

Polarizability of the van der Waals complexes $N_2\dots Y$ and $O_2\dots Y$ ($Y = \text{He, Ne, Ar, Kr, Xe}$).

Part 3. Frequency dependence

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The dependence of the dynamic polarizability of the van der Waals complexes, $X_2\dots Y$, on the distance between the spherically symmetric atom Y and the molecule X_2 , internuclear separation of the molecule X_2 , and on the orientation of X_2 molecule with respect to the complex has been investigated theoretically. Analytical expressions have been derived for the components and invariants of the dynamic polarizability tensor of the $X_2\dots Y$ complex within the framework of the induced point dipoles (IPD) model taking into account the dimensions of the X_2 molecule. The dynamic polarizability of the $X_2\dots Y$ complexes, where $X_2 = N_2, O_2$ and $Y = \text{He, Ne, Ar, Kr, Xe}$, have been calculated.

Introduction

The polarizability of van der Waals molecular complexes generally depends on the qualitative composition of a complex, its spatial structure, and on the frequency of the external electric field. In Refs. 1 and 2, we have studied theoretically the static polarizability of the simplest molecular complexes of the $X_2\dots Y$ type ($X_2 = N_2, O_2$ and $Y = \text{He, Ne, Ar, Kr, and Xe}$) having different geometric structure. This paper continues the theoretical study of the polarizability of such complexes in order to investigate dependence of the components and invariants of the polarizability tensor of the complexes on the frequency of an external electromagnetic field.

Dynamic polarizability of an $X_2\dots Y$ complex

To calculate the dynamic polarizability of atom–molecule complexes, the modified induced point dipoles (IPD) model³ was used. Within the framework of this model, each molecule of the complex is represented as a set of effective atoms, whose polarizability depends on the internuclear distances in the molecule and on the frequency ω of the electric field. In this case, there is no interaction between the effective atoms of the same molecule, and the total polarizability of these atoms coincides with the polarizability of the molecule itself. As a result, the atom–molecule complex can be represented as a set of actual and effective atoms that interact. Within such an approach, the dynamic polarizability tensor of the complex is determined from the system of equations, which can be solved using different methods.⁴

The dynamic polarizability of an $X_2\dots Y$ complex is calculated in the Cartesian coordinate system X ,

Y, Z , bound to the complex (the axis Z passes through the center of gravity of the molecule X_2 and through the atom Y). Assume that the molecule X_2 lies in the plane XZ , and its orientation in the complex is determined by the angle θ (Fig. 1).

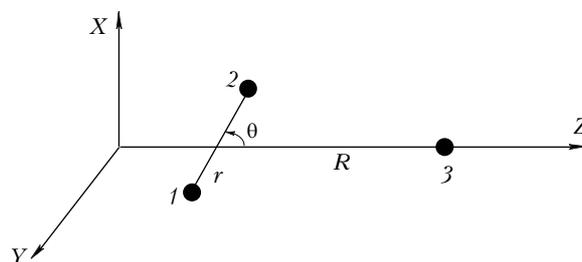


Fig. 1. Cartesian coordinate system, bound to the complex: atoms of the molecule X_2 (1, 2); atom Y (3); r is the internuclear distance of the molecule X_2 ; R is the intermolecular distance in the complex. The angle θ determines the orientation of the molecule X_2 with respect to the complex.

In the coordinate system chosen in this way, the dynamic polarizability of the $X_2\dots Y$ complex depends on the distance R between the atom Y and the center of gravity of the molecule X_2 , the separation r between the nuclei of the molecule X_2 , the orientation of the molecule X_2 with respect to the complex (angle θ), and on the polarizability $\alpha(\omega)$ of the spherically symmetric atom Y and the polarizability tensor $\alpha_{ii}^m(r, \omega)$ of the molecule X_2 . The polarizability tensor of the molecule $\alpha_{ii}^m(r, \omega)$ is defined in the Cartesian coordinate system x, y, z , bound with the molecule X_2 (the axis z coincides with the molecular axis).

The analytical equations for the components of the dynamic polarizability tensor $\alpha_{\alpha\beta}(r, R, \theta, \omega)$ at

arbitrary configurations of the $X_2...Y$ complex are omitted in this paper, because they can be derived from the corresponding equations for $\alpha_{\alpha\beta}(r, R, \theta, \omega)$ [Refs. 1, 2], if we substitute $\varphi = 0$ and take into account the frequency dependence of the atomic and molecular polarizability.

In the problems of atmospheric optics not only individual components of the polarizability tensor of the complex are of interest, but also its invariants, such as the mean polarizability

$$\alpha(r, R, \theta, \omega) =$$

$$= \frac{1}{3}[\alpha_{XX}(r, R, \theta, \omega) + \alpha_{YY}(r, R, \theta, \omega) + \alpha_{ZZ}(r, R, \theta, \omega)] \quad (1)$$

and the polarizability anisotropy

$$\begin{aligned} \gamma(r, R, \theta, \omega) = & \left\{ [\alpha_{XX}(r, R, \theta, \omega) - \alpha_{YY}(r, R, \theta, \omega)]^2 / 2 + \right. \\ & + [\alpha_{YY}(r, R, \theta, \omega) - \alpha_{ZZ}(r, R, \theta, \omega)]^2 / 2 + \\ & + [\alpha_{ZZ}(r, R, \theta, \omega) - \alpha_{XX}(r, R, \theta, \omega)]^2 / 2 + \\ & + 3[\alpha_{XY}(r, R, \theta, \omega)]^2 + 3[\alpha_{YZ}(r, R, \theta, \omega)]^2 + \\ & \left. + 3[\alpha_{XZ}(r, R, \theta, \omega)]^2 \right\}^{1/2}. \quad (2) \end{aligned}$$

The invariants of the polarizability tensor of the $X_2...Y$ complex are calculated accurate to R^{-7} terms inclusive. As a result, the following analytical equations are obtained:

$$\begin{aligned} \alpha(r, R, \theta, \omega) = & \alpha^m(r, \omega) + \alpha(\omega) + \frac{2\alpha(\omega)\gamma^m(r, \omega)}{3R^3}(3\cos^2\theta - 1) + \\ & + \frac{r^2\alpha(\omega)\gamma^m(r, \omega)}{4R^5}(35\cos^4\theta - 30\cos^2\theta + 3) + \\ & + \frac{\alpha(\omega)}{3R^6} \left\{ 6[\alpha^m(r, \omega)]^2 + 6\alpha(\omega)\alpha^m(r, \omega) + \right. \\ & + \gamma^m(r, \omega)(2\alpha^m(r, \omega) + \alpha(\omega))(3\cos^2\theta - 1) + \\ & + [\gamma^m(r, \omega)]^2(\cos^2\theta + 1) \left. \right\} + \frac{5\alpha(\omega)r^4\gamma^m(r, \omega)}{64R^7} \times \\ & \times (231\cos^6\theta - 315\cos^4\theta + 105\cos^2\theta - 5); \quad (3) \\ \gamma(r, R, \theta, \omega) = & \gamma^m(r, \omega) + \\ & + \frac{\alpha(\omega)}{R^3} (3\alpha^m(r, \omega) + \gamma^m(r, \omega))(3\cos^2\theta - 1) + \\ & + \frac{3r^2\alpha(\omega)}{8R^5} (3\alpha^m(r, \omega) + \gamma^m(r, \omega))(35\cos^4\theta - 30\cos^2\theta + 3) + \\ & + \frac{\alpha(\omega)}{2R^6\gamma^m(r, \omega)} \left\{ 36\alpha(\omega)[\alpha^m(r, \omega)]^2 + \alpha(\omega)[\gamma^m(r, \omega)]^2 \right\} \times \\ & \times (36\cos^4\theta - 33\cos^2\theta + 7) + 6\alpha^m(r, \omega)[\gamma^m(r, \omega)]^2(\cos^2\theta + 1) + \\ & + 3\alpha^m(r, \omega)\gamma^m(r, \omega)(5\alpha(\omega) + \alpha^m(r, \omega))(3\cos^2\theta - 1) + \end{aligned}$$

$$\begin{aligned} & + [\gamma^m(r, \omega)]^3(3\cos^2\theta + 1/3) - \\ & - 1/2\alpha^2(\omega)[3\alpha^m(r, \omega) + \gamma^m(r, \omega)]^2(3\cos^2\theta - 1)^2 \left. \right\} + \\ & + \frac{15\alpha(\omega)r^4\gamma^m(r, \omega)}{128R^7} (3\alpha^m(r, \omega) + \gamma^m(r, \omega)) \times \\ & \times (231\cos^6\theta - 315\cos^4\theta + 105\cos^2\theta - 5), \quad (4) \end{aligned}$$

where

$$\alpha^m(r, \omega) = 1/3[\alpha_{xx}^m(r, \omega) + \alpha_{yy}^m(r, \omega) + \alpha_{zz}^m(r, \omega)]$$

is the mean dynamic polarizability of the molecule X_2 ; $\gamma^m(r, \omega) = \alpha_{zz}^m(r, \omega) - \alpha_{xx}^m(r, \omega)$ is the anisotropy of its polarizability tensor.

Calculated dynamic polarizability of the complexes

This section presents the frequency dependences of the components and invariants of the polarizability tensors of the van der Waals $X_2...Y$ complexes ($X_2 = N_2, O_2, Y = He, Ne, Ar, Kr, Xe$). The polarizability of the complexes studied is calculated as functions of the frequency ω of the external electromagnetic field for the most stable configurations ($R = R_e, r = r_e, \theta = 0^\circ$ and $\theta = 90^\circ$) by the equations from Ref. 1. In the calculations, we used the dynamic polarizability functions $\alpha_{yy}^m(r_e, \omega) = \alpha_{xx}^m(r_e, \omega)$ and $\alpha_{zz}^m(r_e, \omega)$ of the molecules N_2 and O_2 from Refs. 5 and 6 and the dynamic polarizabilities $\alpha(\omega)$ of noble gas atoms from Refs. 7–9. The calculated functions of dynamic polarizability of the complexes under consideration are shown in Figs. 2 and 3.

Analysis of the dependences obtained allows us to draw the following conclusions:

1. As the frequency ω of the external electromagnetic field increases, the diagonal components of the polarizability tensor of the $X_2...Y$ complex increase smoothly, and this increase is more significant for heavy noble gas atoms. This is caused by the decreasing frequency of the first resonance transition of the atom Y upon the increase of the nuclear charge.

2. The difference between the frequency dependences of the polarizability tensor components of different $X_2...Y$ complexes is associated with the stronger frequency dependence of the component $\alpha_{zz}^m(r_e, \omega)$ of the molecule O_2 as compared to α_{zz}^m of the molecule N_2 . This is a consequence of the fact that the frequency of the resonance electron transition ${}^3\Sigma_g^- \rightarrow {}^3\Sigma_u^-$ (Schumann–Runge band) of the molecule O_2 is much lower than that of the transition ${}^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ of the molecule N_2 .

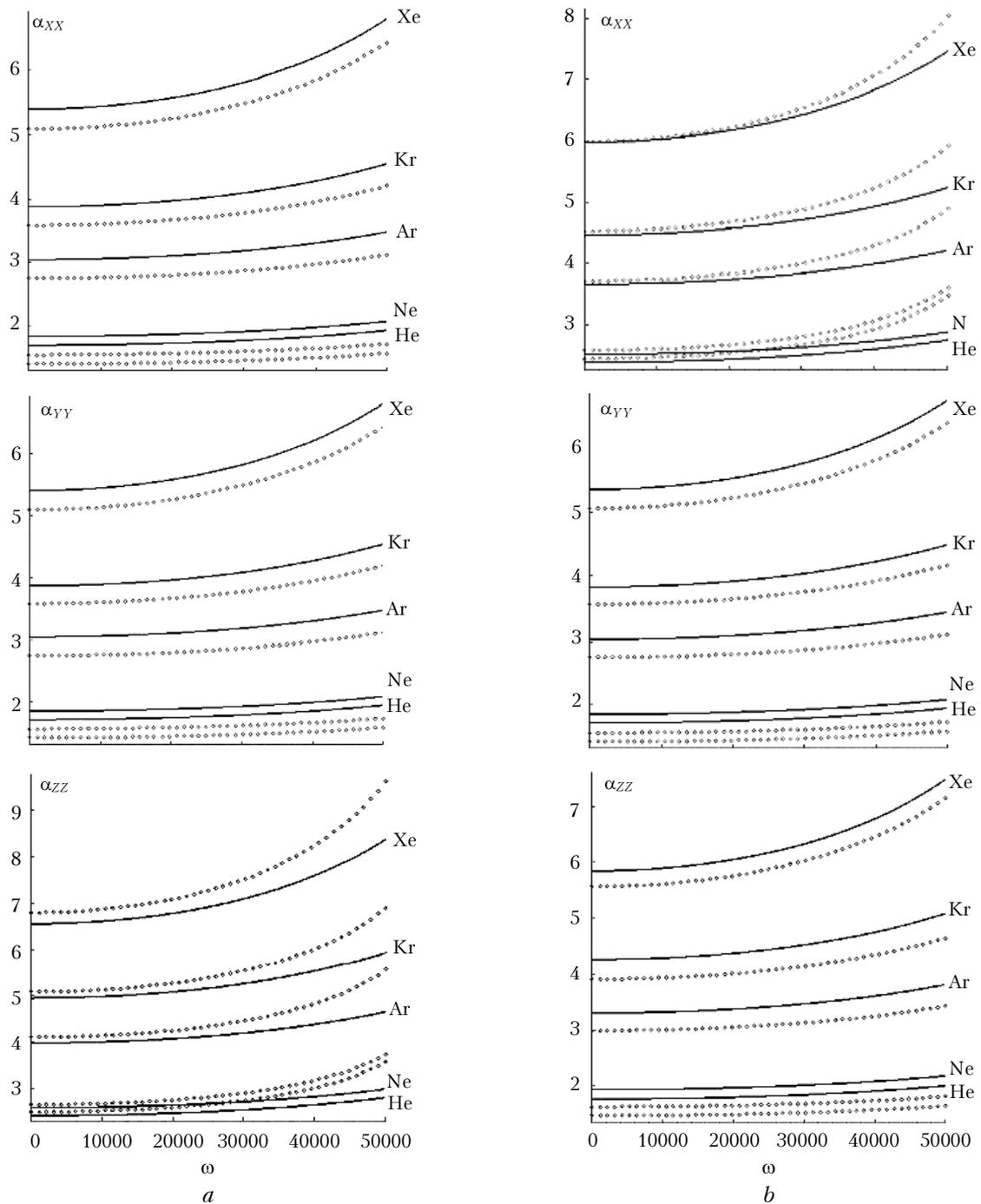


Fig. 2. Components of the dynamic polarizability tensor $\alpha_{\alpha\beta}(r_e, R_e, \theta, \omega)$ (\AA^3) of the complexes $\text{N}_2 \dots \text{Y}$ (solid curves) and $\text{O}_2 \dots \text{Y}$ (dashed curves): L-configuration ($\theta = 0^\circ$) (a); T-configuration ($\theta = 90^\circ$) (b); the frequency ω is given in cm^{-1} .

3. The invariants of the polarizability tensor of the complex $\text{X}_2 \dots \text{Y}$ also increase with the frequency of the external electromagnetic field. However, it should be noted that the anisotropy of the $\text{X}_2 \dots \text{Y}$ complex in the T-configuration ($\theta = 90^\circ$) decreases with the increase of the charge of the atom Y, whereas in the L-configuration ($\theta = 0^\circ$) it increases.

The dependence of the polarizability tensor invariants of the van der Waals $\text{X}_2 \dots \text{Y}$ complexes on the frequency of the electromagnetic field and on the

complex configuration can be presented in a more clear way by the polarizability surfaces. Such surfaces of the polarizability tensor invariants of the van der Waals $\text{X}_2 \dots \text{Y}$ complexes were calculated by Eqs. (3) and (4). As an example, Fig. 4 shows such surfaces for the complex $\text{O}_2 \dots \text{Ar}$. The polarizability surfaces of other complexes under consideration have analogous shapes. It is obvious that at $\theta = 0$ and 90° these surfaces degenerate into the functions of dynamic polarizability shown in Fig. 3.

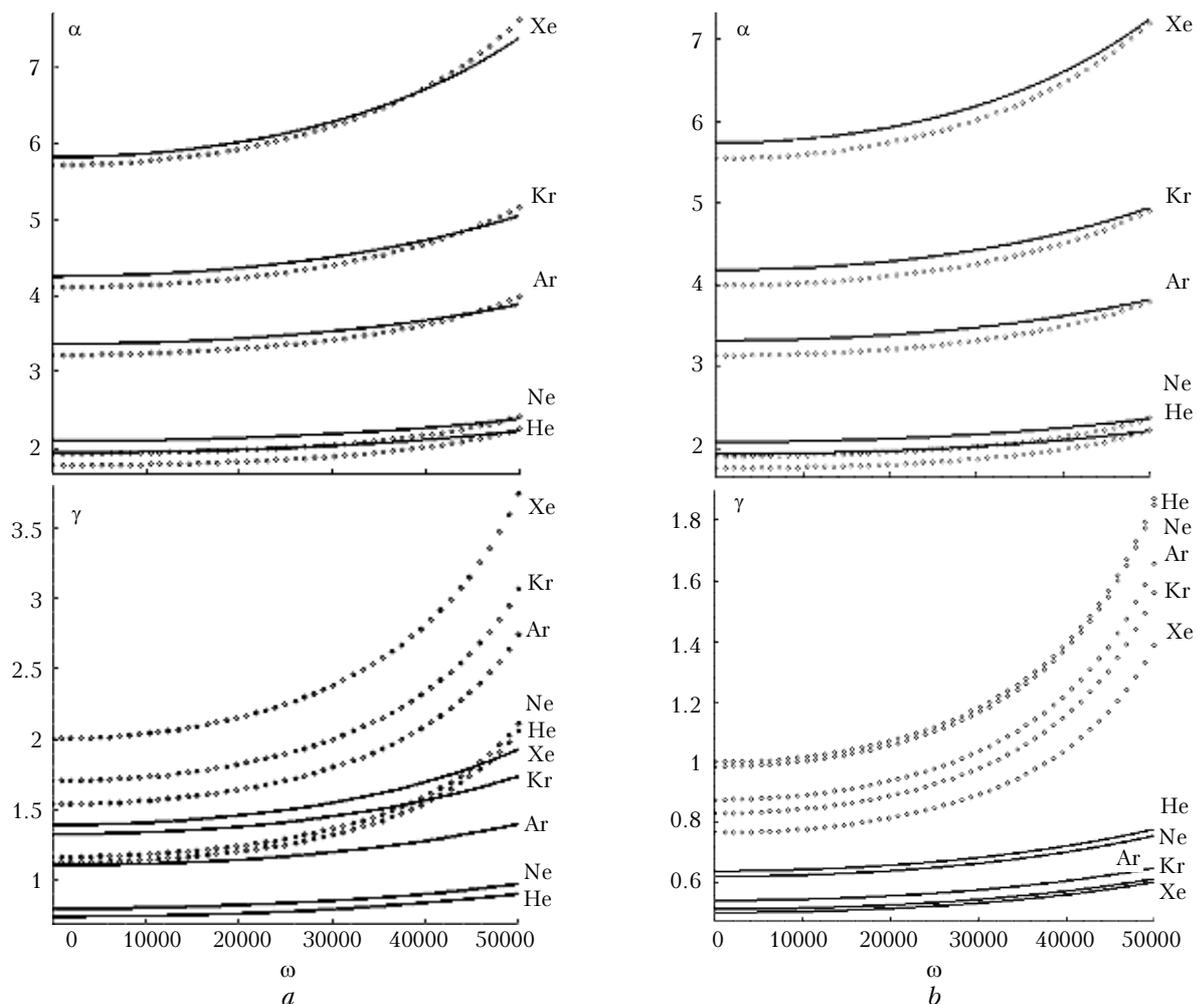


Fig. 3. Invariants of the dynamic polarizability tensor $\alpha(r_e, R_e, \theta, \omega)$ and $\gamma(r_e, R_e, \theta, \omega)$ (\AA^3) of the complexes $N_2 \dots Y$ (solid curves) and $O_2 \dots Y$ (dashed curves): (a) L-configuration ($\theta = 0^\circ$), (b) T-configuration ($\theta = 90^\circ$); the frequency ω is given in cm^{-1} .

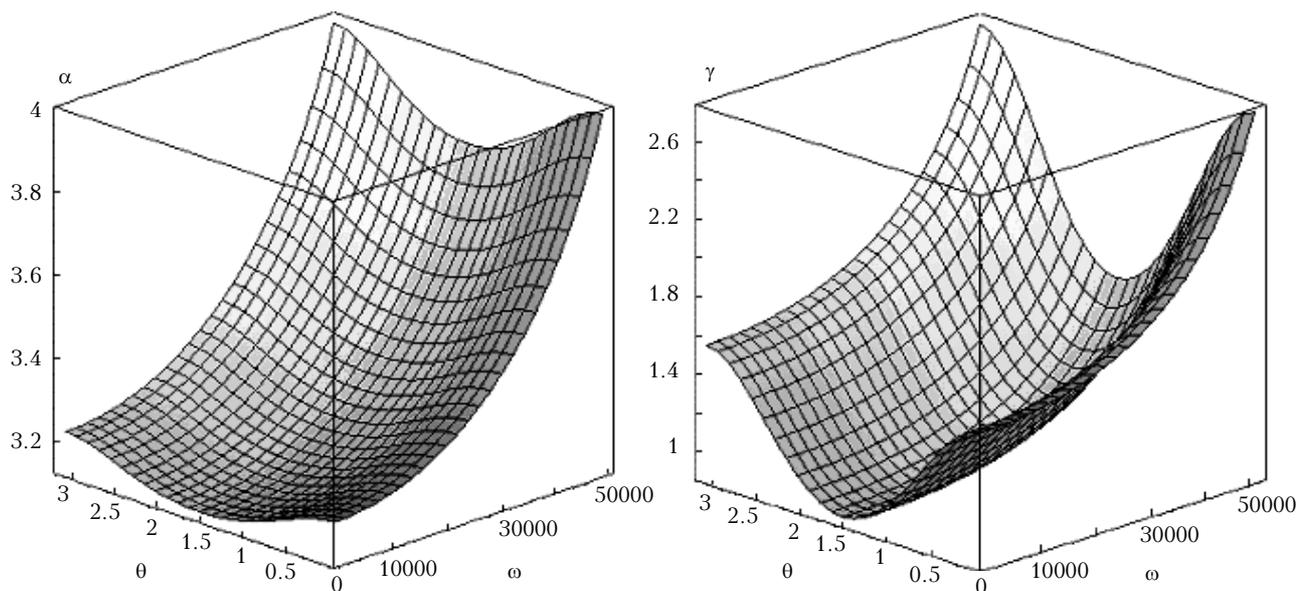


Fig. 4. Invariants of the dynamic polarizability tensor $\alpha(r_e, R_e, \theta, \omega)$ and $\gamma(r_e, R_e, \theta, \omega)$ (\AA^3) of the complex $O_2 \dots Ar$; the angle θ is given in radians; the frequency ω is given in cm^{-1} .

Conclusions

This paper closes the cycle of papers^{1,2} devoted to the analytical description of polarizability surfaces of the van der Waals complexes $X_2...Y$ ($X_2 = N_2, O_2$ and $Y = He, Ne, Ar, Kr, Xe$) as functions of their geometric structure and the frequency of the external electromagnetic field. The polarizability surfaces of the $X_2...Y$ complex have been calculated with the use of the modified Silberstein method,³ which has allowed us to express them through the dynamic polarizability of the atom Y , the dynamic polarizability tensor of a nonrigid molecule X_2 , and the geometric parameters of the complex.

The application of this method to calculation of the polarizability of the complexes under study is justified, because the van der Waals interactions between the complex components are weak and the distances between them are long enough. The efficiency of the modified Silberstein method is confirmed by a good agreement between our calculations of the polarizability of the van der Waals dimer $N_2...N_2$ [Ref. 3] and the *ab initio* calculations from Ref. 10.

References

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