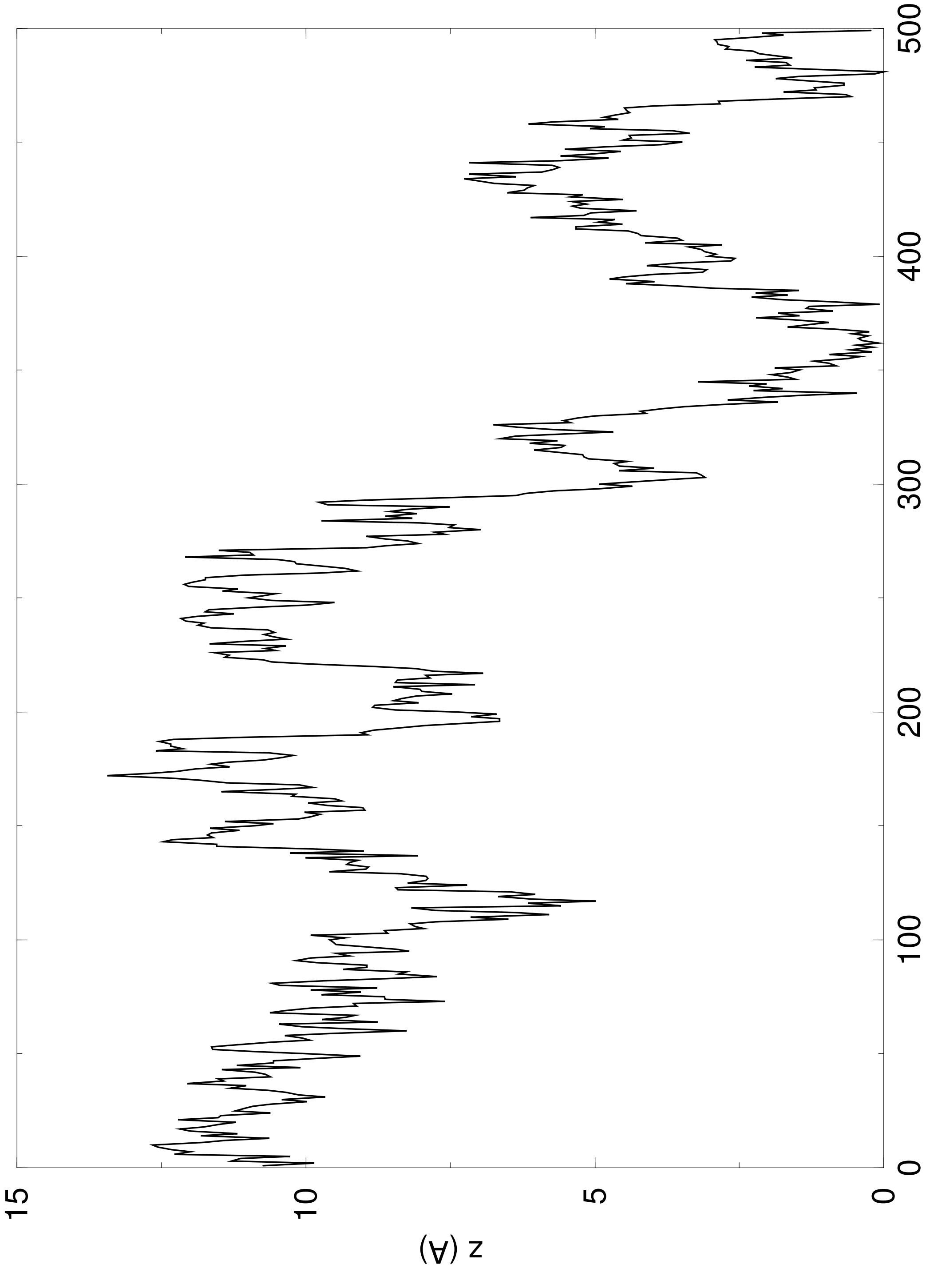


Figure 2a, Jungwirth and Tobias



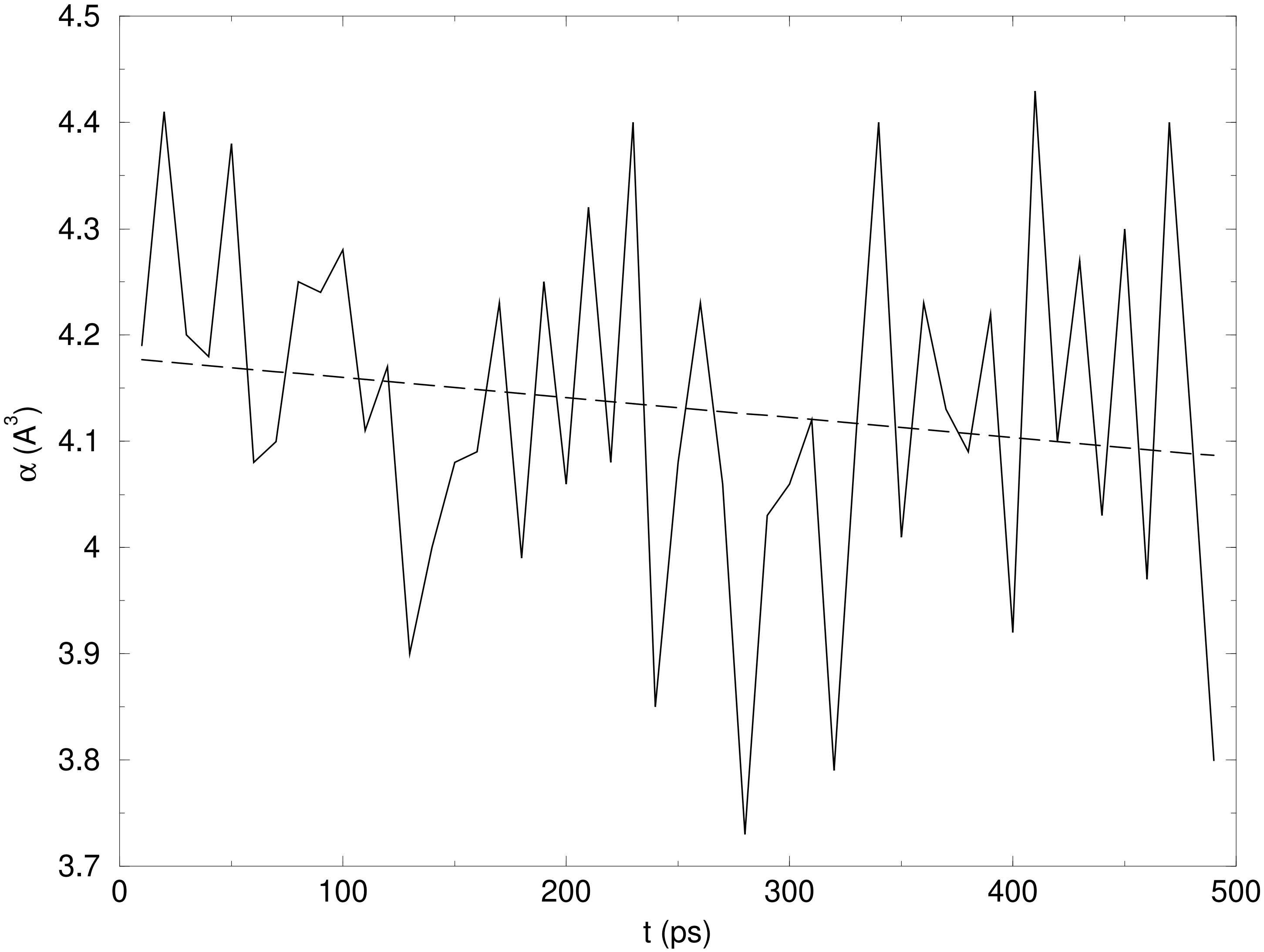


Figure 2b, Jungwirth and Tobias

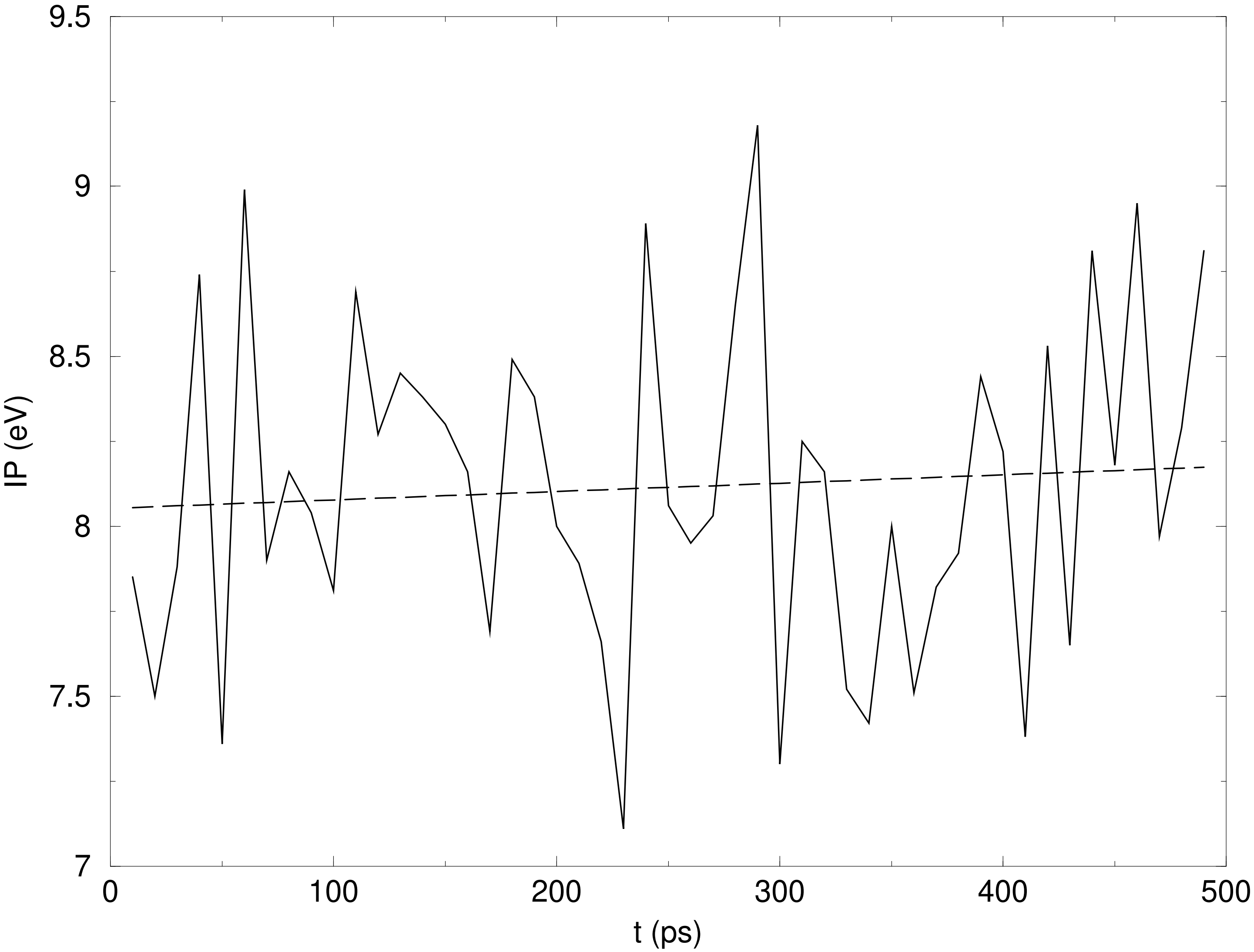


Figure 2c, Jungwirth and Tobias