

MOLECULAR DYNAMICS SIMULATION

OF OZONE DISTRUCTION

O.R. Rakhmanova, A.Y. Galashev

*Institute of industrial ecology UB RAS,
Ekaterinburg, Russia*

rahmanova@ecko.uran.ru

Computer model

$$U_{tot} = U_{pair} + U_{pol} \quad (1)$$

$$U_{pair} = \sum_{j>i} \left(4\epsilon_{LJ} \left[\left(\frac{\sigma_{LJ}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{LJ}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \right) \quad (2)$$

$$U_{pair} = \sum_{j>i} \{ b_i b_j \exp[-(c_i + c_j)r_{ij}] - a_i a_j r_{ij}^{-6} \}$$

$$U_{pol} = -\frac{1}{2} \sum_i \mathbf{d}_i \mathbf{E}_i^0 \quad (3)$$

$$\mathbf{E}_i^0 = \sum_{j \neq i} \frac{q_j \mathbf{r}_{ij}}{r_{ij}^3} \quad (4)$$

$$\mathbf{d}_i = \mathbf{d}_{i,0} + \alpha_{i,0} \sum_{j \neq i} \mathbf{T}_{ij} \mathbf{d}_j \quad (5)$$

$$\alpha_i = \alpha_{i,0} + \alpha_{i,0} \sum_{j \neq i} \mathbf{T}_{ij} \alpha_j$$

$$\mathbf{E}_i = \mathbf{E}_i^0 + \sum_{j \neq i} \mathbf{T}_{ij} \cdot \mathbf{d}_j \quad (6)$$

$$\mathbf{T}_{ij} = \frac{1}{r_{ij}^3} \left(\frac{3\mathbf{r}_{ij} \mathbf{r}_{ij}}{r_{ij}^2} - 1 \right) \quad (7)$$

Dielectric properties

1. Dielectric permittivity

$$L_{i\omega}[-\dot{f}] = \frac{\varepsilon(\omega) - 1}{\varepsilon_0 - 1} = 1 - i\omega L_{i\omega}[f]$$

2. Total dipole moment

$$\mathbf{M}(t) = \sum_{i=1}^N \mathbf{d}_i(t)$$

3. Static dielectric constant

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

4. Autocorrelation function of the total dipole moment

$$f(t) = \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle / \langle \mathbf{M}^2 \rangle$$

5. Absorption section of IR-radiation

$$\sigma(\omega) = \left(\frac{2}{\varepsilon_v c \hbar n} \right) \omega \tanh\left(\frac{\hbar\omega}{2kT} \right) \operatorname{Re} \int_0^{\infty} dt e^{i\omega t} \langle \mathbf{M}(t) \mathbf{M}(0) \rangle$$

6. Raman spectrum

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

$$\Pi(t) \equiv \sum_{j=1}^N \left[\mathbf{a}_j(t) - \langle \mathbf{a}_j \rangle \right]$$

7. Absorption and reflection coefficients

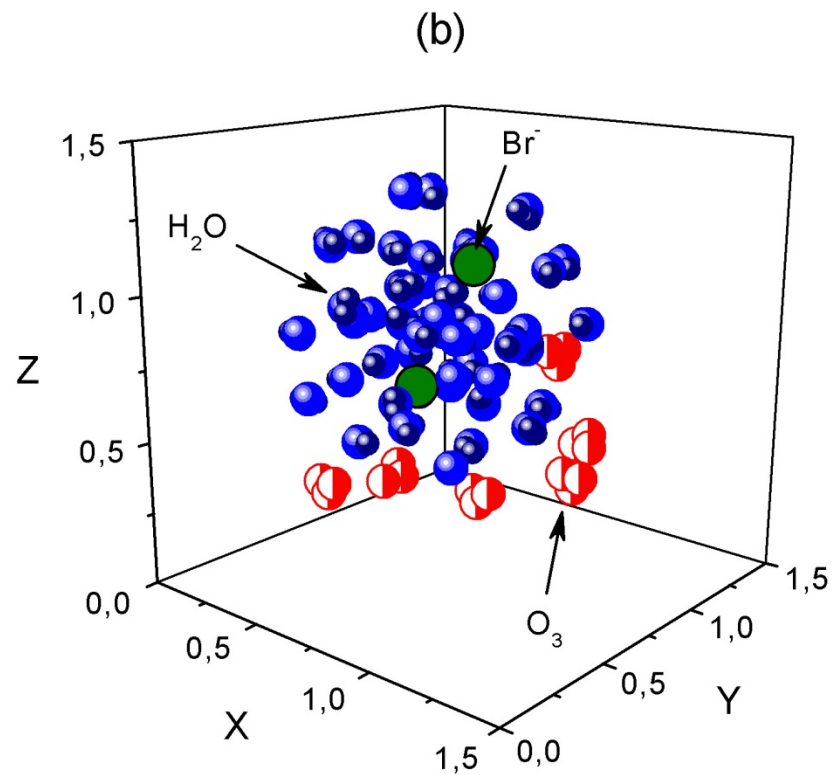
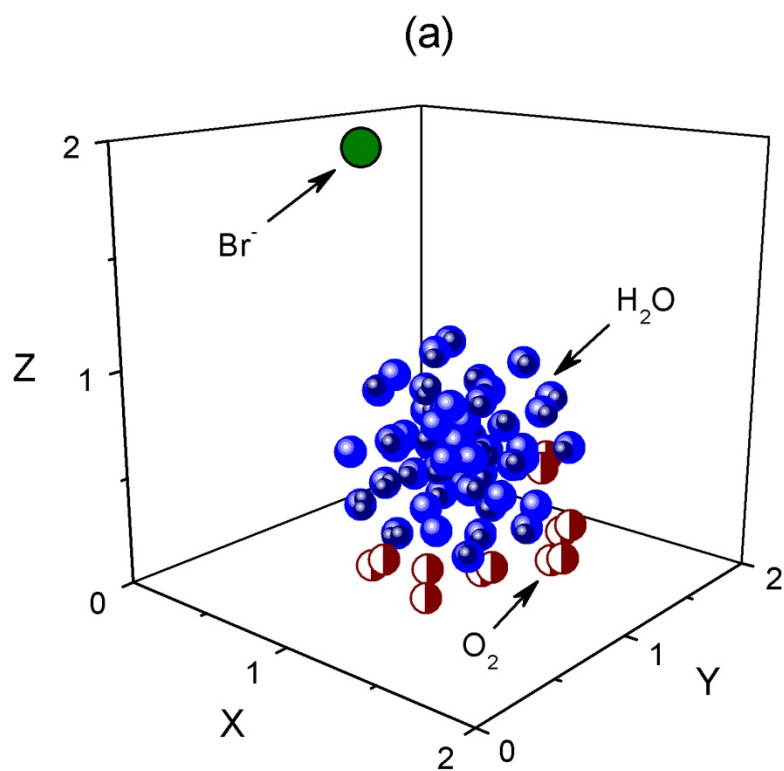
$$\alpha(\omega) = 2 \frac{\omega}{c} \operatorname{Im}[\varepsilon(\omega)^{1/2}]$$

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

8. Emitted power of IR-radiation

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

Fig. 1. Configurations of systems: (a) - $2\text{Br}^- + (\text{O}_2)_6(\text{H}_2\text{O})_{50}$ (free boundary conditions-fbc), (b) - $2\text{Br}^- + (\text{O}_3)_6(\text{H}_2\text{O})_{50}$ (random boundary conditions-rbc) corresponding to the time moment of 25 ps; molecule coordinates are represented in nm.



**Fig. 2. Infrared absorption spectra for systems: (a): 1 – $(\text{O}_2)_6(\text{H}_2\text{O})_{50}$, 2 – $2\text{Br}^- + (\text{O}_2)_6(\text{H}_2\text{O})_{50}$ (fbc), 3 – $2\text{Br}^- + (\text{O}_2)_6(\text{H}_2\text{O})_{50}$ (rbc), 4 – experiment for bulk water; 5 – experiment for gaseous O_2 ;
 (b): 1 – $(\text{O}_3)_6(\text{H}_2\text{O})_{50}$, 2 – $2\text{Br}^- + (\text{O}_3)_6(\text{H}_2\text{O})_{50}$ (fbc), 3 – $2\text{Br}^- + (\text{O}_3)_6(\text{H}_2\text{O})_{50}$ (rbc), 4 – experiment for gaseous O_3 , 5 – experiment for gaseous HBr .**

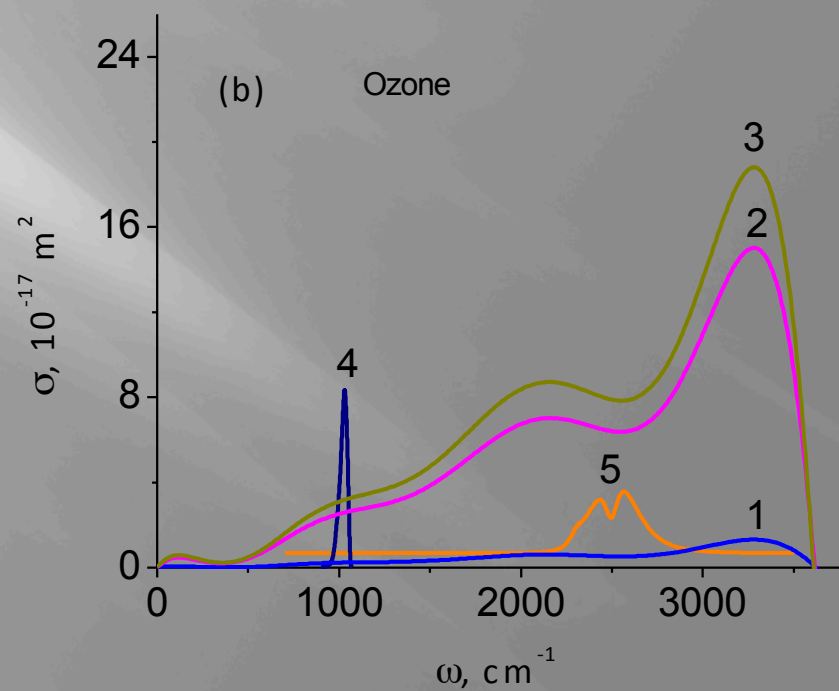
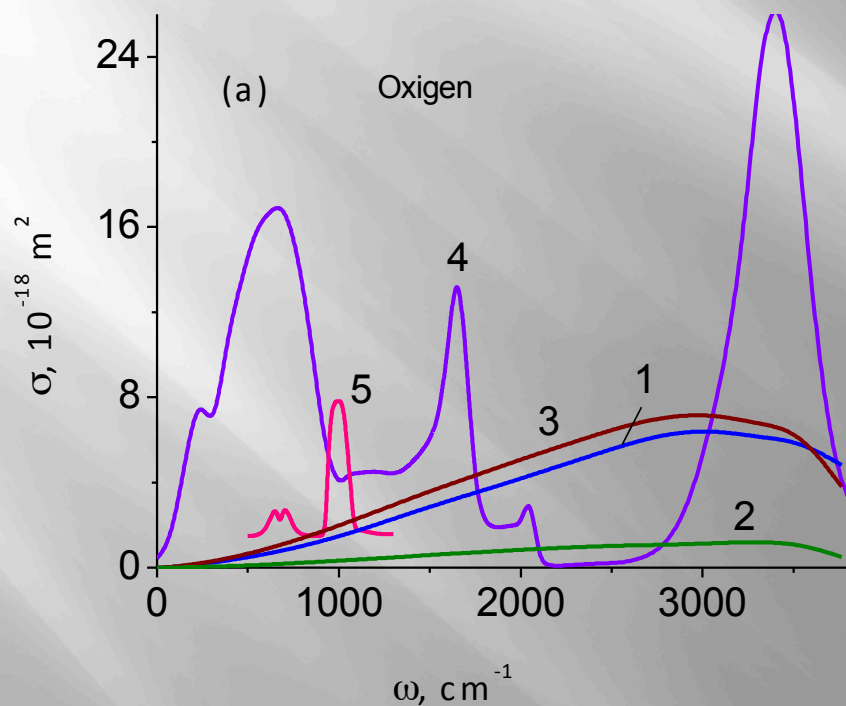


Fig. 3. Raman spectra: (a): 1 – $(\text{O}_2)_6(\text{H}_2\text{O})_{50}$, 2 – $2\text{Br}^- + (\text{O}_2)_6(\text{H}_2\text{O})_{50}$ (fbc), 3 – $2\text{Br}^- + (\text{O}_2)_6(\text{H}_2\text{O})_{50}$ (rbc), 4 – experiment for bulk water at $T = 293$ K; (b): 1 – $(\text{O}_3)_6(\text{H}_2\text{O})_{50}$, 2 – $2\text{Br}^- + (\text{O}_3)_6(\text{H}_2\text{O})_{50}$ (fbc), 3 – $2\text{Br}^- + (\text{O}_3)_6(\text{H}_2\text{O})_{50}$ (rbc), 4 – experiment for gaseous O_3 , 5 – experiment for gaseous HBr at $T = 266$ K.

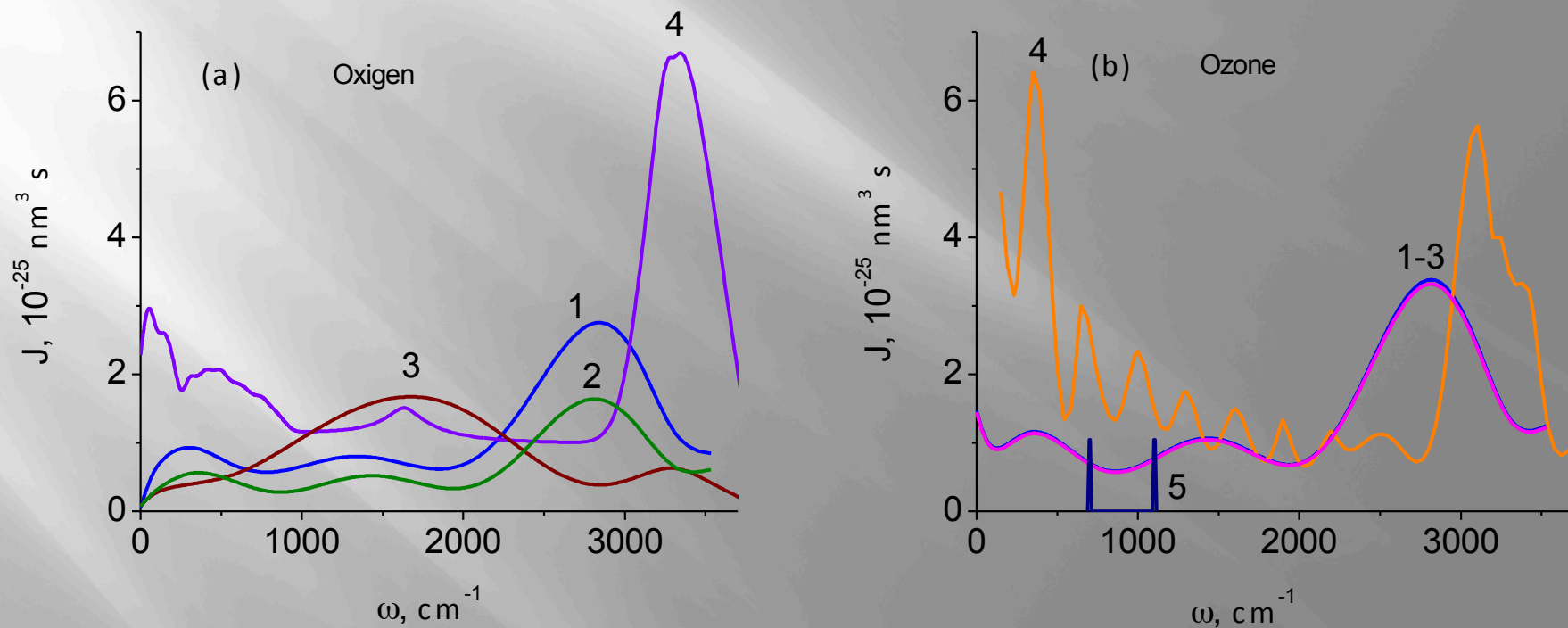


Fig. 4. Spectra of IR radiation emission power: (a): 1 – $(\text{H}_2\text{O})_{50}$, 2 – $(\text{O}_2)_6(\text{H}_2\text{O})_{50}$,

3 – $2\text{Br}^- + (\text{O}_2)_6(\text{H}_2\text{O})_{50}$ (fbc), 4 – $2\text{Br}^- + (\text{O}_2)_6(\text{H}_2\text{O})_{50}$ (rbc);
 (b): 1 – $(\text{H}_2\text{O})_{50}$, 2 – $(\text{O}_3)_6(\text{H}_2\text{O})_{50}$, 3 – $2\text{Br}^- + (\text{O}_3)_6(\text{H}_2\text{O})_{50}$ (fbc),
 4 – $2\text{Br}^- + (\text{O}_3)_6(\text{H}_2\text{O})_{50}$ (rbc),

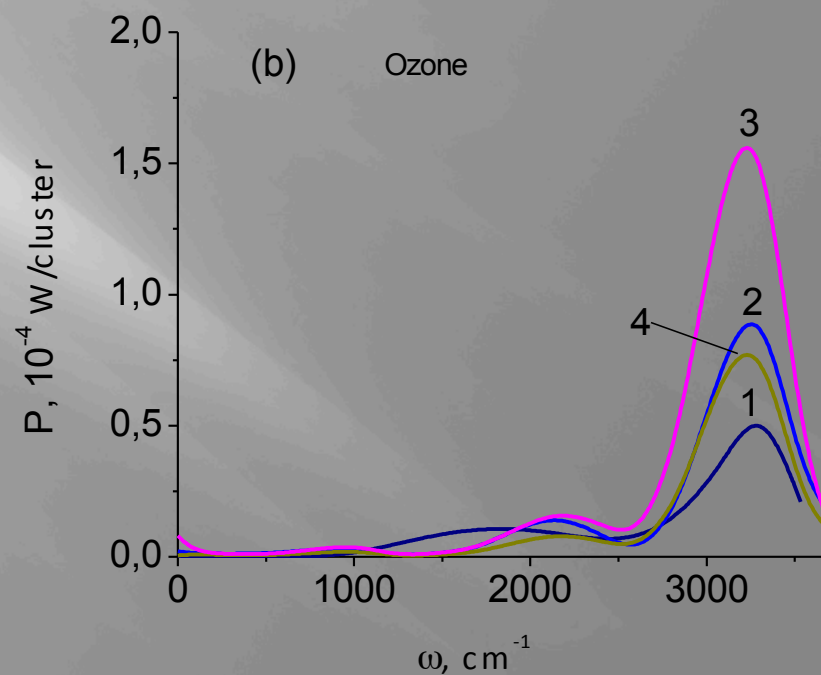
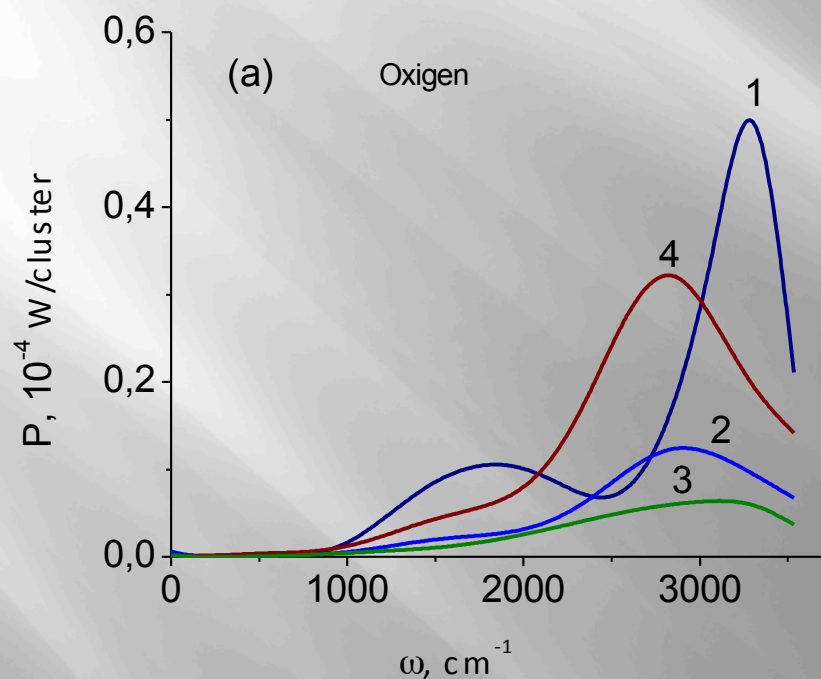


Fig. 5. Refraction spectra of IR radiation for systems: (a) – $6\text{O}_2+(\text{H}_2\text{O})_{50}$, (b) – $2\text{Br}^+(\text{O}_2)_6(\text{H}_2\text{O})_{50}$ (fbc), (c) - $2\text{Br}^+(\text{O}_3)_6(\text{H}_2\text{O})_{50}$ (fbc).

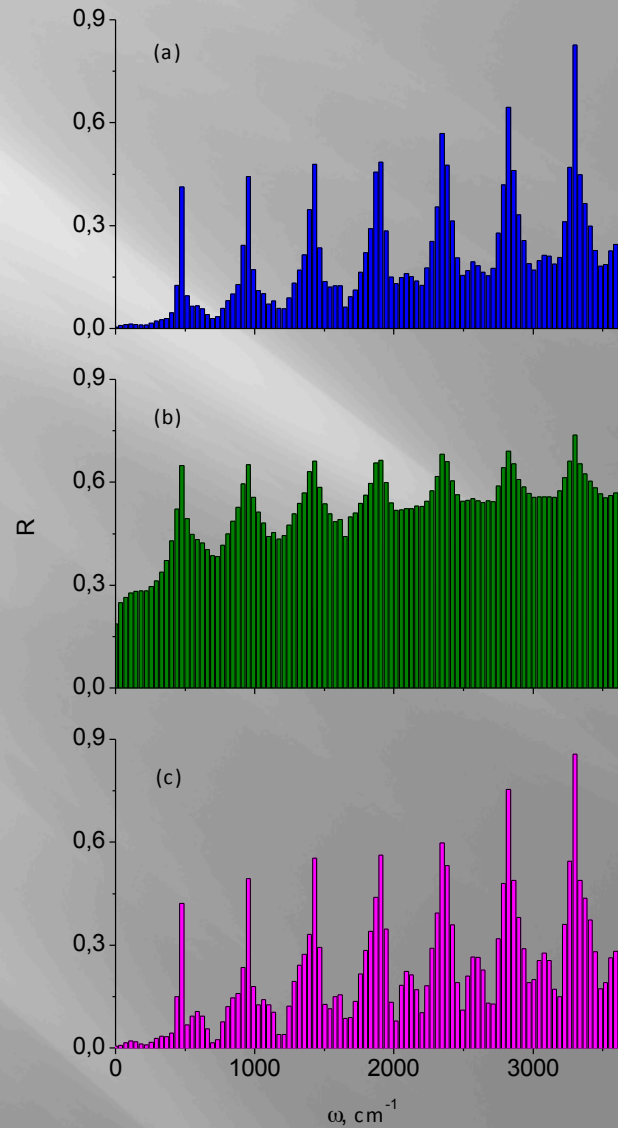
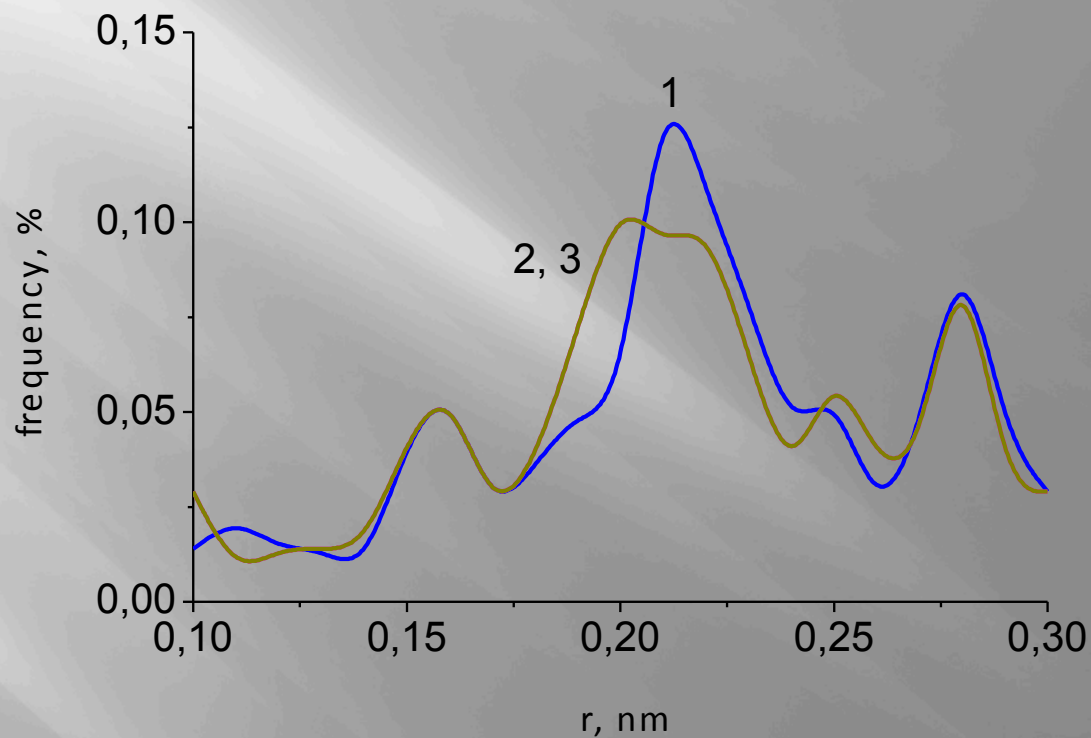


Fig. 6. Length distribution of hydrogen bond in systems: 1 – $6\text{O}_3+(\text{H}_2\text{O})_{50}$,
2 – $2\text{Br}^+(\text{O}_3)_6(\text{H}_2\text{O})_{50}$ (fbc), 3 - $2\text{Br}^+(\text{O}_3)_6(\text{H}_2\text{O})_{50}$ (rbc).



CONCLUSION

1. Different behavior of water-ion systems depending on presence of oxygen or ozone molecules is shown during MD simulation by duration of 25 ps. All six O₃ molecules and Br⁻ ions present in the system up to the end of calculation. In the case of O₂ molecules absorption the application of free boundary conditions results in evaporation of bromine ions and a part of O₂ molecules leave the system when random boundary conditions are used.
2. Under the influence of Br⁻ ions the integral intensity of IR absorption spectra of the systems absorbing ozone increases without dependence of used boundary conditions. On the contrary, in case of oxygen containing system the use of free boundary conditions gives essential reduction of IR spectra integral intensity and the application of random boundary conditions results in some increase of this characteristic values.
3. Raman spectra of water system with ozone molecules are poorly sensitive to influence of Br⁻ ions and type of used boundary conditions. At the same time, Raman spectra for water systems with oxygen molecules are changed significantly under influence of Br⁻ ions and they change their shape considerably at transition from using of free boundary conditions to random ones.
4. It is shown in MD experiment that except for the well-known mechanisms of ozone destruction in result of gas phase reactions, water clusters containing a small amount of bromine ions can also give the contribution to processes of tropospheric ozone destruction.

THANK YOU FOR YOUR ATTENTION