Acid Dissociation in HCl-Water Clusters is Temperature Dependent and Cannot be Detected Based on Dipole Moments

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The dissociation of acids in aqueous environments at low temperatures in the presence of a limited amount of water is underlying a wealth of processes from atmospheric to interstellar science. For the paradigmatic case of $HCl(H_2O)_n$ clusters, our extensive *ab initio* path integral simulations quantify in terms of free energy differences and barriers that $n = 4$ water molecules are indeed required to dissociate HCl at low temperatures. Increasing the temperature, however, reverses the process and thus counteracts dissociation by fluctuation-driven recombination. The size of the electric dipole moment is shown to not correlate with the acid being in its dissociated or molecular state, thus rendering its measurement as a function of n unable to detect the dissociation transition.

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The dissociation of acids, thus producing protons and the counter-anions, is an elementary process that is required to enable many subsequent chemical reactions. For instance, it is a key player in the complex chemistry taking place in the atmosphere of Earth [1–5] or other planets [6], either within water droplets [7–13] or on ice surfaces [1,2,14–16]. Moreover, acids also play a prominent role in reactive processes within the interstellar medium [16,17]. Yet, the fundamental question of how many water molecules are required for the dissociation of an acid molecule is both long-standing and controversial [18–27]. In particular, HCl interacting with H_2O molecules serves as a paradigmatic showcase [12,18–42]. HCl is known to be a strong acid that is essentially fully dissociated in bulk water, thus yielding solvated Cl^- and H^+ ions. In the opposite limit, it is well established that HCl interacting with a single water molecule does not dissociate but forms the $HCl(H_2O)$ heterodimer instead. Given these limiting scenarios, it is obvious that a certain number n of water molecules must be necessary in order to allow the HCl molecule to split into its ionic components. Upon successively adding water molecules to HCl in a superfluid helium matrix, convincing evidence has been given that an ion pair, and thus the dissociated acid molecule, can be stabilized at low temperatures using a minimum number of only four H_2O molecules [20,24,25]. However, the issue of acid dissociation in HCl-water clusters remains experimentally controversial [21–23,25]. Unfortunately, acid dissociation is also theoretically intricate in view of significant quantum and thermal fluctuations effects which can shift dissociation equilibria [33,34,38] combined with difficulties to predictively compute vibrational frequencies [12,31,40,41] as previously used experimentally to monitor acid dissociation.

For these reasons, a recent publication [26] appeared particularly promising since the electric dipole moment of $DCl(H_2O)_n$ clusters has been measured by the beam deflection method as a function of cluster size from $n = 3$ to 8, thus contributing a novel observable that might settle the case. In fact, the assumption that a microsolvated charge-separated species implies a higher dipole moment of the whole cluster has already been used in the literature for a long time [43–47]. Based on such dipole measurements, it has been concluded in the abstract of Ref. 26: "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."

The aim of this work is to provide solid evidence that the rise in the dipole moment in $HCl(H_2O)_n$ clusters is not an indicator that allows one to probe the onset of ionic dissociation. Our data even disclose that the magnitude of the electric dipole moment of these clusters does not correlate at all with the microsolvated acid being dissociated or not. Moreover, upon probing the temperature dependence of acid dissociation for the critical $n = 4$ case, we discover that increasing thermal fluctuations systematically counteracts dissociation. Given four H_2O molecules, HCl strongly prefers indeed to be dissociated into an ion pair in the realm of low temperatures [20,24,25], whereas an undissociated molecular cluster structure is stabilized at sufficiently high temperatures as shown in what follows.

In order to achieve our goal, large-scale *ab initio* path integral simulations [48] have been carried out, thus including nuclear quantum effects at finite temperatures. These simulations of $HCl(H_2O)_n$ from $n = 1$ up to 8 using several isomers have been carried out at $T = 200$ K in order to match the experimental conditions of Ref. [26] using our well-tested and validated approach [31,33,34,38] (i.e., all-electron Becke-Lee-Yang-Parr (BLYP) calculations using the aug–cc–pVTZ basis set and $P = 12$ Trotter beads within the CP2k software package [49]). Additional benchmarks compiled in the Supplemental Material [50] confirm that our

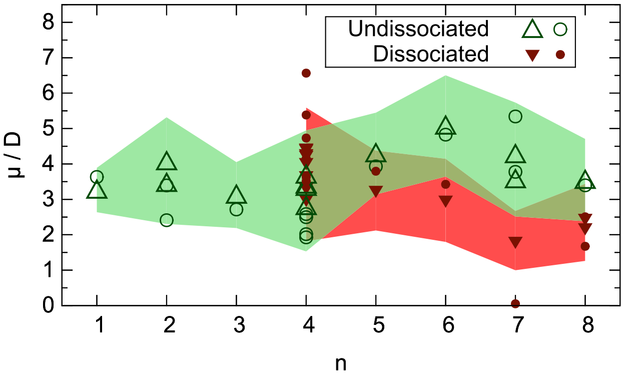

FIG. 1. Quantum-statistical expectation values $\langle\mu\rangle$ of the dipole moment operator at 200 K (triangles) and equilibrium dipole moments μ from static optimization (circles) for $HCl(H_2O)_n$, $n = 1, \ldots, 8$. Filled and open symbols refer to the respective dissociated and undissociated species. The green and red areas correspond to the standard deviation for undissociated and dissociated clusters, respectively, according to the underlying probability distribution functions; see Fig. 2.

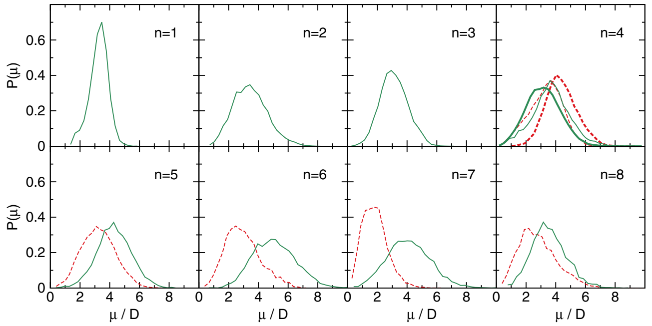

FIG. 2. Quantum-statistical distribution functions $P(\mu)$ of the dipole moment operator for $HCl(H_2O)_n$, $n = 1, \ldots, 8$ at 200 K. The green solid and red dashed lines correspond to undissociated and dissociated clusters, respectively; thin (thick) green and red lines correspond to PA (UD) and SIP (CIP) species, respectively, for $n = 4$.

approach is also valid to compute the dipole moments. In an effort to quantify temperature effects on the dissociation process, the stability of dissociated versus undissociated clusters is quantified by computing quantum and classical free energy profiles of the $n = 4$ species at 50, 100, 200, and 300 K; see the Supplemental Material [50] for details. Last but not least, in addition to computing the dipole expectation values we also optimized more than 2500 structures for $n = 1, \ldots, 8$ to scrutinize possible correlations of the cluster dipole moment and the dissociation state of HCl.

The finite-temperature expectation values of the dipole operator $\langle\mu\rangle$ of the investigated $HCl(H_2O)_n$ clusters at 200 K are compiled in Fig. 1 as a function of n together with dipole moments μ of optimized structures. As expected, for small clusters with up to three water molecules only undissociated structures are found starting at $n = 1$ with the $HCl(H_2O)$ heterodimer. Dissociated species become available only for clusters containing four or more water molecules. What is immediately apparent from Fig. 1 is that clusters containing undissociated and dissociated HCl cannot be distinguished based on the magnitude of their electric dipole moments. The lowest-energy dissociated $n = 7$ case provides a particularly stunning example: the huge dipole created by the separated charges is essentially fully quenched by an arrangement of the water molecules such that the vector sum of their dipoles largely compensates the former; see Supplemental Material [50]. Apart from that illustrative case, the *undissociated* clusters for $n > 4$ even display a tendency to possess *larger dipoles* compared to the corresponding dissociated ones, which is nicely revealed at the level of the full distribution functions at 200 K as presented in Fig. 2. When it comes to the impact of quantum fluctuations on the dipole moments of the static structures, it is not only stunning to see that the quantum averages $\langle\mu\rangle$ at 200 K deviate strongly from the corresponding equilibrium dipole moments μ, but also that fluctuations can both increase *and* decrease it. The clue comes from the very broad dipole distribution functions in Fig. 2, which moreover significantly overlap. Thus, adding their standard deviations to the averages in Fig. 1 leads to a broad "fluctuation window" (shaded area) that covers the total variations of the mean values as a function of n.

The $n = 4$ cluster turns out to be particularly puzzling. For this specific cluster size, our *ab initio* path integral simulations confirm the previous finding [26] of an interconversion between a dissociated and undissociated form of $HCl(H_2O)_4$ at 200 K. The dissociated species represents the long-known solvent-shared ion pair (SIP), whereas the undissociated species is identified here to correspond to the partially aggregated (PA) structure [20,24]. The aggregation-induced dissociation mechanism that leads to dissociation of HCl upon successively adding four H_2O molecules in superfluid helium clusters implies the transient formation of a distinct undissociated structure being the PA species [20,24]. In this species, the fourth water molecule accepts a hydrogen bond from a water molecule within the cyclic $HCl(H_2O)_3$ (quasiplanar undissociated) cluster; see Table I in the Supplemental Material [50]. Once PA is formed, the dangling water eventually reaches the HCl molecule in the ring as a result of large-amplitude motion that readily triggers the dissociation process to yield the SIP species [24]. Upon ion pair formation, the Cl^- and the H_3O^+ ions get separated by a minimal layer of three water molecules via a concerted double proton transfer process (see Fig. 11 in Ref. [38]). Thus, PA and SIP are the relevant species that are involved in the interconversion process, rather than the global undissociated (UD) and dissociated (SIP) minima [27] being separated by high-energy barriers [20,24].

At variance with the $n > 4$ clusters, for $n = 4$ the largest dipole moments are found for dissociated contact ion pairs (CIP), $\langle\mu\rangle \approx 4.4$ D, whereas the lowest ones correspond to

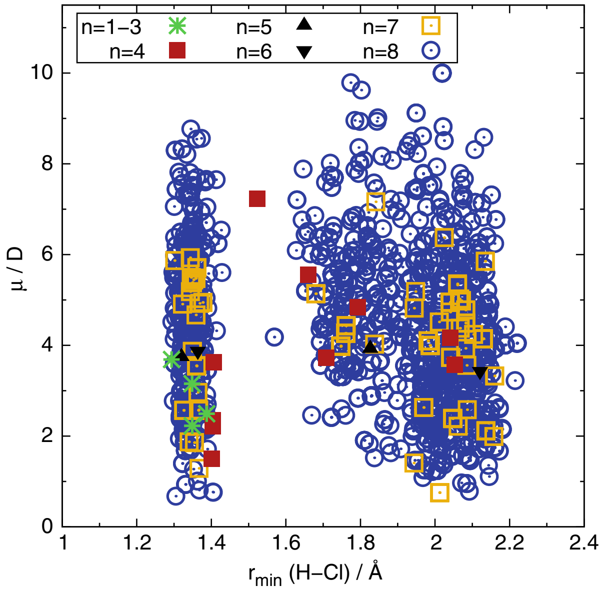

FIG. 3. Dipole moments μ of $HCl(H_2O)_n$ clusters, $n = 1, \ldots, 8$, obtained from more than 2500 optimized structures versus the shortest $H \cdots Cl$ distance r of the respective structure, where $r < 1.4$ Å and $r > 1.6$ Å corresponds to undissociated and dissociated HCl molecules, respectively.

undissociated quasiplanar ring (UD) species with $\langle \mu \rangle \approx 3.0$ D. Moreover, the undissociated PA and the dissociated SIP_{C3} isomers share essentially the same dipole moment in between these limits, namely $\langle \mu \rangle \approx 3.7$ D. All this strengthens our conclusion that the dipole moment is *not* an indicator of HCl-water clusters being in an undissociated or dissociated state. In particular, the measured [26] rise in the electric dipole from $n = 5$ to 6 water molecules does not challenge the conclusion [20,24,25] that $n = 4$ is the smallest HCl-water cluster which supports an ion pair.

Next, independent analysis based on a large ensemble of optimized $HCl(H_2O)_n$ structures in Fig. 3 supports this finding by showing that there is no useful correlation between the magnitude of the total dipole moment μ of the entire $HCl(H_2O)_n$ cluster and the microsolvated HCl molecule being dissociated or not. As one can see, the cluster dipole moments span about the same range from close to zero until roughly 10 D irrespective of the $H \cdots Cl$ distance being below ≈ 1.4 Å (corresponding to an undissociated HCl molecule) or above ≈ 1.6 Å (indicating the ionized state). Therefore, the magnitude μ of the dipole moment of $HCl(H_2O)_n$ clusters in the investigated size range is unrelated to the dissociation state of the microsolvated HCl molecule.

In view of the particular complexity of the $HCl(H_2O)_4$ cluster, for which interconversion between undissociated and dissociated structures at 200 K has been reported [26], we additionally computed both classical and quantum free energy profiles in order to fully quantify relative cluster stabilities and heights of the separating energetic barrier as

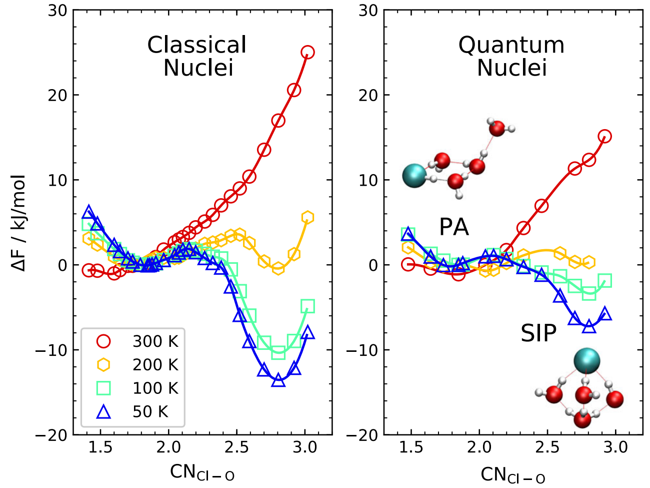

FIG. 4. Classical (left) and quantum (right) free energy profiles connecting the partially aggregated (PA) undissociated to the fully dissociated solvent-shared ion pair (SIP) species for the $HCl(H_2O)_4$ cluster at 50, 100, 200, and 300 K. The order parameter is the coordination number of the chlorine atom with respect to the oxygen atoms (see text).

a function of temperature. In Fig. 4, these free energy landscapes are depicted as a function of the $Cl \cdots O$ coordination number, $CN_{Cl \cdots O}$ serving as an order parameter [24], where minima around 1.85 and 2.80 correspond to the undissociated PA and dissociated SIP structures, respectively. In the low temperature regime, the free energy profiles clearly feature a global minimum that corresponds to the SIP conformer independently from a classical or quantum treatment of the nuclei in agreement with previous findings [20,24]. Second, the barrier that separates the PA local minimum from the dissociated preferred structure is small. The resulting shallowness of the PA minimum substantially supports the aggregation-induced dissociation mechanism disclosed in Refs. [20,24].

In stark contrast to the low temperature scenario, the $n = 4$ cluster offers a much richer behavior as temperature rises. First of all, regarding the free energy differences between the PA and SIP minima, it can be extracted from Fig. 4 that the relative stability of these undissociated and dissociated structures, respectively, experiences a drastic change at around 200 K. Below this crossover temperature the system behaves qualitatively as just described; i.e., SIP remains energetically preferred. At higher temperatures, on the contrary, the SIP minimum along the order parameter completely disappears whereas PA remains a stable species. We note in passing that quantum chemistry approaches [27] that consider harmonic zero-point energies and rigid rotor-harmonic oscillator thermal corrections based on normal modes analysis of optimized equilibrium structures and thus on local minima of the potential energy surface cannot predict the qualitative topology change of the free energy landscape as observed in the present *ab initio* path integral simulations; estimating similarly the temperature dependence of the average dipole moment based on local minima is also limited if species become unstable. Thus, fluctuation effects greatly *destabilize* the ion pair with respect to the undissociated species despite the corresponding SIP structure, of course, remains the global minimum of the underlying potential energy surface.

Given that intriguing temperature dependence for the particularly important $n = 4$ case, we finally come back to the behavior of the electric dipole moment, now as a function of temperature. To this end, we constrain the order parameter to those values that definitely correspond to SIP and PA structures, thus using $\mathrm{CN}_{\mathrm{Cl}\cdots\mathrm{O}} = 2.80$ and 1.85, respectively, and compute the resulting quantum-statistical distributions of the dipole operator at the different temperatures; see Fig. 2 in the Supplemental Material [50]. Corroborating furthermore our previous conclusions, it is confirmed that neither the expectation value of the dipole moment operator $\langle \mu \rangle$ nor its full quantum distribution function $P(\mu)$ can be used to distinguish dissociated from undissociated clusters; note that the structures sampled with $\mathrm{CN}_{\mathrm{Cl}\cdots\mathrm{O}} = 2.80$ still correspond to proper SIP species even at 300 K. The same conclusion is reached upon distance-resolving these distributions akin to Fig. 3; see Fig. 3 in the Supplemental Material [50]. It therefore occurs to us that vibrational spectroscopy should still be the most reliable experimental tool used to distinguish between microsolvated $\mathrm{HCl(H_2O)}_n$ clusters that either host an intact HCl molecule or an $\mathrm{Cl^-}$-$\mathrm{H_3O^+}$ ion pair if combined with accurate computations [12,37,39,40].

We conclude that our results unequivocally demonstrate that the magnitude of the total electric dipole moment of $\mathrm{HCl(H_2O)}_n$ clusters, at least up to $n = 8$, does not probe the dissociation state of the microsolvated acid. Depending on the species, the water molecules might arrange themselves such that their effective molecular dipole moments largely compensate the huge dipole that is generated by the separated charges due to $\mathrm{Cl^-}$ and $\mathrm{H_3O^+}$. This is reminiscent to dielectric shielding, well known from aqueous bulk electrolyte solutions, now in the realm of microsolvating ion pairs. Our finding implies the far-reaching conclusion that beam deflection cannot be used to probe ion pair formation within clusters—contrary to long-standing belief. For the distinct $n = 4$ case, our free energy calculations, which include thermal activation and nuclear quantum effects, provide further support that the fully dissociated solvent-shared ion pair is the preferred low-temperature structure [20] and thus the smallest droplet of acid [20,32]. Unexpectedly, however, we discovered a temperature-driven recombination transition in the sense that simply heating the preferred dissociated ion-paired low-temperature structure of $\mathrm{HCl(H_2O)}_4$ reverses the acid dissociation process. Given the shape of the free energy profile, this "association" reaction becomes eventually barrierless, whereas an intermediate temperature regime is predicted where both dissociated and undissociated species coexist in thermal equilibrium. The fundamental nature of these findings should provide plenty of stimulation to look more broadly into temperature-driven dissociation versus association reactions of strong and also weak acids in microsolvation environments. Beyond simple acids, research into zwitterionization processes of amino acids or even short peptides in small water droplets in the gas phase is expected to disclose yet unknown phenomena related to charge separation and recombination processes in solvent-restricted aqueous environments.

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