IR Absorption, Reflection, and Emission Spectra of Aqueous Disperse Systems Interacting with Nitric Oxide

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Abstract—IR absorption, reflection, and emission spectra of aqueous disperse systems that absorbed molecules of nitric oxide are calculated. In order to reveal the effect of the absorption of NO molecules on the dielectric properties of water clusters with different sizes, clusters are divided into two groups. The first group consists of clusters containing two to ten water molecules, while the second group contains from 11 to 20 H₂O molecules. Six systems of clusters are studied, e.g., $(H_2O)_n$, and $(NO)_2(H_2O)_n$ with $2 \le n \le 10$ and $11 \le n \le 20$ ranges. An increase in the cluster size in each group leads to the amplification of absorption, reflection, and the power of emission of IR radiation. The doubling of the NO concentration in the disperse system results in weak changes in the absorption of IR radiation, reduces the reflection and decreases the number of electrons participating in the interaction with external IR radiation, as well as significantly lowers the power of thermal radiation emitted by the system.

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INTRODUCTION

Nitrogen oxides are classified as primary contaminants of the atmosphere. In a number of complex chemical reactions proceeding in atmosphere, primary contaminants are transformed into secondary contaminants, many of which are potentially more harmful than their precursors [1]. The majority of these transformations occur in the sunlight. Therefore, secondary contaminants are usually considered to be photochemical contaminants. The best-known secondary photochemical contaminant is ozone O₃. Ozone is formed upon the oxidation (with oxygen) of some organic substances of benzene type in sunlight in the presence of nitrogen oxides, NO_r. In this process, the most significant role is played by nitric oxide NO and nitrogen dioxide NO₂. Upon the formation of ozone in the absence of other competing reactions, predominantly NO is consumed and a certain correlation is established between the NO, NO₂, and O₃ concentrations. Nitrogen oxides scattered in the atmosphere are imparted to chemical transformation that results in the formation of nitric acid HNO₃, which can precipitate in the form of acid rain.

Nitric oxide is a colorless, poisonous, and inflammable gas. Nitrogen dioxide is a nonflammable and strongly poisonous substance, which, at high concentrations, can seriously damage human organism with a delayed effect. The other form of nitrogen oxide is the most reactive nitrate radical NO₃, which is formed in the dark and plays an important role in the chemistry of the night atmosphere. Atmosphere contains another important gaseous components containing nitrogen. Such as nitrous oxide N_2O and ammonium NH_3 . Nitrous oxide is formed upon the degradation of microbiological organisms, while ammonium resulted from agricultural activity. Gaseous N_2O does not react in the troposphere but destroys ozone in the stratosphere. Atmospheric moisture may contain sulfuric, nitric, formic, oxalic, and acetic acids. Ammonium reacts with these acids. Crystals of ammonium sulfate are formed upon the interaction between ammonium and sulfuric anhydride. Aerosol particles are formed due to chemical reactions. The lifetime of aerosols is 6–40 days.

Generally, the amount of nitrogen oxides produced in nature due to bacterial activity, volcano eruption, and lightning discharges exceeds their artificial emission [2]. Artificial emission is associated mainly with the incomplete combustion of hydrocarbon fuel. Nitrogen oxides are mixed in atmosphere with water vapor, thus forming nitric acid. This acid contamination can be spread over the large distances.

NO molecules in atmosphere can be captured by water clusters forming an ultradisperse aerosol. The absorption of nitric oxide molecules by the aqueous dispersion medium should result in changes in the optical characteristics of this medium such as IR absorption, reflection, and emission spectra. The most constructive way of the study of these changes are the methods of computer simulation. Atmospheric water clusters are capable of growing by the addition of other water molecules, as well as molecules of atmospheric gases. The capture of most widespread atmospheric gases (N₂, O₂, and Ar), as well as greenhouse gases (CO₂, N₂O, CH₄, C₂H₂, and C₂H₆), under conditions resembling atmospheric conditions has been studied by the molecular dynamics technique in [3–8].

The goal of this work is to study the absorption of nitric oxide molecules by the ultradisperse aqueous medium to define the infrared (IR) spectra of absorption, reflection, and emission by $(H_2O)_n$, $NO(H_2O)_n$, and $(NO)_2(H_2O)_n$ systems under conditions typical for troposphere.

MOLECULAR DYNAMICS MODEL

The simulation of water clusters was performed using modified interaction potential TIP4P for water and a rigid four-center model of H₂O [9]. The modification of the interaction potential for water deals with the changes in the parameters of the Lennard-Jones part of interaction potential and the location of negative charge. As a result, permanent dipole moment of water molecules becomes equal to its experimental value (1.848 D). The geometry of this molecule corresponds to experimental parameters of a molecule in the gaseous phase as follows: $r_{\rm OH} = 0.09572$ nm and H–O–H angle is equal to 104.5° [10]. Fixed charges ($q_{\rm H} = 0.519e$ and $q_{M} = -1.038e$) are assigned to H atoms and point M on the bisectrix of H–O–H angle at distance of 0.0215 nm from oxygen atom. The charge values and position of point M are chosen so as to reproduce experimental values of dipole and quadruple moments [11, 12], as well as the energy of the dimer and relevant characteristic distances calculated ab initio [13]. Stable short-range order in water clusters is mainly achieved due to short-range Lennard-Jones potential with an interaction center belonging to an oxygen atom. The induced dipole moment of the molecule, which must be accounted for to describe nonadditive polarization energy, is also assigned to point M in addition to electric charge. Standard iteration procedure [9] is used to calculate induced dipole moments at each time step. The accuracy of determining \mathbf{d}_i is set in the 10⁻⁵–10⁻⁴ D range.

Atom-atom interactions in NO- H_2O and NO-NO systems were set by the sum of repulsive, dispersion, and Coulombic contributions

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

where parameters a_i , b_i , and c_i of the potential that describes these interactions were takes from [14]. In the case of NO, electrostatic interactions were determined by charges $q_N = 0.189 e$ and $q_O = -0.189e$ placed in the centers of N and O atoms. The distance between atoms in NO molecule is $r_{NO} = 0.12$ nm. NO molecules are characterized by higher polarizability (1.8 Å³) than water molecule (1.49 Å³) [15].

Based on high-level ab initio calculations, it was shown [16] that the most favorable structure of $(H_2O)_{20}$ cluster is formed based on a pentagonal prism $(U_{tot} = -(9.32 - 9.44) \text{ eV})$ rather than on a dodecahedron (-8.67 eV) or melted cubes (-9.21 eV). Molecular dynamics calculations performed using different empiric potentials so far cannot unambiguously decide what structure of $(H_2O)_{20}$ cluster corresponds to the lowest energy. Internal energy of $(H_2O)_{20}$ cluster in the model presented here is equal to -8.66 eV.

Trajectories of the centers of molecule mass were determined by the fourth-order Gear method [17]. Time step Δt of integration was equal to 10^{-17} s. Initially, in the molecular dynamics calculations with durations of $2 \times 10^6 \Delta t$, the equilibrium state at T = 233 K was established for water clusters containing no impurity molecules. The configuration of the $(H_2O)_{20}$ cluster at time instant 20 ps was used hereafter as the initial configuration for the simulation of $NO(H_2O)_n$ and $(NO)_2(H_2O)_n$ clusters. Each added NO molecule was initially arranged so that the least distance between atoms of this molecule and atoms of water molecule was equal to approximately 0.5 nm. The molecule of nitric oxide was positioned so that its axis coincides with the line connecting the centers of the masses of $(H_2O)_n$ cluster and considered diatomic molecule, the oxygen atom of NO molecule being closer to water cluster than nitrogen atom. The newly formed cluster was equilibrated within time interval of $0.6 \times 10^6 \Delta t$ at T = 233 K and then, at the same temperature, necessary physicochemical parameters were calculated within a time interval of $2.5 \times 10^6 \Delta t$. The analytical solution of motion equations for the rotation of molecules was conducted using Rodrigues–Hamilton parameters [18]; the scheme of integration of motion equations for rotations agreed with the approach proposed by Sonnenschein [19]. Calculations were performed on a quad core Pentium-IV computer with processor clock frequency of 2.67 GHz. About 12 h of computation time were spent for the calculation (lasted $10^6 \Delta t$) of the (NO)₂(H₂O)₂₀ cluster.

DIELECTRIC PROPERTIES

We studied six types of ultradisperse systems combined into two groups. The first group was composed of clusters in which the number of water molecules did not exceed ten; the second group included larger clusters with 11–20 water molecules. Group 1 is formed by systems I, III and IV. System I is represented by water clusters containing two to ten molecules; the system III is composed of NO(H₂O)_n (n = 2, ..., 10) clusters; the system IV contains the set of (NO)₂(H₂O)_n clusters containing the same amount of H₂O molecules. Group 2 is formed by systems II, V and VI, which correspond to systems I, III and IV in composition but contain larger numbers of water molecules. It was assumed that the

cluster containing *i* molecules of nitric oxide and *n* molecules of water has the following statistical weight:

$$W_{in} = \frac{N_{in}}{N_{i\Sigma}}, i = 0, 1, 2, n_1 = 2, ..., 10; n_2 = 11, ..., 20,$$

where N_{in} is the number of clusters with *i* molecules of impurity and *n* molecules of water in 1 cm³, $N_{i\Sigma} = \sum_{n=2(11)}^{10(20)} N_{in}$. The N_{in} value was estimated as follows. Let us consider the case of the scattering of unpolarized light when the free path *l* of molecules is much shorter than wavelength λ . The extinction ratio (attenuation coefficient) *h* of incident light is determined, on one hand, by the Rayleigh formula [20] and, on the other hand, by the scattering coefficient ρ ($h = \frac{16\pi}{3}\rho$) [21] in the scattering approximation at an angle of 90°. Taking into account that $h = \alpha + \rho$, where α is the absorption

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$$N_{in} = \frac{2\omega^4}{3\pi c^4} \frac{(\sqrt{\epsilon}-1)^2}{\alpha} \left(1 - \frac{3}{16\pi}\right)$$

where *c* is the speed of light, ε is the dielectric permittivity of a medium, and ω is the frequency of incident light. The calculation of all spectral characteristics was performed taking into account the accepted statistical weights W_{in} . The procedure of the formation of cluster systems suggests the uniform distribution of these systems and is valid at low numerical density of clusters; because of this, clusters do not interact with one another. The average number of each type of clusters per 1 cm³ in studied systems is 12–13 decimal orders of magnitude smaller than the Loschmidt number.

The total dipole moment \mathbf{d}_{cl} of cluster was calculated by the following formula:

$$\mathbf{d}_{\rm cl}(t) = Z_{+} \sum_{i=1}^{N_{\rm tot}} \mathbf{r}_{i}(t) + Z_{-} \sum_{j=1}^{N_{\rm tot}^{+}} \mathbf{r}_{j}(t),$$

where $\mathbf{r}_i(t)$ is the vector indicating the position of atom *i* or point *M* in time *t*, *Z* is the electric charge in the considered center, index + refers to hydrogen or nitrogen atoms carrying a positive electric charge, index – refers to point *M* or oxygen atoms, N_{tot}^+ and N_{tot}^- are the numbers of positive and negative charges in a cluster.

Dielectric permittivity $\varepsilon(\omega)$ as a function of frequency ω is a complex value $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ and is

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determined by the equation [22, 23]

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

where F(t) is the normalized autocorrelation function of the total dipole moment of the cluster

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

The absorption coefficient α of external IR radiation can be presented via the imaginary part of frequencydependent dielectric permittivity $\epsilon(\omega)$ in the following form [24]:

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

Reflection coefficient R is defined as the ratio of the average flux of energy reflected from the surface to the incident flux. At normal incidence of plane monochromatic wave, the reflection coefficient is given by the formula [20]

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

It is suggested here that the wave passes from a transparent medium (medium 1) to a medium that can be either transparent or opaque, i.e., absorbing or scattering medium (medium 2). Indices at dielectric permittivity in expression (1) denote the medium.

The frequency dependence of dielectric permittivity determines the frequency dependence $P(\omega)$ in accordance with expression [21]

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

where E^2 is the average number of squared strength of electric field and ω is the frequency of emitted electromagnetic wave.

The total number of electrons $N_{\rm el}$ in unit volume of a cluster interacting with external electromagnetic field is set in the following form [20]:

$$N_{\rm el} = \frac{m}{2\pi^2 e^2} \int_0^{\infty} \omega \varepsilon''(\omega) d\omega,$$

where e and m is the charge and mass of electron, respectively.



Fig. 1. Configuration of (NO)₂(H₂O)₂₀ cluster at time moment of 25 ps. Coordinates of molecules are presented in nm.

The motion with frequency lower than 1200 cm⁻¹ complies with the vibrations of molecules, while frequencies higher than 1200 cm⁻¹ describe mainly intramolecular vibrations [25]. As intramolecular vibrations are absent in the considered model, in the analysis of frequency-dependent characteristics, we confine ourselves to the $0 \le \omega \le 1000$ cm⁻¹ frequency range.

CALCULATION RESULTS

The configuration of (NO)₂(H₂O)₂₀ cluster corresponding to time moment 25 ps is shown in Fig. 1. It is seen that, by this time, NO molecules rather closely approach water molecules and do not tend to leave the cluster. Water molecules closest to NO molecules, as a rule, are oriented so that their oxygen atoms are directed toward the N atom (more clear smaller circle), while some hydrogen atoms are oriented toward O atom. However, in each case, (N-)O-H angles formed by neighbor H₂O and NO molecules are smaller than 90°. Usually, these angles are not taken into account upon the formation of hydrogen bond [26]. One NO molecule occupies an intermediate position between two peripheral molecules and the core of $(H_2O)_{20}$ cluster. Thus, all features testify to the absence of hydrogen bond between NO and H₂O molecules.

In order to study the effect of the size of clusters forming disperse system on their ability to absorb IR radiation, we consider two systems of $(H_2O)_n$ clusters, i.e., systems that are formed in $2 \le n \le 10$ (system I) and $11 \le n \le 20$ (system II) size ranges. We will also study the effect of the absorption of NO molecules by these systems on their ability to absorb IR radiation. For this purpose, we consider the following systems of clusters such as $(NO)(H_2O)_n$ (system III) and $(NO)_2(H_2O)_n$ (system IV), where $2 \le n \le 10$, and analogous systems V and VI with $11 \le n \le 20$.

Figure 2 demonstrates the frequency dependences of real and imaginary parts of the dielectric permittivity of systems under consideration. The addition of NO molecules to water clusters leads to an increase in the values of both real and imaginary parts of the dielectric permittivity of disperse systems. The ε' and ε'' values for a system of small clusters appeared to be lower than analogous values characterizing larger clusters. However, the addition of two molecules of nitric oxide to clusters is always accompanied by a decrease in ε' and ε'' values. The ε' values averaged over $0 \le \omega \le 1000 \text{ cm}^{-1}$ interval for systems I–VI are related as 1:3.5:2.4:1.4:3.8:2.6, while the ε " values of these systems are related as 1: 14.0: 10.2: 5.5: 12.9: 10.2. The $\varepsilon'(\omega)$ function of bulk water rapidly decays with increasing ω and, at $\omega > \omega$ 560 cm⁻¹, acquires lower values than corresponding value for system I characterized by the lowest values of the dielectric permittivity. The $\varepsilon''(\omega)$ function of bulk water that decreases with small oscillations decays



Fig. 2. Frequency on dependences of (a) real and (b) imaginary parts of the dielectric permittivity of ultradisperse systems: (1) system I, (2) system II, (3) system III, (4) system IV, (5) system V, (6) system VI, and (7) molecular dynamics calculations for bulk water in (a) TIP4P model [27] and (b) experimental data for liquid water [28].

slower and, at $\omega = 1000 \text{ cm}^{-1}$ still does not achieve the ε'' value corresponding to this frequency for system I.

Frequency dependences of absorption coefficient α of IR radiation for systems I, III, and IV are shown in Fig. 3a; for systems II, V, and VI, in Fig. 3b. The absorption of nitric oxide results in an increase in the integral intensity I_a of the absorption of IR radiation by aqueous disperse system. The ratio of integral intensities of $\alpha(\omega)$ spectra for systems of the first group is equal to 1 : 1.5 : 1.5; for systems of the second group, 1 : 1.5 : 1.4. It is evident that the amount of impurity does not substantially affect the I_a value; a twofold increase in the number of NO molecules in clusters in the first case does not lead to changes in I_a , whereas, in the second case, it only leads to a slight (by factor of 1.1) decrease in the I_a value. The addition of one NO molecule to each cluster shifts the

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Fig. 3. Absorption coefficients of IR radiation for systems: (a) (1) system I, (2) system III, (3) system IV, (4) experimental data for gaseous NO [29], and (b) (1) system II, (2) system V, (3) system VI, and (4) experimental data for bulk water [30].

principal maximum of $\alpha(\omega)$ spectrum toward high frequencies, from 812 cm⁻¹ for system I to 983 cm⁻¹ for system III and from 770 cm⁻¹ for system II to 975 cm⁻¹ for system V. A twofold increase in the number of NO molecules in clusters shifts the principal maximum of $\alpha(\omega)$ spectrum back to low frequencies to 927 cm⁻¹ for system IV and 951 cm⁻¹ for system VI. Note that deformation vibrations of molecules of the gaseous nitric oxide are characterized by weakly pronounced maximum at 807 cm⁻¹ [29]; for liquid water, the principal maximum in the $\alpha(\omega)$ spectrum falls at 700 cm⁻¹ [30].

The $\alpha(\omega)$ spectra of single clusters of systems V and VI are presented in Fig. 4. As a rule, spectra of water clusters that absorb one NO molecule have three or five maxima, except for the $\alpha(\omega)$ spectrum with one peak



Fig. 4. Absorption spectra of IR radiation for clusters: (a) $NO(H_2O)_n$ and (b) $(NO)_2(H_2O)_n$, $11 \le n \le 20$.

for a cluster containing 20 water molecules. The addition of a second NO molecule to clusters makes the pattern of the $\alpha(\omega)$ spectra more uniform with three or four maxima. The ratios of maximum-to-minimum integral intensity of absorption for $\alpha(\omega)$ spectra of systems V and VI are 1.85 and 1.25, respectively.

The reflection of IR radiation by cluster systems also depends on the size of constituent aggregates. The

larger the cluster size in a system, the larger its reflection coefficient R (Fig. 5). The ratio of integral reflection coefficients for systems III and V is 1 : 1.5; for systems IV and VI, 1 : 2.2. The reflection coefficient of a single-type cluster system decreases with increasing number of NO molecules. For example, integral coefficient R decreases by 2.0 and 1.4 times, respectively, when passing from systems III and V with one NO molecule in each cluster to systems IV and VI containing two NO molecules in each aggregate. An increase in coefficient R for systems of larger clusters is caused by the rise in the total reflecting surface area, whereas a decrease of R after absorption of second NO molecules by clusters is attributed to the loosening of clusters and the roughening of their surfaces.

Reflection spectra of single clusters for systems V and VI are shown in Fig. 6. The $R(\omega)$ spectra of each of the system are characterized by a high diversity of relief. The addition of second NO molecules to clusters leads not to the leveling of integral intensities of reflection for single $R(\omega)$ spectra but, on the contrary, to increasing differences between these characteristics. For example, the ratio of maximum-to-minimum integral intensity for $R(\omega)$ spectra of system V is 2.62; for analogous spectra of system VI is 2.93.

Clusters that absorb IR radiation are capable of reemitting. Power P of IR radiation of the systems of small clusters containing NO molecules rapidly decreases (Fig. 7a) so that the ratio of integral intensities of emission power for systems I, III, and IV is equal to 1:0.24 : 0.13. However, when IR radiation is emitted by the systems of larger clusters, the ratio of integral intensities of emission power changes (Fig. 7b). For systems II, V, and VI, this ratio is equal to 1: 5.03: 1.38. The large value of total emission power for system V composed of water clusters with $11 \le n \le 20$ absorbing each one NO molecule is due to the large value of the imaginary part of the dielectric permittivity of this system. This is related to the fact that NO molecule is capable of penetrating inside the cluster and thereby compacting the cluster. When two NO molecules are added to the cluster, at least one of these molecules is usually located on the surface, i.e., it tends to loosen the cluster. The imaginary part of the dielectric permittivity of the cluster decreases, thus lowering power P of emitted IR radiation.

The number of electrons $N_{\rm el}$ in clusters that participate in the interaction with external electromagnetic radiation increases unmonotonously upon the absorption of NO molecules by clusters (Fig. 8). However, when the number of NO molecules in the clusters increases twofold, the number of active electrons reduces. The ratio between the total number of active electrons in clusters of pure water, as well as in clusters containing one or two NO molecules equals 1 : 6.05 : 2.78. In general, the $N_{\rm el}$ function is an increasing function. The (H₂O)₄ cluster has



Fig. 5. Reflection coefficients of cluster systems: (a) III, (b) V, (c) IV, and (d) VI.

the least number of active electrons; the $(NO)_2(H_2O)_{19}$ cluster, the largest number.

CONCLUSIONS

The influence of nitric oxide on the greenhouse effect is hard to determine. This is related to the relatively short residence of this contaminant and its indirect effect on climate. This gas changes the concentrations of major greenhouse gases, such as methane, ozone, and fluorocarbons, due to a number of chemical processes occurring in the troposphere. Short- (about 10 years) and longer-term effects associated with the emission of nitrogen oxides are distinguished. Shortterm effects of the emission of nitrogen oxides are



Fig. 6. Reflection spectra of IR radiation for clusters: (a) NO(H₂O)_n and (b) (NO)₂(H₂O)_n, $11 \le n \le 20$.

explained by the production of ozone in the troposphere whose increase in concentration leads to atmospheric warming. During the next decade and over even longer periods of time, this emission will lead to a reduction in the content of both methane and ozone and, thus, to the cooling of atmosphere.

In this work, it was demonstrated that NO molecules could be captured by water clusters. NO molecules can penetrate the water cluster and be held there for ≈ 25 ps. The detection of nitric oxide in aqueous dispersion



Fig. 7. Frequency dependences $P(\omega)$ of the power of IR radiation for different systems: (a) (1) system I, (2) system III, and (3) system IV: (b) (1) system II, (2) system V, and (3) system VI.

medium is not a simple task due to the absence of strong intermolecular bonds. Reflection and emission spectra depend to a significant extent on the size of clusters composing the system, whereas absorption spectra are more stable with respect to the dispersity of the system. In regard to the greenhouse effect, the main quantitative characteristic is the integral intensity of the $\alpha(\omega)$ -spectrum. However, changes in spectral characteristics related to the absorption of NO molecules involve also the values of characteristic frequencies. For small clusters, the power of IR radiation decreases with an increase in the number of captured NO molecules; for larger clusters, values of this characteristic increases; moreover, initially drastic rise of the emission power caused by the addition of NO molecules is replaced by its fast fall. In this fall, the integral emission power that characterizes the system of pure water clusters with $11 \le n \le 20$ is not achieved. In reflection spectra, the relief of R distributions is also changed, in addi-



Fig. 8. Number of electrons interacting with external electromagnetic radiation in clusters containing *n* water molecules: (1) $(H_2O)_n$, (2) $NO(H_2O)_n$, and (3) $(NO)_2(H_2O)_n$.

tion to integral intensity, depending on the cluster size. In particular, for the system composed of smaller clusters, peaks in the R spectrum turned out to be more resolved. Additionally, the absorption of NO molecules by water clusters is accompanied by an increase in the number of electrons interacting with external IR radiation. In essence, atmospheric moisture acts as an absorbent that cleans Earth's atmosphere from small impurities, e.g., nitric oxide, that impart harmful effect on biosphere. Small impurities, including nitric oxide, noticeably influence the transfer of radiation in troposphere only in atmospheric transparency windows for water vapor and carbon dioxide. However, the role of NO rises upon the formation of the radiation regime of stratosphere.

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