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ABSORPTION BANDS OF NEGATIVELY CHARGED POLAR CLUSTERS

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Experimental data on photoabsorption of negatively charged clusters $(H_2O)_n^-$ and $(NH_3)_n^-$ are explained on the basis of the polaron model. Experimental and calculated curves of light absorption are compared for these clusters. The problem of transition to the limit of a boundless condensed medium, is discussed.

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Currently a great experimental data array is collected on photoabsorption of negatively charged clusters $(H_2O)_n^-$ and $(NH_3)_n^-$. According to [1,2], if the number of molecules in such clusters exceeds the critical value n_c ($n_c = 11$ and 41 for water and ammonium clusters, respectively), the absorption curve represents an asymmetric peak with a steep slope at lower energies and a long smooth tail in the range of high energies. The peak energy can be interpreted as the energy of vertical transition of an excessive electron or as the ionization potential. Extrapolation of the experimental data to the limit $n \to \infty$ should lead to an ionization potential corresponding to the volume value of energy for solvated electron photodetachment from a solution.

Currently at least two problems are not solved. First, the above extrapolation yields the photodetachment energy lower than the experimental value for a volume solvent. The second problem concerns explanation of the asymmetric shape and broadening of absorption peak. In particular, the latter effect was related in [2] to the contribution of molecular vibrations controlled by the cluster temperature into absorption. At the same time, this temperature was believed in [2] to be so low that the cluster is in a solid state. In this case, the temperature line broadening is insignificant and cannot explain the experimental absorption bandwidth. In [1,2], the extrapolation dependency of the ionization potential on the number of cluster molecules was found from absorption maxima. The absorption curve portion found there is very strange in the long-wave spectral region. If, as was believed in [1,2], the electron transitions are vertical (proceed at a fixed cluster molecule configuration), the light absorption should be zero at quantum energies lower than the ionization potential.

To explain the spectroscopic data, we employ the polaron model. According to [3], this model yields accurate critical numbers of molecules in the polar cluster as well as dependencies of the ionization potential of negatively charged clusters $(H_2O)_n^-$ and $(NH_3)_n^-$ on n. The model predicts a single stable coupled state for the electron in the cluster for all the values $n > n_c$ in experiments on electron photodetachment. Thus, the photoexcited electron can transit only into a delocalized state. It is of utmost importance that, according to the polaron model, the transitions are allowed energetically if the light quantum energy exceeds the absolute total energy of polaron state in the cluster. According to [3], this energy is significantly lower than the ground state energy and vanishes as the cluster radius tends to R_1, ($R_1 > R_c$, where R_c is the critical size, at which the electron coupled state is possible in the cluster). At $R = R_1$, the electron energy remains finite. As will be shown, these polaron model properties can explain the nonzero

light absorption at energies lower than the ionization potential defined as an energy spacing between the lowest electron state in vacuum and the ground state in the cluster.

In the considered model, the impact of an electromagnetic field with the vector potential **A** on an excessive electron in the cluster is a weak perturbation causing transitions between states. The transition probability $W(q)$ is given by the Fermi formula

$$W(q) = \frac{2\pi}{\hbar} \sum_{k,s,s'} \left| \langle \Psi_{0s} | H' | \Psi_{ks'} \rangle \right|^2 \delta(\epsilon_{ks'} - \epsilon_{0s} - \hbar\omega_q), \quad (1)$$

where Ψ_{0s} is the wavefunction of the cluster and the ground-state electron, $\Psi_{k's'}$ is the wavefunction of the cluster and the electron in delocalized vacuum state with wavenumber **k**, subscripts s and s' indicate sets $(s_1, ..., s_n)$ and $(s'_1, ..., s'_n)$ of cluster quantum states in the ground and excited electron states, respectively, and ϵ_{0s} and $\epsilon_{ks'}$ are energies of the system in states Ψ_{0s} and $\Psi_{ks'}$. In adiabatic approximation, the functions Ψ_{0s} and $\Psi_{ks'}$ are multiplicative,

$$\Psi_{0s} = \psi_0 \chi_s, \quad \Psi_{ks'} = \psi_k \chi_{s'}, \quad (2)$$

where $\psi_0(r)$ and $\psi_k(r)$ are the electron wavefunctions in ground and excited states, respectively.

When calculating (1), we believe that the basic contribution into absorption is given by such transitions, due to which the cluster transits from the polarized state of energy ϵ_{0s} equal to the total energy ϵ_0 of the cluster ground state into a state with zero polarization corresponding to the energy $\epsilon_{ks'} = \epsilon_k$, where $\epsilon_k = k^2/2m$ is the free electron energy in vacuum. The perturbation Hamiltonian in (1) is given by

$$H' = -\frac{e}{m} \mathbf{A}\hat{\mathbf{p}}, \quad \mathbf{A} = \left(\frac{2\hbar n_q}{V \epsilon_\infty \omega_q} \right)^{1/2} \mathbf{e}, \quad (3)$$

where **e** is the polarization vector, n_q is the number of photons with momentum q, V is the system volume, and ϵ_∞ is the high-frequency dielectric constant.

As wavefunctions ψ_k, we choose these functions $\psi_k = V^{-1/2} \exp(i\mathbf{kr})$ of a free electron in vacuum for the photoionization cross section $\sigma_q = (V/n_q c) W_q$, where c is the speed of light. Then, using (2) and (3), we arrive at

$$\sigma_q = \frac{P(\omega_q) e^2 m^{1/2}}{3\sqrt{2}\,\hbar^3 \epsilon_\infty} \frac{1}{\omega_q \bar{c}} (\epsilon_0 + \hbar\omega_q)^{3/2} \times \left| \int \psi_0 \exp(i\mathbf{kr})\, d^3 r \right|^2, \quad (4)$$

where

$$k = \frac{\sqrt{2m(\epsilon_0 + \hbar\omega_q)}}{\hbar}, \quad P(\omega_q) = \sum_{s,s'} \left| \langle \chi_s | \chi_{s'} \rangle \right|^2$$

Wavefunctions ψ_0 in (4) were tabulated in [4] for negatively charged clusters $(H_2O)_n^-$ and $(NH_3)_n^-$ at various n. For states localized inside the cluster, the wavefunction ψ_0 was approximated in [4] as

$$\psi_0(r, R) = \exp\left[-\alpha(R) r\right] \sum_{j=0}^{3} C_j(R) r^j, \quad (5)$$

where $\alpha(R)$ and $C_j(R)$ were tabulated also for various cluster radii. Taking into account the relation between cross section $\sigma(q)$ and absorptivity $I(\omega_q)$, one writes the latter as

$$I(\omega_q) = C \frac{(\hbar\omega_q - |\epsilon_0|)^{3/2}}{\hbar\omega_q} \frac{\alpha_y C_0}{\left[16\alpha_y^2(\mathrm{eV}) + \hbar\omega_q - |\epsilon_0|\right]^4} \left(1 + A + B + C\right), \quad (6)$$

where

$$A = \frac{48\alpha_y^2(\mathrm{eV}) - \hbar\omega_q + |\epsilon_0|}{16\alpha_y^2(\mathrm{eV}) + \hbar\omega_q - |\epsilon_0|} \frac{C_1}{\alpha_y C_0}, \quad B = 652.8 \frac{\tilde{\epsilon}}{\mu}(\mathrm{eV}) \frac{\hbar\omega_q - |\epsilon_0| - 16\alpha_y^2(\mathrm{eV})}{\left[16\alpha_y^2(\mathrm{eV}) + \hbar\omega_q - |\epsilon_0|\right]^2} \frac{C_2}{C_0},$$

$$C = 652.8 \frac{\tilde{\epsilon}}{\mu}(\mathrm{eV}) \frac{160\alpha_y^2(\mathrm{eV})(\hbar\omega_q - |\epsilon_0|) - (\hbar\omega_q - |\epsilon_0|)^2 - 1280\alpha_y^4(\mathrm{eV})}{\left[16\alpha^2(\mathrm{eV}) + \hbar\omega_q - |\epsilon_0|\right]^3} \frac{C_3}{\alpha_y C_0}.$$

Values α_y (designated as α in [4]), C_0, C_1, C_2, and C_3 were tabulated in [4] for various cluster radii. The value C in (6) is independent of that radius, however, in general, C depends on ω_q. The

values that enter C and depend on the absorbed light frequency are the high-frequency dielectric constant $\epsilon_\infty(\omega_q)$ and $P(\omega_q)$. A neglect of the ϵ_∞ dispersion in the frequency range of interest causes an error not exceeding 5%. The value $P(\omega_q)$ at photon energies exceeding the ionization potential depend also weakly on ω_q since the cluster state depends weakly on the wavenumber k gained by the delocalized electron due to photoexcitation. Therefore, in further estimates we neglect the contribution of $\epsilon_\infty(\omega_q)$ and P into the frequency dependency of light absorption.

The threshold frequency, at which the absorption is nonzero, is defined by

$$I(\omega_q) = 0, \tag{7}$$

where $|\epsilon_0|$ is determined by (6) and by the condition

$$\left.\frac{\partial I(\omega_q)}{\partial \omega_q}\right|_{\omega_q=\omega_{\max}} = 0, \tag{8}$$

here $\omega_{\max}$ is the frequency of the absorption $I(\omega_q)$ maximum (see Figs. 1 and 2). The dependency of $\omega_{\max}$ on the number n of cluster molecules was approximated in [2] as

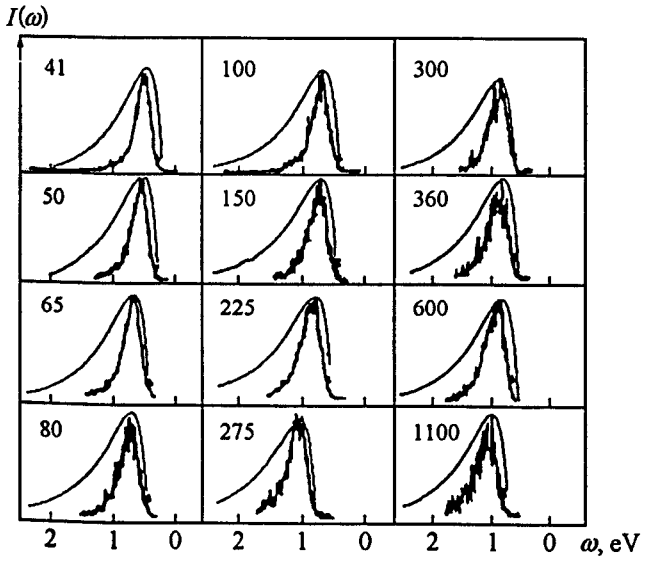

Figure 1. Experimental and calculated (thin lines) light absorption for clusters of ammonia molecules. The number of cluster molecules is shown in each panel.

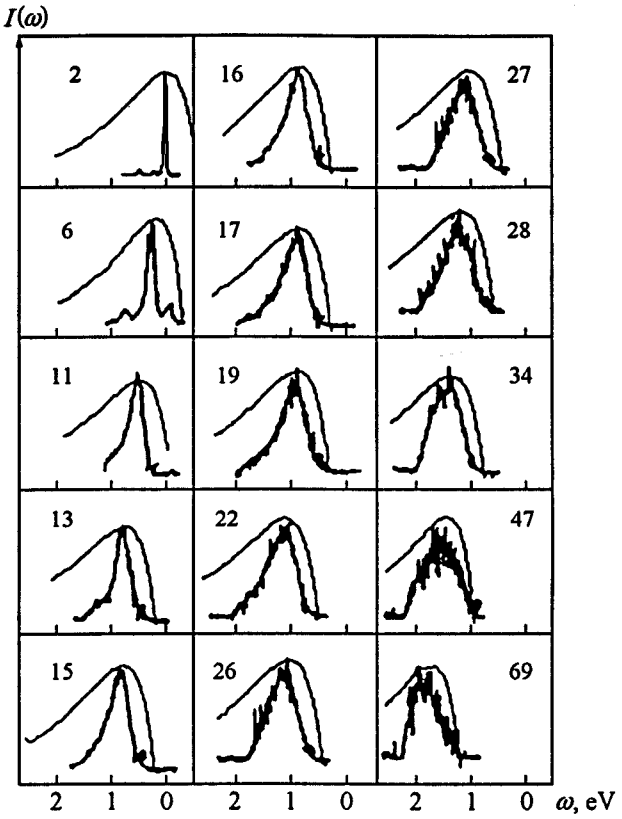

Figure 2. Same as in Fig. 1 for water molecules.

$$\omega_{\max} = \begin{cases} -1.25 + 2.63n^{-1/3}\,(\text{eV}) & \text{for ammonia,} \\ -3.30 + 5.73n^{-1/3}\,(\text{eV}) & \text{for water.} \end{cases} \tag{9}$$

The values $\tilde{\epsilon}$ and μ appearing in (6) are equal respectively to 1.92 and 1.04 for ammonia and 1.81 and 2.44 for water. The relation of the cluster radii given in [4] to the number of cluster molecules has the form

$$R = \begin{cases} 5.836n^{1/3}\,(\text{Å}) & \text{for ammonia,} \\ 5.293n^{1/3}\,(\text{Å}) & \text{for water.} \end{cases} \tag{10}$$

Figures 1 and 2 show the experimental and calculated light absorption in ammonia and water clusters for various numbers of cluster molecules. Notwithstanding a qualitative agreement between the calculation and experiment, the difference is significant at large ω_q, which cannot be explained by the approximations when deriving the formula for $I(\omega_q)$. It follows from (3) that the basic contribution into

the short-wave range is given by Fourier components of the cluster ground state wavefunction Ψ_0 taken from the polaron model. It seems to be insufficiently accurate to represent the electron potential well outside the cluster, since the neglected image forces decrease as r^{-4} at the distance r from the cluster. Notwithstanding its right asymptotics as $r \to \infty$, the wavefunction deviates significantly at distances of order of the cluster size. Thus, correction of the results found calls for more detailed calculations of the electron wavefunction.

As has been indicated, there exists a single coupled state at all n used in the experiments on electron photodetachment from water ($n < 150$) and ammonium ($n < 1100$) clusters. The first coupled excited state in ammonium clusters appears approximately at $n = 2500$. Then the absorption can exhibit some features. However, these can be totally smeared by a wide absorption band caused by the electron transition into vacuum. The data found confirm the hypothesis about an identical nature of electron states in clusters $(NH_3)_n^-$ with $n > 36$, which are seeding states of a solvated electron.

We consider also the widely discussed problem of the transition to the limit $n \to \infty$, that is to a boundless condensed medium. In ammonium clusters, extrapolation of the vertical transition energy as $n \to \infty$ yields the ionization potential of 1.2 eV for an electron solvated in ammonia. This is much lower than the photoabsorption threshold of 1.45 eV measured for such an electron. Therefore, the data interpretation of [1,2] was subject to criticism in [5]. According to [1,2], a dimensional cluster equation, that is the extrapolation of cluster $(NH_3)_n^-$ ionization potentials, linear in $n^{-1/3}$, is applicable beginning from $n_c = 41$, at which the electron–cluster coupled state is possible. In this case, a constructed straight line crosses the ionization potential axis at $I = 1.2$ eV (line *2* in Fig. 3). According to [5], the above equation is applicable only to very large clusters with $n > 150$. Then, one can draw a straight line within experimental error bars so that the crossing point is $I = 1.7$ eV (line *1* in Fig. 3). This level substantially exceeds the experimental value of 1.45 eV [1,2].

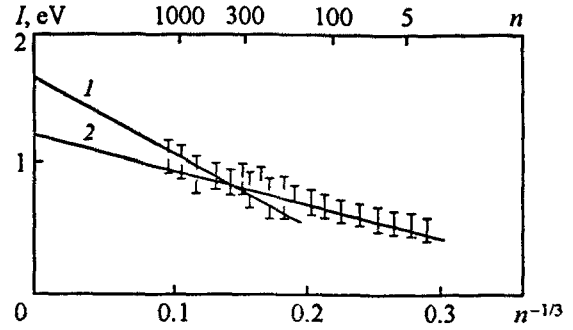

Figure 3. Dependency of the vertical phototransition energy on the cluster size. Bars correspond to experimental data for clusters $(NH_3)_n^-$ of $n = 40-1100$ with experimental errors; straight lines *1* and *2* correspond to the data interpretation according to [5] and [1,2], respectively.

To achieve the latter, it is sufficient to accept that the dimensional cluster equation becomes valid already at $n > 100$.

For our description, both approaches of [1,2] and [5] are not valid. We yield the ionization potential $I = 1.2$ eV for a cluster of infinite radius. However, this result does not mean that it is the ionization potential in volume ammonia since our case differs from the conditions of electron photodetachment from it. Notwithstanding the transition to limit $n \to \infty$, the electron + cluster system is charged negatively. Then, during photoionization, final-state electron wavefunctions correspond exactly to plane waves used by us when calculating the photoionization cross section of a negatively charged cluster. At the electron photodetachment from volume ammonia, the final-state wavefunctions are not plane waves but the waves in the field of a positive Coulomb center due to general electroneutrality of the electron + solvent system. The ionization potential in such a system was calculated earlier in [6] and yields $I = 1.5$ eV for the chosen parameters, which conforms totally to the experiment.

One more problem is further development of the polaron model for clusters of polar molecules. According to this model used by us to explain absorption spectra, the critical cluster radius R_c is a bifurcation point, at which two solutions are generated. One of them, put

into the basis of calculation, corresponds to internal states of a bound electron. This solution is stable since its total energy is negative. Another solution corresponds to surface states whose total energy is positive. Such states are metastable and their contribution into absorption is not considered. The excessive electron binding energy in polar clusters $(H_2O)_n^-$, calculated by the quantum molecular dynamics method [5], shows possibly stable coupled surface states with a negative total energy of the excessive electron. Therefore, the clusters $(H_2O)_n^-$ with $n = 8-32$ are characterized by a single, surface type of coupled states. Only at $n > 32$ internal states of an excessive cluster electron are possible. However, up to $n \leqslant 60$ the internal states are less favorable energetically than surface ones. Thus, at $n \sim 60$ absorption spectra should be reorganized, which has not yet been observed experimentally.

Nevertheless, stable surface states cannot be impossible absolutely. Further detailed calculations based on the polaron model, in particular, including image forces, could yield new facts in favor of the presence of stable electron surface states in clusters with small n, which seems to call for more detailed experiments.

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