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THERMOPHYSICAL PROPERTIES OF MATERIALS

Molecular-Dynamic Modeling of the Spectral Characteristics of the Ozone–Water Cluster System

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Abstract—The absorption of one to six ozone molecules by the $(H_2O)_{25}$ cluster is studied by the method of molecular dynamics under near-atmospheric conditions. The capture of O_3 molecules by a water cluster produces a decrease in the integrated intensity of IR absorbance, reflectance, and Raman spectra. IR absorbance spectra are highly sensitive to the number of ozone molecules absorbed by a water cluster. The observed photon emission time and the radiation intensity of a dispersed aqueous system with absorbed ozone molecules are appreciably reduced relative to the analogous characteristics of a pure water cluster system.

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INTRODUCTION

The study of the properties of clusters is usually considered as a way of investigating the transition from gas to condensed liquid. In the case of water clusters, it is also possible to estimate the effect of hydration on the dynamics of chemical reactions in a regulated form. For example, the reaction between SO_3 and water vapor consisting of both monomers and clusters is extremely important from the standpoint of heterogeneous atmospheric chemistry [1], as it represents the final stage in SO_2 tropospheric oxidation, which eventually leads to the formation of sulfuric acid aerosols and acid rains. These reactions also result in the depletion of ozone, thus weakening the absorption of incident solar radiation and influencing the Earth's climate.

Atomic oxygen plays an important part in the formation of atmospheric ozone. Oxygen atoms formed in the dissociation of an O_2 molecule either associate again in the presence of another particle M necessary to withdraw the energy from a formed molecule according to the equation

$$O + O + M \rightarrow O_2 + M,$$

or interact with an O_2 molecule also in the presence of another particle and form an ozone molecule as follows:

$$O_2 + O + M \rightarrow O_3 + M.$$

Physically, an ozone molecule is stable, but the decomposition rate of gaseous ozone grows appreciably with an increase in the temperature and amounts of some gases, for example, NO, Cl_2, Br_2 and I_2, and also under the action of different radiations and particle fluxes.

The structure of clusters formed by water and ozone is partly caused by relatively weak van der Waals interactions between H_2O and O_3 molecules. An ozone molecule can not disrupt the strong H bonds between water molecules, so it is highly probable that it will be located near the surface of a cluster and bonded with one or two neighboring H_2O molecules in the network of hydrogen bonds. Quantum chemical calculations also show the possibility of forming an ordinary bond between the oxygen atom of an O_3 molecule and the hydrogen atom of an H_2O molecule [2]. In small water–ozone complexes, the length of this bond can amount to 0.22–0.26 nm; i.e., it proves to be 0.05 nm longer than that in the respective water systems.

The modified time-dependent density functional theory method was used in the calculations of the excitation energy [3] and spectral shifts [4] of O^3–$(H_2O)_n$ complexes, $n = 1$–4. It was found that, at $n = 1$, a water molecule is bonded with an ozone molecule in such a way that the oxygen atom in an H_2O molecule is oriented to the central atom in an O_3 molecule. At $n = 2$, a water dimer and an O_3 molecule form a more stable cyclic structure. At $n = 3$ and 4, a cyclic water trimer (tetramer) adheres to an ozone molecule through the formation of a hydrogen bond. The interaction between a water cluster and an ozone molecule leads to a blue shift in the first and second excitation energies. The IR absorbance, emittance, and reflectance spectra of water clusters and absorbed oxygen molecules were studied by the method of molecular dynamics in [5–8].

The objective of the given work is to study the IR absorbance, emittance, reflectance, and Raman spectra of the system formed by $(H_2O)_{25}$ clusters absorbing one to six ozone molecules.

CALCULATION MODEL

In the present work, we use the new TIP4P water model [9]. The dynamics of a molecular system is realized with the water–water intermolecular interaction potential [9] and the description of the oxygen–oxygen and oxygen–water interactions as the sum of repulsion, dispersion, and Coulomb contributions [10] as follows:

$$\Phi(r_{ij}) = b_i b_j \exp[-(c_i + c_j) r_{ij}] - a_i a_j r_{ij}^{-6} + \frac{q_i q_j}{r_{ij}},$$

where a_i, b_i, and c_i are the parameters of the potential describing these interactions, their values taken from [11]. The electrostatic interactions between O_3 molecules are determined by the charges $q_{\text{cen}} = 0.19e$ and $q_{\text{side}} = -0.095e$ [12] placed at the localization points of the central and side atoms, respectively. The O_{side}–O_{cen}–O_{side} angle in an ozone molecule is equal to 116.8° [13]. The distance between the central and side atoms is $r_{\text{OO}} = 0.1278$ nm. The polarizability of an O_3 molecule α^p (2.85 Å^3) is higher than that of a water molecule (1.49 Å^3) [12, 13].

The study of the absorption of ozone by water clusters was begun with creating the configuration of an equilibrium water cluster surrounded by ozone molecules. The initial equilibrium configurations of water clusters were obtained in independent molecular-dynamic calculations, in which the kinetic energy of molecules in a cluster corresponded to the temperature of 233 K. Initially, the center of a free ozone molecule was placed on one of the coordinate axes at a distance of 0.6–0.7 nm from the center of the nearest water molecule incorporated in a cluster. As a result, each ozone molecule was involved in the molecular interaction field. In this model, the trimming radius of all the interactions was 0.9 nm. A nonlinear O_3 molecule has originally a random orientation. The dielectric properties were determined for two cluster systems: $(O_3)_i(H_2O)_{25}$, $1 \le i \le 6$, and $(H_2O)_n$, where n = 10, 15, 20, ..., 50. The spectra of the system represented the superposition of the spectra of individual clusters. The number of scattering centers was determined by the procedure described below. In the studied systems, the average concentration of each cluster type was 12–13 orders of magnitude less than the Loschmidt number.

The newly formed system was equilibrated on the time interval of $0.6 \times 10^6 \Delta t$, where the time step $\Delta t = 10^{-17}$ c s, and then the required physicochemical properties were calculated on the time interval $2.5 \times 10^6 \Delta t$. The equations describing the motion of the centers of mass of molecules were integrated with the use of the fourth-order Gear method [14]. The equations describing the motion of rotating molecules were solved analytically with the use of the Rodrigues–Hamilton parameters [15], and the scheme of their integration corresponded to the approach suggested by Sonnenschein [16].

DIELECTRIC PROPERTIES

Let us consider the scattering of nonpolarized light when the molecule path length l is much less than the light wavelength λ. The extinction (attenuation) coefficient ξ of an incident ray can be determined both by the Rayleigh formula [17]

$$\xi = \frac{2\omega^4}{3\pi c^4}\frac{(\sqrt{\varepsilon}-1)^2}{N},$$

and through the scattering coefficient ρ by the expression $\left(\xi = \frac{16\pi}{3}\rho\right)$ [18] in the right-angle scattering approximation. Here, N is the concentration of scattering centers, c is the light velocity, ε is the dielectric permittivity of the medium, and ω is the incident wave frequency.

Taking into consideration that $\xi = \alpha + \rho$, where α is the absorption coefficient, we obtain

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

Let us determine the following types of ultradispersed systems

(1) a space filled by water clusters consisting of 10, 15, 20, ..., 50 molecules;

(2) a medium consisting of $(H_2O)_{25}$ clusters with one to six absorbed O_3 molecules.

Let us describe system 2 in such a way that the statistical weight of a cluster containing i impurity molecules and n water molecules can be expressed as follows:

$$W_{in} = \frac{N_{in}}{N_\Sigma}, \quad i = 1\text{–}6, \quad n = 25,$$

where N_{in} is the concentration of clusters with i impurity molecules and 25 water molecules, $N_\Sigma = \sum_{i=1}^{6} N_i$, and i can take values from 1 to 6. Similar weights were used for $(H_2O)_n$ clusters constituting system 1. In this case, $i = 0$, and n takes values from 10 to 50 in steps $\Delta n = 5$, so that the upper summation index is equal to 9. The further calculation of all the spectral characteristics was performed with consideration for the assumed statistical weights W_{in}.

The static dielectric constant ε_0 was calculated through the fluctuations of the total dipole moment [19], and the complex value $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ was determined through the autocorrelation function of the total dipole moment of a cluster [20, 21]. The absorption coefficient α of incident IR radiation can be expressed through the imaginary component of the frequency-dependent dielectric permittivity $\varepsilon(\omega)$ as follows [22]:

$$\alpha(\omega) = 2\frac{\omega}{c}\mathrm{Im}\left[\varepsilon(\omega)^{1/2}\right].$$

The reflection coefficient R is determined as the ratio of the average reflected energy flux to the incident flux. In the case of normal incidence of a flat monochromatic wave, the reflection coefficient is calculated by the formula [17]

$$R = \left|\frac{\sqrt{|\varepsilon_1|} - \sqrt{|\varepsilon_2|}}{\sqrt{|\varepsilon_1|} + \sqrt{|\varepsilon_2|}}\right|^2. \qquad (1)$$

Here, it is assumed that a wave passes from a transparent medium (medium 1) into a medium which can be either transparent or opaque, i.e., absorbing or scattering (medium 2). The lower indexes of the dielectric permittivity in Eq. (1) denote the medium.

In the case of depolarized light, the Raman spectrum $J(\omega)$ is determined as follows [21]:

$$J(\omega) = \frac{\omega}{(\omega_L - \omega)^4}\left(1 - e^{-\hbar\omega/kT}\right)$$
$$\times \mathrm{Re}\int_0^\infty dt e^{i\omega t}\langle \Pi_{xz}(t)\Pi_{xz}(0)\rangle$$

where

$$\Pi(t) \equiv \sum_{j=1}^{N}\left[\boldsymbol{\alpha}_j^p(t) - \left\langle \boldsymbol{\alpha}_j^p\right\rangle\right],$$

$\hbar = h/2\pi$, h is the Planck constant, ω_L is the exciting laser frequency, Π_{xz} is the xz component of the $\Pi(t)$ value, the x axis is directed along the molecular dipole, and xy is the molecular plane.

The frequency dispersion of the dielectric permittivity determines the frequency dependence of dielectric losses $P(\omega)$ according to the equation [18]

$$P = \frac{\varepsilon''\langle E^2\rangle\omega}{4\pi},$$

where $\langle E^2\rangle$ is the average squared intensity of an electrical field, and ω is the frequency of an emitted electromagnetic wave.

CALCULATION RESULTS

The configuration of an $(O_3)_6(H_2O)_{25}$ cluster corresponding to the time moment of 25 ps is shown in Fig. 1. It can be seen that the cluster central part (skeleton) consisting of water molecules has an elongated form. Ozone molecules evenly surround the skeleton formed by water molecules and do not strive to get inside it. The orientation of ozone molecules is caused by the character of their contact with the water skeleton. An ozone molecule is bonded with one or, more rarely, two water molecules. As a rule, the side atoms of O_3 molecules are located more closely to the hydrogen atoms of H_2O molecules. Since the hydrogen atoms are mainly oriented outward from the water skeleton, the central atom of three of six O_3 molecules is oriented outwards. The molecular planes of two O_3 molecules are positioned tangentially to the skeleton, and the central atom of one O_3 molecule is closer to the water skeleton than its side atoms.

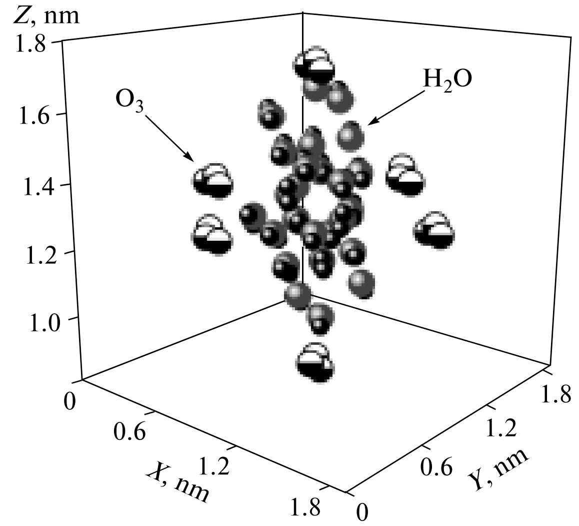

Fig. 1. Configuration of the $(O_3)_6(H_2O)_{25}$ cluster at a time moment of 25 ps.

The IR absorbance spectrum $\alpha(\omega)$ of the dispersed water system is appreciably changed after ozone has been absorbed (Fig. 2). The main peak in the $\alpha(\omega)$ spectrum of the pure water system at a frequency of 843 cm^{-1} is transformed into two peaks corresponding to the frequencies of 690 and 970 cm^{-1}. The location of the first of these peaks coincides with that of the main peak in the IR absorbance spectrum of volumetric water [23], and the second one is positioned close to the peak typical of the atmospheric ozone spectrum $\alpha(\omega)$ obtained by a satellite at a height of 83 km [24]. The absorption of ozone leads to a 14.1% decrease in the integrated intensity of the IR absorbance spectrum of the dispersed water system.

The IR absorbance spectra of individual $(O_3)_i(H_2O)_{25}$ clusters are illustrated in Fig. 3. It can be seen that their shapes and the intensities of peaks are substantially changed with addition of new ozone molecules to a water cluster. The $\alpha(\omega)$ spectra of the clusters forming system 2 have two to four peaks. The integrated intensity I_{tot} of the $\alpha(\omega)$ spectrum is minimal for the $(O_3)_6(H_2O)_{25}$ cluster and maximal for the $(O_3)_4(H_2O)_{25}$ aggregate. The value of I_{tot} of the clusters of system 2 changes within 25.0%, and that of the

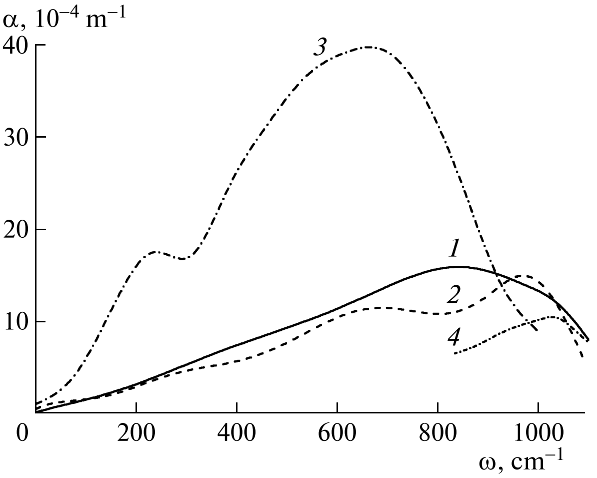

Fig. 2. IR absorbance spectra of (*1*) $(H_2O)_n$, $10 \le n \le 50$, and (2) $(O_3)_i(H_2O)_{25}$ clusters, $1 \le i \le 6$; (*3*) the experimental α(ω) function of volumetric liquid water [23]; and (*4*) experimental spectrum of gaseous O_3 [24].

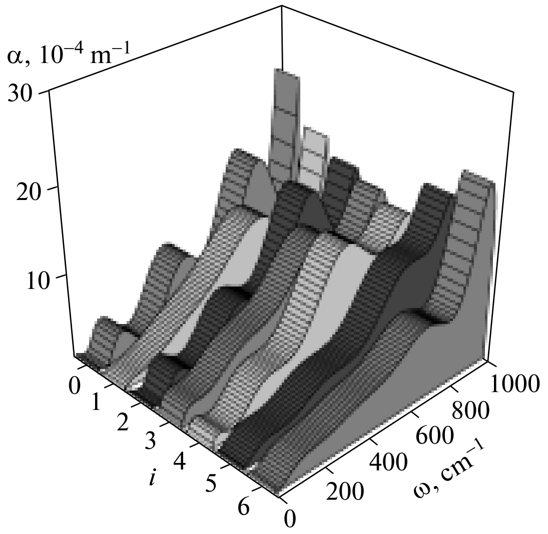

Fig. 3. IR absorbance spectra of $(O_3)_i(H_2O)_{25}$ clusters, $1 \le i \le 6$.

water clusters, which have captured from two to five ozone molecules, becomes ~10.8% higher on average in comparison with I_{tot} of the $(H_2O)_{25}$ cluster.

The IR reflectance spectrum *R*(ω) of system 2 in the form of a histogram is compared with that of the $(H_2O)_{25}$ cluster in Fig. 4. The absorption of O_3 molecules by the $(H_2O)_{25}$ cluster has resulted in a slight ~2.3% decrease in the integral intensity I_R of the reflectance spectrum. In the first half of the *R*(ω) spectrum (up to 500 cm^{-1}) we can observe even a slight ~1.2% increase in the integrated intensity I_R, whereas the frequency interval from 501 to 1000 cm^{-1} is characterized by an appreciable ~5.1% decrease in the value of I_R. The capture of ozone molecules by water clusters increased the number of peaks in the *R*(ω) spectrum of system 2 from eight to ten, but these peaks became less resolvable. The changes observed in the *R*(ω) spectrum of system 2 indicate a slight modification in the structure of the surface of water clusters owing to the absorption of O_3 molecules.

The difficulties in studying the Raman spectra *J*(ω) of ozone are connected with its high sensitivity to photodecomposition. Nevertheless, in [25], the Raman spectrum of gaseous ozone was obtained with the use of a He–Ne laser at a pressure of 0.2–0.4 MPa. It has been established that the basic $^{16}O_3$ transition frequencies ω_1 and ω_2 are 1103.3 and 702.1 cm^{-1}, respectively, and correspond to individual weak spectral lines shown in Fig. 5. The calculated Raman spectra of systems 1 and 2 and also the Raman spectrum of volumetric water [26] are illustrated in the same figure. It can be seen that the absorption of ozone leads to an appreciable change in the Raman spectrum of the dispersed water system. The integrated intensity of the Raman spectrum of system 2 consisting of heterogeneous clusters was reduced by 1.8 times. The peaks at 402, 830, and 1016 cm^{-1} were formed instead of the peaks at 240, 561, and 821 cm^{-1} in the *J*(ω) spectrum of system 1. The main peak of the *J*(ω) spectrum reduced its intensity by 1.9 times and underwent a blue shift from 30 to 65 cm^{-1}. The combination principle consists in that the transitions with the frequencies equal to the combinations (sums or differences) of the frequencies of other transitions can be observed. Taking into account anharmonicity, the weak peak at 830 cm^{-1} can be considered as an overtone of the peak at 402 cm^{-1}. In the anti-Stokes region of the Raman spectrum of volumetric water, the Raman frequency shifts correspond to 53, 143, and 447 cm^{-1} (Fig. 5,

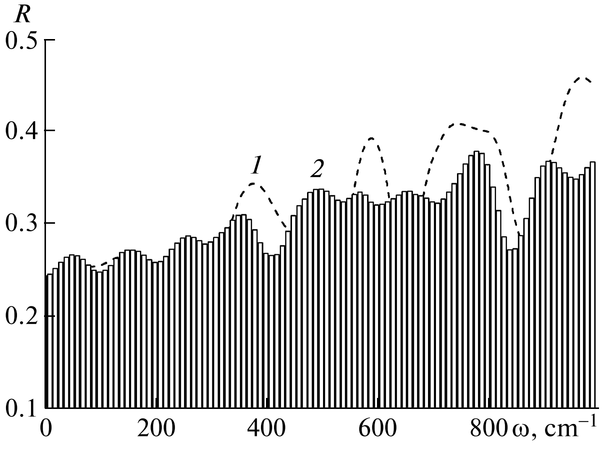

Fig. 4. Reflection coefficients of (*1*) $(H_2O)_{25}$ and (*2*) $(O_3)_i(H_2O)_{25}$ clusters, $1 \le i \le 6$.

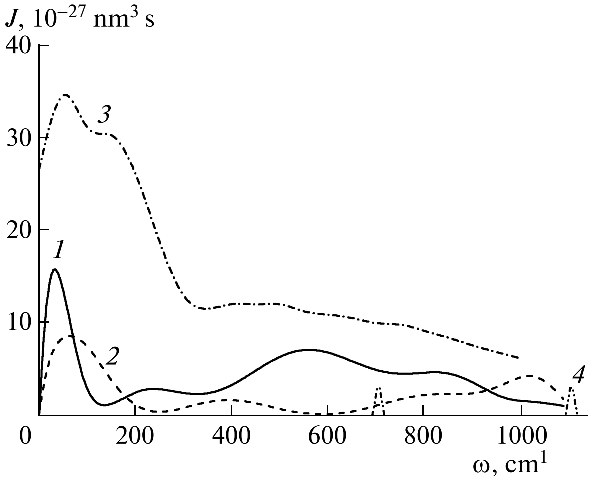

Fig. 5. Raman spectra of (*1*) $(H_2O)_n$, $10 \le n \le 50$, and (*2*) $(O_3)_i(H_2O)_{25}$ clusters, $1 \le i \le 6$; (*3*) liquid water (experimental) [26]; and (*4*) gaseous O_3 (experimental) [25].

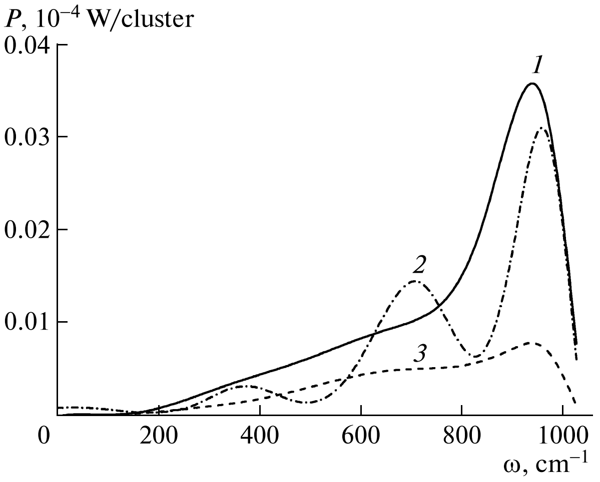

Fig. 6. IR emittance spectra of (*1*) $(H_2O)_n$, $10 \le n \le 50$; (*2*) $(H_2O)_{25}$; and (*3*) $(O_3)_i(H_2O)_{25}$ clusters, $1 \le i \le 6$.

curve *3*). The study of a Raman spectrum makes it possible to determine the lifetime of a system in an excited state, or the radiation time τ. After absorbing a photon, a system transfers to a higher energy level, i.e., becoming excited. In the absence of external actions, an excited system loses its energy in the form of emitted photons, so its lifetime is finite. The time τ is reciprocal to the change in the collective oscillation frequency (mode difference Δω). To estimate the upper boundary of τ, we choose the minimum Δω value, which corresponds to the width of the first Raman spectrum peak at half height $\Delta\omega_1$ equal to 71.4 cm^{-1} for system 1 and 133.3 cm^{-1} for system 2. Hence, the minimum radiation time τ is 0.51 ps for system 1 and 0.25 ps for system 2. Therefore, the absorption of ozone molecules by the dispersed water system reduces appreciably the observed photon emission time. As the lifetime τ_{cl} of the clusters studied in the given work exceeds the time of computational experiments, i.e., the clusters are not decomposed during the calculations, the radiation time τ of $(O_3)_i(H_2O)_{25}$ clusters, where $11 \le i \le 6$, is at least an order of magnitude less than τ_{cl}.

The radiation source power indicates how quickly the intensity of this radiation is changed. The particle-scattered radiation power density determines how clearly these particles are visible. The frequency dependence of the cluster-scattered IR radiation power $P(\omega)$ is shown in Fig. 6. In system 1, the radiation power per cluster (curve *1*) is ~1.3 times higher than the value of P for the $(H_2O)_{25}$ cluster (curve *2*). The $P(\omega)$ spectrum is characterized by a single minimum at 939 cm^{-1} for system 1 and by three minima at 369, 709, and 956 cm^{-1} for the $(H_2O)_{25}$ cluster. The scattered IR radiation power is appreciably reduced in the system of $(H_2)_{25}$ clusters with absorbed ozone molecules (system 2). In this case, the $P(\omega)$ spectrum is also characterized by a single maximum at 942 cm^{-1}. The integrated intensity of the scattered radiation power for system 2 is 3.4 times lower than that for system 1.

CONCLUSIONS

From the standpoint of climatic changes, the most important greenhouse gases are tropospheric water vapor and stratospheric ozone. The latent heat accompanying the condensation and evaporation of water vapor has a significant effect on the energy balance in the atmosphere. Ozone absorbs ultraviolet radiation of the most biologically hazardous ranges. The discovery of "ozone holes" in the stratosphere is spurring in-depth study of atmospheric processes at a molecular level.

In the present work, it is shown that, under near-atmospheric conditions, ozone is easily absorbed by water clusters and retained for several tens of picoseconds. The emission time of the IR radiation energy absorbed by water clusters is much lower than their lifetime. Therefore these clusters take an active part in the processes of absorption, reflection, and scattering of radiation energy. The spectral characteristics of the dispersed water medium are appreciably changed owing to the absorption of ozone. The integrated intensities of the absorbance, reflectance, emittance, and Raman spectra are decreased. Consequently, the greenhouse effect produced by ozone molecules must be reduced at the expense of their absorption by water clusters.

It is difficult to predict the future of the ozone layer because of the fact that Earth is currently entering a new geophysical regime, in which the concentrations of greenhouse gases grow, thus changing the temperature of the stratosphere. The recovery of the ozone concentration is caused by different factors, among which the changes in the temperature and water concentration and the transfer of various atmospheric components should be mentioned. Here, even the concentration of trace components is of great importance.

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