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EXCESS ELECTRONS BOUND IN CLUSTERS RELATED TO HYDROGEN- BONDED CONDENSED PHASES

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Prompted by the work of Kim & co. on electrons interacting with water hexamer clusters of different geometries [*Phys. Rev. Lett.*, **76**, 956 (1996)], we have analyzed data for electron binding by water and ammonia clusters of various sizes [Haberland & co. 1991, Jortner & co. 1988]. Three regimes of cluster sizes are delineated. I: large clusters containing $n \geq 300$ molecules, which join the cluster regimes to the liquid phase, and which completely encompass the wave function of the excess electron. II: intermediate clusters with $300 < n \leq 20$, which internally contain most but not all of the wave function of the excess electron. III: small clusters with $n_{\max} \geq n \geq n_{\min}$, on which the excess electron is bound to polar hydrogens that project from the surface of the cluster, and for which the electron binding energy is very sensitive to the molecular arrangement in the cluster.

The rest of the paper is largely devoted to (a) suggestions of further experiments and (b) the possible use of an excess electron as a probe to herald the nucleation of a condensed phase.

Keywords: Clusters; ammonia; water; electron capture

1. BACKGROUND

The study of excess electrons in hydrogen bonded liquids such as ammonia, water and alcohols has a long history [1–3]. Mobility [4] and optical absorption [5,6] measurements are the most popular ways to study whether the excess electrons are to be described by well-localized or delocalized wave functions. With the growth of cluster science, a large body of work is building up on anions of clusters of various sizes.

The present investigation has been prompted by the recent work of Kim & co [7], who have used conventional quantum-chemical techniques as well as density functional theory to calculate the binding energy of an electron to a hexamer of six H_2O molecules. A focus of their study was to attempt to find the stable cluster geometry of such an anion. They suggest two favorable geometries: two staggered triangular rings, and a triangular prism; a regular octahedral structure is unstable. In the two favorable structures, which are similar to those found by Combariza, Kestner and Jortner [8] for a Cl^- anion in water hexamers, the vertical ionization energies are calculated to be 0.5 eV for the two-rings and 0.1 eV for the prism. These are near to experimental values 0.5 and 0.2 eV [9, 10], which therefore Kim & co. interpret as arising from the two different cluster geometries, each of which is metastable [7].

Here we shall be concerned with the change in binding regimes of excess electrons as we pass from such a small, structure-sensitive assembly of six water molecules through an experimentally and theoretically studied regime from ~ 20 –130 molecules, through to the limit of the condensed phase. The proposal is made in the following section that there are essentially three regimes, which we shall delineate below.

2. DELINEATION OF THREE REGIMES OF EXCESS ELECTRON BINDING IN CLUSTERS AND CONDENSED PHASES WITH HYDROGEN BONDING

In the hexamer calculations of Kim & co. [7], it is useful language to say that the excess electron in $(\text{H}_2\text{O})_6^-$ is in an s-like orbital. Naturally, superposed on this spherical wave function are corrugations, the main features of which correspond to some pile-up of probability density of the excess electron around the six non-hydrogen-bonded H atoms in the least unstable negative cluster. The regime of structure-sensitive binding will be referred to as region III (see Fig. 1). At some small value of n in $(\text{H}_2\text{O})_n^-$ the excess electron is no longer bound. We shall exclude in all hydrogen bonding systems the anionic dimer, which we felt must be handled separately.

Regime II is classified as follows. If we define α_n as the total polarizability of an intermediate size cluster, regime II is defined as that

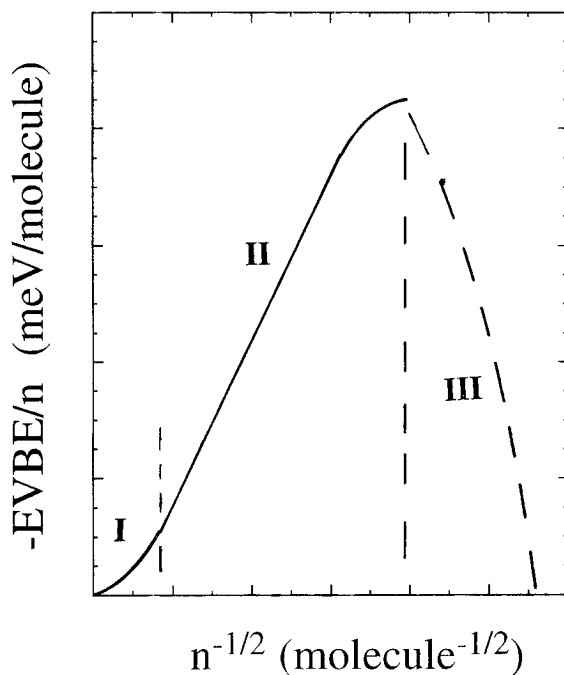


FIGURE 1 Schematic sketch of the shape of the variation of the vertical ionization energy $-EVBE$, of an electron bound to a hydrogen-bonded cluster, with the number n of molecules in the cluster. For reasons given in the text, the plot is of $-EVBE/n$ against $n^{-1/2}$. Regimes I, II and III are described in the text (see Section 6).

range of n over which a reasonable approximation is

$$\alpha_n \simeq \alpha_1 n \quad (1)$$

where α_1 is the known polarizability of a single molecule (say H₂O, NH₃ or CH₃OH). Eqn. (1) is roughly equivalent to the statement, elaborated for example by Brinck & co. [11], that polarizability correlates with volume. We emphasize that Eqn. (1) is useful only over a restricted range of n (say 20–200 for H₂O).

Following Barnett & co. [12], we expect that the long-range form of the polarization contribution to the pseudopotential $V_{ps}(r)$ is $-\alpha_n/2r^4$. This must be cut off, to avoid the pronounced singularity at $r = 0$ and should be supplemented by Coulomb, exclusion and exchange

contributions [12]. We expect a spherically averaged potential to exhibit a minimum of depth V_{\min} say, at a position reflecting the size of the cluster. We anticipate (see, for example, Eqn. (1) for the polarization term) that V_{\min} will scale linearly with n in the limited range of n in regime II.

This then motivates studying, instead of the binding energy E_b of the excess electron, the binding energy E_b/n per molecule. Elementary analysis of the lowest level in the above well centered on V_{\min} suggests that there is a correction to V_{\min} for "zero-point energy" $1/2 \hbar \omega$, where the phase angular speed $\omega = (k/m)^{1/2}$, with m the electron mass and force constant k proportional to n . Thus $E_b/n = \text{constant} + \text{term proportional to } n^{-1/2}$. Without pressing the detail of the above argument, it motivates plotting E_b/n against $n^{-1/2}$, and this is the representation in the schematic plot of Figure 1.

Regime I simply reflects the fact that, in large water or ammonia clusters or droplets, $E_b \rightarrow \text{constant}$ in the liquid regime, and hence $E_b/n \rightarrow 0$ as $n \rightarrow \infty$ and $n^{-1/2} \rightarrow 0$. Regime I therefore corresponds to the saturation regime in which E_b becomes essentially E_v beyond a certain value n_{sat} of the number of molecules in the cluster.

We turn from the schematic form shown in Figure 1, in which the three regimes are labeled, to detailed results for H_2O and NH_3 clusters.

3. DETAILED RESULTS FOR H_2O AND NH_3 CLUSTERS

The objective of this section is to present available results on water clusters and ammonia clusters [13] in a manner which makes contact with the three regimes labeled in the schematic Figure 1. We have, for $(\text{H}_2\text{O})_n$ clusters, taken data from Figure 8 of the review by Barnett & co. [14]. From their curve labeled EVBE, which denotes the excess electron vertical binding energy but is actually the negative of the vertical ionization energy, we have read off the values -1.92 , -2.38 , -3.21 and -3.54 eV for the four points marked. We have also utilized a curved extrapolation of these four results to -4.5 eV at the limit $n^{-1/3} \rightarrow 0$ ($n \rightarrow \infty$). The dashed parabola in regime I of Figure 2 for H_2O corresponds to 4.5 eV/ n plotted against $n^{-1/2}$.

The four points for EVBE of electrons in clusters of $n = 18$ to 128 lie satisfactorily around a straight line, and conform with the polarizability Eqn. (1).

It remains therefore to link this mainly linear regime II with regimes I and III as marked in Figure 1. For regime III, we need to know the minimum number n_{\min} of molecules that bind an excess electron. Experimentalists have observed anions for $n = 2, 6$ and 7 [10]. The dimer requires a separate treatment, so we have assumed $n_{\min} = 6$ in Figure 2. The clusters with $n = 6$ and 7 each displayed two values of binding energy, one near 0.5 eV and the other near 0.2 eV [10].

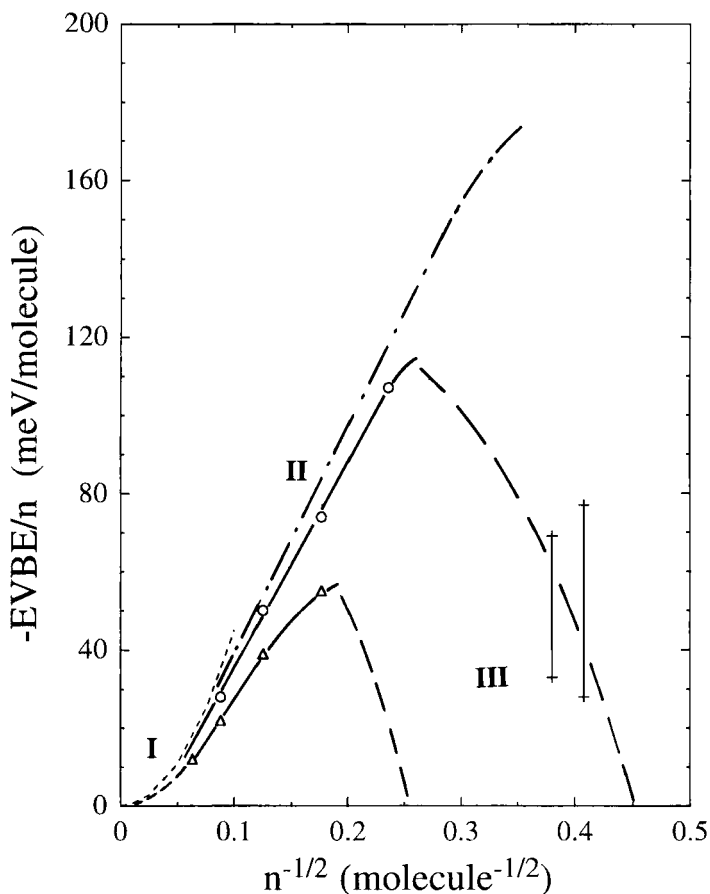


FIGURE 2 Plots of $-EVBE/n$ against $n^{-1/2}$ for electrons bound to clusters of NH₃, H₂O, and CH₃OH molecules. NH₃, Δ ref. 13; H₂O, O ref. 13, ‡ ref. 10; CH₃OH, ---, hypothetical (see text).

Kim & co. attributed the two energies to different molecular arrangements in the clusters [7], discussed in the Introduction. We have drawn a dashed curve for regime III which has a maximum of $-EVBE/n \approx 110$ meV/molecule at $n^{-1/2} = 0.26$, or $-EVBE = 1.7$ eV at $n = 15$ molecules.

By comparing measured Vertical Detachment Energies (VDEs) of electrons from clusters of various sizes [10] with values calculated [13] for interior states (excess electron wave function predominantly inside the cluster) and for states in which the excess electron has high probability near the surface of the cluster (called surface states in refs. 7 and 13; see Fig. 2 of ref. 7) it appears that all the VDEs refer to surface states. However the four points plotted in regime II of Figure 2 correspond to interior states, where most of the electron wave function is localized inside the cluster. For clusters below a certain size, interior states are unstable with respect to surface states [13]. Regime II of Figure 2 therefore corresponds to interior states, and regime III to surface states of the electron on the cluster. The $n = 2$ case [10] is in a category by itself, not included in ref. 13 or here.

In joining regime II onto regime I, we use a tangent construction, the approximately straight line of regime II becoming tangential to the parabola of regime I when $n \approx 300$ molecules. This we take to be a measure of the size of the $(H_2O)_n$ cluster required to essentially reach the condensed phase value of $(EVBE)_{n \rightarrow \infty}$, by completely enclosing the wave function of the electron. The equation of the upper parabola in regime I of Figure 2 is $-EVBE/n$ (meV/molec) = $4500 (n^{-1/2})^2$.

Turning to discuss more briefly the corresponding curve for ammonia clusters, we have utilized the data from Figure 1 of Barnett & co. [13]. These workers calculated EVBE for interior states in ammonia clusters in the range of $n = 32$ to 256 molecules, using as for water, path-integral molecular simulations. In these simulations, an electron-molecule pseudopotential was invoked which embodied Coulomb, polarization, exclusion and exchange contributions. The EVBE values are -1.76 , -2.51 , -2.86 and -3.15 eV for $n = 32$, 64, 128 and 256 molecules. These have been plotted in Figure 2, and again form an almost linear regime II. Barnett & co. [13] stress the weaker binding in ammonia relative to water. They estimated that interior states would not be stable with respect to surface states for n somewhat below 18 in water and somewhat below 32 in ammonia. We therefore

put the peaks of the curves in Figure 2 at $n = 15$ for water and $n = 30$ for ammonia, both of which correspond to $-EVBE \approx 1.7$ eV as a minimum vertical ionization energy from an interior state.

Regime III corresponds to states in which the excess electron wave function is mainly near the surface of the cluster, and the energy is very sensitive to the particular arrangement of the molecules in the cluster. We take $n_{\min} \approx 16$ for ammonia, following ref. 13.

For regime I in ammonia we made a curved extrapolation of the four interior state points in Figure 1 of ref. 13 to $-EVBE \approx 3.4$ eV at $n^{-1/3} = 0$. The equation of the lower parabola in regime I of Figure 2 is therefore $-EVBE/n$ (meV/molec) = $3400(n^{-1/2})^2$.

4. PREDICTIONS FOR METHANOL

An attempt to form negative clusters of methanol and ethanol failed [15]. Large neutral clusters were identified by impact ionization and quadrupole mass spectrometry, but the clusters did not capture electrons as $(H_2O)_n$ and $(NH_3)_m$ did in the same apparatus [15]. In the liquid phase, solvated electrons are more strongly bound in methanol than in water or ammonia [1], and hence the optical absorption energy is larger [16] and the mobility is smaller [3] in methanol than in the other two liquids. In the light of these observations on the liquid phase, it seems important to reopen the question of the binding of an excess electron to a methanol cluster.

There are several possibilities to explore. (1) Haberland & co. [15] referred to the presence of a microplasma near the gas expansion nozzle, and it seems important to examine the effect of the electric discharge on the methanol itself and on the metal point around which the discharge forms (does the point become coated with carbonaceous deposit?). (2) The attachment of an electron to an ammonia or water cluster probably first occurs to the polar hydrogen atoms projecting from the surface of the cluster, and for the larger clusters [13] the electron moves from the surface state to an interior state of lower energy. Clusters of alcohol molecules have nonpolar alkyl groups on the surface, the cluster being bound by the polar OH groups, which would therefore be oriented toward the interior of the cluster. The nonpolar exterior would not capture an electron with high probability,

and therefore some external driving force, such as about 1 eV kinetic energy, may be required to penetrate the surface. This would decrease the capture probability compared to that of lower energy electrons impinging on clusters of water or ammonia, and sensitive detection of the signal will be needed.

A qualitative estimate of $-EVBE/n$ in methanol clusters is drawn in Figure 2. Only interior states are expected, so regime III might not exist for methanol. In regime II, where a minimum of two layers of water or ammonia molecules interact with the excess electron, the methyl group in methanol acts as the second (polarizable) layer, so fewer molecules are needed. We therefore terminated the curve at $n = 8$, compared to 15 for water and 30 for ammonia.

Phase I, through which large clusters evolve to bulk liquid, would be similar for methanol and water.

5. POSSIBLE RELEVANCE TO NUCLEATION

Henson [17] measured the swarm time of flight of $H^+(H_2O)_n$ and $OH^-(H_2O)_n$ in saturated water vapor. The ion mobilities, normalized for vapor density, were found to increase with increasing vapor temperature (and concomitantly increasing density). The mobilities were relatively low and were ascribed to nanodroplets that condensed around the ions.

Freeman [18] analyzed the data of Henson, assuming that the density d of the nanodroplet was approximately the same as that of the bulk liquid at the corresponding temperature. He then approximated the average number z of molecules in the droplet to be

$$z = (4\pi/3) R^3 d (6 \times 10^{23}/18) \quad (2)$$

Using mobilities and temperatures from the work of Henson [17] and density data from Gallant [19], an Arrhenius plot was made of the average number of molecules per droplet in the water vapor, each droplet being nucleated by a positive or negative ion. The equation of the straight line obtained was

$$\ln z = -7.96 + (3850/T): \quad 293 \leq T \leq 343 \text{ K}, \quad (3)$$

yielding $z \sim 180$ at 293 K and ~ 30 at 343 K. Noteworthy is the fact that, in this particular system, with $\text{H}^+(\text{H}_2\text{O})_m$ and $\text{OH}^-(\text{H}_2\text{O})_m$ ions, the measured mobilities of the anions and cations were the same, hence $m \approx n$. We anticipate that if OH^- ions could be replaced by excess electrons, nanodroplets $e^-(\text{H}_2\text{O})_p$ could nucleate, with p not necessarily equal to m .

It is relevant in the present context to note the independent experiment of Wada and Freeman [20] with cations in isobutene vapor. Mobilities were measured in saturated and unsaturated vapors over the entire temperature range of the liquid phase. Droplet formation at each gas density began at a temperature somewhat greater than the vapor-liquid coexistence temperature at that density. Average droplets in the vapor in equilibrium with its liquid contained $\sim 7 \times 10^5$ molecules at 297 K and 2×10^3 molecules at 397 K. Droplets began forming at somewhat below the vapor pressure of the liquid, depending on the liquid surface tension at the onset temperature. One must recognize however that isobutene vapor consists of highly polarizable molecules that do not hydrogen bond.

In relation to the regimes delineated in Figures 1 and 2, the above numbers of molecules in droplets nucleated by anions and cations place us in Regimes II and I. (The work of Berry and Wales [21] on freezing, melting, spinodals and clusters is also particularly noteworthy in the present context.)

6. SUMMARY AND FUTURE DIRECTIONS

After giving a qualitative account of three regimes of hydrogen-bonded clusters that bind an excess electron, we used available results for vertical ionization energies for (a) H₂O and (b) NH₃ to construct Figure 2. This then highlights the following points.

Regime I: The curvature of the limiting parabola in the plots in Figures 1 and 2 is determined by the binding energy of the electron in the condensed phase. The extent of regime I is then essentially determined by the number of molecules needed in the cluster to give the condensed phase binding, where the electron wave function is entirely contained within the cluster.

Regime II: This is characterized by a linear plot and corresponds to the “extensive” regime of polarizability α_n governed by Eqn. (1). It corresponds to clusters that contain most, but not all, of the electron wave function in their interiors. When the number of molecules in a cluster is reduced sufficiently the “interior state” becomes unstable with respect to a “surface state”, and the system enters Regime III. The transition between Regimes II and III is represented by the maximum in the plots of Figures 1 and 2. The positions and heights of the maxima are characteristic features; position and height are strongly correlated. This has led us to sketch a curve for an excess electron bound to methanol clusters in Figure 2, to indicate where to search in the proposed experiment of Section 3. Also, we conjecture that in terms of the vertical ionization energy of the interior states, the maximum $-EVBE/n$ corresponds in each case to a similar ionization energy of the excess electron, ~ 1.5 eV.

Regime III: The clusters are too small to contain most of the electron wave function internally. The excess electron is bound to polar hydrogens that project from the surface of the cluster, hence the designation as surface states [7, 13]. The transition from Regime II to III when the cluster size is reduced is probably not as smooth as the transition from II to I when the size is increased, so the maxima in the curves of Figures 1 and 2 are possibly jagged. Regime III terminates at the minimum number n_{\min} of molecules required to bind an electron (excluding the water dimer, which needs a separate treatment). Values of n_{\min} are about 16 for ammonia and 6 for water. Small clusters of methanol molecules probably have no —O—H groups projecting the polar hydrogen out of the surface, so Regime III probably does not exist for methanol.

The value of n_{\min} especially for $(\text{NH}_3)_n^-$, might change in applied magnetic flux densities of the order of 10 T: see the discussion of effects of large magnetic fields on electron binding, by Freeman and March [22].

Finally, in Section 5, we have indicated how the use of an excess electron as a probe may have implications for nucleation. Further work, both experiment and theory, in this general area would seem to be worthwhile.

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