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Molecular Dynamics Investigation of the Interaction between IR Radiation and an Ammonia–Water Medium

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Abstract—The frequency dependence of the absorption factor and refractive index of a dispersion water system absorbing ammonia are studied by means of molecular dynamics. It is found that the capture of the ammonia molecules by water clusters is accompanied by a substantial reduction in their ability to absorb IR radiation in the frequency range $0 \leq \omega \leq 3500 \text{ cm}^{-1}$, and the refractive index of the ammonia–water system of clusters is lowered. It is shown that the maxima of the absorption spectra and the refractive index shift to higher frequencies. Starting from a certain concentration of ammonia in the clusters, however, the integral intensity of the spectra increases.

Keywords: ammonia, adsorption, water, clusters.

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INTRODUCTION

$\text{NH}_3(\text{H}_2\text{O})$ complexes were studied experimentally by means of microwave and IR spectroscopy in [1] as well as by ab initio calculations in [2]. The structure and thermodynamic and kinetic properties of $\text{NH}_3(\text{H}_2\text{O})_n$ complexes, where $n = 1$ or 2 , were studied in [3]. The results from [4] illustrate there must be at least four water molecules in a cluster in order to dissociate and form NH_4^+ and OH^- ions. Theoretical data on, among other things, the structure and dissociation energy of systems $\text{NH}_4^+ \cdots (\text{H}_2\text{O})_n \cdots \text{OH}^-$, where $n = 5, 8, 9$, and 21 , were obtained in [5].

The aim of this work was to study the effect of ammonia adsorbed on atmospheric water clusters on the optical properties (absorption and refraction) of disperse systems.

MOLECULAR DYNAMICS MODEL

The interaction between the water molecules in the clusters was described via the nonadditive potential, the additive part of which was the TIP4P potential for water modified in [6] (including the Lennard–Jones and Coulomb interactions) [7], while the nonadditive part took the form of polarization interaction [8]. In this work, we used the flexible molecular models in [9–11], in which the deformation of a molecule is determined by balancing the total potential force

$\mathbf{f}(\mathbf{u}) = -\frac{\partial \mathbf{r}}{\partial \mathbf{u}} \nabla \Phi(\mathbf{r})$ of centrifugal force $-\mu\omega^2$, where μ is reduced mass, u is distance between two atoms, ω is

the vibration frequency, and \mathbf{r} determines the point at which force is applied.

Ammonia–ammonia and ammonia–water atom–atom interactions were described using the Lennard–Jones and Coulomb contributions:

$$\Phi_{\text{aw}}(r) = \varepsilon_{\text{aw}} \left[\left(\frac{r_0}{r_{ij}} \right)^{12} - 2 \left(\frac{r_0}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}}.$$

Parameter values ε_{aw} , r_0 , and q_i for the H and N atoms belonging to molecule NH_3 were taken as 0.038 kcal/mol, 0.28525 nm, 0.333e, and 0.41314 kcal/mol, 0.38171 nm, and $-0.999e$ respectively [12]. The parameters of the Lennard–Jones potential describing ammonia–water interaction were determined using the Lorentz–Berthelot formula,

$$\varepsilon_{\text{aw}} = (\varepsilon_{\text{a}} \varepsilon_{\text{w}})^{1/2}, \quad \sigma_{\text{aw}} = \sigma_{\text{a}} + \sigma_{\text{w}}/2,$$

where ε_{a} , ε_{w} depths of the potential wells, and σ_{a} , σ_{w} are geometrical parameters of the potential for the N and H atoms of the ammonia molecule and the O atom of the water molecule, respectively.

The trajectories of the mass centers of the molecules were determined using the fourth-order Gear method [13]. The time step Δt of integration was 0.2×10^{-16} s. In our initial molecular dynamics calculations with a duration of $4 \times 10^6 \Delta t$, an equilibrium state at $T = 233$ K was prepared for pure water clusters containing no impurity molecules. The $(\text{H}_2\text{O})_{50}$ cluster configuration associated with the 80 ps point in time was then used as the initial configuration for simulating heteroclusters of $(\text{NH}_3)_i(\text{H}_2\text{O})_{50}$, $1 \leq i \leq 6$.

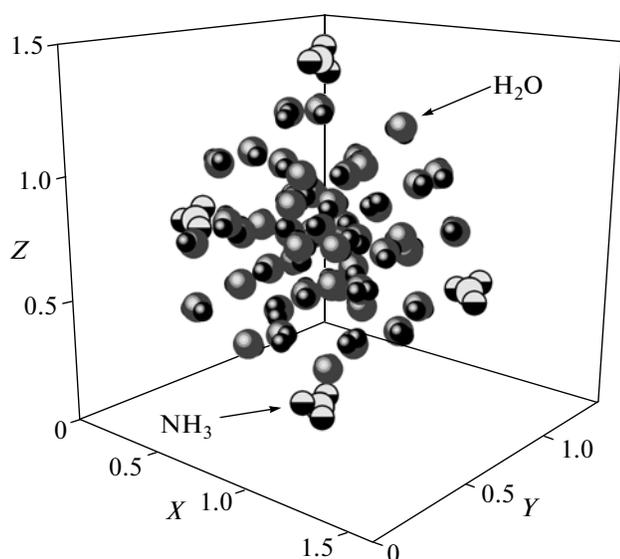


Fig. 1. Configuration of a $(\text{NH}_3)_4(\text{H}_2\text{O})_{50}$ cluster corresponding to a time of 50 ps.

Each added molecule of NH_3 was originally placed in such a way that the minimum distance between the atoms of its molecules and the atoms of the water molecules were ~ 0.6 nm. Initially, the mass centers of the NH_3 molecules were located on axes outside the cluster of water.

The initial orientation of the ammonia molecules was arbitrary. A newly formed cluster was balanced in the time interval of $1.2 \times 10^6 \Delta t$ at $T = 233$ K, and the necessary physical and chemical properties were then calculated at the same temperature for the range of $5 \times 10^6 \Delta t$.

The system of $(\text{NH}_3)_i(\text{H}_2\text{O})_{50}$ clusters was formed in accordance with statistical weights established in the following manner. Let us consider the case of non-polarized light when length l of a molecule's flight is much smaller than the light's wavelength λ . The extinction coefficient (attenuation) h of the incident beam is determined by the Rayleigh formula on the one hand [14], and by the scattering coefficient ρ ($h = (16\pi/3)\rho$) on the other [15], in approximation of a scattering angle of 90° . Since $h = \alpha + \rho$, where α is the absorption factor, we have

$$N = \frac{2\omega^4 (\varepsilon^{1/2} - 1)^2}{3\pi c^4 \alpha} \left(1 - \frac{3}{16\pi}\right),$$

where N is the number of scattering centers in 1 cm^3 . Here, c is speed of light, ε is the dielectric constant of the medium, and ω is frequency of the incident wave.

Systems I and II are formed from clusters of $(\text{H}_2\text{O})_n$ and $(\text{NH}_3)_i(\text{H}_2\text{O})_{50}$, respectively, so that a cluster containing i impurity molecules and n water molecules has the statistical weight

$W_{in} = N_{in}/N_{\Sigma}$, $1 \leq i \leq 6$, $10 \leq n \leq 50$ ($\Delta n = 5$), where N_{in} is the number of clusters with n water molecules and i is the number of NH_3 molecules in 1 cm^3 , $N_{1\Sigma} = \sum_{n=1}^9 N_{i=0,n}$, $N_{2\Sigma} = \sum_{i=1}^6 N_{i,n=50}$. In subsequent calculations, all spectral characteristics were incorporated with statistical weights W_{in} .

The analytical solution of the equations of motion for molecular rotation was found using the Rodrigues–Hamilton parameters [16], and the scheme for integrating the equations of motion in the case of rotation corresponds to the approach proposed by Sonnenschein in [17].

DIELECTRIC PROPERTIES

Static dielectric constant ε_0 was calculated in terms of fluctuations of the total dipole moment of \mathbf{d}_{cl} [18],

$$\varepsilon_0 = 1 + \frac{4\pi}{3VkT} \left[\langle \mathbf{d}_{cl}^2 \rangle - \langle \mathbf{d}_{cl} \rangle^2 \right],$$

where V is the volume of a cluster, and k is the Boltzmann constant.

Relative permittivity $\varepsilon(\omega)$ as a function of frequency ω is the complex quantity $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, for whose determination we use the equation [18, 19]

$$\begin{aligned} \frac{\varepsilon(\omega) - 1}{\varepsilon_0 - 1} &= - \int_0^\infty \exp(-i\omega t) \frac{dF}{dt} dt \\ &= 1 - i\omega \int_0^\infty \exp(-i\omega t) F(t) dt, \end{aligned}$$

where the function $F(t)$ is the normalized autocorrelation function of a cluster's total dipole moment

$$F(t) = \langle \mathbf{d}_{cl}(t) \cdot \mathbf{d}_{cl}(0) \rangle / \langle \mathbf{d}_{cl}^2 \rangle.$$

Refractive index n and the absorption factor of the medium κ are given by [14]

$$n = \left[\frac{\varepsilon' + (\varepsilon'^2 + \varepsilon''^2)^{1/2}}{2} \right]^{1/2}, \quad \kappa = \left[\frac{-\varepsilon' + (\varepsilon'^2 + \varepsilon''^2)^{1/2}}{2} \right]^{1/2}.$$

Factor κ determines the rate of decay of a wave as it propagates in the medium.

RESULTS AND DISCUSSION

The configuration of a $(\text{NH}_3)_4(\text{H}_2\text{O})_{50}$ cluster with a duration of 50 ps is shown in Fig. 1. All of the NH_3 molecules were adsorbed by water clusters in the indicated period of time. A similar pattern was observed for other cases where ammonia was adsorbed by water clusters. The NH_3 molecules tended to orient themselves in such a way that the N atom was closer to the H atom of one of the water molecules. In reality, a water molecule acts as an acceptor during the interaction between ammonia and water.

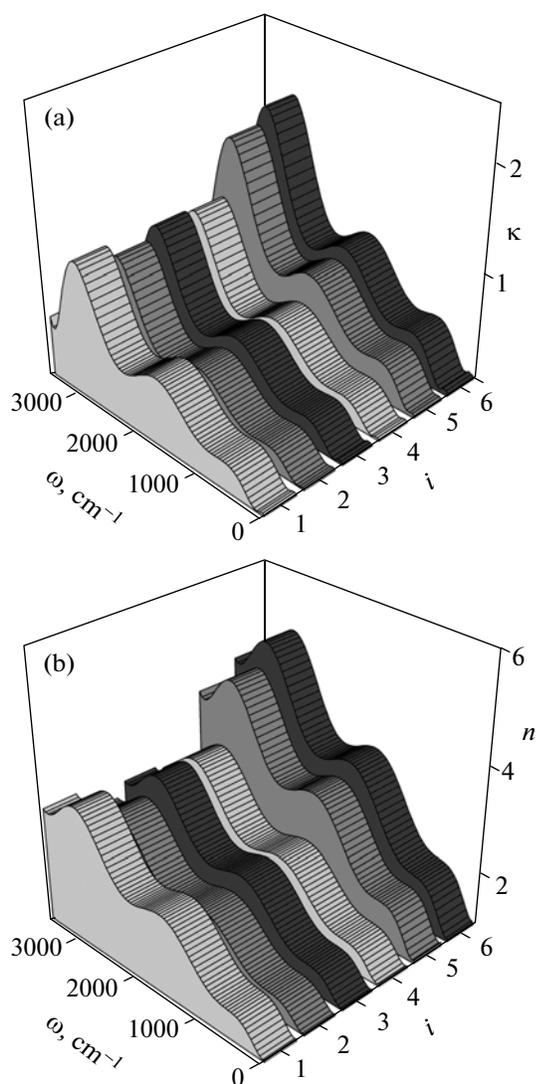


Fig. 2. Frequency dependence of the (a) absorption factors and (b) refractive indices of IR radiation for clusters $(\text{NH}_3)_i(\text{H}_2\text{O})_{50}$, $1 \leq i \leq 6$.

The frequency spectra of absorption factor κ and refractive index n for individual clusters of $(\text{NH}_3)_i(\text{H}_2\text{O})_{50}$ are shown in Fig. 2. When added to a water cluster of four NH_3 molecules, the integrated intensities I_κ of the $\kappa(\omega)$ spectrum change only slightly (within 18%). However, the $(\text{NH}_3)_4(\text{H}_2\text{O})_{50}$ cluster's acquisition of the next two NH_3 molecules raises the intensity of the $\kappa(\omega)$ spectrum considerably. As a result, the ratio of the integrated intensities of the $\kappa(\omega)$ spectrum for clusters with $i = 6$ (where I_κ is the maximum) and $i = 2$ (where I_κ is the minimum) is 1.77. The frequency spectra of refractive index $n(\omega)$ behave this way as one to six ammonia molecules are added to a water cluster. The variation of integrated intensity I_n does not exceed 13% if up to four NH_3 molecules are

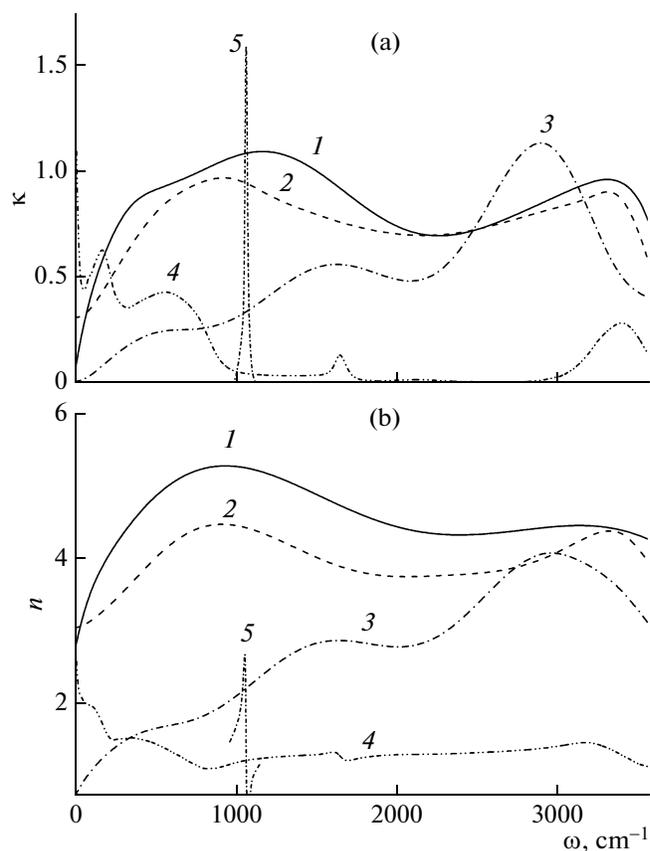


Fig. 3. Frequency dependence of the (a) absorption factors and (b) refractive indices for different systems: (1) cluster $(\text{H}_2\text{O})_{50}$; (2) I; (3) II; (4, 5) experimental data for liquid water [20] and NH_3 cryogenic film [21].

added to the cluster, and the ratio of the extreme intensities $I_{n=6}/I_{n=2}$ is 1.54. For clusters of water adsorbed NH_3 molecules, $n(\omega)$ and the main peaks of the $\kappa(\omega)$ and $n(\omega)$ spectra correspond to frequencies of 2929 and 2971 cm^{-1} , respectively.

The frequency dependence of the medium absorption factor $\kappa(\omega)$ and the refractive index $n(\omega)$ for the $(\text{H}_2\text{O})_{50}$ cluster and systems I and II are shown in Fig. 3, along with the relevant experimental spectra for liquid water [20] and cryogenic film NH_3 [21]. It can be seen that factor κ for the $(\text{H}_2\text{O})_{50}$ cluster and system $(\text{H}_2\text{O})_{n=10-50}$ is higher than for system $(\text{NH}_3)_i(\text{H}_2\text{O})_{50}$ over the range of frequencies. Factor κ determines the rate of decay of the wave as it propagates. The speed of wave damping for all of the investigated frequencies is therefore higher in cluster systems of pure water than in system II. The average (in terms of frequency) value of factor κ for an $(\text{H}_2\text{O})_{50}$ cluster and system I was 0.81 and 0.72, while for system II it was 0.48. At frequencies $\omega > 1100 \text{ cm}^{-1}$, the value of factor κ for cluster systems everywhere has a higher value than for liquid water or cryogenic NH_3 film. The values of refractive index n

for an $(\text{H}_2\text{O})_{50}$ cluster and system I are almost everywhere higher than for system II; i.e., systems of clusters of pure water are optically denser than system II. In addition, the refractive index for system II has a periodically increasing frequency dependence. The index n of cluster systems at frequencies $\omega > 370 \text{ cm}^{-1}$ is higher than the corresponding characteristics of liquid H_2O . Cryogenic film NH_3 exhibits a sharp spike in the characteristics of κ and n near the frequency 1058 cm^{-1} .

CONCLUSIONS

Our modeling showed that close to the surface of a water cluster, NH_3 molecules are adsorbed by the cluster. As result, we obtained stable clusters of $(\text{NH}_3)_i(\text{H}_2\text{O})_{50}$ with i of 1 to 6 molecules. The water clusters thus have a high degree of lyophilicity. Due to the internal flexibility of molecules, the local distortions of the structure related to the adsorption of NH_3 molecules by a water cluster are minimized. Ammonia molecules are added to a cluster due to the formation of new $\text{N} \cdots \text{H}$ hydrogen bonds. The characteristics of their geometrical optics (the absorption factor and the refractive index) reduce its value throughout the considered frequency range after the adsorption of ammonia molecules by water clusters. At low values (up to 7 wt %) of the proportion of ammonia in water clusters, the form and spectra intensity of the absorption factor and the refractive index are weakly dependent on the number of ammonia molecules contained in the clusters. However, a further increase in the proportion of ammonia in the cluster results in a marked rise in the integrated intensity of the spectra.

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