

Polarizability of the van der Waals complexes N₂...Y and O₂...Y (Y=He, Ne, Ar, Kr, Xe). Part 2. Unstable configurations

M.A. Buldakov,¹ V.N. Cherepanov,² and N.S. Nagornova²

¹ *Institute of Monitoring of Climatic and Ecological Systems,
Siberian Branch of the Russian Academy of Sciences, Tomsk*

² *Tomsk State University*

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The dependence of the molecular complexes X₂...Y polarizability on the distance between the atom Y and the molecule X₂, the internuclear separation of the molecule X₂, and on the orientation of the molecule X₂ with respect to the complex has been investigated theoretically and analytical description is proposed. The polarizability of the complex was calculated within the framework of modified DID model, in which a molecule that enters a dimer is represented as two anisotropic effective atoms. The polarizability of these effective atoms was determined by the polarizability of the molecule X₂ and its orientation in the dimer. The polarizability of the complexes X₂...Y (X₂=N₂, O₂ and Y=He, Ne, Ar, Kr, Xe) has been calculated.

Introduction

A characteristic feature of the van der Waals complexes is weak interaction between the complex components. This manifests itself in the low bond energies. The potential energy surface of complexes usually has a very complicated shape with one or several minima, giving the stable configurations of the complexes.^{1,2} However, even small rotation-vibration excitation of the complexes leads to appearance of large-amplitude internal motions, due to which the complexes are mostly in unstable configurations. The complexes in stable configurations obviously play the dominant role only at a very low gas temperature. As the temperature increases, the role of the complexes in unstable configurations increases and becomes quite noticeable at atmospheric temperatures.

In Part 1 of this paper,³ we have calculated the polarizability of the van der Waals complexes X₂...Y in stable configurations. For unstable configurations, the method of polarizability calculation used in Ref. 3 gives very cumbersome expressions, practically unsuitable for analysis. That is why in this paper we use the iterative method of calculation, which is less accurate, but gives rather compact analytical expressions for the components and invariants of the polarizability tensor of the X₂...Y complexes in an arbitrary configuration.

Analytical representation of the X₂...Y complex polarizability

To calculate the polarizability of molecular complexes, we use the dipole-induced-dipole (DID) model, formulated by Silberstein for a system of

interacting atoms^{4,5} and then adapted to molecular systems.⁶ Within the framework of the modified DID model, each molecule of the complex is represented as a set of effective atoms, whose polarizability depends on the internuclear separations in the molecule. In this representation, there is no interaction between the effective atoms of the same molecule, and their total polarizability coincides with the polarizability of the molecule itself. As a result, the atom–molecule complex can be represented as a set of interacting real and effective atoms, and the polarizability tensor of such a complex $\alpha_{\alpha\beta}$ can be written as a series⁶:

$$\alpha_{\alpha\beta} = \sum_{m=1}^N \alpha_{\alpha\beta}^m + \sum_{m,n=1}^N \alpha_{\alpha\delta}^m T_{\delta\gamma}^{mn} \alpha_{\gamma\beta}^n + \sum_{m,n,k=1}^N \alpha_{\alpha\delta}^m T_{\delta\gamma}^{mn} \alpha_{\gamma\epsilon}^n T_{\epsilon\rho}^{nk} \alpha_{\rho\beta}^k + \dots \quad (1)$$

where $\alpha_{\alpha\beta}^m$ is the polarizability tensor of a real or effective atom m ; N is the total number of the real and effective atoms in the complex. The subscripts α , β , γ , δ , ϵ , and ρ stand for X , Y , Z of the Cartesian coordinate system (repeating Greek subscripts denote summation). The tensor $T_{\beta\gamma}^{mn}$ in Eq. (1) has the form

$$T_{\beta\gamma}^{mn} = -\frac{1}{(r^{mn})^5} \left(3r_{\beta}^{mn} r_{\gamma}^{mn} - (r^{mn})^2 \delta_{\beta\gamma} \right). \quad (2)$$

Here r^{mn} is the distance between the atoms m and n ; r_{β}^{mn} are the components of the vector r^{mn} . Equation (1) describes the polarizability tensor of any atom–molecule complex in an arbitrary configuration.

To calculate the polarizability of the $X_2\dots Y$ complex, introduce two Cartesian coordinate systems: the complex-fixed coordinate system X, Y, Z (the axis Z passes through the center of the molecule X_2 and the atom Y) and the X_2 molecule-fixed coordinate system x, y, z (nuclei of the molecule lie on the axis z). The orientation of the molecule in the complex is described by the Euler angles θ and φ (Fig. 1). In the coordinate systems chosen in this way, the polarizability of the complex $X_2\dots Y$ depends on the distance R between the atom Y and the center of the molecule X_2 , on the distance r between the nuclei of the molecule X_2 , and on the orientation of the molecule X_2 in the complex (angles θ and φ), as well as on the polarizability α of the spherically symmetric atom Y and the polarizability tensor $\alpha_{ij}^m(r)$ of the molecule X_2 .

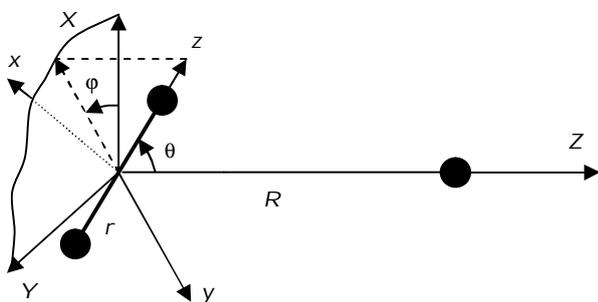


Fig. 1. Cartesian coordinate systems used in this work.

The components of the polarizability tensor of the complex $X_2\dots Y$ have been calculated by Eqs. (1) and (2) accurate to R^{-6} terms inclusive. As a result, the following analytical expressions have been obtained:

$$\begin{aligned} \alpha_{xx}(r, R, \theta, \varphi) = & \alpha_{xx}^m(r)(1 - \sin^2 \theta \cos^2 \varphi) + \\ & + \alpha_{zz}^m(r) \sin^2 \theta \cos^2 \varphi + \alpha - \\ & - \frac{2\alpha}{R^3} \left[\alpha_{xx}^m(r)(1 - \sin^2 \theta \cos^2 \varphi) + \alpha_{zz}^m(r) \sin^2 \theta \cos^2 \varphi \right] + \\ & + \frac{3r^2 \alpha}{4R^5} \left\{ \alpha_{xx}^m(r) (15 \cos^2 \theta \sin^2 \theta \cos^2 \varphi - \right. \\ & \quad \left. - \sin^2 \theta \cos^2 \varphi - 5 \cos^2 \theta + 1) - \right. \\ & \quad \left. - 3 \alpha_{zz}^m(r) \sin^2 \theta \cos^2 \varphi (5 \cos^2 \theta - 1) \right\} + \\ & + \frac{\alpha}{R^6} \left\{ (\alpha_{xx}^m(r))^2 (3 \cos^2 \theta \sin^2 \theta \cos^2 \varphi - \sin^2 \theta \cos^2 \varphi + 1) + \right. \\ & \quad + (\alpha_{zz}^m(r))^2 \sin^2 \theta \cos^2 \varphi (3 \cos^2 \theta + 1) - \\ & \quad - 6 \alpha_{xx}^m(r) \alpha_{zz}^m(r) \cos^2 \theta \sin^2 \theta \cos^2 \varphi + \\ & \quad \left. + \alpha \alpha_{xx}^m(r) (1 - \sin^2 \theta \cos^2 \varphi) + \alpha \alpha_{zz}^m(r) \sin^2 \theta \cos^2 \varphi \right\}; \quad (3) \\ \alpha_{yy}(r, R, \theta, \varphi) = & \alpha_{xx}^m(r)(1 - \sin^2 \theta \sin^2 \varphi) + \\ & + \alpha_{zz}^m(r) \sin^2 \theta \sin^2 \varphi + \alpha - \end{aligned}$$

$$\begin{aligned} & - \frac{2\alpha}{R^3} \left[\alpha_{xx}^m(r)(1 - \sin^2 \theta \sin^2 \varphi) + \alpha_{zz}^m(r) \sin^2 \theta \sin^2 \varphi \right] + \\ & + \frac{3r^2 \alpha}{4R^5} \left\{ \alpha_{xx}^m(r) (15 \cos^2 \theta \sin^2 \theta \sin^2 \varphi - \right. \\ & \quad \left. - \sin^2 \theta \sin^2 \varphi - 5 \cos^2 \theta + 1) - \right. \\ & \quad \left. - 3 \alpha_{zz}^m(r) \sin^2 \theta \sin^2 \varphi (5 \cos^2 \theta - 1) \right\} + \\ & + \frac{\alpha}{R^6} \left\{ (\alpha_{xx}^m(r))^2 (3 \cos^2 \theta \sin^2 \theta \sin^2 \varphi - \sin^2 \theta \sin^2 \varphi + 1) + \right. \\ & \quad + (\alpha_{zz}^m(r))^2 \sin^2 \theta \sin^2 \varphi (3 \cos^2 \theta + 1) - \\ & \quad - 6 \alpha_{xx}^m(r) \alpha_{zz}^m(r) \cos^2 \theta \sin^2 \theta \sin^2 \varphi + \\ & \quad \left. + \alpha \alpha_{xx}^m(r) (1 - \sin^2 \theta \sin^2 \varphi) + \alpha \alpha_{zz}^m(r) \sin^2 \theta \sin^2 \varphi \right\}; \quad (4) \end{aligned}$$

$$\begin{aligned} \alpha_{zz}(r, R, \theta) = & \alpha_{xx}^m(r) \sin^2 \theta + \alpha_{zz}^m(r) \cos^2 \theta + \alpha + \\ & + \frac{4\alpha}{R^3} (\alpha_{xx}^m(r) \sin^2 \theta + \alpha_{zz}^m(r) \cos^2 \theta) + \\ & + \frac{3r^2 \alpha}{R^5} \left\{ \alpha_{xx}^m(r) (4 \cos^2 \theta \sin^2 \theta - \sin^4 \theta) - \right. \\ & \quad \left. - \alpha_{zz}^m(r) (3 \cos^2 \theta \sin^2 \theta - 2 \cos^4 \theta) \right\} + \\ & + \frac{\alpha}{R^6} \left\{ (\alpha_{xx}^m(r))^2 (\cos^2 \theta \sin^2 \theta + 4 \sin^4 \theta) + \right. \\ & \quad + (\alpha_{zz}^m(r))^2 (\cos^2 \theta \sin^2 \theta + 4 \cos^4 \theta) + \\ & \quad + 6 \alpha_{xx}^m(r) \alpha_{zz}^m(r) \cos^2 \theta \sin^2 \theta + \\ & \quad \left. + 4 \alpha \alpha_{xx}^m(r) \sin^2 \theta + 4 \alpha \alpha_{zz}^m(r) \cos^2 \theta \right\}; \quad (5) \end{aligned}$$

$$\begin{aligned} \alpha_{xy}(r, R, \theta, \varphi) = & \sin^2 \theta \cos \varphi \sin \varphi \times \\ & \times \left\{ (\alpha_{zz}^m(r) - \alpha_{xx}^m(r)) - \frac{2\alpha}{R^3} (\alpha_{zz}^m(r) - \alpha_{xx}^m(r)) + \right. \\ & \left. + \frac{3r^2 \alpha}{4R^5} \left[\alpha_{xx}^m(r) (15 \cos^2 \theta - 1) - \alpha_{zz}^m(r) (15 \cos^2 \theta - 3) \right] + \right. \\ & \quad \left. + \frac{\alpha}{R^6} (\alpha_{zz}^m(r) - \alpha_{xx}^m(r)) \times \right. \\ & \quad \left. \times \left[\alpha_{zz}^m(r) (3 \cos^2 \theta + 1) - \alpha_{xx}^m(r) (3 \cos^2 \theta - 1) + \alpha \right] \right\}; \quad (6) \\ \alpha_{xz}(r, R, \theta, \varphi) = & \sin \theta \cos \theta \cos \varphi \left\{ (\alpha_{zz}^m(r) - \alpha_{xx}^m(r)) + \right. \\ & \quad + \frac{\alpha}{R^3} (\alpha_{zz}^m(r) - \alpha_{xx}^m(r)) - \\ & \quad - \frac{3r^2 \alpha}{8R^5} \left[\alpha_{xx}^m(r) (5 \cos^2 \theta + 7) - \alpha_{zz}^m(r) (5 \cos^2 \theta - 9) \right] + \\ & \quad \left. + \frac{\alpha}{R^6} (\alpha_{zz}^m(r) - \alpha_{xx}^m(r)) \times \right. \\ & \quad \left. \times \left[\alpha_{zz}^m(r) (3 \cos^2 \theta + 1) - \alpha_{xx}^m(r) (3 \cos^2 \theta - 4) - 2\alpha \right] \right\}; \quad (7) \end{aligned}$$

$$\begin{aligned} \alpha_{\gamma Z}(r, R, \theta, \varphi) = & \sin\theta \cos\theta \sin\varphi \left\{ (\alpha_{ZZ}^m(r) - \alpha_{XX}^m(r)) + \right. \\ & + \frac{\alpha}{R^3} (\alpha_{ZZ}^m(r) - \alpha_{XX}^m(r)) - \\ & - \frac{3r^2\alpha}{8R^5} \left[\alpha_{XX}^m(r) (5\cos^2\theta + 7) - \alpha_{ZZ}^m(r) (5\cos^2\theta - 9) \right] + \\ & + \frac{\alpha}{R^6} (\alpha_{ZZ}^m(r) - \alpha_{XX}^m(r)) \times \\ & \left. \times \left[\alpha_{ZZ}^m(r) (3\cos^2\theta + 1) - \alpha_{XX}^m(r) (3\cos^2\theta - 4) - 2\alpha \right] \right\}. \quad (8) \end{aligned}$$

In some cases, of interest are not the components of the polarizability tensor of the complex, but the tensor invariants, such as the mean polarizability

$$\begin{aligned} \alpha(r, R, \theta) = \\ = \frac{1}{3} [\alpha_{XX}(r, R, \theta, \varphi) + \alpha_{YY}(r, R, \theta, \varphi) + \alpha_{ZZ}(r, R, \theta, \varphi)] \quad (9) \end{aligned}$$

and the square polarizability anisotropy

$$\begin{aligned} \gamma^2(r, R, \theta) = & \frac{1}{2} \left[(\alpha_{XX}(r, R, \theta, \varphi) - \alpha_{YY}(r, R, \theta, \varphi))^2 + \right. \\ & + (\alpha_{YY}(r, R, \theta, \varphi) - \alpha_{ZZ}(r, R, \theta, \varphi))^2 + \\ & + (\alpha_{ZZ}(r, R, \theta, \varphi) - \alpha_{XX}(r, R, \theta, \varphi))^2 + \\ & + 6[\alpha_{XY}(r, R, \theta, \varphi)]^2 + 6[\alpha_{YZ}(r, R, \theta, \varphi)]^2 + \\ & \left. + 6[\alpha_{XZ}(r, R, \theta, \varphi)]^2 \right]. \quad (10) \end{aligned}$$

Note that $\alpha(r, R, \theta)$ and $\gamma^2(r, R, \theta)$ are independent of the angle φ , because the invariants of the polarizability tensor do not depend on the orientation of the complex as a whole. The calculation has yielded the following analytical expressions for the invariants of the polarizability tensor of the complex $X_2\dots Y$:

$$\begin{aligned} \alpha(r, R, \theta) = & \alpha^m(r) + \alpha + \frac{2\alpha\gamma^m(r)}{3R^3} (3\cos^2\theta - 1) + \\ & + \frac{r^2\alpha\gamma^m(r)}{4R^5} (35\cos^4\theta - 30\cos^2\theta + 3) + \\ & + \frac{\alpha}{3R^6} \left\{ 6(\alpha^m(r))^2 + 6\alpha\alpha^m(r) + \gamma^m(r) (2\alpha^m(r) + \alpha) \times \right. \\ & \left. \times (3\cos^2\theta - 1) + (\gamma^m(r))^2 (\cos^2\theta + 1) \right\}, \quad (11) \end{aligned}$$

$$\begin{aligned} \gamma^2(r, R, \theta) = & (\gamma^m(r))^2 + \frac{2\alpha\gamma^m(r)}{R^3} (3\alpha^m(r) + \gamma^m(r)) \times \\ & \times (3\cos^2\theta - 1) + \frac{3r^2\alpha\gamma^m(r)}{4R^5} (3\alpha^m(r) + \gamma^m(r)) \times \\ & \times (35\cos^4\theta - 30\cos^2\theta + 3) + \frac{\alpha}{R^6} \left\{ 36\alpha(\alpha^m(r))^2 + \right. \\ & \left. + \alpha(\gamma^m(r))^2 (36\cos^4\theta - 33\cos^2\theta + 7) + \right. \end{aligned}$$

$$\begin{aligned} & \left. + 6\alpha^m(r) (\gamma^m(r))^2 (\cos^2\theta + 1) + \right. \\ & \left. + 3\alpha^m(r) \gamma^m(r) (5\alpha + \alpha^m(r)) (3\cos^2\theta - 1) + \right. \\ & \left. + (\gamma^m(r))^3 (3\cos^2\theta + 1/3) \right\}, \quad (12) \end{aligned}$$

where

$$\alpha^m(r) = \frac{1}{3} [\alpha_{XX}^m(r) + \alpha_{YY}^m(r) + \alpha_{ZZ}^m(r)]$$

is the mean polarizability of the molecule X_2 and

$$\gamma^m(r) = \alpha_{XX}^m(r) - \alpha_{ZZ}^m(r)$$

is the anisotropy of its polarizability tensor.

Calculated results

The analytical expressions presented above have been used in calculating the components and invariants of the polarizability tensor of $X_2\dots Y$ complexes ($X=N, O$ and $Y=He, Ne, Ar, Kr, Xe$) as functions of the angles θ and φ assuming the equilibrium distances r_e and R_e corresponding to the most stable configuration of the complex. In the calculations, we used the components of the polarizability tensor of N_2 and O_2 molecules: $\alpha_{YY}(r) = \alpha_{XX}(r)$ and $\alpha_{ZZ}(r)$ from Ref. 7, as well as the polarizability α of atoms of the inert gases from Refs. 8–11. As an example, Fig. 2 depicts the components of the polarizability tensor of the $N_2\dots Ar$ complex as functions of the angles θ and φ . It is clearly seen that the complex polarizability strongly depends on the orientation of the molecule N_2 , and the variability range of the diagonal components of the polarizability tensor significantly (roughly by 10 times) exceeds that of the off-diagonal components. The dependences shown in Fig. 2 are characteristic of the other studied complexes as well.

It is interesting to consider how the invariants of the polarizability tensor of the complex vary at different values of the angle θ . For this purpose, by analogy with Ref. 3, introduce the non-additive parts of the invariants of the complex polarizability tensor

$$\Delta\alpha(r_e, R_e, \theta) = \alpha(r_e, R_e, \theta) - \alpha^m(r_e) - \alpha \quad (13)$$

and

$$\Delta\gamma^2(r_e, R_e, \theta) = \gamma^2(r_e, R_e, \theta) - (\gamma^m(r_e))^2. \quad (14)$$

The calculated dependences $\Delta\alpha(r_e, R_e, \theta)$ and $\Delta\gamma^2(r_e, R_e, \theta)$ on the angle θ for the complexes $N_2\dots Y$ ($Y=He, Ne, Ar, Kr, Xe$) are shown in Fig. 3.

The analysis of these dependences suggests the following:

1. The invariants of the polarizability tensor of the complex in its most stable configuration ($\theta = 90^\circ$) are smaller than the sums of the corresponding invariants of the polarizability tensors of the non-interacting atom and molecule.

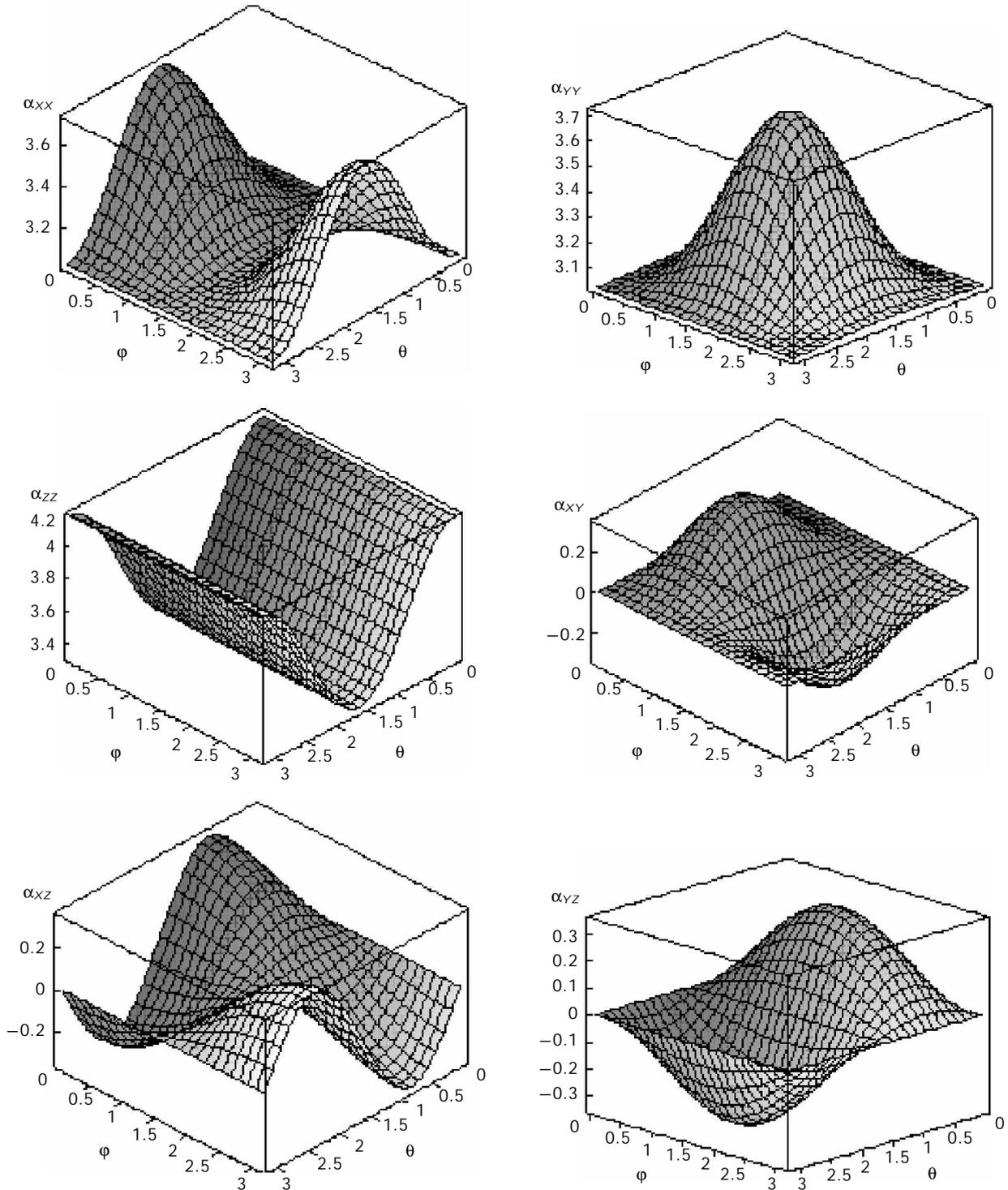


Fig. 2. Components of the polarizability tensor (in Å³) of N₂...Ar complex at $R = R_e$ and $r = r_e$; the angles θ and φ are measured in radians.

2. The invariants of the polarizability tensor of the complex increase as its geometry alternates from the *T*-configuration ($\theta = 90^\circ$) to the *L*-configuration ($\theta = 0^\circ$).

3. The range of possible variations of the invariants of the complex polarizability tensor increases with the increase in the polarizability α of the atom of an inert gas.

4. The relative change of the mean polarizability of the complex is much smaller (1–2 orders of magnitude) than the relative change of the square polarizability anisotropy:

$$\begin{aligned} & \left(\Delta\alpha(r_e, R_e, \theta = 0^\circ) - \Delta\alpha(r_e, R_e, \theta = 90^\circ) \right) / \left(\alpha^m(r_e) + \alpha \right) \ll \\ & \ll \left(\Delta\gamma^2(r_e, R_e, \theta = 0^\circ) - \Delta\gamma^2(r_e, R_e, \theta = 90^\circ) \right) / \left(\gamma^m(r_e) \right)^2. \end{aligned}$$

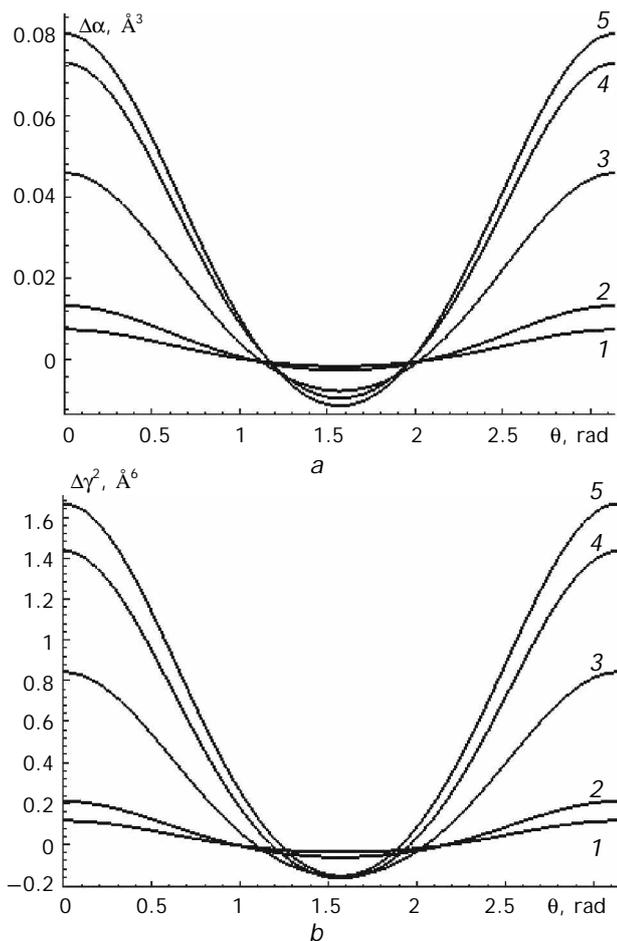


Fig. 3. Variation of the non-additive part of the mean polarizability (a) and the square polarizability anisotropy (b) of $N_2...Y$ complexes at $R = R_e$ and $r = r_e$: $N_2...He$ (1), $N_2...Ne$ (2), $N_2...Ar$ (3), $N_2...Kr$ (4), $N_2...Xe$ (5).

The calculation of the components and invariants of the polarizability tensor by Eqs. (3)–(8) and (11), (12) includes an error, because the series (1) is restricted to the terms $\sim R^{-6}$. For the considered complexes (at $R = R_e$), this error amounts to $\sim 0.001 \text{ \AA}^3$ for the components of the polarizability tensor and the mean polarizability and $\sim 0.01 \text{ \AA}^6$ for the square

polarizability anisotropy. It should be noted that this error does not include the errors inherent in the modified DID model. However, the check of this model with $N_2...N_2$ complex taken as an example showed that it provides for the reliable values of polarizability of the van der Waals complexes.⁶

Conclusions

The analytical expressions for the polarizability of $X_2...Y$ complexes have been derived within the framework of the modified DID model. These expressions reflect the regularities in the transformation of the polarizability tensor of such complexes as functions of the internuclear separation of the molecule X_2 , the distance between the atom Y and the molecule X_2 , as well as the orientation of the molecule X_2 in the complex. The results of this work can be used in studies of the influence of van der Waals complexes on the properties of gaseous media under various thermodynamic conditions and, in particular, to determine the role of $X_2...Y$ complexes in physical and chemical processes in the Earth's atmosphere.

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