

## *F'*-CENTER MODEL OF NEGATIVELY CHARGED METAL–AMMONIUM CLUSTERS

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The excess electron state in  $\text{Li}(\text{NH}_3)_n^-$  cluster is shown to have the same nature as the electron state in ionic crystals. The calculated results conform to available experimental data.

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Mass spectrometry and photoelectron data point to the absence of a critical size for the negatively charged metal–ammonium cluster  $\text{Li}(\text{NH}_3)_n^-$  [1]. At first sight this is not surprising because lithium has positive electron affinity that means existence of a stable ion  $\text{Li}^-$ . However, the experimental data [1] show that in  $\text{Li}(\text{NH}_3)_n^-$  the lithium excess electron is in a solvated state not bound to the lithium atom. At the same time, according to the experimental data of [2], the electron in the ammonium cluster can be in the solvated state only if the  $\text{NH}_3$  molecules exceed 35 in number. The existence of the negative critical size of ammonium cluster relates to the polaron nature of the electron state in the cluster, thus, the main role in this state is played by a bulk effect [3–5]. A separate molecule contribution into the polaron state is small, but the total field created by dipoles of all polar molecules forms a potential well deep

enough to hold the electron in the cluster. In the framework of this continual approach, a lithium atom added in any area of the cluster has no effect on the quantitative data. In other words, the  $\text{Li}(\text{NH}_3)_n^-$  cluster, like  $(\text{NH}_3)_n^-$  one, would have a critical size. However, this speculation does not accept the possibility for the Li neutral atom included into the cluster to transit into the state  $\text{Li}^+$  after the valent electron going into the solvated state.

To describe this phenomenon, let us assume the  $\text{Li}^+$  ion to locate at the cluster center in agreement with experimental data of [6]. In the continual approach, the ion can be taken as a point. Hence, two electrons in the cluster  $\text{Li}(\text{NH}_3)_n^-$  interact with the cluster polarization, with each other, and with the positively charged  $\text{Li}^+$  ion placed in the cluster center. The total energy functional of this system is written as

$$\begin{aligned}
 I_{F'} = & \frac{\hbar^2}{2m_{\text{cl}}} \int |\nabla_{r_1} \Psi(r_1, r_2)|^2 dV_1 dV_2 + \frac{\hbar^2}{2m_{\text{cl}}} \int |\nabla_{r_2} \Psi(r_1, r_2)|^2 dV_1 dV_2 \\
 & - e \int_{\Omega} |\Psi(r_1, r_2)|^2 \Pi(r_1) dV_1 dV_2 - e \int_{\Omega} |\Psi(r_1, r_2)|^2 \Pi(r_2) dV_1 dV_2 \\
 & - \frac{Ze^2}{\epsilon_{0\text{cl}}} \int \frac{|\Psi(r_1, r_2)|^2}{r_1} dV_1 dV_2 - \frac{Ze^2}{\epsilon_{0\text{cl}}} \int \frac{|\Psi(r_1, r_2)|^2}{r_2} dV_1 dV_2 \\
 & + \frac{\tilde{\epsilon}_{\text{cl}}}{8\pi} \int [\nabla_r \Pi(r)]^2 dV - \frac{e^2}{\epsilon_{\infty\text{cl}}} \int \frac{|\Psi(r_1, r_2)|^2}{|r_1 - r_2|} dV_1 dV_2.
 \end{aligned} \tag{1}$$

The first two terms in the right side of (1) correspond to the electron kinetic energy ( $m_{cl}$  is the electron mass in the cluster); the next two terms are related to the electron potential energy ( $\Pi(r)$  is the polarization potential and  $e$  is the electron charge); the two following terms describe the interaction of electrons with the positive charge  $Ze$ ; the next to last term corresponds to the polarization potential energy; and the last term describes repulsion between the electrons. Values  $\epsilon_{0cl}$  and  $\epsilon_{\infty cl}$  are the static and high-frequency dielectric constants,  $\tilde{\epsilon}_{cl}^{-1} = \epsilon_{\infty cl}^{-1} - \epsilon_{0cl}^{-1}$  is the inverse effective dielectric constant.

In functional (1) we take into account a few cases.

(i) Both electrons are distributed mainly inside the cluster. In this case, the third, fourth and eight terms in the functional (1) right side should be integrated only over the cluster volume  $\Omega$ .

(ii) Both electrons are distributed mainly outside the cluster. This case is analogous to a negatively charged  $H^-$  ion in vacuum, thus is not realistic. Here the stable state would correspond

to the electron radius shorter than the cluster one, that contradicts the assumption made.

(iii) As the final case, one electron locates inside the cluster while the other is outside. In the continual approximation, this case is similar to the problem of an electron distributed outside of the cluster. This problem solution leads to unstable surface states [3–5].

Thus, only case (i) is realized. It is noteworthy that in the limit of the infinite size  $R_{cl} \rightarrow \infty$  the considered problem transforms to the case of  $F'$  center in ionic crystals [7].

To find an approximate solution to (1), we write the two-electron wave function in a multiplicative form

$$\Psi(r_1, r_2) = \Psi(r_1) \Psi(r_2). \quad (2)$$

From variation of functional (1) with respect to  $\Pi(r)$ , one gets for the potential  $\Pi(r)$  the Poisson equation coinciding with that for a polaron [8]. Substituting this equation solution from [8] into functional (1) and taking into account relation (2) for the functional  $I_{F'}$ , we have

$$I_{F'} = \frac{\hbar^2}{2m_{cl}} \int |\nabla \Psi|^2 dV - \left( \frac{1}{\epsilon_{\infty cl}} - \frac{2}{\epsilon_{0cl}} \right) e^2 \int_{\Omega} \frac{|\Psi(r)|^2 |\Psi(r')|^2}{|r - r'|} dV dV' + \frac{2e^2}{\tilde{\epsilon}_{cl} R_{cl}} - \frac{2Ze^2}{\epsilon_{0cl}} \int \frac{|\Psi(r)|^2}{r} dV. \quad (3)$$

Functional (3) coincides with the functional considered in [9] for the case of a neutral cluster when substituting  $\epsilon_{\infty cl}$ ,  $\epsilon_{0cl}$ ,  $\tilde{\epsilon}_{cl}$  and  $m_{cl}$  in (3) with  $\epsilon_{\infty}$ ,  $\epsilon_0$ ,  $\tilde{\epsilon}$ , and  $m$  from [9] by relations

$$m_{cl} = 2m, \quad (4)$$

$$\epsilon_{\infty cl}^{-1} - 2\epsilon_{0cl}^{-1} = 2\tilde{\epsilon}^{-1}, \quad (5)$$

$$2\epsilon_{0cl}^{-1} = \epsilon_0^{-1}, \quad (6)$$

$$\frac{2(\epsilon_{\infty cl}^{-1} - \epsilon_{0cl}^{-1})}{R_{cl}} = \frac{1}{\tilde{\epsilon}R}. \quad (7)$$

Hence, after substitution of the cluster parameters into the left side of (4)–(7), we get in the right side of (4) and (5) the values of  $m$ ,  $\tilde{\epsilon}$ ,  $\epsilon_0$ , and  $R$  for introduction into the solution of [9]. For the ammonium cluster, we put  $\epsilon_{\infty cl} = 1.77$  and  $\epsilon_{0cl} = 22$ . According to (5), this corresponds to  $\tilde{\epsilon} = 1.054$ . From relation (4)

with  $m_{cl} = m_0$  it follows that  $m = 0.5m_0$ . Respectively, from (6) we find  $\epsilon_0 = 11$ , and from (7) we derive  $R = 0.9R_{cl}$ . The found values are reasonably close to those parameters for water clusters ( $\tilde{\epsilon} = 1.012$  and  $m = 0.7m_0$ ), to which the model [9] is most sensitive. According [9], the results depend only slightly on the cluster size  $R_{cl}$  at  $n \geq 4$ . This means that the electron bound state exists virtually at any ammonium cluster size (in [1] clusters  $Li(NH_3)_2^-$  were not observed due to insufficient installation sensitivity). Thus, for  $Me(NH_3)_n^-$  clusters, where  $Me$  is a metal atom, the considered model suggests the absence of the critical cluster size. Let us note that this conclusion is true even for metals of negative electron affinity: Be, Mg, Zn, Sr, Cu, Ba, Hg, and Rn.

To estimate the photoionization energy of a negatively charged metal–ammonium cluster, we use the approximation [9] of electron en-

ergy  $W$  corresponding to the functional  $I_F$ . According to [9], for great  $n$  the electron energy  $W = W_{F'}$  is well approximated by the dependence

$$W = -\frac{2}{\Gamma^2} \frac{e^4 m}{\tilde{\epsilon}^2 \hbar^2} + \frac{B(\epsilon, Z\tilde{\epsilon})}{R}, \quad (8)$$

where  $B$  and  $\Gamma$  are numerical coefficients depending on the ratio  $Z\tilde{\epsilon}/\epsilon_0$ ;  $\Gamma$  is tabulated in [9] for the problem of  $F$ -center. For the parameters derived by us,  $\tilde{\epsilon} = 1.054$  and  $\epsilon = 11$ , using results of [10], we get  $\Gamma = 2.9$  and  $B \approx 0$  [9]. Taking  $m = 0.5$ , from (8) we find  $W_{F'} = -2.91$  eV. This value correlates with the energy of electron states in the negatively charged metal–ammonium cluster, which fits functional (3) of the  $F'$ -center model. To estimate the ionization potential, we can use the energy  $W \equiv W_F$  value derived for various  $n$  in a neutral ammonium cluster (dependence  $W(n)$  in [9]). In particular, for  $n = 10$  we find  $W_F = -2.4$  eV [9]. The ionization potential in this case is  $IP =$

$W_F - W_{F'} = 0.51$  eV, which is close to 0.48 eV measured experimentally in [1].

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