Electric Dipole Moments of Nanosolvated Acid Molecules in Water Clusters

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The electric dipole moments of $(H_2O)_n DCl$ (n=3-9) clusters have been measured by the beam deflection method. Reflecting the (dynamical) charge distribution within the system, the dipole moment contributes information about the microscopic structure of nanoscale solvation. The addition of a DCl molecule to a water cluster results in a strongly enhanced susceptibility. There is evidence for a noticeable rise in the dipole moment occurring at $n \approx$5-6. This size is consistent with predictions for the onset of ionic dissociation. Additionally, a molecular dynamics model suggests that even with a nominally bound impurity an enhanced dipole moment can arise due to the thermal and zero point motion of the proton and the water molecules. The experimental measurements and the calculations draw attention to the importance of fluctuations in defining the polarity of water-based nanoclusters, and generally to the essential role played by motional effects in determining the response of fluxional nanoscale systems under realistic conditions.

Introduction. Water clusters are convenient experimental platforms for the study of the microscopic physics and chemistry of solvation. By monitoring cluster properties as a function of the number of water molecules, it is possible to follow the step-by-step progression of intermolecular interactions [1], following the transition from isolated molecule to bulk By virtue of having a large fraction of their molecules located near the surface, clusters can serve as surrogates for important processes occurring on aerosols and hydrometeors [2,3]. Composed of only a finite number of constituents, they often serve as test beds for theoretical methods and models.

Small water clusters doped with an acid molecule – here, for concreteness, hydrogen chloride – have been the subject of a great number of theoretical papers and a sizeable (but regrettably much smaller) number of experimental ones. Hydrogen chloride readily dissociates into H_3O^+ and Cl^- and the dissociation also takes place in HCl hydrates [4-8], on the ice surface [9-12] or on larger water nanoparticles [13-15] and protonated water cluster ions [16,17]. One inquiry that persistently threads its way through this subject is: what is the minimum quantity of water molecules, $(H_2O)_n$, required to dissociate the acid [18]? According to calculations, the acidically dissociated structure is supported starting from *n*=4; most of the theoretical approaches agree that at this size the dissociated form represents the global minimum on the potential energy surface [18-24]. Experimentally, for neutral clusters the question has been probed by laser spectroscopy (see, e.g., [25-28]) but finding a conclusive spectroscopic signature of the onset of dissociation in a nanocluster is not straightforward.

As a matter of fact, the challenge is not just experimental but conceptual. The free water clusters in natural and laboratory environments generally exist at temperatures appreciably above absolute zero [29]. (Our focus is on this regime, as opposed to the environment in superfluid

helium droplets [26].) To build a constructive bridge between theory and experiment, it is important to address the question: To what extent do parameters observable at finite temperatures either retain or lose the specificity assigned by optimization of the cluster structure? (See, e.g., Ref. [31] as well as [32-35].) In the bulk, dissociation of an acid molecule clearly implies separation of its charged constituents. But within a small water cluster the anion and the proton are confined to a finite volume, while the proton is highly mobile. Hence in the presence of thermal as well as zero-point motion it is not obvious to what degree ionic dissociation in a realistic cluster environment translates into an unambiguous change in the distribution of charge within the cluster. There exists a convenient observable which directly reflects electrical charge distribution within a system: the electric dipole moment $\boldsymbol{p}$. Indeed, measurements of $|\boldsymbol{p}|$ by electrostatic deflection of cluster beams have served as a valuable probe of structure and bonding [36-38]. However, there have been only few applications of the method to water clusters [39-41]. In the present report we use beam deflection to provide a new experimental angle onto the problem of acidic dissociation: a measurement of the electric dipole moment of $(H_2O)_n$ clusters carrying a DCl molecule. The measurements yield what may be the first direct evidence for a transition occurring between $n=5$ and 6.

The data are considered within the context of a theoretical analysis of proton delocalization and the associated time-averaged dipole moment (or, equivalently, the rovibrational polarizability) of a doped cluster. We point out that the dynamically averaged dipole moment within a finite highly fluxional system can be qualitatively different from that computed for a static minimum-energy framework.

Experimental results. Dipole moments were deduced from a beam-deflection measurements of the susceptibility (effective polarizability α_{eff}) of clusters. Experimental details

are described, in the Supplemental Materials section [42]. Mass spectrometric detection of water clusters doped with a molecule of hydrochloric acid is impeded by the fact that electron-impact ionization of the complex always results in a complete loss of the chlorine atom [54] making the mass spectrum indistinguishable from that of neat water clusters. To identify mass peaks deriving from doped species, it is therefore necessary to deuterate one of the partners. We used a supersonic oven filled with H_2O vapor and injected DCl gas from a capillary into the expansion zone.

In a system whose dipole moment undergoes fluctuations and is statistically oriented along the electric field (often referred to as a "floppy" cluster), the probability of sampling a particular dipole configuration approximates a canonical distribution, and the effective linear susceptibility is then given by the Langevin-Debye formula with the temperature corresponding to the cluster's internal rovibrational temperature [36-38]: $\alpha_{eff} = \bar{p}^2 / (3 k_B T)$. Here $\bar{p} = |\bar{\mathbf{p}}|$ is the time-averaged value of the cluster dipole moment along the deflection field direction. It is important to emphasize (see, e.g., the incisive discussion in the classic book of Van Vleck [55]) that the numerator represents the statistical mean square of the vector dipole moment of the system (in the absence of an external field). It is a more general quantity than a permanent moment, and can be temperature-dependent. Thus it also incorporates the effects of rovibrational polarization and screening (cf., e.g., Ref. [56]). This correlates with the assertion above that discussions of the structure of molecular clusters must be supplemented by considerations of the dynamics of their constituents.

The experimentally measured effective polarizabilities are plotted in Fig. 1(a). The first important observation is that peaks assigned to mixed clusters display a much larger response, attesting to the presence of a polar impurity.

4

Water clusters formed in a hot nozzle expansion will cool by evaporation, and evaporative ensemble theory [57-59] predicts a resultant $T \approx 200$ K. This temperature was employed previously with the same setup to analyze the deflection of neat water clusters [39] and is close to $T_{rot}=167$ K fitted to the deflection profiles of the D_2O molecule [60]. Using this value and the measured α_{eff}, we obtain the root-mean-square (rms) values of the dipole moment $\bar{p}$ plotted in Fig. 1(b). The neat cluster dipole moments are approximately 10-20% higher than the values reported in an earlier measurement [39].

Fig. 1(b) shows that the excess dipole moment carried by the mixed clusters (i.e., the difference between the moment of a mixed and neat cluster) is close to that of the DCl molecule (1.1 D [61,62]). This implies that the peaks detected in the mass spectra do not originate from much heavier precursors: otherwise, the latter would have to possess unrealistically high dipole moments in order to deflect by the observed amount. This is consistent with the assumption that $(H_2O)_nDCl$ does not undergo extensive fragmentation upon electron-impact ionization. Indeed, according to theoretical results [63] ionization of $(H_2O)_4HCl$ dominantly involves the loss of zero or one water molecule; for larger clusters losses may be weaker. Similarly, Refs. [64,65] concluded that the number of water monomers lost by small neat water clusters upon electron bombardment or VUV radiation, respectively, is small. Thus we estimate that the uncertainty in the experimental dependence of cluster properties on size n does not on average exceed one molecule. (The influence of fragmentation merits further investigation but calls for an ionization technique that would not perturb cluster structure and combine softness with efficiency.)

The data reveal a sizeable $\approx 30\%$ increase in the electric dipole moment of $(H_2O)_nDCl$ clusters between $n=5$ and $n=6$. In other words, at this point there occurs a restructuring of the average charge distribution within the cluster (since this is precisely what defines the dipole

moment's magnitude). As remarked in the introduction, it is convenient that a deflection experiment can make such an effect directly apparent. This is the first direct observation of a shift in the electric susceptibility of a small doped water cluster with size.

Calculation and discussion. A strong shift in the magnitude of $\bar{p}$ in a doped water cluster can be due to one or both of the following mechanisms: either a significant increase in the separation between D^+ and Cl^- (i.e., dissociation of the molecule), and/or a strong shift in the rovibrational electric polarizability of the water cluster itself (i.e., a change in how effectively the water network screens the impurity). As emphasized in the introduction, a qualitatively important question in this context is the influence of internal motion on the actual dipole moment of a highly fluxional finite molecular cluster.

The important role played by quantum delocalization in the structure of $(H_2O)_nHCl$ complexes has been addressed a number of times [31,33,35]; cluster structure also exhibits significant variations with temperature. Here, we aim to assess how zero-point and thermally driven structural variations are reflected in the effective electric dipole moments. To our knowledge, this specific angle has not been addressed in previous calculations on doped water clusters and therefore we have supplemented the experiment by calculations which pay particular attention to the difference between minimum-energy structures and systems that exhibit actual motional dynamics [42]. As a first step, such calculations were performed for two selected $(H_2O)_4HCl$ clusters representing the covalent and ionic minima, as well as for pure water clusters. As described below, the calculations suggest that in these conditions the two aforementioned mechanisms – ionic dissociation and polarization of the water cluster matrix - can enhance cluster dipole moments by similar amounts, and it is not straightforward to separate their contributions. Furthermore, it becomes apparent that a "charge-separated structure" no

longer entails full charge separation when thermal and zero-point fluctuations are taken into account.

The dipole moments of minimum energy structures of small pure and doped water clusters are shown in Fig. 2(a). For several of them, the finite-temperature rms dipole moments are also shown. Already for neat water clusters there are significant deviations between the "minimum-energy" dipole moments and the dynamical rms values. This is most dramatically exemplified by the tetramer. $(H_2O)_4$ in its fixed minimum-energy configuration has a zero moment due to symmetry (and as a result is, e.g., invisible in rotational spectroscopy [66-68] The effective moment measured in the present experiment is, however, $\bar{p} \approx 1.9$ D, reflecting the cluster's internal motion. Molecular- (MD) and path integral molecular-dynamics (PIMD) simulations yield an rms value of 1.40 D (taking into account the thermal effects at 200 K) and 1.78 D (considering also the vibrational delocalization) [69].

The analysis of doped water clusters is much more complicated due to their enormous structural diversity. This diversity together with the lack of information on the relative population and intercoversion rates of different isomers in the beam make it impractical, and to a degree unjustified at this stage, to address computationally the experimentally detected change of the dipole moment between the doped pentamer and hexamer structures.

It is instructive, however, to consider again the situation for the doped tetramer, $(H_2O)_4HCl$ [Fig. 2(a)]. This is the first size supporting the existence of the $H_3O^+ \dots Cl^-$ ion pair in the minimum-energy configurations. Here looking at minimum-energy structures would suggest that the dipole moments of the ion pair structures should be almost double that of the covalent form. However, the differences of the PIMD rms dipole moments are substantially smaller,

which means that the dynamic charge distributions become much more similar. This occurs because of the thermal and quantum motion within the cluster.

This highlights the important point that whereas minimum-energy depictions portray distinct and static covalent and ionic structures, in reality the light hydrogen atom travels rather freely within the finite cluster, as illustrated in Fig. 2(b). This conclusion is in accord with previous studies even though the particular structural distribution can depend on the electronic structure method used in the simulations and cluster temperature. This figure shows the probability of finding an H atom near the Cl atom for structures starting out as covalent and ionic configurations. Inclusion of quantum delocalization effects in PIMD points towards partial dissociation of the covalent structure and (even more conspicuously) a partially covalent character acquired by the nominally ion-pair structure. The two corresponding pairs of points marked by dashed circles in Fig. 2(a) show behavior which fully correlates with this observation: the nominally covalent form of the tetramer displays an enhanced rms dipole moment at finite temperature (reflecting partial dissociation), while the corresponding dipole moment of a "solvent-separated-pair" starting structure actually decreases somewhat (reflecting a decrease in the time-average charge separation).

The figure makes it clear that experimentally measurable quantities must be discussed in terms of hydrogen densities rather than precisely defined hydrogen positions. The "fluxional perspective" on the $(H_2O)_n HCl$ clusters is in accord with previous studies [31,33,35], although of course the particular distribution of geometries is sensitive to the electronic structure level employed and to the assumed cluster temperature.

Summary and conclusions. We reported on a measurement of the electric dipole moment of water clusters doped with a molecule of acid. The dipole moment is an important observable because it is directly related to the charge distribution within the system. This is the first such measurement on the archetypal system of a water cluster containing a hydrogen-halide molecule. The addition of a DCl molecule to an $(H_2O)_n$ cluster results in an overall strong enhancement of the dipole moment, and furthermore there is evidence for a significant rise in the dipole moment of $(H_2O)_n$DCl occurring at $n \approx 5\text{-}6$.

This size is consistent with predictions for the onset of ionic dissociation. Alternatively, a molecular dynamics model suggests that the dynamical rovibrational polarization of the cluster's water molecules can give rise to a large dipole moment even when the impurity remains nominally bound. This calculation draws attention to the fact that care is needed in relating the charge distribution in a finite and fluxional cluster to the degree of ionization of an embedded impurity. This is especially important for protons which can undergo strong thermal and zero-point fluctuations. Overall, the role of fluctuations in defining the electric susceptibility of water clusters has not been fully and quantitatively addressed in the literature, and merits in-depth theoretical analysis. Conversely, deflection experiments on pure and doped neutral water clusters can provide important information about their internal motion and about the relative populations and interconversions of structural motifs, thus supplying useful benchmarks for theoretical models. An especially important technical development would be the ability to control and vary the internal temperature of such neutral free clusters.

Note also that notwithstanding the underlying dynamical details, the observed jump in the effective dipole moment of doped water clusters should have important consequences, for

example, for long-range interactions involving these clusters, e.g., for the stability of dipole-bound anions [70-72], and for the rates of cluster reactions with electrons and ions.

Figure captions

Fig. 1. (a) Effective polarizabilities of neat (bottom) and DCl-doped (top) water clusters. Straight lines and bands show the mean value and its standard deviation for the groups n=3-5 and n=6-9. (b) Neat (bottom) and doped (top) time-averaged (rms) electric dipole moments $\bar{p}$ obtained from the data in (a) using the Langevin formula, as described in the text. Straight lines show the mean value for the groups n=3-5 and n=6-9. There is a jump in the $DCl(H_2O)_n$ cluster susceptibilities between n=5 and 6.

Fig. 2. (a) Calculated dipole moments for $(H_2O)_{1-6}$ (diamonds) and $HCl(H_2O)_{0-6}$ (circles) systems. Open symbols correspond to minimum energy structures optimized at the *ab initio* MP2 level, and filled symbols to *rms* moments $\bar{p}$ from path integral molecular-dynamics values at the assumed cluster temperature of 200 K. In the labels, COV stands for a covalently bound HCl in the cluster, CIP stands for a contact-ion pair, and SSP for a solvent-separated ion. Dashed circles highlight two pairs of doped tetramer structures for which minimum-energy and finite-temperature dipole moment values can be compared. See the text and Supplementary Materials [42] for additional information. (b) Density distribution of the closest Cl…H distance for the covalent and solvent separated ion pair of the $HCl(H_2O)_4$ cluster. Black dotted and solid curves: classical and path-integral MD simulations, respectively, for the covalent structure. Red dotted and solid curves: classical and PIMD simulations, respectively, for the ion pair structure.
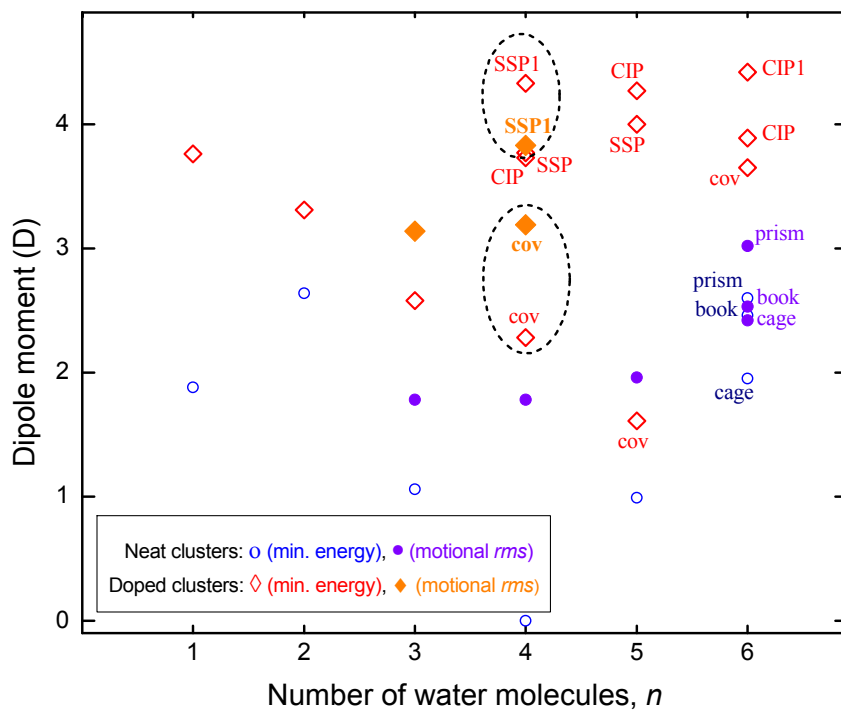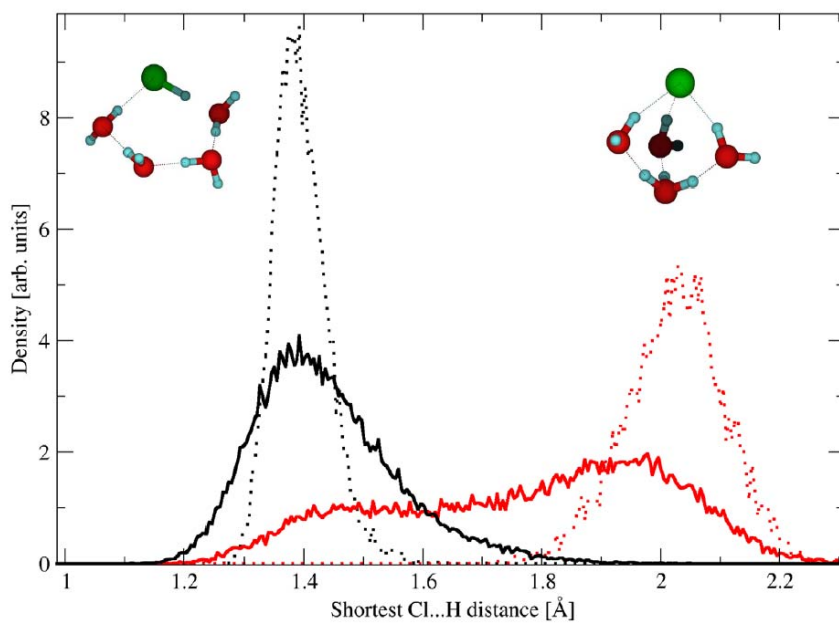
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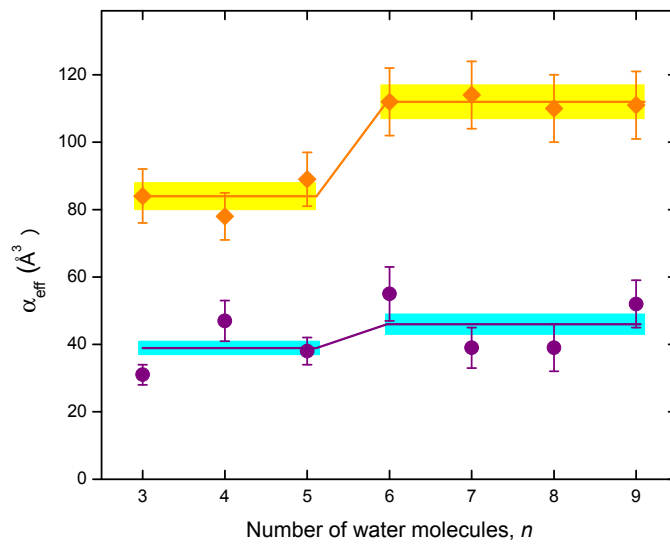
(a)
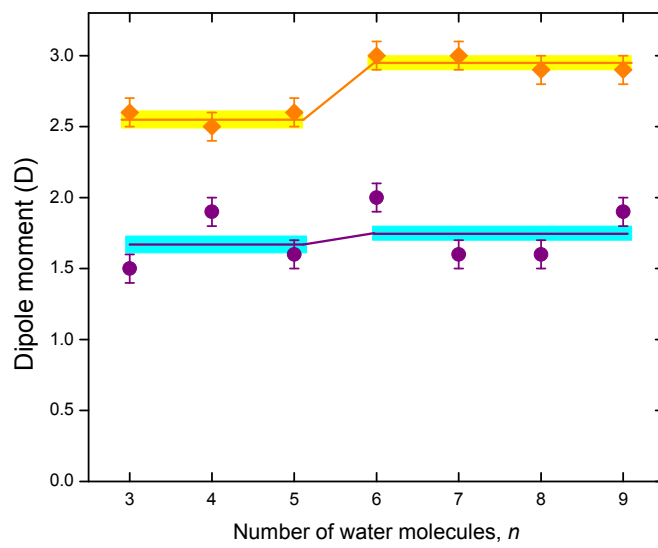
(b)

Fig. 1

(a)

(b)

Fig. 2

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