Polarizability of the van der Waals complexes N₂...Y and O₂...Y (Y=He, Ne, Ar, Kr, Xe). Part 1. Stable configurations

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Within the framework of the modified DID theory, the analytical expressions for the polarizability tensor components of the van der Waals complexes $X_2...Y$ (Y = He, Ne, Ar, Kr, Xe, and X = N, O), being in stable configurations, have been obtained. The polarizability of these complexes has been calculated assuming their stable configurations. It has been estimated how the complex polarizability tensor changes as its component molecule approaches the atom of a noble gas.

Introduction

A van der Waals complex is a bound state of several atoms and molecules due to the van der Waals interactions. Such complexes are characterized by low bonding energy, joining atoms and molecules into a complex (much lower than the bonding energy in ordinary molecules) and by large distances between the particles in a complex (essentially exceeding the internuclear separations in molecules). For this reason, the complex components keep their individuality in the first approximation. In spite of this, the properties of a complex are not simple sums of the analogous properties of its components. To be mentioned in the first place is the change of moments of inertia and selection rules and the appearance of additional degrees of freedom of the components due to intermolecular vibrations and rotations, which give rise to new spectral bands and some distortions of the bands, belonging to the complex components.

One more feature of the van der Waals complexes is a non-rigid structure. Thus, the quantum-chemical calculations of the potential energy surface of complexes[1,2] indicate that the complexes can exist in several configurations with different dissociation energies. As a result, even a small rotation-vibration excitation is sufficient for a complex to change its configuration for a different one.

The content of van der Walls complexes in a gas under normal conditions is relatively low, but as the gas temperature grows, it increases markedly and becomes quite significant at high temperatures. Being present in all gas media, complexes take an active part in all physical-chemical processes and exert a marked influence on the gas properties. Thus, the presence of complexes in a gas significantly changes the relaxation rates of the rotation-vibration energy and, consequently, the time needed for establishing thermodynamic equilibrium. On the other hand, the presence of complexes in gases leads to more efficient chemical and photochemical reactions.[3,4]

At the same time, the van der Walls complexes are not studied thoroughly by now. The main progress is achieved in the field of quantum-chemical calculations of the potential energy surfaces of relatively simple molecular complexes. In this way, the parameters of the stable configurations of these complexes have been determined with high reliability. The electric characteristics of van der Waals complexes (dipole moments and polarizability) are studied much more poorly.

The aim of this work was theoretical investigation of the polarizability of the simplest molecular complexes $X_2...Y$ in the stable configurations, where X_2 is a diatomic homonuclear molecule, and Y is an atom of a noble gas.

Method for calculation of the polarizability of molecular complexes

To calculate the polarizability of molecular complexes, let us use the dipole-induced-dipole (DID) model formulated by Silberstein for a system of N interacting atoms.[5,6] Within this model, the induced dipole moment μ^m of an atom m can be written in the form

$$\mu_\alpha^m = \alpha_{\alpha\beta}^m \left(E_\beta^m - \sum_{n \neq m} T_{\beta\gamma}^{mn} \mu_\gamma^n \right), \qquad (1)$$

where $\alpha_{\alpha\beta}^m$ is the polarizability tensor of the atom m; E_β^m is the external electric field, applied to the atom m; $T_{\beta\gamma}^{mn} \mu_\gamma^n$ is the electric field at the atom m, caused by the induced dipole of the atom n. The subscripts α, β, γ can be equal to X, Y, Z of the Cartesian coordinate system (from here on, the repeating

subscripts β and γ denote summation). The tensor $T_{\beta\gamma}^{mn}$ has the form

$$T_{\beta\gamma}^{mn} = -\frac{1}{(r^{mn})^5}\left[3r_\beta^{mn}r_\gamma^{mn} - (r^{mn})^2\delta_{\beta\gamma}\right], \qquad (2)$$

where r^{mn} is the distance between the atoms m and n; r_β^{mn} are the components of the vector r^{mn}. The expression in parentheses in Eq. (1) is the total electric field, acting on the atom m. This field consists of the external field and the fields of the induced dipole of all other atoms.

To solve the system of equations (1), we use the method proposed in Ref. 7 and further developed in Ref. 8. As a result, Eq. (1) takes the form

$$\mu_\alpha^m(\alpha_{\alpha\beta}^m)^{-1} + \sum_{n\neq m} T_{\beta\gamma}^{mn}\mu_\gamma^n = E_\beta^m, \qquad (3)$$

which is equivalent to the system of $3N$ equations

$$\begin{bmatrix} \alpha_1^{-1} & T_{12} & \diagdown & T_{1N} \\ T_{21} & \alpha_2^{-1} & \diagdown & T_{2N} \\ \wedge & \wedge & \diagdown & \wedge \\ T_{N1} & T_{N2} & \diagdown & \alpha_N^{-1} \end{bmatrix} \begin{bmatrix} \mu_1 \\ \mu_2 \\ \wedge \\ \mu_N \end{bmatrix} = \begin{bmatrix} E_1 \\ E_2 \\ \wedge \\ E_N \end{bmatrix}. \qquad (4)$$

For brevity, the following designations are introduced here: $\alpha_m \equiv \alpha_{\alpha\beta}^m$; $T_{mn} \equiv T_{\beta\gamma}^{mn}$; $\mu_m \equiv \mu_\gamma^m$, and $E_m \equiv E_\beta^m$. The matrices α_m and T_{mn} are 3×3, and μ_m and E_m are the 3×1 matrices.

The solution of the system of equations (4) can be presented in the form

$$\begin{bmatrix} \mu_1 \\ \mu_2 \\ \wedge \\ \mu_N \end{bmatrix} = \begin{bmatrix} \alpha_1^{-1} & T_{12} & \diagdown & T_{1N} \\ T_{21} & \alpha_2^{-1} & \diagdown & T_{2N} \\ \wedge & \wedge & \diagdown & \wedge \\ T_{N1} & T_{N2} & \diagdown & \alpha_N^{-1} \end{bmatrix}^{-1} \begin{bmatrix} E_1 \\ E_2 \\ \wedge \\ E_N \end{bmatrix} \qquad (5)$$

or

$$\mu_\alpha^m = \sum_n B_{\alpha\beta}^{mn} E_\beta^n, \qquad (6)$$

where the explicit form of the matrix $B_{\alpha\beta}^{mn}$ is given by Eq. (5). Since the external field is the same for all the atoms ($E_\beta^n \equiv E_\beta$), the total dipole moment of all the atoms can be written as

$$\mu_\alpha = \sum_m \mu_\alpha^m = E_\beta \sum_{n,m} B_{\alpha\beta}^{mn}. \qquad (7)$$

The resulting equation for the polarizability tensor of the system of interacting atoms takes the form

$$\alpha_{\alpha\beta} = \sum_{n,m} B_{\alpha\beta}^{mn}. \qquad (8)$$

The equation obtained for the polarizability tensor of the system of interacting atoms is exact within the chosen model.

The method considered above has been modified in Ref. 9 for the calculation of the polarizability of molecular complexes. In this modified method, every molecule in a complex is represented as a set of effective atoms, whose polarizability depends on the internuclear separations in the molecule. The total polarizability of the effective atoms of every molecule coincides with the polarizability of this molecule, and the interaction between the effective atoms of the same molecule is absent. The concept of effective atoms, allows one to take into account the size of the interacting molecules and to use the above mathematical apparatus for the calculation of polarizability of molecular complexes.

Polarizability of the complex $X_2...Y$

The calculations of the potential energy surfaces for the complexes $N_2...Y$ and $O_2...Y$ (Y = He, Ne, Ar, Kr, Xe) have shown that the complexes $N_2...Y$ exist in one stable configuration (T-configuration),[10–23] while the complexes $O_2...Y$ exist in two stable configurations (L- and T-configurations),[24–28] and the T-configuration is the most stable among them. The stable configurations of these complexes are shown in Fig. 1, in which atoms 1 and 2 belong to the molecule X_2, and atom 3 is the atom Y.
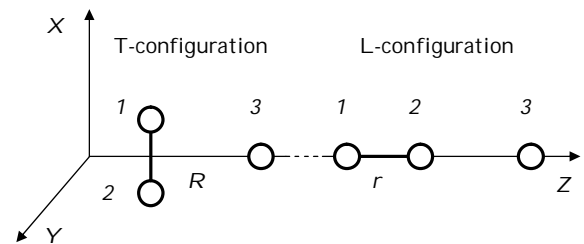

Fig. 1. Stable configurations of the complexes $X_2...Y$.

Atom 3 is a noble gas atom in the ground state, and therefore its polarizability tensor α is isotropic. Within the modified method, atoms 1 and 2 do not interact with each other ($T_{\beta\gamma}^{12} = T_{\beta\gamma}^{21} = 0$) and are the same effective atoms, whose polarizability is described by the tensor

$$\alpha_{\alpha\beta}^0(r) = \frac{1}{2}\alpha_{\alpha\beta}^m(r),$$

where $\alpha_{\alpha\beta}^m(r)$ is the polarizability tensor of the molecule X_2 in the complex-fixed coordinate system (see Fig. 1), and r is the distance between atoms in the molecule.

In the further calculations, it is more convenient to use the polarizability tensor of the molecule $\alpha_{ij}^m(r)$, written in the molecular system of coordinates ($i, j = x, y, z$). In this coordinate system (the axis z coincides with the molecular axis), the tensor $\alpha_{ij}^m(r)$ has only three nonzero components: $\alpha_{xx}^m(r) = \alpha_{yy}^m(r)$ and $\alpha_{zz}^m(r)$.

Polarizability of the complex X₂...Y in the L-configuration

In this case, the complex-fixed coordinate system (see Fig. 1) is the main one for the polarizability tensor of the complex, and therefore in this coordinate system it has the diagonal form $\alpha_{\beta\beta}(r, R)$. A feature of the L-configuration of the complex $X_2...Y$ is that the coordinate system chosen coincides with the molecular coordinate system of the molecule X_2, and thus

$$\alpha_{XX}^m(r) = \alpha_{YY}^m(r) = \alpha_{xx}^m(r) = \alpha_{yy}^m(r)$$

$$\text{and } \alpha_{ZZ}^m(r) = \alpha_{zz}^m(r) .$$

Following the calculation scheme considered above, we obtain the following equations for the components of the polarizability tensor of the complex $X_2...Y$ in the L-configuration:

$$\alpha_{XX}(r,R) = \alpha_{YY}(r,R) =$$

$$= \left\{ \alpha_{xx}^m(r) + \alpha - \alpha\alpha_{xx}^m(r)\left(\frac{1}{R_{13}^3} + \frac{1}{R_{23}^3}\right) - \frac{1}{4}\alpha\left[\alpha_{xx}^m(r)\right]^2 \times\right.$$

$$\left.\times\left(\frac{1}{R_{13}^3} - \frac{1}{R_{23}^3}\right)^2\right\} \Big/ \left\{1 - \frac{1}{2}\alpha\alpha_{xx}^m(r)\left(\frac{1}{R_{13}^6} + \frac{1}{R_{23}^6}\right)\right\}, \quad (9)$$

$$\alpha_{ZZ}(r,R) = \left\{ \alpha_{zz}^m(r) + \alpha + 2\alpha\alpha_{zz}^m(r)\left(\frac{1}{R_{13}^3} + \frac{1}{R_{23}^3}\right) - \right.$$

$$\left. -\alpha\left[\alpha_{zz}^m(r)\right]^2\left(\frac{1}{R_{13}^3} - \frac{1}{R_{23}^3}\right)^2\right\} \Big/ \left\{1 - 2\alpha\alpha_{zz}^m(r)\left(\frac{1}{R_{13}^6} + \frac{1}{R_{23}^6}\right)\right\},$$

$$(10)$$

where

$$R_{13} = R + \frac{r}{2}, \quad R_{23} = R - \frac{r}{2},$$

and R is the distance between the atom Y and the center of gravity of the molecule X_2.

Polarizability of the complex X₂...Y in the T-configuration

In this case, the chosen coordinate system (see Fig. 1) is also the main one for the polarizability tensor of the complex, but it does not coincide with the molecular coordinate system of the molecule X_2. However, in these coordinate systems there is a unique correspondence between the components of the polarizability tensor of the molecule X_2:

$$\alpha_{XX}^m(r) = \alpha_{zz}^m(r) \text{ and } \alpha_{YY}^m(r) = \alpha_{ZZ}^m(r) = \alpha_{xx}^m(r) .$$

As a result, the calculation of the components of the polarizability tensor of the complex $X_2...Y$ in the T-configuration yields the following analytical expressions:

$$\alpha_{XX}(r,R) =$$

$$= \left\{ \alpha_{zz}^m(r) + \alpha + 2\alpha\alpha_{zz}^m(r)\left[\left(\frac{r^2}{2} - R^2\right)\Big/\left(R^2 + \frac{r^2}{4}\right)^{5/2}\right] - \right.$$

$$\left. -\frac{9}{4}\alpha\alpha_{xx}^m(r)\alpha_{zz}^m(r)\left[r^2R^2\Big/\left(R^2 + \frac{r^2}{4}\right)^5\right]\right\} \times$$

$$\times\left\{1 - \alpha\alpha_{zz}^m(r)\left[\left(\frac{r^2}{2} - R^2\right)^2\Big/\left(R^2 + \frac{r^2}{4}\right)^5\right] - \right.$$

$$\left. -\frac{9}{4}\alpha\alpha_{xx}^m(r)\left[r^2R^2\Big/\left(R^2 + \frac{r^2}{4}\right)^5\right]\right\}^{-1}, \quad (11)$$

$$\alpha_{YY}(r,R) = \left\{\alpha_{xx}^m(r) + \alpha - 2\alpha\alpha_{xx}^m(r)\Big/\left(R^2 + \frac{r^2}{4}\right)^{3/2}\right\} \times$$

$$\times\left\{1 - \alpha\alpha_{xx}^m(r)\Big/\left(R^2 + \frac{r^2}{4}\right)^3\right\}^{-1}, \quad (12)$$

$$\alpha_{ZZ}(r,R) =$$

$$= \left\{\alpha_{xx}^m(r) + \alpha + 2\alpha\alpha_{xx}^m(r)\left[\left(2R^2 - \frac{r^2}{4}\right)\Big/\left(R^2 + \frac{r^2}{4}\right)^{5/2}\right] - \right.$$

$$\left. -\frac{9}{4}\alpha\alpha_{xx}^m(r)\alpha_{zz}^m(r)\left[r^2R^2\Big/\left(R^2 + \frac{r^2}{4}\right)^5\right]\right\} \times$$

$$\times\left\{1 - \alpha\alpha_{xx}^m(r)\left[\left(2R^2 - \frac{r^2}{4}\right)^2\Big/\left(R^2 + \frac{r^2}{4}\right)^5\right] - \right.$$

$$\left. -\frac{9}{4}\alpha\alpha_{zz}^m(r)\left[r^2R^2\Big/\left(R^2 + \frac{r^2}{4}\right)^5\right]\right\}^{-1}. \quad (13)$$

Thus, the polarizability of the stable configurations of the complex $X_2...Y$ is determined by the polarizability tensor of the molecule X_2, dependent on its internuclear separation r, the polarizability of the noble gas atom, and the distance R.

Note that at $r = 0$ Eqs. (9)–(13) coincide with the corresponding equations for the components of the polarizability tensor of two interacting anisotropic atoms in the classical Silberstein theory.

Results and discussion

The components of the polarizability tensor of the complexes $N_2...Y$ and $O_2...Y$ (Y = He, Ne, Ar, Kr, Xe) as functions of the distances r and R have been calculated by Eqs. (9)–(13) for the T- and L-configurations. In the calculations, we used the components of the polarizability tensor $\alpha_{yy}^m(r) = \alpha_{xx}^m(r)$ and $\alpha_{zz}^m(r)$ of the molecules N_2 and O_2 from

Ref. 29 and the polarizabilities of the noble atoms: $\alpha(He) = 0.205$ Å^3 [Ref. 30], $\alpha(Ne) = 0.352$ Å^3, $\alpha(Ar) = 1.594$ Å^3 [Ref. 31], $\alpha(Kr) = 2.488$ Å^3, $\alpha(Xe) = 4.114$ Å^3 [Ref. 33]. Figure 2 shows the calculated surfaces of the components of the polarizability tensor of the $N_2...Ar$ complex (T-configuration) for the distances r and R ranging in the intervals $0 \le r \le 5$ Å and 3 Å $\le R \le 5$ Å.

The surfaces of the components of the polarizability tensors for other $X_2...Y$ complexes (T-configuration) have similar shapes. As would be expected, the polarizability of the complexes changes significantly as a function of the internuclear separation of the molecule r and weakly depends on the distance R. This conclusion is also valid for the $O_2...Y$ complexes in the L-configuration.

It is interesting to consider the variation of the polarizability tensor of the complex $X_2...Y$ as the molecule X_2 and the noble atom Y approach each other. For this purpose, let us separate a non-additive part of the complex polarizability tensor

$$\Delta\alpha_{\beta\beta}(r, R) = \alpha_{\beta\beta}(r, R) - \alpha_{\beta\beta}(r, \infty), \qquad (14)$$

where $\alpha_{\beta\beta}(r, \infty)$ is the polarizability tensor of the complex, when the atom and the properly oriented molecule are far separated. Using Eq. (14), we have calculated the dependence of the non-additive parts of the polarizability tensor on the distances r and R for the T- and L-configurations of the complexes studied.
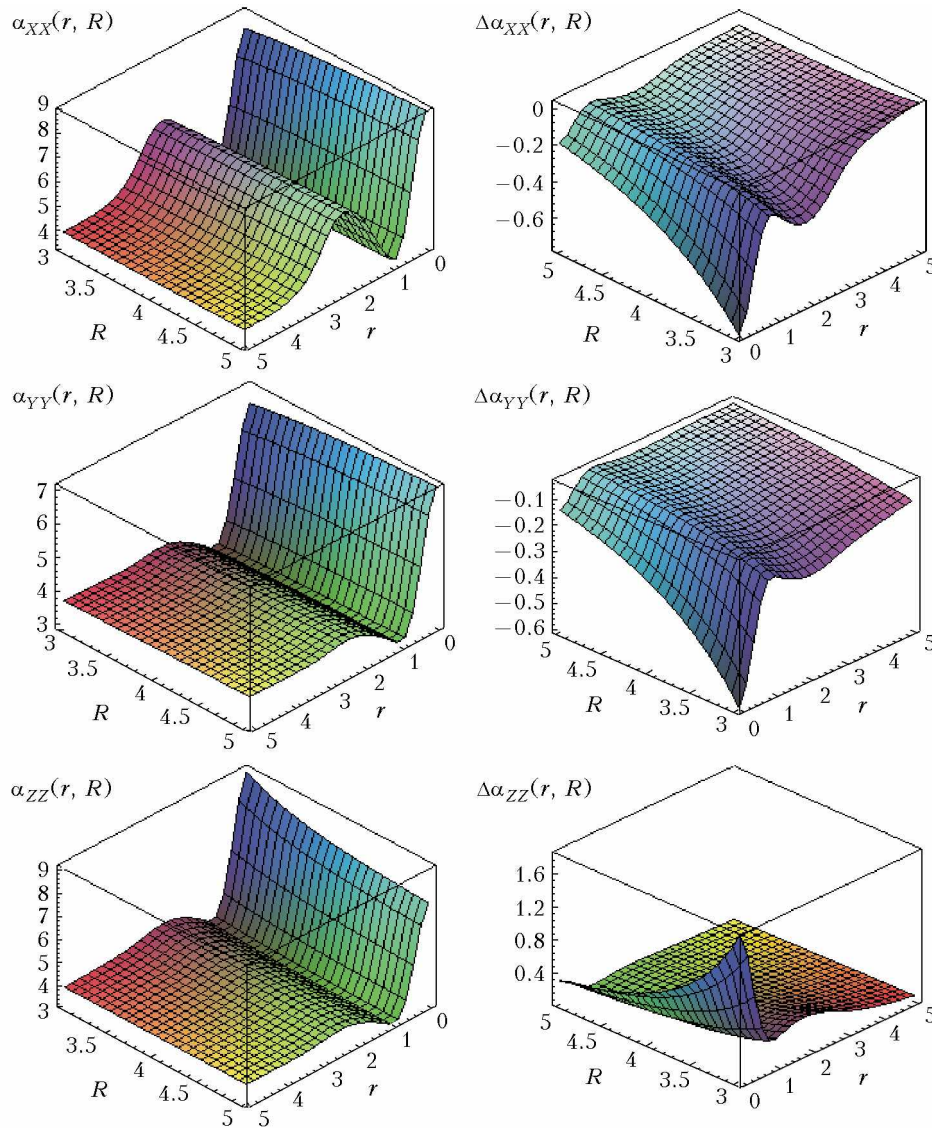

Fig. 2. Components $\alpha_{\beta\beta}(r, R)$ of the polarizability tensor and their non-additive parts $\Delta\alpha_{\beta\beta}(r, R)$ for the $N_2...Ar$ complex in the T-configuration (in Å^3); the distances r and R are given in Å.

Polarizability tensors $\alpha_{\beta\beta}$ (Å^3) and their non-additive parts $\Delta\alpha_{\beta\beta}$ (Å^3)
for the complexes $N_2...Y$ and $O_2...Y$ (Y = He, Ne, Ar, Kr, Xe) in the stable configurations

Complex	Configuration			α_{XX}	α_{YY}	α_{ZZ}	$\Delta\alpha_{XX}$	$\Delta\alpha_{YY}$	$\Delta\alpha_{ZZ}$
	Form	ΔE_e, cm^{-1}	R_e, Å						
$N_2...He$		23.2 (Ref. 10)	3.39 (Ref. 10)	2.43	1.72	1.77	−0.02	−0.02	0.03
$N_2...Ne$		53.3 (Ref. 10)	3.37 (Ref. 10)	2.56	1.86	1.94	−0.04	−0.03	0.05
$N_2...Ar$	T	104.8 (Ref. 10)	3.70 (Ref. 10)	3.71	3.04	3.32	−0.12	−0.09	0.19
$N_2...Kr$		138.2 (Ref. 22)	3.74 (Ref. 22)	4.55	3.89	4.32	−0.19	−0.14	0.30
$N_2...Xe$		91.2 (Ref. 23)	4.22 (Ref. 23)	6.14	5.49	5.99	−0.22	−0.16	0.35
$O_2...He$		27.9 (Ref. 24)	3.18 (Ref. 24)	2.51	1.44	1.48	−0.03	−0.02	0.03
$O_2...Ne$		58.1 (Ref. 26)	3.36 (Ref. 26)	2.65	1.58	1.65	−0.04	−0.02	0.04
$O_2...Ar$	T	117.0 (Ref. 27)	3.55 (Ref. 27)	3.78	2.76	3.01	−0.14	−0.08	0.18
$O_2...Kr$		127.8 (Ref. 28)	3.72 (Ref. 28)	4.63	3.63	3.98	−0.19	−0.11	0.24
$O_2...Xe$		144.1 (Ref. 28)	3.87 (Ref. 28)	6.16	5.20	5.73	−0.28	−0.16	0.36
$O_2...He$		25.6 (Ref. 24)	3.65 (Ref. 24)	1.44	1.44	2.58	−0.01	−0.01	0.05
$O_2...Ne$		27.6 (Ref. 26)	4.03 (Ref. 26)	1.59	1.59	2.74	−0.02	−0.02	0.06
$O_2...Ar$	L	104.0 (Ref. 27)	4.02 (Ref. 27)	2.78	2.78	4.21	−0.07	−0.07	0.28
$O_2...Kr$		87.1 (Ref. 28)	4.13 (Ref. 28)	3.64	3.64	5.23	−0.10	−0.10	0.41
$O_2...Xe$		104.4 (Ref. 28)	4.30 (Ref. 28)	5.22	5.22	7.05	−0.14	−0.14	0.60

It can be seen from Fig. 2 that all the components of the polarizability tensor $\Delta\alpha_{\beta\beta}(r, R)$ have quite a complicated dependence on the distances r and R, and the component $\Delta\alpha_{ZZ}(r, R)$ is positive, while the components $\Delta\alpha_{XX}(r, R)$ and $\Delta\alpha_{YY}(r, R)$ are negative. Thus, upon the formation of the complex, the component $\alpha_{ZZ}(r, R)$ increases, while the components $\alpha_{XX}(r, R)$ and $\alpha_{YY}(r, R)$ decrease as compared with the sum of the corresponding polarizability components of the non-interacting atom and molecule. This is also valid for other $X_2...Y$ complexes in the T- and L-configurations.

The polarizability $\alpha_{\beta\beta} \equiv \alpha_{\beta\beta}(r_e, R_e)$ and the non-additive part of polarizability $\Delta\alpha_{\beta\beta} \equiv \Delta\alpha_{\beta\beta}(r_e, R_e)$ for the stable configurations of the considered complexes were calculated by Eqs. (9)−(14). The dissociation energies ΔE_e and the equilibrium distances R_e of the stable configurations are summarized in the Table.

In the calculations, we also used the values of the equilibrium internuclear separations r_e of the molecules N_2 and O_2 from Ref. 34. The obtained values of $\alpha_{\beta\beta}$ and $\Delta\alpha_{\beta\beta}$ are tabulated as well. The analysis of these data indicates that $\alpha_{\beta\beta}$ and $|\Delta\alpha_{\beta\beta}|$ of the $X_2...Y$ complexes increase with the increase in the polarizability of the noble atom, despite the increase of the equilibrium distance R_e in the complexes.

Conclusions

Within the framework of the modified DID theory, the analytical expressions have been derived for the components of the polarizability tensor of the simplest molecular complexes $X_2...Y$ in their stable configurations. The complex polarizability is determined by the polarizability of its component atom, the polarizability tensor of the non-rigid molecule, and the complex geometry. The expressions for the polarizability tensor of the complex $X_2...Y$ have been obtained for the isotropically polarized atom, but they can be easily modified for the case of an atom with anisotropic polarizability.

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