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Hydration of N_2 and Cl_2 Molecules

A. E. Galashev, G. I. Pozharskaya, and V. N. Chukanov

Institute of Thermal Physics, Ural Division, Russian Academy of Sciences, Ekaterinburg, Russia
Institute of Industrial Ecology, Ural Division, Russian Academy of Sciences, Ekaterinburg, Russia

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Abstract—The behavior of N_2 and Cl_2 molecules in H_2O clusters was studied by the molecular dynamics method. Structural, thermodynamic, kinetic, and electrical properties of water aggregates containing N_2 and Cl_2 molecules were examined. The energy of the admixture–water interaction is negative and decreases as the cluster size increases. The electrostatic potential and the field strength undergo strong changes in the vicinity of aggregate border. The effect of hydration on the rate of some atmospheric reactions was considered.

In the lowest gaseous mantle of the Earth, troposphere, the atmospheric air is weakly ionized, and the role of water vapor is especially great. On the average, specific humidity decreases with height, i.e. the diffusion vapor flow in the atmosphere is directed upward. Nitrogen is one of the most abundant elements on the Earth, its main body being concentrated in the atmosphere, where the content of N_2 is ~78.09 vol%. Chlorine occurs in nature only as compounds but can be released as the result of chemical reactions. In the gas phase, N_2 and Cl_2 molecules have neither electric charge nor dipole and quadrupole moments [1], i.e. they are nonpolar.

In the atmosphere, Cl_2 is not as stable as N_2 and can be destroyed under sunlight. The photodissociation of gaseous Cl_2 in the wavelength range of 250–450 nm have been intensively studied over the last decade. It was found that the resulting Cl^- radicals can be present in two spin-orbital states [2]. The energy of N_2 dissociation is almost by a factor of four higher than that of Cl_2. The energy of dissociation of nitrogen oxide is lower than that of nitrogen. The charged nitrogen trioxide NO_3^+ undergoes photodissociation to form NO_2^+ and NO^+ ions, the fraction of the former ion being $26 \pm 4\%$ at irradiation wavelengths of 460–660 nm [3].

The aim of this work was to study the possibility of hydration of N_2 and Cl_2 molecules under near-atmospheric conditions by the molecular dynamics method. Traditionally, the chemistry of atmosphere considers hydration of ions [4–6] but not of electrically neutral inorganic molecules. An exception is the work of Sigon *et al.* [7] who have studied the hydrophilicity of polar NaCl molecules.

Molecular dynamics model. The simulation is based on the molecular dynamics method applied to water molecules with a fixed point distribution of masses and effective charges and to admixture molecules (N_2 or Cl_2) having no distributed charges. The additive part of the interaction between water molecules was described by a potential function $U_{\mathrm{ww}}^{(2)}(1)$ corresponding to the SPC/POL1 model [8].

$$U_{\mathrm{ww}}^{(2)} = \sum_{i<j} \left[\frac{q_i q_j}{r_{ij}} + \frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}} \right]. \tag{1}$$

Here q_i is the electric charge ascribed to the ith atom, r_{ij} is the distance between the ith and jth atoms, and A_{ij} and C_y are empirical parameters.

The first term in the brackets in Eq. (1) describes the electrostatic interaction between the ith and jth centers, and two other terms reflect the effective non-Coulomb pair interaction in view of $A_{\mathrm{OH}} = A_{\mathrm{HH}} = C_{\mathrm{OH}} = C_{\mathrm{HH}} = 0$.

The energy of pair interaction between admixture and water molecules was calculated on the basis of the atom–atom potential $U_{\mathrm{aw}}^{(2)}$ [9] given by Eq. (2).

$$U_{\mathrm{aw}}^{(2)} = \sum_{i<j} [-a_i aj/r^6 + b_i b_j \exp\{-(c_i + c_j)r\}]. \tag{2}$$

Here a_i, b_i, and c_i are coefficients individual for each kind of atoms.

The polarization term U_{pol} was calculated for the whole system by Eq. (3), where summation is carried out over all polarized centers.

$$U_{\mathrm{pol}} = -\frac{1}{2} \sum_j \alpha_j (E_j E_j^0). \tag{3}$$

Here a_j is the polarizability of the centers, E_j is the electric field induced on a specified center by all other

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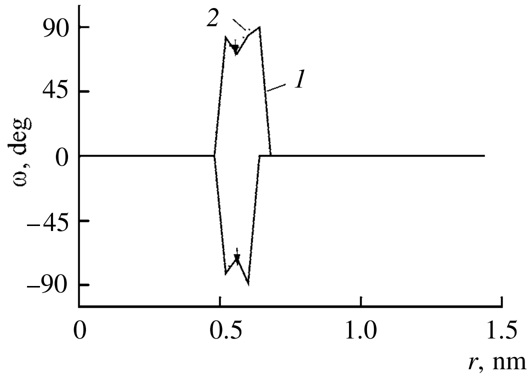

Fig. 1. Radial distribution of angles ω formed by a linear admixture molecule and the HH intercepts in water molecules in clusters with N_w 14. (*1*) N_2 and (*2*) Cl_2.

charges and induced dipoles belonging to any other water molecule falling within the interaction sphere (with a radius of 8 Å) and E_j^0 is the electric field induced on a specified center exclusively by all other charges falling within the interaction sphere.

The isotropic atomic polarizabilities were taken from [10]. The polarization energy was calculated by a self-consistent procedure, i.e. induced moments in each center were determined by an iterative procedure and used to calculate U_{pol} which relates to the contribution of multiparticle polarization effects to the total interaction energy.

We used a 4-th order Gear predictor–corrector algorithm [11]. Instead of integrating rotary motion equations, we used the method of free charge motion with the SHAKE procedure [12], that recovers the shape of water molecules. The time step Δτ was 10–15 s. The calculation at each temperature consisted of two parts: preliminary (3×10^5 Δτ) and principal (2×10^6 Δτ. In both cases we divided the calculations into macrosteps of 1×10^5 Δτ. In the preliminary, required structural relaxation was achieved. As the starting configuration we took fragments of an ideal body-centered crystal lattice, but for certain numbers of water molecules N_w regular geometric figures were used: triangle (3), tetrahedron (4), bipyramid (5), octahedron (6), icosahedron (12), and dodecahedron (20). The number of water molecules located at the apexes of the figure is given in parentheses. The admixture molecule was located in its center. The calculations were carried out for 240 K.

Results of simulation. Visual examination of cluster configurations showed that an admixture molecule first placed in the center of the cluster remained there also at the end of the calculations, i.e. it did tend to be expelled from the cluster. The volume *V* of the clusters approximated by the volume of a sphere drawn around the center of the cluster and passing through the mass center of the most remote water molecule is not a monotonous function of N_w. The minima of the *V*(*N*) dependence fell at N_w of 4, 7, and 12. The mutual angular orientations of the molecules were estimated by the distribution of angles ω formed by linear molecules (N_2 and Cl_2) with the HH intercepts of water molecules, as the centers of water molecules recede from the center of the admixture molecule, i.e. as the distance *r* (Fig. 1) increased. Starting with N_w 6, the ω angles generally varied from ±70 to ±90°. Closely similar ω(*r*) distributions were obtained for water clusters containing polar admixture molecules (CO, HF, and HCl). The location of the minima in the ω(*r*) distribution (Fig. 1) almost coincides with the location of the maxima of the frequencies of appearance of these events, marked off by arrows in Fig. 1.

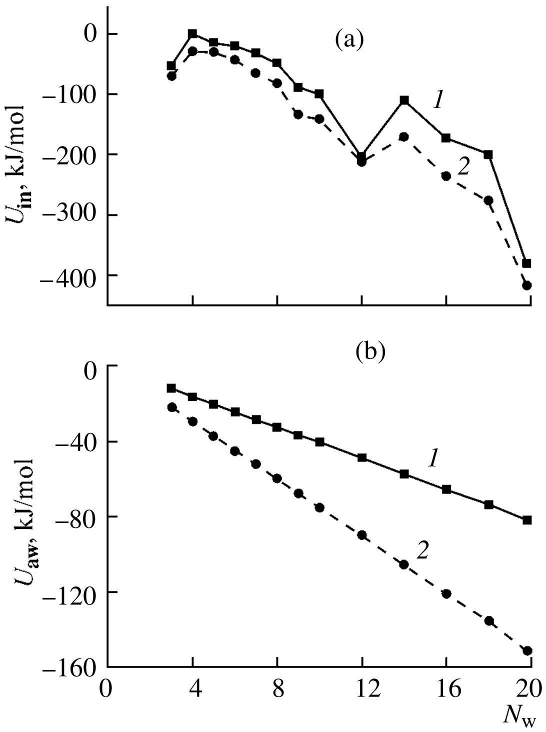

Fig. 2. (a) Intrinsic energy U_{in} and (b) energy of admixture–water interaction U_{aw} for molecular clusters. (*1*) N_2 and (*2*) Cl_2.

In general, the intrinsic energy U_{in} decreases as N_w increases (Fig. 2a) for both types of clusters, but there are a local maximum at N_w 4 and a local minimum at N_w 12. The U_{in} values at N_w 20 are –380.8 (N_2) and –418.0 kJ/mol (Cl_2). The energy of a pure water cluster with N_w 20, calculated with an empirical pair interaction potential, is –367.4 kJ/mol [13]. The energy of the admixture–water interaction U_{aw} steadily decreases as N_w increases (Fig. 2b). Therewith, the U_{aw} energies for clusters with Cl_2 are invariably lower than for those with N_2 at all N_w. The negative U_{aw} values are unambiguous evidence showing that N_2 and Cl_2 molecules tend to hydration.

The heat capacity c_p (the equations for calculation of c_p can be found in [14]) that characterize kinetic energy fluctuations behaves rather smoothly for the clusters under study starting with clusters with N_w 4. Such behavior of c_p differentiates clusters with N_2 and Cl_2 from aggregates with HCl and HF, whose heat capacity exhibits a splash at N_w 7–8, implying strong thermal perturbations attendant in formation of the second hydration layer for the admixture molecule.

The diffusion coefficients for admixture molecules in clusters with N_w 20, calculated by the autocorrelation rate function, differed from one another more than three times: 0.82×10^{-10} (N_2) and 2.59×10^{-10} m^2/s (Cl_2), whereas the diffusion coefficients for water molecules in these clusters (3.85×10^{-10} and 3.73×10^{-10} m^2/s, respectively) were close to each other. The molecular dynamics data show [15] that the self-diffusion coefficient of overcooled pure water (1.4×10^{-10} m^2/s) at 238.2 K is lower by a factor of 2.7 than in the clusters under consideration.

Electrically neutral admixture molecules in clusters were surrounded by water molecules bearing distributed electric charges [8]. The electrostatic potential determined by distributed charges can be found in any point of space. Let us determine it for the mass center of an admixture molecule. In the SPC/POL1 model, water molecules are represented as a rigid construction consisting of point charges. Draw a sphere of radius r from a point where the potential is to be determined. The potential of the field induced by charges falling within the sphere is determined in terms of the principle of electric field superposition [16] [Eq. (4)], performing summation over all charges falling within the sphere of radius r; r_i is the distance from the center of the sphere to the point charge i.

$$\Phi_{\mathrm{int}}(r) = a \sum_{i, r_i < r} \frac{q_i}{r}. \quad (4)$$

On the other hand, charges located outside of the sphere create potential (5).

$$\Phi_{\mathrm{out}}(r) = a \sum_{i, r_i > r} \frac{q_i}{r_i}. \quad (5)$$

The coefficient a in Eqs. (4) and (5) is equal to 1 for the SGS unit system and $1/4\pi\varepsilon_0$ for the SI system.

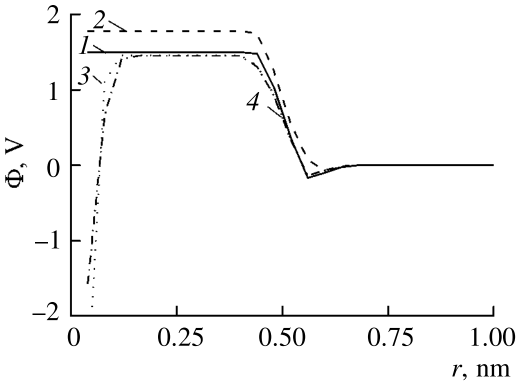

Fig. 3. Electric potential (Φ) in clusters with N_w 14, related to the mass center of the admixture molecule. (*1*) N_2, (*2*) Cl_2, (*3*) HF, and (*4*) HCl.

As there are no charges inside the first coordination sphere drawn around an admixture molecule (N_2 and Cl_2), the Φ_a potential in this region is constant (Fig. 3). This is one of the features of the Φ_a potential which distinguish it from the corresponding function for similar clusters with CO, HF, or HCl molecules (irrespective of N_w), where Φ_a sharply changes as r approaches zero. At r 4.8–6.0 Å for clusters with N_w 14 (Fig. 3), the Φ_a potential sharply decreases attaining small negative values. At $r > 6.8$ Å, the Φ_a function is close to zero. The fast change of Φ_a at the border of the cluster suggests that the admixture molecule exerts a weak long-range (electric) effect on the location and orientation of water molecules. The sharp fall of the electric potential is the second important feature distinguishing N_2 and Cl_2 clusters from water aggregates containing real polar molecules, the fall of Φ_a at the cluster border is smoother.

The strength of the effective field apparent from the mass center of an admixture molecule is determined by formula (6).

$$E_a = -\nabla\Phi_a. \quad (6)$$

By the radial distribution of the electric field strength one can readily distinguish clusters containing N_2 and Cl_2 molecules from aggregates including polar molecules (Fig. 4). In essence, the difference is only in the presence of sharp peaks at $r < 2.5$ Å around the HCl and HF molecules and in the absence of any field in the vicinity of the N_2 and Cl_2 molecules.

Effect of hydration of N_2 and Cl_2 molecules on the composition of the Earth atmosphere. Our study provides unambiguous evidence showing that under near-atmospheric conditions there is a possibility for N_2 and Cl_2 molecules to be surrounded by water

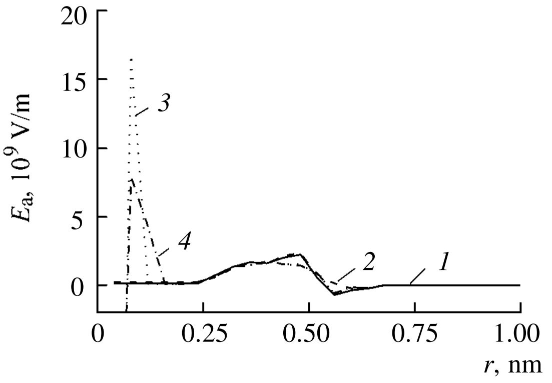

Fig. 4. Electric field strength (E_a) in clusters with N_w 14, related to the mass center of the admixture molecule. (*1*) N_2, (*2*) Cl_2, (*3*) HF, and (*4*) HCl.

molecules, forming stable clusters. The probability of such events seems to be low in spite of the fact that nitrogen dominates in the Earth atmosphere. The insensitivity of nitrogen and chlorine molecules to long-range (electric) interactions does not permit them to initiate cluster formation from available water vapor without assistance. However, the N_2 and Cl_2 molecules present in clouds can be trapped by water molecules during cluster or drop formation even if dissociation of the admixtures is impossible.

The experimental study [17] of condensation of technical water vapor showed that the first condensate contains increased amounts of chlorine (up to 5%). This seems to be associated with the fact that not only Cl^- ions are hydrated, but also electrically neutral Cl_2 molecules, as we showed in the present work. The Cl_2 molecule can appear from $Cl^\cdot$ radicals by reaction (7), for example, when the active particle $Cl^\cdot$ collides with vessel wall (designated by W in the formula). In the case of triple collision, the excess energy of the resulting molecule is transferred to the wall (or to another particle), which prevents the Cl_2 molecule from decomposition.

$$Cl^\cdot + Cl^\cdot + W \longrightarrow Cl_2 + W. \qquad (7)$$

Reactions (8) and (9) activated by chlorine can occur in the South pole zone of the Earth atmosphere.

$$ClONO_2 + HCl \longrightarrow Cl_2 + HNO_3, \qquad (8)$$

$$HOCl + HCl \longrightarrow Cl_2 + H_2O. \qquad (9)$$

The most important is reaction (8), as a result of which chlorine passes from $ClONO_2$ and HCl molecules more resistant to photodissociation to Cl_2 molecules less stable to light. Reflected sunlight during Antarctic spring induces photolysis of Cl_2 molecules to release atomic chlorine, which destroys ozone by catalytic cycles. Most nitric acid formed in reaction (8) remains in the condensed phase. The initiated "blowing-through" with excess nitrogen renders $ClONO_2$ less reactive toward the active chlorine formed [18]. We call attention to reaction (9) yielding water. The abundance of water molecules can result in formation of hydration layer around Cl_2 molecules, thereby protecting them from chlorine detachment by $ClONO_2$ molecules. This favors accumulation of molecular chlorine and, owing to photolysis, of atomic chlorine, resulting in ozone destruction. In this case, a negative role of natural gas hydrates can be traced. A positive effect of natural hydration can be illustrated by natural conservation of CO_2 [19] on the Earth, which decreases emission of this gas into the atmosphere and thus retards the global warming.

Thus, N_2 and Cl_2 molecules interact with atmospheric water vapor and can exist within the hydratione shell for at least 2 ns. This is testified by the negative energies of interaction between an admixture molecule and cluster water molecules. This energy additively decreases as the number of particles in the cluster increases. The lowest intrinsic energy attained at N_w 20 both for N_2 and Cl_2 clusters points to the tendency of neutral molecules for occupying cavities created by the network of hydrogen bonds. This fact distinguishes the molecules under consideration from polar molecules (CO, HF, and HCl) whose $U_{in}(N_w)$ dependence has no absolute minimum at N_w 20. The partial radial distribution functions g_{NH}–r and g_{ClH}–r each have one main peak, and the width of the latter increases with increasing N_w and correlates with a narrow ω range. In fact, cluster water molecules orient themselves around a linear admixture molecule in such a manner that the $\langle\omega\rangle$ angle is from 70 to 90°. The most probable angles are close to the minimal value (~70°). Nitrogen and chlorine are quite similar not only in orienting water molecules, but also in the electrostatic field created around them. This is the main reason for the generation of N–H and Cl–H bonds stabilizing the mutual arrangement of the molecules. At the same time, the electric field created in the mass center of an admixture molecule strongly depends on the molecule being polar or not.

The hydration of Cl_2 molecules in the atmosphere increases the probability of the photolysis yielding atomic chlorine. Chlorine, having a lower interaction energy with water than nitrogen, can remain hydrated in the atomic form, too, thus giving rise to subsequent reactions changing the composition of the atmosphere. The energy of N_2 dissociation is higher by a factor of 2.2 compared with the respective value for the $\dot{O}H$

radical. In this case, dissociation of the N_2 molecule is preceded by destruction of its hydration shell, and, therefore, hydration cannot favor photolysis.

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