Polarizability of nitrogen and oxygen dimers: temperature dependence

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Within the framework of the dipole-induced-dipole (DID) model, a method is proposed for calculation of the temperature dependence of dimer polarizability. The temperature dependence is a consequence of statistical averaging of dimer electronic polarizability over rotational-vibrational states of different dimer configurations. Every molecule in a dimer is considered as an effective atom having the same polarizability tensor as the molecule itself. The interaction between the effective atoms in a dimer is taken in the form of the Lennard–Jones potential. The method proposed is applied to calculation of the temperature dependence for $(N_2)_2$ and $(O_2)_2$ polarizability invariants.

Introduction

It is well-known that all atoms and molecules can form weakly bound complexes. Such complexes are present in all gaseous media, including the Earth's atmosphere, where they take an active part in all physical and chemical processes. Since energy levels, dipole moments, and polarizability of the complexes differ markedly from the corresponding properties of molecules in their composition, the presence of complexes in the Earth's atmosphere leads to appearance of new effects. A prominent example is absorption of longwave radiation by nitrogen dimers due to intermolecular rotational-vibrational transitions in them, while individual nitrogen molecules do not absorb this radiation at all. However, in spite of the importance of this fact for radiation transfer in the Earth's atmosphere, now we have no reliable data both on the concentration of such complexes in the atmosphere and their electrooptical properties.

Determination of electrooptical properties of molecular complexes involves some difficulties caused by peculiarities of their structure. Thus, quantum-chemical calculations of the potential energy surface for such complexes[1,2] show that they can exist in several configurations, and their dissociation energies are low and different for different configurations, so even small rotational-vibrational excitation is enough for a complex to transit from one configuration to another. As a result, molecular complexes of a certain chemical composition are presented in the actual atmosphere by an ensemble of isomers being in the state of dynamic equilibrium with each other; and the complex polarizability due to statistical averaging over rotational-vibrational states of different complex configurations, is some effective parameter depending on temperature.

In this paper, we study theoretically the polarizability of nitrogen and oxygen dimers, belonging to the most abundant molecular complexes in the Earth's atmosphere.

Computational method

Each molecule in a dimer is considered as a model or effective atom, whose polarizability tensor coincides with the polarizability tensor of this molecule, therefore, the dimer is represented as a diatomic molecule, whose axis coincides with axis Z. The dimer polarizability tensor is the function of the separation R between the effective atoms and the Euler angles θ_1, φ_1, and θ_2, φ_2 specifying, respectively the orientation of the first and second molecules in the dimer.[3] To describe the dimer polarizability tensor as a function of R (at fixed Euler angles), we invoke the classical electrostatic dipole-induced-dipole theory,[4] which physically correctly describes the polarizability of van der Waals complexes at characteristic intermolecular separations.[5,6]

Within this dimer model, its polarizability tensor has two independent components $\alpha_{xx}(R) = \alpha_{yy}(R)$ and $\alpha_{zz}(R)$, which can be written in the form

$$\alpha_{xx}(R) = \alpha_{xx}^{(1)} + \alpha_{xx}^{(2)} - \frac{2}{R^3}\alpha_{xx}^{(1)}\alpha_{xx}^{(2)} + \\ + \frac{1}{R^6}\left(\alpha_{xx}^{(1)} + \alpha_{xx}^{(2)}\right)\alpha_{xx}^{(1)}\alpha_{xx}^{(2)} + \ldots \quad (1)$$

and

$$\alpha_{zz}(R) = \alpha_{zz}^{(1)} + \alpha_{zz}^{(2)} + \frac{4}{R^3}\alpha_{zz}^{(1)}\alpha_{zz}^{(2)} + \\ + \frac{4}{R^6}\left(\alpha_{zz}^{(1)} + \alpha_{zz}^{(2)}\right)\alpha_{zz}^{(1)}\alpha_{zz}^{(2)} + \ldots, \quad (2)$$

where $\alpha_{ii}^{(1)}$ and $\alpha_{ii}^{(2)}$ are the components of the polarizability tensor of the first and second molecules in the dimer; they depend respectively on the Euler angles θ_1, φ_1 and θ_2, φ_2. For problems of atmospheric optics, more important parameters are invariants of the polarizability tensor, rather than its components. They are the mean dimer polarizability

$$\alpha(R) = \frac{1}{3}\left[\alpha_{xx}(R) + \alpha_{yy}(R) + \alpha_{zz}(R)\right] \tag{3}$$

and the square dimer anisotropy

$$\gamma^2(R) = \frac{1}{2}\left\{\left[\alpha_{xx}(R) - \alpha_{yy}(R)\right]^2 + \left[\alpha_{xx}(R) - \alpha_{zz}(R)\right]^2 + \right.$$
$$\left. + \left[\alpha_{yy}(R) - \alpha_{zz}(R)\right]^2\right\} + 3\left[\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2\right]. \tag{4}$$

Since a significant share of dimers is in excited rotational-vibrational states of different configurations already at low temperatures, the average values of dimer polarizability invariants are of a practical importance, for example,

$$\alpha(T) = \frac{\sum\limits_{i,\mathrm{v},J} g^{(i)}(2J+1)\langle \mathrm{v},J|\alpha^{(i)}(R)|\mathrm{v},J\rangle \exp\left[-\dfrac{hcE_{\mathrm{v}J}^{(i)}}{kT}\right]}{\sum\limits_{i,\mathrm{v},J} g^{(i)}(2J+1)\exp\left[-\dfrac{hcE_{\mathrm{v}J}^{(i)}}{kT}\right]}, \tag{5}$$

where index i numbers dimer configurations; $g^{(i)}$ is the statistical weight of a configuration; $\langle \mathrm{v},J|\alpha^{(i)}(R)|\mathrm{v},J\rangle$ is the matrix element of the dimer polarizability in the state with the vibrational and rotational quantum numbers v and J, and the rotational-vibrational energy levels can be written as

$$E_{\mathrm{v}J}^{(i)} = \delta^{(i)} + \sum_{nm} Y_{nm}^{(i)}\left(\mathrm{v} + \frac{1}{2}\right)^n J^m (J+1)^m, \tag{6}$$

$\delta^{(i)} = D_\mathrm{e}^{(0)} - D_\mathrm{e}^{(i)}$ is the difference in the dissociation energies between the most stable and ith dimer configurations. The dimer polarizability anisotropy is averaged over the ensemble of configurations in the similar way.

In this paper, the dimer potential energy function was modeled by the 6:12 Lennard–Jones potential depending only on two parameters: equilibrium separation $R_\mathrm{e}^{(i)}$ and the dissociation energy $D_\mathrm{e}^{(i)}$. Thanks to this, within the considered dimer model we determined molecular constants for each configuration: frequency of harmonic vibrations $\omega_\mathrm{e}^{(i)}$, rotational constant $B_\mathrm{e}^{(i)}$, and Dunham anharmonic constants a_j, which, in their turn, were used to calculate spectroscopic constants $Y_{nm}^{(i)}$, rotational-vibrational energy levels $E_{\mathrm{v}J}^{(i)}$, and matrix elements of polarizability. The matrix elements of polarizability were calculated by analytical equations given in Ref. 7. The needed polarizability derivatives were determined through expansion of the dimer polarizability tensor invariants (Eqs. (3) and (4)) into the Taylor series in terms of the variable $x^{(i)} = (R - R_\mathrm{e}^{(i)})/R_\mathrm{e}^{(i)}$ at the point $x^{(i)} = 0$.

Calculated results and discussion

The polarizability of the $(N_2)_2$ and $(O_2)_2$ dimers was calculated for 169 possible configurations obtained by changing the Euler angles θ_1, φ_1, θ_2, φ_2 with a step of 45°. Since only 19 configurations are physically different, just they were used in calculations, while the contribution from the others was taken into account through statistical weights $g^{(i)}$. Figure 1 shows some of possible dimer configurations. The dotted line is the Z-axis between centers of molecules. Parameters of these configurations and dimer characteristics in them are tabulated below. The missing values of $R_\mathrm{e}^{(i)}$ and $D_\mathrm{e}^{(i)}$ for other dimer configurations were estimated by linear interpolation.

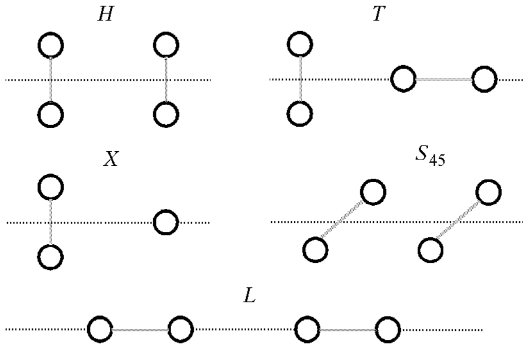

Fig. 1. Dimer configurations of diatomic molecules.

Calculation of average values of the dimer polarizability invariants requires the summation limits in Eq. (5) to be determined, what is a nontrivial problem. In this paper, the maximum values of the quantum numbers v_max and J_max (for each $\mathrm{v} \le \mathrm{v}_\mathrm{max}$) for the dimer configurations considered were determined by the technique described thoroughly in Ref. 9.

Table. Parameters of $(N_2)_2$ and $(O_2)_2$ dimers in some configurations

Configuration						$(N_2)_2$ (Ref. 3)			$(O_2)_2$ (Ref. 8)		
Symbol	θ_1, deg	φ_1, deg	θ_2, deg	φ_2, deg	g	R_e, □	D_e, cm^{-1}	δ, cm^{-1}	R_e, □	D_e, cm^{-1}	δ, cm^{-1}
L	0	0	0	0	1	5.22	6.83	73.96	4.55	45.18	83.42
T	0	0	90	0	8	4.15	75.97	4.82	4.02	61.86	66.84
H	90	0	90	0	4	3.70	44.30	36.49	3.33	128.6	0
X	90	0	90	90	4	3.63	52.01	28.78	3.28	123.0	5.6
S_{45}	45	0	45	0	8	4.09	80.79	0	4.39	37.53	91.07

Within the approach proposed, we calculated $\alpha(T)$ and $\gamma^2(T)$ averaged over the ensemble of dimer configurations with polarizabilities of actual N_2 and O_2 molecules[10] taken as the polarizabilities of model atoms. For analysis of the results obtained, we also calculated $\alpha_i(T)$ and $\gamma_i^2(T)$ for some dimer configurations (in this case, without summation over i in Eq. (5)). The calculated temperature dependence of $\alpha(T)$ and $\gamma^2(T)$ (solid lines), as well as $\alpha_i(T)$ and $\gamma_i^2(T)$ (dashed lines) of the $(N_2)_2$ and $(O_2)_2$ dimers is depicted in Figs. 2–5.

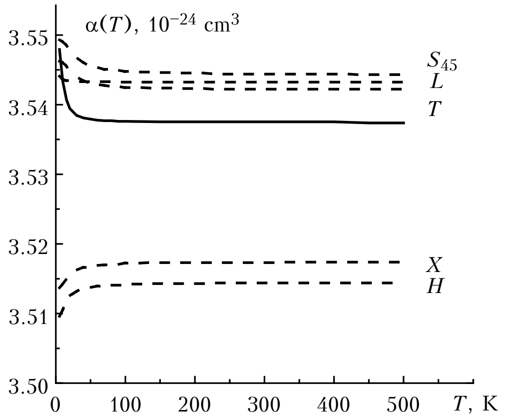

Fig. 2. Average polarizability $\alpha(T)$ and $\alpha_i(T)$ of N_2–N_2 dimer.

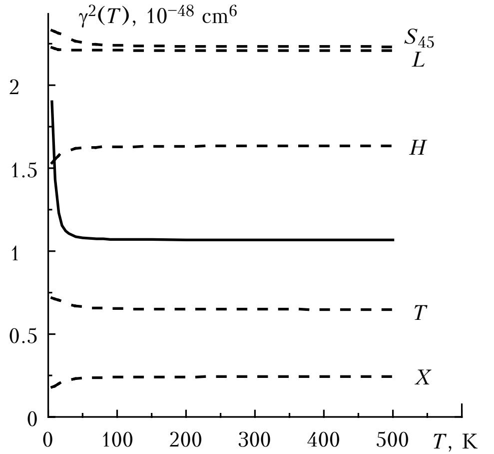

Fig. 3. Polarizability anisotropy $\gamma^2(T)$ and $\gamma_i^2(T)$ of N_2–N_2 dimer.

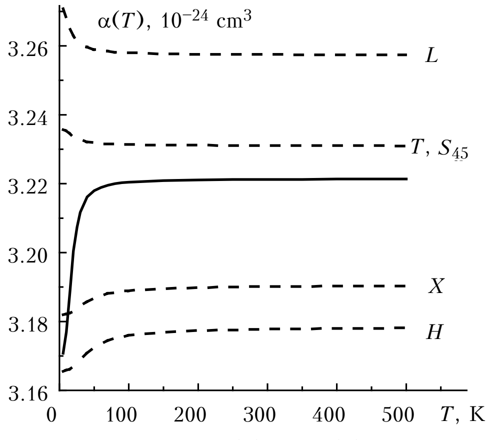

Fig. 4. Average polarizability $\alpha(T)$ and $\alpha_i(T)$ of O_2–O_2 dimer.

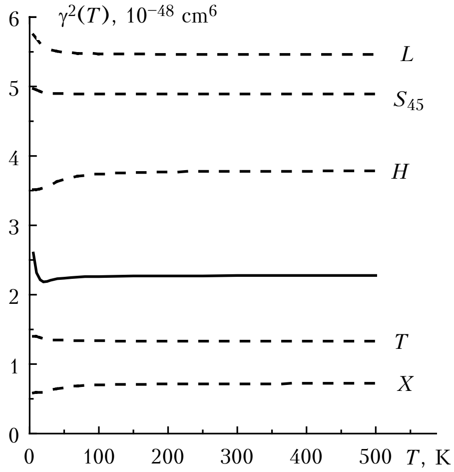

Fig. 5. Polarizability anisotropy $\gamma^2(T)$ and $\gamma_i^2(T)$ of O_2–O_2 dimer.

Analysis of the dependences suggests the following conclusions:

– the functions $\alpha(T)$, $\alpha_i(T)$, $\gamma^2(T)$, and $\gamma_i^2(T)$ change significantly at rather low temperatures $T < 100$ K;

– at $T \to 0$ K $\alpha(T)$ and $\gamma^2(T)$ tend to $\alpha_k(T)$ and $\gamma_k^2(T)$, where the index k corresponds to the most stable dimer configuration;

– at $T > 100$ K $\alpha(T)$ and $\gamma^2(T)$ weakly depend on temperature, tending to the sum of the corresponding polarizability invariants of molecules forming the dimer.

This behavior of the temperature dependences $\alpha(T)$ and $\gamma^2(T)$ of the $(N_2)_2$ and $(O_2)_2$ dimers can be explained based on the following reasoning. At very low temperature, most $(N_2)_2$ and $(O_2)_2$ dimers are in the lowest rotational-vibrational states of the most stable dimer configurations: S_{45} for $(N_2)_2$ and H for $(O_2)_2$. As the temperature increases, other dimer configurations having significantly different polarizabilities become populated. This leads to considerable changes in the temperature dependences $\alpha(T)$ and $\gamma^2(T)$. The character of these changes is different for $(N_2)_2$ and $(O_2)_2$ dimers, because of the different distributions of dimer configurations over the parameter $\delta^{(i)}$. As the temperature reaches $T \approx 100$ K, almost all rotational-vibrational states of all configurations are populated, and the further temperature growth does not lead to redistribution of dimers over configurations. At such temperatures, most molecules in dimers are free-oriented, and just this fact leads to additivity of polarizability invariants of molecules in a dimer.

Conclusion

The method proposed for calculating the temperature dependence of polarizability of molecular dimers is based on the Silbershtein's polarizability theory and representation of molecules in a dimer as model atoms, whose interaction is described by the Lennard–Jones potential.

The use of the Lennard–Jones potential is justified by the absence of reliable quantum-chemical calculations of potential energy surfaces for the $(N_2)_2$ and $(O_2)_2$ dimers in a rather wide range of intermolecular separations in a dimer.

However, in spite of simplicity of this potential, the results obtained are physically reasonable for gaseous media in thermodynamic equilibrium and can be useful in the physics of weakly bound molecular complexes.

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