Computer study of absorption of oxygen and ozone molecules by water clusters with Cl^- and Br^-

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Abstract: Infrared absorption and Raman spectra were calculated by using the molecular dynamics method for water clusters with chlorine and bromine ions in a medium of water and either ozone or oxygen molecules. The intensity of IR absorption spectra of clusters with absorbed oxygen increased and that of clusters with absorbed ozone decreased as the number of chlorine ions grew. When Br^- were present in the system the inverse behaviour was observed. An increase in the number of ions weakened the intensity of the Raman spectra when either oxygen or ozone was absorbed; for ozone this weakening was more noticeable. A stronger reduction of the integrated intensity of the Raman spectrum with an increase in the number of Br^- was observed in the presence of ozone molecules in the system. Cl^- ions caused an amplification of the emission power of the IR radiation for both systems in the presence of oxygen and ozone, and Br^- strengthened the emission of IR radiation for systems containing ozone, and weakened it for systems with oxygen molecules.

Key words: absorption, chlorine and bromine ions, IR and Raman spectra, oxygen, ozone, water clusters.

Résumé : Faisant appel à la méthode de la dynamique moléculaire, on a calculé les spectres d’absorption IR et Raman d’agrégats d’eau avec des ions chlorure et bromure dans un milieu aqueux contenant des molécules d’ozone ou d’oxygène. L’intensité des spectres d’absorption IR des agrégats comportant de l’oxygène absorbé augmente alors que celle des agrégats comportant de l’ozone absorbé diminue avec une augmentation du nombre d’ions chlorures. Dans les systèmes comportant des ions bromures, on a observé un comportement inverse de cette amplitude. En présence d’oxygène ou d’ozone absorbé, une augmentation du nombre d’ions chlorures diminue l’intensité des spectres Raman; avec l’ozone, cette diminution est plus importante. Une réduction encore plus forte de l’intensité intégrée du spectre Raman est observée avec une augmentation du nombre d’ions bromures, en présence de molécules d’ozone dans le système. Les ions chlorures provoquent une amplification de la puissance de l’émission du rayonnement IR pour les deux systèmes en présence d’oxygène ou d’ozone et les ions bromures augmentent l’émission du rayonnement IR des systèmes contenant d’ozone alors que les molécules d’oxygène l’affaiblissent.

Mots-clés : absorption, ions chlorures et bromures, spectres IR et Raman, oxygène, ozone, agrégats d’eau.

[Traduit par la Rédaction]

Introduction

The stratospheric ozone (O_3) layer contains 90% of the atmosphere’s ozone and thus is responsible for the majority of the absorption of solar UV radiation. Halogen atoms are released by the degradation of long-lived halocarbon species (CH_3Cl, $CFCl_3$, CH_3Br, etc.), which are emitted either naturally or anthropogenically in the troposphere and then transported into the stratosphere. Halogen atoms (X = F, Cl, Br, or I), which are released in the degradation processes, react quickly with O_3 to form halogen oxides. In addition, halogen atoms can react with O_2 by association reactions to form halogen peroxide radicals. These radicals are unstable and dissociate by the reverse of their formation reaction, therefore, under atmospheric conditions the XO_2 species exist in equilibrium with X and O_2. The stability of XO_2 decreases in the series F > Cl > Br > I. One of the main causes of formation of the ozone hole is the increase in stratospheric chlorine and bromine levels because of the release of man-made chlorofluorocarbons (CFCs) such as CF_3Cl and CF_2Cl_2. The ClO dimer plays a major part in the catalytic destruction of ozone occurring in the polar lower stratosphere during wintertime, which leads to the formation of the ozone hole over Antarctica. On the other hand, BrO is lost by BrCl production. The behaviour of halogen oxides in the stratosphere is strongly influenced by the chemistry of temporary reservoir species containing chlorine and bromine. The combined Br–Cl catalytic cycles are very efficient in depleting ozone, and can therefore cause equal or even larger ozone destruction than chlorine alone in the lower stratosphere. Although there are significant human sources of Br, the contemporary abundance of total stratospheric Br is only ~0.5% of that of Cl.[1] Owing to the much shorter atmospheric lifetimes of iodine-containing compounds (e.g., CH_3I emitted from the oceans) compared with

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their Cl⁻- and Br⁻-containing analogues, iodine does not reach the stratosphere in significant quantities.

In the chemistry of atmospheric particles, halogen activation, which describes the liberation of halogen containing components from sea salt particles, must be considered. These components undergo subsequent photolysis to release exceedingly reactive Cl and Br atoms. Photochemical reactions in clouds occur in the liquid phase with the participation of $HO^{\bullet}$ and $HO_2^{\bullet}$ radicals and other oxidizing components (H_2O_2 or O_3) supplied from the gas phase. Dense small aggregates of molecules are conventionally called clusters. Water clusters are present in clouds and can also exist in a cloudless atmosphere.[2] Atoms and molecules in the atmosphere experience ionization from the action of cosmic rays, from the radiation of radioactive rocks, and from radon in the air itself. The ionization of molecules releases electrons. Chlorine and bromine atoms easily attract free electrons to produce negatively charged ions. Chlorine or bromine ions interact with ozone and split it into oxygen molecules and atoms (possibly into three oxygen atoms). This reaction is facilitated by the presence of water. In other words, the reaction has its highest rate on the surfaces of water clusters. Fast chlorine or bromine ions are the first to reach the surface of water clusters.

The purpose of this work was to study the interaction of halide-containing electrically charged water clusters with ozone and oxygen molecules, and to determine the character of the changes in the dielectric properties of these aggregates that occur as a result of such interactions.

Model

Water is among the most studied of chemicals, owing in part to its ubiquity and its necessity for all life. In addition to these "natural" reasons, water is an interesting compound because it has unique physical properties and is a model hydrogen-bonded liquid. Most of the available water interaction potentials are parameterized to reproduce the thermodynamic and structural properties of bulk water. The polarizable model allows us to examine the changes in the dipole moment of the individual water molecules as a function of their environment. This can provide insight into many body effects in water clusters at a molecular level. Dang and Chang[3] developed a polarizable potential model for water that behaves reasonably well with changes in the environment (i.e., for clusters, liquid, and liquid–vapor). The simulation of water clusters was performed using a modified transferable intermolecular potential 4 points (TIP4P) interaction potential for water and the rigid four-centre model of the H_2O molecule.[4] The modification of the interaction potential for water by Dang and Chang[3] concerned variation of the parameters of the Lennard–Jones part of the potential and localization of negative charge. As a result, the value of the permanent dipole moment for the water molecule is taken to be equal to its experimentally obtained value of 1.848 D. The geometry of this molecule corresponds to the experimentally obtained parameters of the molecule in the gas phase: $r_{\mathrm{OH}} = 0.09572$ nm and angle HOH = 104.5°.[5] Fixed charges ($q_{\mathrm{H}} = 0.519e$ and $q_{\mathrm{M}} = -1.038e$, where e is electronic charge) are assigned to H atoms and to a point M lying on the bisector of angle HOH at a distance of 0.0215 nm from the oxygen atom. The values of the charges and the position of point M are selected so as to reproduce the experimentally obtained values of the dipole and quadrupole moments[6,7] as well as the ab initio calculated energy of the dimer and the typical distances in the dimer.[8]

The total interaction energy of the system can be written as

$$[1] \qquad U_{\mathrm{tot}} = U_{\mathrm{pair}} + U_{\mathrm{pol}}$$

where the pairwise additive part of the potential is the sum of the Lennard–Jones and Coulomb interactions,

$$[2] \qquad U_{\mathrm{pair}} = \sum_i \sum_j \left\{ 4\varepsilon^{(\mathrm{LJ})} \left[\left(\frac{\sigma_{ij}^{(\mathrm{LJ})}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}^{(\mathrm{LJ})}}{\boldsymbol{r}_{ij}} \right)^{6} \right] + \frac{q_i q_j}{\boldsymbol{r}_{ij}} \right\}$$

Here r_{ij} is the distance between sites i and j, q is the charge, and $\sigma^{(\mathrm{LJ})}$ and $\varepsilon^{(\mathrm{LJ})}$ are the Lennard–Jones parameters.

The nonadditive polarization energy is given by

$$[3] \qquad U_{\mathrm{pol}} = -\frac{1}{2} \sum_i \mathbf{d}_i \cdot \mathbf{E}_i$$

where $\mathbf{d}_i$ is the induced dipole moment at the centre of mass of the ith molecule, $\mathbf{E}_i$ is the total electric field at this centre, and $\mathbf{E}_i^0$ is the electric field at site i produced by the fixed charges in the system,

$$[4] \qquad \mathbf{E}_i^0 = \sum_{j \neq i} \frac{q_j \mathbf{r}_{ij}}{r_{ij}^3}$$

where $\mathbf{r}_{ij}$ is the vector from the centre of mass of the jth molecule to the centre of mass of the ith molecule,

$$[5] \qquad \mathbf{d}_i = \alpha_i \mathbf{E}_i$$

where α_i is the atomic polarizability and

$$[6] \qquad \mathbf{E}_i = \mathbf{E}_i^0 + \sum_{j \neq i} \mathbf{T}_{ij} \cdot d_j$$

where $\mathbf{T}_{ij}$ is the dipole tensor,

$$[7] \qquad \mathbf{T}_{ij} = \frac{1}{|r_{ij}|^3} (3\hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij} - \mathbf{1})$$

where $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$ is the unit vector and $\mathbf{1}$ is the 3 × 3 unit tensor.

The stabilization of short-range order in water clusters is largely attained because of the short-range Lennard–Jones potential with the centre of interaction ascribed to the oxygen atom. Related to point M, in addition to the electric charge, is the polarizability, which is required for the description of nonadditive polarization energy. The standard iterative procedure is used at every time step for calculating induced dipole moments.[3] The accuracy of determination of $\mathbf{d}_i$ was in the range 1×10^{-5} to 1×10^{-4} D.

The additive part of the oxygen–oxygen and oxygen–water interactions is described by an atom–atom potential calculated by the Gordon–Kim approximation with the application of the spherical average of electronic densities,[9,10]

$$[8]\qquad \Phi(r_{ij}) = b_i b_j \exp[-(c_i + c_j) r_{ij}] - a_i a_j r_{ij}^{-6} + \frac{q_i q_j}{r_{ij}}$$

where the parameters a_i, b_i, and c_i of the potential describing these interactions were borrowed from Spackman.[9,10] The $q_+ = 0.19e$ positive charge was set on the central atom of the O_3 molecule and the $q_- = -0.095e$ negative charge on each of its side atoms.[11] The O_3 molecule was electrically neutral as a whole. Atoms in the O_2 molecule had no electric charges.

The Coulomb interaction of Cl^- and Br^- ions with water was determined by their electric charge ($q = -1e$, where e is the elementary charge unit). The ion–H_2O non-Coulomb interaction was included as a Lennard–Jones Cl^-–O or Br^-–O interaction with the parameters from refs. 11 and 12. We also considered atom–atom interaction between Cl^- or Br^- ions described by eq. [8] with the parameters from ref. 10. The nonadditive contribution to interactions between water, oxygen, ozone, chlorine, and bromine was caused by polarization and was taken into account in calculations according to eqs. [3]–[7].

Here, we consider flexible models of molecules. Flexibility was created using the procedure developed in terms of Hamilton dynamics in refs. 13 and 14. Let us consider a diatomic molecule and let atoms a and b in it be separated by the distance

$$[9]\qquad R = \| \mathbf{r}_a - \mathbf{r}_b \|$$

where $\mathbf{r}_a$ and $\mathbf{r}_b$ are the vectors that determine the positions of the atoms. Let $\mathbf{v}_a$ and $\mathbf{v}_b$ be the corresponding velocities and let the reduced mass have the form

$$[10]\qquad \mu = \frac{m_a m_b}{m_a + m_b}$$

The size of the molecule consisting of atoms a and b is determined by the equality of the total potential force $\mathbf{f}(\mathbf{R}) = -\frac{\partial \mathbf{r}}{\partial R} \nabla \Phi(\mathbf{r})$ to the centrifugal force $-\mu R \omega^2$, that is,

$$[11]\qquad -\mu R \omega^2 - \mathbf{f}(\mathbf{r}) \frac{\partial \mathbf{r}}{\partial R} = 0$$

where vector $\mathbf{R} = \mathbf{r}_a - \mathbf{r}_b$, $\mathbf{r}$ is the vector determining distance from atoms a or b up to the external centre interacting with them, and $\omega = \| \mathbf{v}_a - \mathbf{v}_b \| / R$ is the angular velocity. The minimization of contributions to the potential energy U of each generalized coordinate yields

$$[12]\qquad \frac{\partial}{\partial q_i} U(\mathbf{r}, \mathbf{v}) = \frac{\partial}{\partial R_i} \left[\frac{1}{2} \mu_i R_i^2 \omega_i^2 + \Phi(\mathbf{r}) \right] = 0$$

This method is applicable to molecules with arbitrary compositions.[15] The use of the flexible model of molecules allowed us to expand the range of frequencies under study.

The simulation of the interaction of $(Cl^-)_i(H_2O)_{50-i}$ or $(Br^-)_i(H_2O)_{50-i}$ clusters with a gas medium containing iH_2O molecules and six O_2 or O_3 molecules began with creating the configuration of the equilibrium cluster of water $(H_2O)_{50}$ with the kinetic energy corresponding to 250 K in the molecular dynamics calculations. The positions of Cl^- or Br^- in the cluster were determined using a system of coordinates fixed at the centre of mass of the cluster. The cluster was approximated by a sphere and water molecules situated most closely to the coordinate axes from this sphere were found. These molecules (their number was from one to six) were displaced outside along the coordinate axes through distances of 0.6–0.7 nm from the former positions of their centres of mass, into which Cl^- or Br^- were introduced. The number of ions equaled the number of displaced molecules. The interaction of the newly formed $(Cl^-)_i(H_2O)_{50-i}$ or $(Br^-)_i(H_2O)_{50-i}$ cluster with water and O_2 or O_3 molecules was studied in an ensemble with an external thermostat[16] at 250 K. The cutoff radius for intermolecular interactions was 0.9 nm in our model. Six O_2 or O_3 molecules were situated predominantly on the lower side of the cluster. The fairly compact arrangement of these molecules facilitated studies of their influence on the behavior of Cl^- or Br^-. The time instant at which ions were incorporated into the water cluster and O_2 (or O_3) molecules approached this aggregate was taken as time $t = 0$. The calculation of spectral characteristics started with time instant $10^5 \Delta t$ (1 ps), where Δt is the integration time step, and the complete duration of the calculation was $2.5 \times 10^6 \Delta t$ time steps.

The Gear method[17] of the fourth order was used for determining the trajectories of the centres of mass of the molecules. The integration time step was 10^{-17} s. The Rodriguez–Hamilton parameters[18] were used to derive the analytical solution of equations of motion for molecular rotation, and the scheme of integration of the equations of motion in the presence of rotations corresponded to the approach suggested by Sonnenschein.[19]

Dielectric propeties

It was assumed that a cluster containing i molecules of oxygen or ozone and n molecules of water has the statistical weight

$$[13]\qquad W_{i,n} = \frac{N_{i,n}}{N_{i,\Sigma}} \qquad i = 1, \ldots, n$$

where $N_{i,n}$ is the number of clusters with i molecules (ions) of impurity and n molecules of water per 1 cm^3 and $N_{i,\Sigma} = \sum_{i=1}^{n} N_{i,n}$. The value of $N_{i,n}$ was estimated as follows. We considered the case of the scattering of nonpolarized light where the molecular free path l is much less than the wavelength of light λ. The extinction (attenuation) coefficient η of the incident beam may be determined on the one hand by the Rayleigh formula[20] and on the other hand in terms of the scattering coefficient ρ[21] in the approximation of the scattering at an angle of 90°. In view of the fact that η is $\alpha + \rho$, where α is the absorbance, we have

$$[14]\qquad N_{i,n} = \frac{2\omega^4}{3\pi c^4} \frac{(\sqrt{\varepsilon} - 1)^2}{\alpha} \left(1 - \frac{3}{16\pi} \right)$$

Here c is the velocity of light, ε is the permittivity of the medium, and ω is the incident wave frequency. The spectral characteristics of the systems were calculated in view of the adopted statistical weights $W_{i,n}$. The procedure of forming the systems of clusters provided for the uniform distribution of these formations and is valid at a low concentration of clusters, which means that they do not interact with one another. The average value of the concentrations of the clusters of each type in the systems under investigation was 12–13 orders of magnitude lower than the Loschmidt number.

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

$$[15] \qquad \mathbf{d}_{\mathrm{cl}}(t) = q_{+}^{(k)} \sum_{i=1}^{N_{\mathrm{tot1}}} \mathbf{r}_i(t) + q_{-}^{(k)} \sum_{j=1}^{N_{\mathrm{tot2}}} \mathbf{r}_j(t)$$

where $\mathbf{r}_i(t)$ is the vector indicating the location of nucleus i or point M at the instant of time t, q is the electric charge located at the centre under consideration, the index k specifies the type of nucleus (or point M), the subscript + relates to the nucleus carrying a positive electric charge, the subscript – to the nucleus carrying a negative charge, and N_{tot1} and N_{tot2} are the numbers of positively and negatively charged nuclei in the cluster, respectively.

The permittivity $\varepsilon(\omega)$ as a function of frequency is given by the complex quantity $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ (where ε' is the real part and ε'' is the imaginary part of permittivity), which was determined using the equation[22,23]

$$[16] \qquad \frac{\varepsilon(\omega) - 1}{\varepsilon - 1} = -\int_0^\infty \exp(-i\omega t) \frac{\mathrm{d}F}{\mathrm{d}t} \mathrm{d}t = 1 - i\omega \int_0^\infty \exp(-i\omega t) F(t) \mathrm{d}t$$

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

$$[17] \qquad F(t) = \frac{\langle \mathbf{d}_{\mathrm{cl}}(t) \cdot \mathbf{d}_{\mathrm{cl}}(0) \rangle}{\langle \mathbf{d}_{\mathrm{cl}}^2 \rangle}$$

The cross section of IR radiation absorption is given by

$$[18] \qquad \sigma(\omega) = \frac{2}{\varepsilon_v c\hbar n} \omega \tanh\left(\frac{\hbar\omega}{2kT}\right) \mathrm{Re} \int_0^\infty \mathrm{d}t e^{i\omega t} \langle \mathbf{d}_{\mathrm{cl}}(t) \cdot \mathbf{d}_{\mathrm{cl}}(0) \rangle$$

where ε_v is the permittivity of the vacuum, $\hbar = h/2\pi$, h is Planck's constant, and n is the refractive index.

The Raman and IR spectra of the clusters were calculated via the autocorrelation functions of polarizability and dipole moment, respectively. A polar molecule is characterized by a permanent (gas phase) dipole moment $\mathbf{d}_{i,0}$ and polarizability tensor $\boldsymbol{\alpha}_{i,0}$. Interaction with neighbouring molecules creates the induced dipole moment and polarizability of molecule i. Each model molecule was treated as a polarizable point dipole situated in the centre of mass of the molecule. The $\mathbf{d}_i$ dipole moment of molecule i and its polarizability α_i are related because of molecule interactions with the environment.[24]

$$[19] \qquad \mathbf{d}_i = \mathbf{d}_{i,0} + \boldsymbol{\alpha}_{i,0} \sum_{j \neq 1} \mathbf{T}_{ij} \mathbf{d}_j$$

$$[20] \qquad \boldsymbol{\alpha}_i = \boldsymbol{\alpha}_{i,0} + \boldsymbol{\alpha}_{i,0} \sum_{j \neq 1} \mathbf{T}_{ij} \boldsymbol{\alpha}_j$$

We used the anisotropic gas-phase polarizability tensor $\boldsymbol{\alpha}_{xx,yy,zz} = \{1.495, 1.626, 1.286\}$ Å^3 for the water molecule.[24] O_3 and O_2 molecules were characterized by the isotropic experimental polarizability values 2.85 and 0.793 Å^3, respectively.[25] The atomic polarizabilities for Cl^- (3.25 Å^3) and Br^- (3.1 Å^3) were taken from ref. 25.

Equations [19] and [20] for $\mathbf{d}_i$ and $\boldsymbol{\alpha}$ were solved by inverting the matrix and using the $\mathbf{d}_{i,0}$ and $\mathbf{a}_{i,0}$ values on the right-hand side.

For depolarized light, the Raman spectrum is given by the equation[24]

$$[21] \qquad J(\omega) = \frac{\omega}{(\omega_{\mathrm{L}} - \omega)^4} (1 - \mathrm{e}^{-\hbar\omega/kT}) \mathrm{Re} \int_0^\infty \mathrm{d}t e^{i\omega t} \langle \Pi_{xz}(t) \Pi_{xz}(0) \rangle$$

where

$$[22] \qquad \Pi(t) \equiv \sum_{j=1}^{N} [\boldsymbol{\alpha}_j(t) - \langle \boldsymbol{\alpha}_j \rangle]$$

where ω_{L} is the exciting laser frequency, Π_{xz} is the xz component of $\Pi(t)$, the x axis is directed along the molecular dipole, and xy is the molecular plane. Simulations were performed for ω_{L} = 19 436.3 cm^{-1} (the argon laser green line, λ = 514.5 nm).

In liquid water the interaction of Cl^- and Br^- with H_2O molecules is limited to the electrostatic attraction of water dipoles to anions. In a small water cluster Cl^- and Br^- experience mutual repulsion and cannot be held close to water molecules for long. We performed calculations for six $(Cl^-)_i(H_2O)_{50-i}$ + iH_2O + $6O_2$, systems and six $(Cl^-)_i(H_2O)_{50-i}$ + iH_2O + $6O_3$ systems, with i = 1–6. The same calculations were carried out for the corresponding systems containing Br^-. Systems with i = 1–6 are denoted by I–VI in the presence of oxygen and by VII–XII in the presence of ozone. We put one stroke at the number of the system containing Cl^- and two strokes at the system number including Br^-. The criterion for the addition of O_3 or O_2 molecules to a water cluster was the establishment of $r_{\mathrm{o-o}} \leq$ 0.35 nm distances.

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

$$[23] \qquad P = \frac{\varepsilon'' < E^2 > \omega}{4\pi}$$

where $< E^2 >$ is the average value of the square of the electric field strength and ω is the frequency of the emitted electromagnetic wave.

Motions with a frequency of <1200 cm^{-1} correspond to the liberation of molecules and those with a frequency >1200 cm^{-1} largely describe intramolecular vibrations.[26]

Results and discussion

Chlorine-containing systems

Because of Coulomb repulsion from negatively charged oxygen ions and mutual repulsion, the Cl^- in $(Cl^-)_i(H_2O)_{50-i}$ clusters rushed to the outside of the cluster. The ions leaving a cluster pushed water molecules apart. This and the interaction with the environment molecules (H_2O and either O_2 or O_3) heated the $(Cl^-)_i(H_2O)_{50-i}$ + iH_2O + $6O_3$ (or $6O_2$) system.

The strongest heating, to 311 K (at time $t \sim 3$ ps), was observed when the cluster of water with six chlorine atoms was surrounded by O_3 molecules. The algorithm that we used allowed for the decomposition of O_3 molecules with energies of 1.3 eV or higher. This energy is sufficient for splitting an ozone molecule surrounded by water molecules. However, in reality there was no decomposition of ozone. As a rule, in 2 ps, that is by the time that $t = 5$ ps, the system was cooled because of velocity scaling and reached its initial temperature of ~250 K. Two Cl^- leave the $(Cl^-)_6(H_2O)_{44}$ cluster in both O_2- and O_3-containing systems by the time $t = 1.2$ ps (Fig. 1). One of the Cl^- hit an O_2 molecule (Fig. 1A). In the same system with ozone, two ions directly interacted with O_3 molecules (one of these ions interacted with two O_3 molecules at once), one ion was “bound" to a water molecule, and one ion was almost free (Fig. 1B). By $t = 2.8$ ps all Cl^- ions had left the cluster and, conversely, O_3 molecules had approached it. Clusters with four and two Cl^- lost these ions in 2.8 and 2.2 ps, respectively. A similar interaction picture was observed when O_2 rather than O_3 molecules approached the cluster. The system was then free of ions in 2.8 ps (six Cl^-), 2.4 ps (four Cl^-), and 2.2 ps (two Cl^-).

The IR absorption spectra are determined by the behaviour of the autocorrelation function of the total $\mathbf{d}_{cl}$ of a cluster. When O_2 molecules without permanent dipole moments are added to a water cluster, they weakly influence the $\mathbf{d}_{cl}$ value determined by the aqueous component of the cluster. For this reason, the perturbation force introduced by Cl^- is approximately proportional to the number of ions (N_{Cl^-}). The integral intensities of the IR absorption spectra (I_{tot}s) therefore grow as N_{Cl^-} increases (Fig. 2A). The opposite situation arises if O_3 molecules are absorbed. When O_3 molecules, whose permanent dipole moment (0.12 D) is lower than that of water, are added to a cluster they create additional “beats” during the evolution of the $\mathbf{d}_{cl}$ value.

The action of Cl^- on the cluster strengthens these oscillations with different frequencies and phases. The larger the number of Cl^- in the cluster, the stronger the beats created by the O_3 molecules. As a result, the ability of the system to absorb IR radiation decreases (I_{tot} decreases) as the number of ions increases (Fig. 2B). The I_{tot} values for systems I′–VI′ increase nonmonotonically and those for systems VII′–XII′ decrease as the number of Cl^- grows. The I_{tot} ratios are 1:0.80:1.22:1.10:2.83:1.83 for systems I′–VI′ and 1:1.04:0.86:0.79:0.99:0.94 for systems VII′–XII′. In all cases the absorption peak is in the vicinity of the frequency $\omega = 960 \pm 20$ cm^{-1}. The main absorption of liquid water is observed at 690 cm^{-1},[27] and that of ozone–oxygen gas mixtures in the vicinity of 996 cm^{-1}.[28]

The Raman spectra of aqueous systems containing oxygen or ozone are differ more than the IR spectra (Fig. 3). The Rayleigh line at $\omega = 0$ is excluded from the spectra. The positions of the first peaks coincide (26 cm^{-1}), but there is no correspondence between the other peaks. In addition, the integral intensities of Raman spectra are noticeably higher with oxygen than with ozone in aqueous systems. The Raman spectrum for liquid water is characterized by low-frequency peaks at 60 cm^{-1} as well as by a peak near 170 cm^{-1}.[29] The peak at 60 cm^{-1} is caused by the bending of hydrogen bonds between water molecules; the peak at

Fig. 1. Configurations of systems $(Cl^-)_6(H_2O)_{44}$+ $6H_2O$+ 6X at time $t = 1.2$ ps. (A) X = O_2. (B) X = O_3. Coordinates of the molecules are presented in nm.

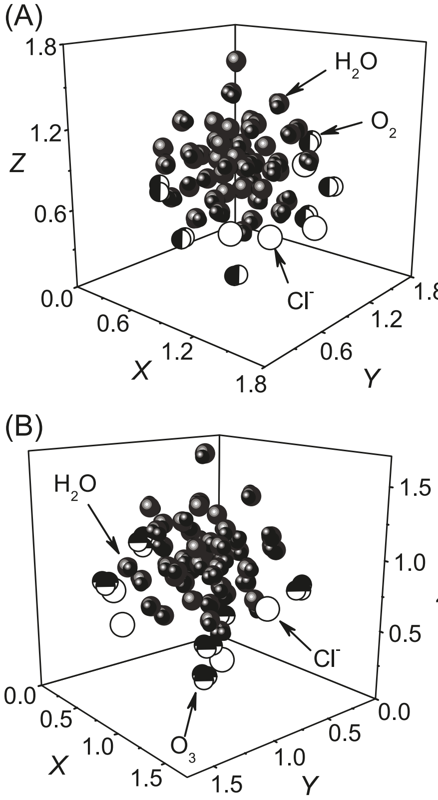


Fig. 2. IR absorption spectra of systems with (A) oxygen and (B) ozone: (1) systems I′ and VII′, (2) III′ and IX′, (3) VI′ and XII′, (4) $\sigma(\omega)$ function of bulk liquid water, experimental,[27] and (4′) experimental spectrum of an O_2 + O_3 mixture of gases.[28]

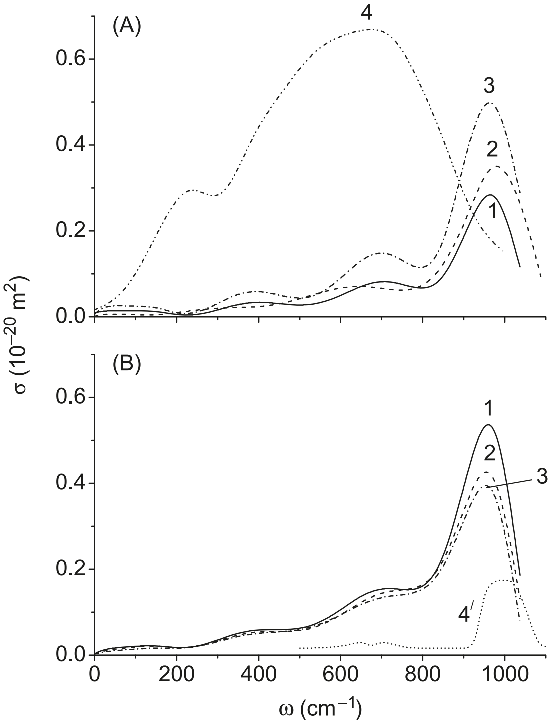
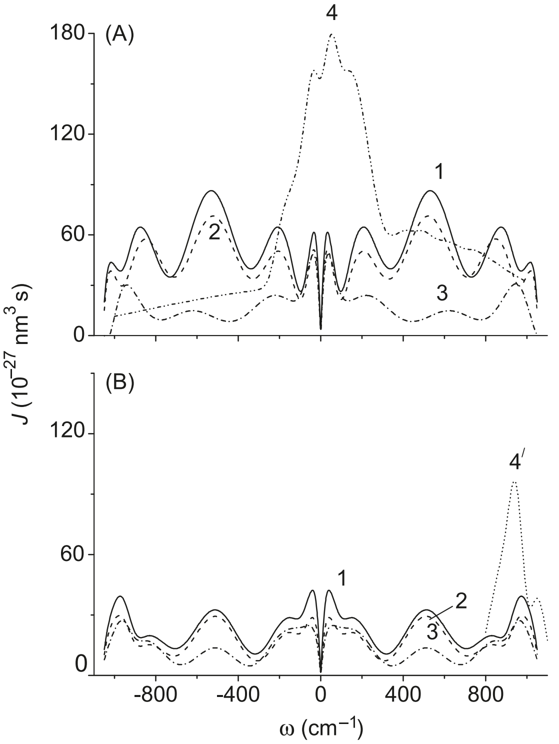


Fig. 3. Raman spectra of systems with (A) oxygen and (B) ozone: (1) systems I′ and VII′, (2) III′ and IX′, (3) VI′ and XII′, (4) liquid water experimental,[29] and (4’) a solution of OClO in water, experimental.[30]



170 cm^{-1} appears because of bond stretching.[24] The position of the newly formed last peak at 950 cm^{-1} in the spectrum of the system with six O_2 molecules and six Cl^- is close to the position of the peak in the Raman spectrum of an aqueous solution of chlorine dioxide (945 cm^{-1}) determined experimentally.[30] The peak observed in femtosecond measurements of a solution of OClO in water was assigned to a fundamental transition to a new energy level with symmetrical dilatation of the OClO molecule.

A study of the photolysis of OClO in aqueous solution showed the possibility of separation of dielectric relaxation related to solvent (water) libration modes and mechanical solvation caused by low-frequency translational motion.[31] The mechanical response of a solvent is usually provided by one or two molecules in its first solvation shell. According to the computer simulation results, 80% of water solvation that follows OClO photoexcitation occurred during a 2×10^{-14} s time interval, whereas the remaining 20% of the response was diffusive in nature and could be observed on a picosecond time scale.[31]

Two characteristic times can also be identified for excitation related to the removal of Cl^- from a water cluster. A short time interval (~3 ps) corresponds to the excitation or interaction of ions with water and O_3 (or O_2) molecules. The dielectric relaxation interval is ~10 ps. During this time, the cluster “forgets” the value and direction of its dipole moment at time $t = 0$. The dissociation of the free O_3 molecule (in the vacuum) usually occurs when energy of 4–5.5 eV is imparted to it. Chlorine ions moving out of the cluster do not possess such energy. For this reason, we did not observe the decomposition of ozone molecules.

As the strength and duration of perturbation caused by the “bombardment” of molecules (H_2O and O_3 or O_2) by Cl^- increased, the integral intensity of the IR absorption spectrum decreased in the presence of ozone and increased with the addition of oxygen. The main absorption frequency remained constant. The Raman spectra substantially changed their shape and intensity when absorbed oxygen was replaced with ozone. Irrespective of the number of Cl^- initially contained in a water cluster and the molecules it absorbs (O_3 or O_2), the main Raman spectrum frequency remains unchanged. The absorption of ozone causes a more rapid decrease in the intensity of Raman spectra compared with the absorption of oxygen.

IR emission $P(\omega)$ spectra for oxygen-containing systems are characterized by the presence of a principal band in the $800 \le \omega \le 1000$ cm^{-1} frequency range (Fig. 4A). The integral intensity (I_{rad}) of the emission spectra of the systems under consideration increased significantly in the presence of Cl^-. The ratio of I_{rad} values for the $P(\omega)$ spectra of the $(O_2)_6(H_2O)_{50}$ cluster and systems II′, IV′, and VI′ is 1:1.45:1.09:1.70. The intensity of IR radiation emission by the $(O_3)_6(H_2O)_{50}$ cluster increases as a result of the action of chlorine ions (Fig. 4A). The ratio of I_{rad} in the $P(\omega)$ spectra of the $(O_3)_6(H_2O)_{50}$ cluster and systems VIII′, X′, and XII′ is 1:1.34:1.16:1.07. In the presence of ions, Cl^- displacement of the main maximum of the $P(\omega)$ spectrum in the area of low frequencies occurs more strongly for the systems containing oxygen. The increase in the number of Cl^- acting on the cluster results in a better resolution of the second and third peaks of the $P(\omega)$ spectrum.

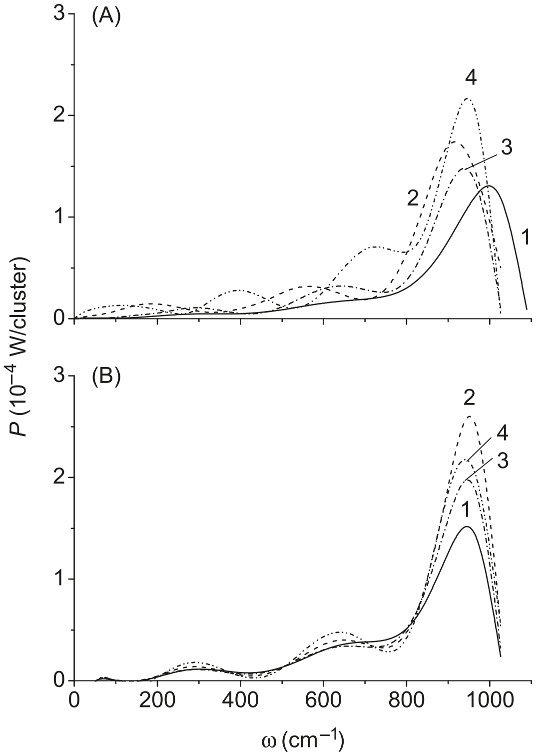
Bromine-containing systems

Differences in the behaviour of Br^- in water clusters, when interacting with O_2 or O_3 molecules, can appear because of their greater weight than that of Cl^- ($m_{\text{Br}}/m_{\text{Cl}} = 2.25$). Configurations of the $6Br^-(H_2O)_{44}$+ $6H_2O$ + 6X cluster systems, obtained up to t = 25 ps, are shown in Fig. 5. Here, X refers to O_2 molecules (Fig. 5A) or O_3 molecules (Fig. 5B). In both cases six free water molecules have joined the $6Br^-(H_2O)_{44}$ cluster. Three of six Br^- have abandoned the cluster in the presence of oxygen in the system. One of these ions is depicted in the bottom part of Fig. 5A. Three O_2 molecules also evaporated with the left ions that left the cluster, while three other molecules of oxygen joined the cluster. The effect of the presence of ozone molecules produced a different result. All six O_3 molecules were adsorbed by cluster. Thus, six Br^- have left the cluster surface, but they have are not at such a great distance that we could consider them as evaporated ones. We consider ions or molecules for which non-Coulomb interaction with other molecules vanishes at a distance of 0.9 nm as evaporated ones. These types of ions or molecules do not come back to the cluster.

Frequencies and intensities of normal vibrations are defined by the weight and kind of atoms, the bonding force, and the spatial arrangement of the atoms (lengths and corners of the bond). Absorbed ions change the cluster structure and influence the intensity of the IR spectrum and to a smaller degree the intensity of the Raman spectrum.

Absorption IR spectra of some systems containing bromine are depicted in Fig. 6. The addition of six O_2 molecules

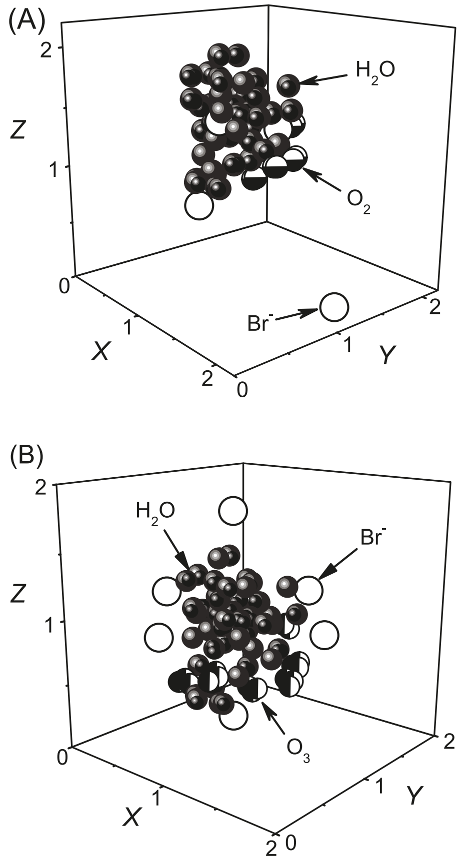
Fig. 4. IR emission spectra of systems $(Cl^-)_i(H_2O)_{50-i} + iH_2O + 6X$ for (A) X = O_2 and (B) X = O_3. (1) $i = 2$, (2) $i = 4$, (3) $i = 6$, (4) the $P(\omega)$ function of the $(O_3)_6(H_2O)_{50}$ cluster.



to the $(H_2O)_{50}$ cluster resulted in an increase of the integrated I_{tot} of IR radiation absorption by a factor of 2.3. However, if a water cluster initially absorbed Br^- ions (at the equivalent desorption of water molecules), then such an amplification of I_{tot} value was not observed, and the I_{tot} magnitude in the presence of four or more Br^- and the absorption of oxygen, decreases. The position of the main peak of the IR spectrum of the dispersed water system with molecular oxygen did not change, and the next highest intensity peak is deformed into a shoulder. The location of the basic peak shifted (by ~100 cm^{-1}) in the of low-frequency area with respect to the position of the main peak of an experimental IR spectrum of liquid bulk water.[27] Localization of the minimum between two peaks of the $\sigma(\omega)$ spectra of the cluster systems falls within an interval of the maximal intensity of an experimental IR spectrum of gaseous bromine hydride,[32] and the fast rise in spectrum intensity of the systems under consideration corresponds to the position of the main maximum of an experimental IR spectrum of a gaseous $O_2 + O_3$ mix.[28]

Opposite transformations of the $\sigma(\omega)$ spectrum occur with a change in the number of Br^- in the cluster with ozone present in the system. The addition of O_3 molecules to the cluster gives a reduction in the I_{tot} magnitude by a factor of 7.3. This decrease is less observed with the growth of the number of Br^- in the cluster. In other words, adsorption of ozone follows the increase of the I_{tot} values if the water cluster consistently attaches Br^-. Therefore, with two Br^- the intensity of the IR spectrum on adsorption of ozone decreases by a factor of 2.1, and when four Br^- are in the cluster the I_{tot} magnitude is reduced by only a factor of 1.07. The increase of intensity of the $\sigma(\omega)$ spectra stops when the number of Br^- ions exceeds four.

Fig. 5. Configurations of the systems $(Br^-)_i(H_2O)_{44} + 6H_2O + 6X$ corresponding to time (t) = 25 ps: (A) X = O_2 and (B) X = O_3. Coordinates of the molecules are presented in nanometers.



The position of the main peak of the IR spectrum hardly changes and approximately corresponds to the frequency 3300 cm^{-1} during the change of the number of Br^- within a cluster. Here (as well as in the presence of oxygen in the system), a red shift of the position of the main maximum of the spectrum concerning localization of the basic peak of the experimental IR spectrum of liquid water was observed. The minimum dividing peak of the $\sigma(\omega)$ spectra of the cluster systems falls into an area of the greatest intensity of the IR spectrum of gaseous bromine hydride. The fast increase in intensities of the $\sigma(\omega)$ spectra of these systems occurs in the frequency range where the peak of the IR spectrum of gaseous ozone[33] is located.

Nonpolar O_2 molecules create a “dilution” effect owing to the decrease in the total dipole moment magnitude. The Br^- perturb an internal electric field of the cluster, accelerating the attenuation of the autocorrelation function of $\mathbf{d}_{cl}$ magnitude. As a result the intensity of the IR spectrum decreases with an increase in the number of bromine ions. The grouped polar O_3 molecules create a poorly varying electric field that orders the dipole moments of the water molecules. As a result the $\mathbf{d}_{cl}$ magnitude is increased, and the intensity of the IR spectrum grows with the increase in the number of Br^- in the system. Amplification of the perturbation owing to the addition to the cluster of more than

Fig. 6. IR absorption spectra for systems $(Br^-)_i(H_2O)_{50-i} + iH_2O + 6X$: (A) X = O_2 and (B) X = O_3. (1) $i = 0$. (2) $i = 2$. (3) $i = 4$. (4) $i = 6$. For (A): (5) the $\sigma(\omega)$ function of bulk liquid water, experiment;[27] (6) experimental spectrum of an $O_2 + O_3$ mixture of gases;[28] and (7) $\sigma(\omega)$ of gaseous HBR, experiment.[32] For (B): (5) the $\sigma(\omega)$ function of the $(H_2O)_{50}$ cluster and (6) the experimental spectrum of gaseous O_3.[33]

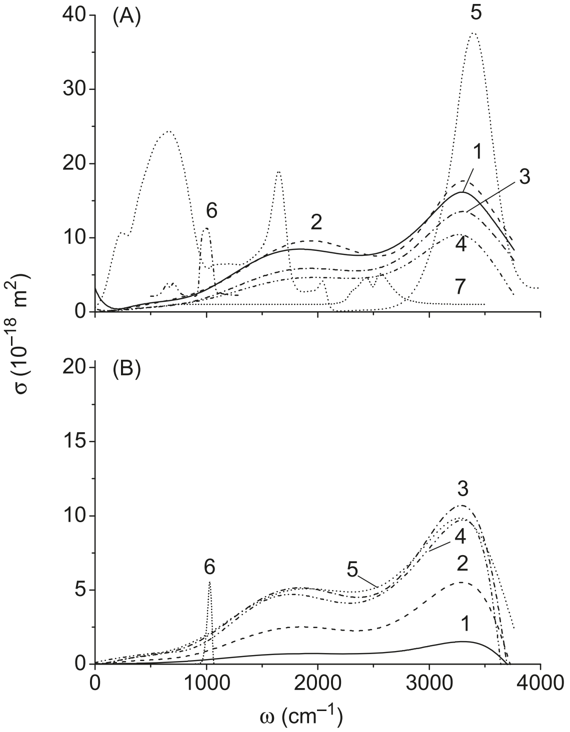
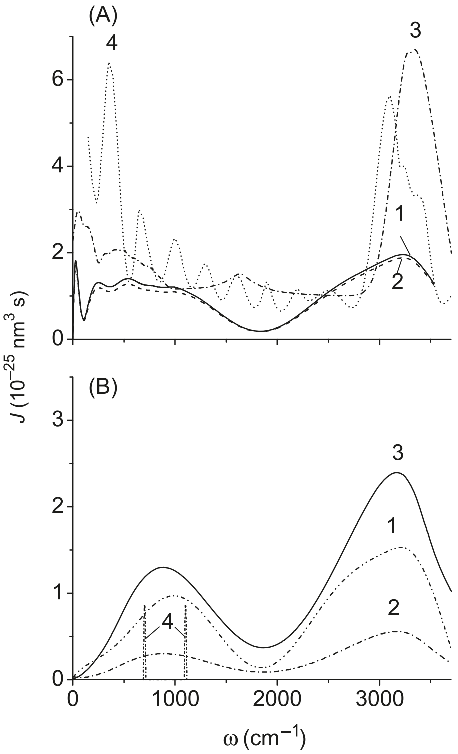


Fig. 7. Raman spectra of the $(Br^-)_i(H_2O)_{50-i} + iH_2O + 6X$ systems: (A) X = O_2 and (B) X = O_3. (1) $i = 0$. (2) $i = 6$. For (A): (3) liquid water at 293 K, experiment[34] and (4) the Br_2 clathrate hydrates at 266 K, experiment.[35] For (B): (3) the $(H_2O)_{50}$ cluster and (4) gaseous O_3, experiment.[36]



four Br^- results in faster attenuation of the autocorrelation function of the $\mathbf{d}_{cl}$. As a consequence, the intensity of the IR spectrum in an aqueous–ozone system at $i = 4$ starts to lessen.

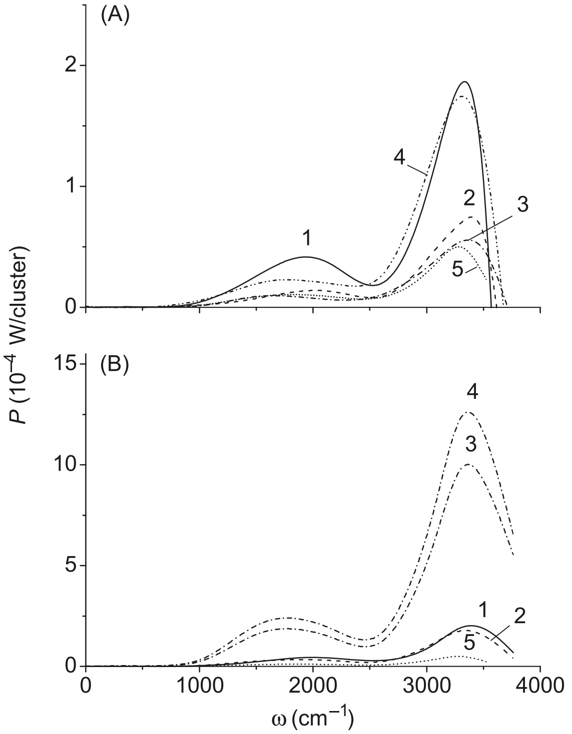
Raman spectra for bromine-containing systems (I″, VI″, VII″, and XII″) are shown in Fig. 7. Adsorption of six oxygen molecules resulted in an increase in the integrated intensity of the Raman spectrum (J_{tot}) for the $(H_2O)_{50}$ cluster by a factor of 1.6. In the presence of oxygen, the $J(\omega)$ spectrum poorly changed the intensity and the shape with variation in the number of Br^- in a cluster. When absorption of six Br^- by the aqueous–oxygen system occurred, the J_{tot} magnitude decreased by only 7.1%. In the systems containing up to six Br^-, a red shift of the basic peak at ~110 cm^{-1} relative to the main peak in the experimental Raman spectrum of liquid water[34] was observed. This peak has blue shift on quantity ~130 cm^{-1} with respect to the localization of the expressed peak in the similar experimental spectrum of the Br_2 clathrate hydrates.[35] The addition of six ozone molecules resulted in a decrease in the J_{tot} of the Raman spectrum for the $(H_2O)_{50}$ cluster by a factor of 1.5. The quantity of Br^- within the clusters is essentially reflected in the shape of the $J(\omega)$ spectra of the cluster systems containing ozone. $J(\omega)$ spectra considerably reduced the intensity with an increase in the number of Br^-. The J_{tot} magnitude of the aqueous–ozone system in the presence of six Br^- is lower by a factor of 4.3 than the J_{tot} value of this system in the absence of Br^-.

Red and blue (~170 and 20 cm^{-1}, respectively) shifts of the maximum position of the Raman spectra of cluster systems with respect to the corresponding peaks of the experimental spectra for water and bromine clathrate hydrates were observed. The position of the first (less intense) peak in the $J(\omega)$ spectra of cluster systems containing ozone lies in the interval between the two peaks of the experimental spectrum of gaseous ozone.[36]

The average polarizability per molecule ($\bar{\alpha}$) goes down in comparison with the designated α magnitude for water clusters with the addition of nonpolar molecules having a lower α (0.793 Å^3) than the α magnitude for molecules of liquid water (1.49 Å^3). In this case the presence of bromine ions exerts a weak influence on chaotization of the dipole moments of water molecules. Thus, fluctuations of α magnitude and behaviour of the appropriate correlation function poorly change. It results in minor alterations of the Raman spectrum at a variation in the number of Br^- in the system. Another situation arises for the systems containing ozone. The polar molecules of ozone have a higher polarizability (α = 2.7 Å^3) than water molecules. Therefore, the $\bar{\alpha}$ magnitude in the ozone system is higher than α for the water cluster. Disordering of the dipole moments was amplified with an increase in the number of Br^- and the polarizability values were smoothly reduced. Fluctuations of the α magnitude were lower than those for systems with oxygen. As a result, the intensities of the $J(\omega)$ spectra for the systems containing ozone was reduced with an increase in the number of Br^-.

Adsorption of molecules of both oxygen and ozone by the $(H_2O)_{50}$ cluster strengthens the integrated intensities of the emission spectra of IR radiation (P_{tot}). As a result of the

Fig. 8. IR emission spectra of systems $(Br^-)_i(H_2O)_{50-i}$+ iH_2O + 6X. (A) X = O_2, and (B) X = O_3 (1) i = 0. (2) i = 2. (3) i = 4. (4) i = 6. (5) The $P(\omega)$ function of the $(H_2O)_{50}$ cluster.



addition of six O_2 molecules, the P_{tot} magnitude increased by a factor of 3.8, and with the addition of six O_3 molecules to the cluster by a factor of 4.1 (Fig. 8). Emission spectra of cluster systems essentially change in intensity with a variation of the number of Br^- in the cluster. As a rule, the intensities of emission spectra are reduced in the presence of oxygen in the system and grows when the clusters adsorb ozone. For example, with six Br^- the $P(\omega)$ spectrum P_{tot} was reduced by a factor of 1.1 on adsorption of oxygen and it was increased by a factor of 6.4 when ozone joins. When bromine ions are added into an oxygen-containing system, the main peak of the emission spectrum, on average, is displaced by 20 cm^{-1} aside high frequencies. But addition of Br^- into ozone-containing systems results in a shift of the main peak up to 35 cm^{-1} aside low frequencies. The maximal reduction of the intensities of emission spectra for systems with oxygen occured in the presence of four Br^- in the cluster, and the maximal increase of this characteristic was observed for systems with ozone in the presence of six Br^- in the aggregate.

Conclusion

Ozone depletion occurs when the natural balance between the production and destruction of stratospheric ozone is tipped in favour of destruction. Although natural phenomena can cause temporary ozone loss, chlorine and bromine released from man-made compounds such as CFCs are now accepted as the main cause of this depletion. Emissions of CFCs have accounted for roughly 80% of total stratospheric ozone depletion. CFCs are photolyzed by UV radiation that breaks the weakest bond, usually a C–Cl or C–Br bond. Naturally occurring chlorine has the same effect on the ozone layer, but has a shorter life span in the atmosphere.

The present work demonstrates that water clusters are capable of adsorbing ozone and of detaining its molecules on the cluster surface over a significant time. Clusters consisting of polar molecules can hold Cl^- and Br^-. Thus, on the surface of a water cluster favourable conditions are created for the reaction of chlorine or bromine with ozone to proceed, which results in the destruction of the latter. The time that Br^- remain in water clusters is at least 10 times more than the time that Cl^- remain. Therefore, bromine ions destroy ozone more effectively. The intensities of IR absorption spectra essentially increase as the number of Br^- per cluster increases. Raman spectra of dispersed aqueous–ozone systems considerably reduce intensities with an increase in the number of Br^- contained in them. Emission spectra of IR radiation essentially have an increase in their intensities only at significant concentrations of Br^- in clusters.

In summary, the more massive Br^- are held in water clusters much longer than Cl^-, allowing the addition of ozone molecules to the cluster. At the same time absorption of oxygen molecules, as a rule, leads to evaporation of some of the Br^- from the cluster and to a loss of some oxygen molecules from its environment.

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