

## MULTIPLY CHARGED CLUSTER IONS

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Conditions are found for producing a stable state of an electron bound to negatively charged clusters of polar molecules  $X^-(H_2O)_n$  and  $X^-(NH_3)_n$ , where  $X^-$  is a negative ion placed in the cluster center. The critical cluster size  $R_c$ , at which the electron is trapped by the cluster, is 16.6 Å for the water cluster and 45 Å for the ammonium one. Ionization potential of the water cluster  $[X(H_2O)_n]^{-2}$  with  $R = R_c$  is equal to 2 eV, while that of the ammonium cluster  $[X(NH_3)_n]^{-2}$  is 0.72 eV.

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Multiple clusters have been an objective of intense research [1]. Since the multiply charged cluster cations are easier to prepare experimentally, their properties have been studied much better than those of cluster anions. In the present paper we determine conditions for formation of an electron state bound to a negatively charged cluster of polar molecules.

Below we assume a cluster to consist of quite many polar molecules, thus to be spherical, and to have a negative ion  $X_c$  with the charge  $q$  at the center. For water and ammonium clusters considered, the difference  $V_0$  between the conduction band bottoms in an infinite medium and vacuum is supposed to be zero.

Obviously an electron can be bound to such a cluster only if the latter is sufficiently large. The bound state is formed by two competing forces: the Coulomb repulsion between the cluster and the negative ion and the attraction between them due to the cluster polarization. The total electron energy functional in this case has the form

$$I = -\frac{\hbar^2}{2m} \int |\nabla \Psi(r)|^2 dV - e \int |\Psi(r)|^2 \Pi(r) dV + \frac{\tilde{\epsilon}}{8\pi} \int (\nabla_r \Pi(r))^2 dV - \int e \Phi(r) |\Psi(r)|^2 dV, \quad (1)$$

where  $e$  is the electron charge. The first term in the right side of (1) represents the kinetic energy of an electron with the effective mass  $m$ ; the second term corresponds to the electron interaction with the cluster polarization; the third term determines the cluster polarization potential energy, where  $\tilde{\epsilon}^{-1} = \epsilon_\infty^{-1} - \epsilon_0^{-1}$  is the inverse effective dielectric constant ( $\epsilon_\infty^{-1}$  and  $\epsilon_0^{-1}$  are the high-frequency and static dielectric constants); and the last term describes the electron interaction with the negative ion of the potential  $\Phi$ ,

$$\Phi(r) = \begin{cases} -\frac{q}{\epsilon_0 r} - \frac{q}{R(1 - \epsilon_0^{-1})}, & r \leq R, \\ -\frac{q}{r}, & r > R, \end{cases} \quad (2)$$

where  $-q$  is the ion charge and  $R$  is the cluster radius. The second and third terms in (1) are integrated only over the cluster volume  $\Omega$ .

Hereafter we assume the electron to locate mainly inside the cluster. On the opposite assumption, the Coulomb repulsion would dominate in the electron-cluster interaction and hence the electron could not be bound. We also restrict ourselves to the case of rather high dielectric constant  $\epsilon_0$ , that is characteristic of the clusters  $(\text{H}_2\text{O})_n$  ( $\epsilon_0 = 80$ ) and  $(\text{NH}_3)_n$  ( $\epsilon_0 = 22$ ). Thus, invoking relation (2), functional (1) is approximately rewritten as

$$I = \frac{\hbar^2}{8m} \int |\nabla\Psi|^2 dV - e \int_{\Omega} |\Psi|^2 \Pi(r) dV + \frac{\tilde{\epsilon}}{8\pi} \int_{\Omega} (\nabla\Pi)^2 dV + \frac{qe}{R}. \quad (3)$$

Functional (3) differs from that investigated in [2-4] only by the constant term  $qe/R$  in the right side of (3). Using the results of [2-4] we have for (3)

$$I = -1.48 \frac{\mu}{\tilde{\epsilon}^2} + \frac{7.2}{R} \left( \frac{1}{\tilde{\epsilon}} + 2 \frac{q}{e} \right) [\text{eV}] \quad (4)$$

Here the energy is given in electronvolts, while the cluster size is measured in angstroms;  $\mu = m/m_0$ , where  $m_0$  is the mass of a free electron in vacuum. The critical cluster size  $R_c$ , at which the stable state is possible, is determined from the condition  $I \leq 0$ ,

$$R_c = 4.88 \frac{\tilde{\epsilon}^2}{\mu} \left( \frac{1}{\tilde{\epsilon}} + 2 \frac{q}{e} \right) \quad (5)$$

To calculate the electron energy  $W$  in the cluster, one can use the approximation for  $W$  derived in [2] at  $q=0$ . As a result,  $W$  takes on the form

$$W = -4.43 \frac{\mu}{\tilde{\epsilon}^2} + \frac{14.4}{R} \left( 1 + \frac{1}{\tilde{\epsilon}} \right) \quad (6)$$

The parameter  $|W|$  represents the cluster ionization potential and can be measured in experiments on electron photodetachment from the cluster.

Let us estimate the critical size (5) for clusters  $(\text{H}_2\text{O})_n^{-2}$  and  $(\text{NH}_3)_n^{-2}$ . For the water cluster with  $\tilde{\epsilon} = 1.81$ ,  $q = e$ , and  $\mu = 2.44$  [2] we get  $R_c = 16.6 \text{ \AA}$ . For the ammonium cluster with  $\tilde{\epsilon} = 1.92$ ,  $q = e$ , and  $\mu = 1$  the critical size is  $R_c = 45 \text{ \AA}$ .

The electron energy  $W(R_c)$  for the cluster with  $R = R_c$ , according to (5) and (6), is given

by

$$W(R_c) = -\frac{\mu}{\tilde{\epsilon}^2} \frac{1.49\tilde{\epsilon}^{-1} + 8.86q/e - 2.94}{\tilde{\epsilon}^{-1} + 2q/e} \quad (7)$$

From (7) for the water cluster with  $q = e$  we have  $W(R_c) = -2 \text{ eV}$ . For the ammonium cluster with  $q = e$  we find  $W(R_c) = -0.72 \text{ eV}$ .

It is useful to compare the found data with those for bipolaron states [5]. This shows that the cluster critical size required for the stable electron state at a negatively charged water cluster is less than that required for the bipolaron state ( $R_c = 21 \text{ \AA}$ ). The same conclusion is true for the ammonium cluster where bipolaron states can exist at  $R_c = 80 \text{ \AA}$ .

These data makes it possible to recognize the state nature at the close charge-to-mass ratio in mass spectroscopy experiments with the water and ammonium clusters considered.

Above we assumed the negative ion ( $X^-$ ) to be at the cluster center. More complicated is the case when the ion is not there. For example, according to [6], the halide ions  $X^- = \text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  solvated in water clusters localize not at the center but at the cluster surface. In particular, this follows from the solvation energy [7] estimated by the continual model. In this case conditions for formation of the two-charged cluster  $[\text{X}(\text{H}_2\text{O})_n]^{-2}$  can be more favorable, because, due to a longer effective distance between the ion and the electron, the electron repulsion by the  $X^-$  ion is weaker than in the case of ion central position. Thus, one can expect the critical size of water cluster  $[\text{X}(\text{H}_2\text{O})_n]^{-2}$  with ion  $X^-$  at its surface to be of the same order of magnitude as in the absence of  $X^-$ , that is  $n_c = 11-17$  [2-4]. For  $[\text{X}(\text{NH}_3)_n]^{-2}$  this value is  $n_c = 20-40$  [2-4].

### References

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