COMMUNICATIONS

Excess electrons in polar molecular clusters

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(Received 24 February 1988; accepted 9 March 1988)

Studies of electron localization in finite clusters of polar molecules, e.g., $(H_2O)_n$ and $(NH_3)_n$, open new avenues for probing the microscopic energetics and mechanisms of solvation and of size effects on chemical and physical phenomena, pertaining to the questions of the modes of electron localization and the minimal cluster sizes which sustain bound states of an excess electron. While single water and ammonia molecules do not attach an excess electron readily (if at all), negatively charged free water[1-5] $(H_2O)_n^-$, and ammonia,[6] $(NH_3)_m^-$ clusters have recently been observed for $n \geqslant 11$ and $m \geqslant 30$, respectively, and accurate values of the vertical binding energies for $(H_2O)_n^-$ cluster, $11 \leqslant n \leqslant 20$ have been obtained via photoelectron spectroscopy.[3] These systems provide an immense theoretical challenge due to their complexity and the delicate dependence of their stability on the nature of the electron–molecule and interatomic interactions.

Employing the recently developed quantum path-integral molecular dynamics method (QUPID) which is based on the path-integral formulation of quantum statistical mechanics[7] and an isomorphism between the quantum problem and a classical one and in conjunction with a newly developed electron molecule pseudopotential,[8-10] we have studied for the first time the microscopic energetics, structure and stability of electron attachment to clusters of $(H_2O)_n$ and $(NH_3)_n$ for a wide range of cluster sizes and temperatures. In these studies the molecular degrees of freedom are treated classically (no significant isotopic dependence has been observed) employing known intra- and intermolecular interactions for water[11] and ammonia,[12] and the electron–molecule interaction was described via a pseudopotential, constructed[8-10] in the spirit of density functional method and consisting of Coulomb, polarization, exclusion, and exchange contributions. The energetics of the systems can be expressed in terms of the electron vertical and adiabatic binding energies, EVBE and EABE, respectively, where the former is the electron ionization energy of the negatively charged cluster with no cluster reorganization and EABE = EVBE + E_c, where E_c is the cluster reorganization energy, i.e., the difference between the equilibrium intra- and intermolecular energies of the negatively charged cluster and the corresponding neutral. Energetic stability is inferred from the magnitude and sign of EABE (which at the limit of $n \rightarrow \infty$ is the heat of electron solvation in the bulk) with EABE < 0 corresponding to an energetically stable bound state.

The results of our studies are summarized in Fig. 1 where the binding energies are plotted vs $n^{-1/3}$ (full and empty symbols correspond to EVBE and EABE, respectively, circles and squares to interior and surface states, respectively). We observe first that for small to intermediate size $(H_2O)_n$ $(12 < n < 64)$ clusters stable well-bound electron localization occurs via *surface states* (SS) while localization in interior states (IS) requires cluster sizes $n \gtrsim 64$. The electron charge distributions of these bound states, characterized by the radius of gyration R_g, varies from $R_g \sim 6\ a_0$ for the SS of the $n = 12$ cluster to $R_g \sim 4.0\ a_0$ of the IS for $n = 128$. Furthermore the EVBEs of the SS states for the $12 \leqslant n \leqslant 18$ water clusters are in quantitative agreement with the measured values.[3] We remark that the discovery of the energetically favored surface mode of localization in small and intermediate $(H_2O)_n$ clusters[8-10] points to the inadequacy of previous models[13,14] where a cavity-like (internal) binding geometry was assumed and which have failed to explain the observed energetic stability of these clusters. The measurement of the transition from surface to internal localization upon increasing cluster size (signified by a marked increase in EVBE) is left as an experimental challenge.

In contrast to the case of the $(H_2O)_n^-$ clusters we observe that the onset of stable electron attachment to ammonia clusters (signified by EABE < 0, open squares and circles for SS and IS, respectively) occurs via *internal localization*, requiring $n \gtrsim 32$ molecules, and is *not preceded* by

0021-9606/88/106670-02$02.10

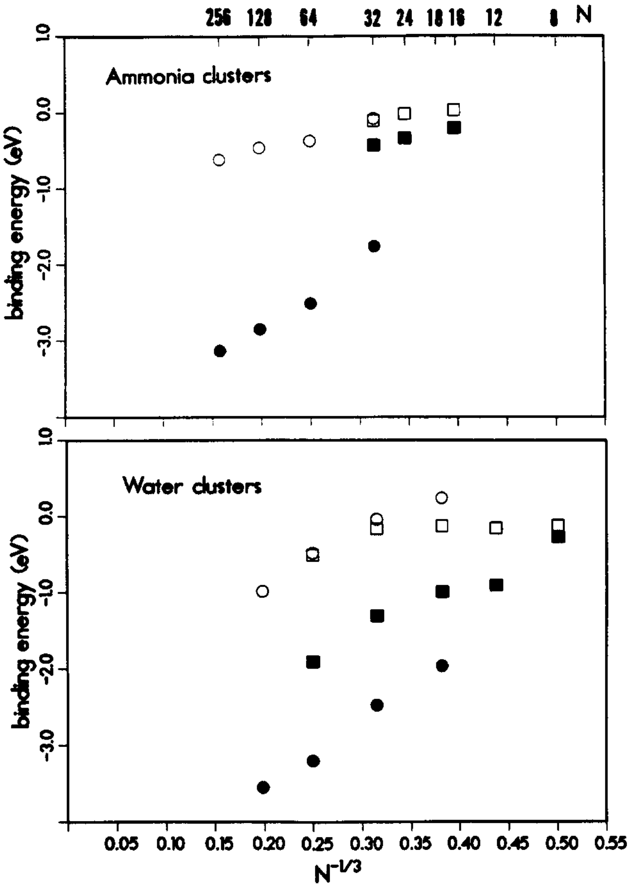

FIG. 1. Calculated excess electron binding energies (in electron volts) vs $n^{-1/3}$ for $(NH_3)_n^-$ (a) and $(H_2O)_n^-$ (b) clusters. Circles and squares correspond to interior and surface states, respectively. Full and empty symbols correspond to the vertical (EVBE) and adiabatic (EABE) binding energies, respectively. The ammonia results were obtained at $T = 189.5$ K and those for water (Refs. 8–10) at $T = 300$ K for $n \gg 32$ and $T = 79$ K for $n < 32$. Note the weaker binding in ammonia relative to water, in particular for the surface states, and the linear dependence on $n^{-1/3}$ for the internal states.

well-bound surface localized states for smaller clusters. In addition, attempts to bind an electron via surface states to $n > 32$ clusters resulted in a transition to the internally localized states.

Finally, as evident, the energies of the internal states of both materials (circles) exhibit linear dependence vs $n^{-1/3}$. An adaptation[10,15] of a dielectric continuum model,[16] where the molecular cluster is described by a dielectric sphere of radius $\bar{R} = r_s n^{-1/3}$ [where r_s the (mean) radius of the molecular constituent] yields[10,15] EVBE $(\bar{R}) =$ EVBE $(\infty) + An^{-1/3}$ and EVBE $(\bar{R}) =$ EVBE $(\infty) + Bn^{-1/3}$, where $A = e^2/2r_s(1 - D_s^{-1})$ and $B = (e^2/2r_s)(1 + D_{\rm op}^{-1} - 2D_s^{-1})$ with D_s and $D_{\rm op}$ the static and optical dielectric constants of the material. The values of the predicted slopes (A and B) agree with those obtained from the simulations results (Fig. 1). Furthermore, an extrapolation of the electron adiabatic binding energies (EABE) to $n \to \infty$ yields values in agreement with current experimental estimates[17] (-1.7 and -1.1 eV for water and ammonia, respectively) for the bulk heats of solution in these materials.

To summarize, we conclude that electron localization in $(H_2O)_n^-$ clusters[1-5] occurs via two modes depending on the cluster size (surface states for $8 < n < 64$) with a transition from surface to internal localization for $n \sim 64$. The interplay between the competing effects of the interaction of the electron with the molecular constituents, the kinetic energy of localization and the intermolecular interactions (underlying cluster reorganization) precludes the formation of stable well-bound surface states in ammonia clusters, resulting in the onset of excess electron binding via internal localization for $n \gtrsim 32$, in agreement with experimental observations.[6]

This research was supported by the U.S. Department of Energy under Grant No. FG05-86ER45234 (to U.L.).

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