Polarizability of diatomic homonuclear molecules: internuclear dependence

M.A. Buldakov

Institute of Optical Monitoring,
Siberian Branch of the Russian Academy of Sciences, Tomsk

Received July 1, 2002

A semiempirical method has been developed for calculation of the polarizability tensor components of diatomic homonuclear molecules as functions of the internuclear separation $R \in [0, \infty)$. The method is based on the known polarizability function of a molecule for small R, the values of polarizability and its derivatives for the equilibrium configuration, and improved polarizability functions of oriented interacting atoms at large R. The latter accounts for multipole interactions between the atoms and for the change in atomic polarizabilities as atoms approach each other. The atomic multipole interactions are taken into account using a model of two interacting dielectric spheres. The method proposed has been tested with the H_2 molecule as a case study and was applied to calculation of the polarizability functions of the N_2 and O_2 molecules.

Introduction

The dependence of molecular electronic polarizability tensor components on the spatial position of nuclei in a molecule is one of the fundamental characteristics, which, along with the dipole moment function, determines optical and electric properties of a molecule. It is too a complicated problem to find this dependence even for diatomic molecules, whose electronic polarizability tensor has only two independent components and, correspondingly, there are only two polarizability functions $\alpha_{zz}(R)$ and $\alpha_{xx}(R) = \alpha_{yy}(R)$, where R is the internuclear separation, and the axis Z coincides with the molecular axis.

The current concepts of polarizability functions of diatomic molecules are based on analytical description of these functions for some ranges of internuclear separations and on the results of *ab initio* calculations. Thus, in the range of small R, the polarizability function can be described analytically through united atom treatment.[1] Near the equilibrium configuration of the nuclei, the polarizability function is usually specified by a Taylor series, whose parameters (derivatives of the polarizability tensor components) can be determined experimentally from Raman spectra.[2] To describe the polarizability functions at large R, the classical Silberstein's electrosctatic model is used, which considers the interacting atoms as point dipoles induced by an external electric field that are localized on the molecular nuclei.[3,4] Such an approach allows the molecular polarizability functions to be calculated from known values of the polarizability of atoms forming the molecule.

Later on the Silberstein's model was improved in Refs. 5 and 6. This improvement consisted in accounting for the changes in the polarizability of atoms as they approach each other. The quantum-chemistry calculations of the polarizability functions are usually conducted for relatively narrow ranges of the internuclear separation near the equilibrium separation R_e for diatomic molecules (see, for example, Refs. 7 and 8), and only for H_2 molecule such calculations were conducted for the whole range of R (Refs. 9 and 10) with the use of specialized *ab initio* methods applicable only to single- and two-electron molecules. Besides, in a number of papers one can find *ab initio* calculations of the polarizability function for pairs of interacting atoms of noble gases (for example, Ref. 11 and references therein).

These investigations have attracted the interest in the development of semiempirical methods suitable for calculation of the polarizability functions of any diatomic molecules at an arbitrary internuclear separation. Now we know three such methods[12–14] that differ by the degree and ways of using the available information. Thus, formulas suggested in Ref. 12, though giving the general idea of the polarizability functions of N_2 molecule, do not provide physically correct description of their behavior neither at small nor at large internuclear separations.

The method for constructing the polarizability functions used in Ref. 13 is based on the empirical regularities of their behavior near peaks and on the known asymptotic dependence at large R (Refs. 5 and 6). However, this method does not describe correctly behavior of the polarizability functions at small R, and the versatility of the correlations found there raises certain doubts. The method for calculation of the polarizability functions used in Ref. 14 is based on their asymptotic at small[1] and large[3,4] R and derivatives in the equilibrium. Disadvantages of this method are, first of all, underestimation of the polarizability functions in the range of medium R.

In this paper, refining the behavior of the polarizability functions in the range of medium R by taking into account the multipole interactions between atoms and the change in the polarizability as atoms approach each other develops a semiempirical method proposed in Ref. 14.

0235-6880/02/09 752-05 $02.00

Polarizability of a couple of interacting dielectric spheres

To take into account the multipole interactions between two identical atoms, let us use the model of two interacting dielectric spheres.[15,16] In this model, the polarizability of two dielectric spheres of radius r_0 located on the axis Z of the Cartesian coordinate system at the distance R from each other in the static electric field can be presented as[16]

$$\alpha_{zz}(R)=2\alpha_0\frac{\varepsilon+2}{\varepsilon-1}(2\sinh\eta_0)^3\times$$
$$\times\sum_{p=0}^{\infty}\left[\frac{2}{\varepsilon+1}\right]^p\sum_{n=1}^{\infty}n\chi_n^{(p)}(R), \tag{1}$$

$$\alpha_{xx}(R)=2\alpha_0\frac{\varepsilon+2}{\varepsilon-1}(2\sinh\eta_0)^3\times$$
$$\times\sum_{p=0}^{\infty}\left[\frac{2}{\varepsilon+1}\right]^p\sum_{n=1}^{\infty}\frac{n(n+1)}{2}\omega_n^{(p)}(R), \tag{2}$$

where ε is the dielectric constant of the sphere; α_0 is the sphere polarizability; $\cosh\eta_0 = R/(2r_0)$, and the coefficients $\chi_n^{(p)}(R)$ and $\omega_n^{(p)}(R)$ are specified by cumbersome recurrences (27)–(35) in Ref. 16. Within this model, Eqs. (1) and (2) are exact in the range $R \in (2r_0, \infty)$, but the polarizability can be calculated by them only numerically, because they include infinite weakly convergent series.

To present the polarizability functions $\alpha_{zz}(R)$ and $\alpha_{xx}(R)$ analytically, Eqs. (1) and (2) are to be expanded into a series over powers of the small parameter $\delta = r_0/R$, and after summation over p and n the following simple asymptotic equations are obtained:

$$\frac{\alpha_{zz}(R)}{2\alpha_0}=1+2\frac{\varepsilon-1}{\varepsilon+2}\delta^3+$$
$$+4\left(\frac{\varepsilon-1}{\varepsilon+2}\right)^2\delta^6+18\frac{(\varepsilon-1)^2}{(\varepsilon+2)(2\varepsilon+3)}\delta^8+$$
$$+8\left(\frac{\varepsilon-1}{\varepsilon+2}\right)^3\delta^9+48\frac{(\varepsilon-1)^2}{(\varepsilon+2)(3\varepsilon+4)}\delta^{10}+\cdots, \tag{3}$$

$$\frac{\alpha_{xx}(R)}{2\alpha_0}=1-\frac{\varepsilon-1}{\varepsilon+2}\delta^3+$$
$$+\left(\frac{\varepsilon-1}{\varepsilon+2}\right)^2\delta^6+6\frac{(\varepsilon-1)^2}{(\varepsilon+2)(2\varepsilon+3)}\delta^8-$$
$$-\left(\frac{\varepsilon-1}{\varepsilon+2}\right)^3\delta^9+18\frac{(\varepsilon-1)^2}{(\varepsilon+2)(3\varepsilon+4)}\delta^{10}+\cdots. \tag{4}$$

Using the equation

$$\alpha_0=\frac{\varepsilon-1}{\varepsilon+2}r_0^3, \tag{5}$$

we can write Eqs. (3) and (4) in a more convenient form:

$$\alpha_{zz}(R)=2\alpha_0+4\alpha_0^2\frac{1}{R^3}+$$
$$+8\alpha_0^3\frac{1}{R^6}+18\alpha_0^3\left(1+\frac{1}{2\varepsilon+3}\right)\frac{r_0^2}{R^8}+$$
$$+16\alpha_0^4\frac{1}{R^9}+32\alpha_0^3\left(1+\frac{2}{3\varepsilon+4}\right)\frac{r_0^4}{R^{10}}+\cdots, \tag{6}$$

$$\alpha_{xx}(R)=2\alpha_0-2\alpha_0^2\frac{1}{R^3}+$$
$$+2\alpha_0^3\frac{1}{R^6}+6\alpha_0^3\left(1+\frac{1}{2\varepsilon+3}\right)\frac{r_0^2}{R^8}-$$
$$-2\alpha_0^4\frac{1}{R^9}+12\alpha_0^3\left(1+\frac{2}{3\varepsilon+4}\right)\frac{r_0^4}{R^{10}}+\cdots. \tag{7}$$

It is seen from Eqs. (6) and (7) that the polarizability functions of a couple of interacting dielectric spheres include, besides the well known terms of the Silberstein's model, additional terms caused by the multipole interaction. Note that at $\varepsilon \to \infty$ the equations obtained correspond to the model of metal spheres.[17]

Method for construction of the polarizability functions

The method for construction of the polarizability functions of diatomic molecules comprises three stages.

1. At small R, the polarizability functions are specified as[1]

$$\alpha_{ii}(R) = \alpha_{ii}^{(0)} + A_{ii}R^2 + B_{ii}R^3 + C_{ii}R^4, \tag{8}$$

where $\alpha_{ii}^{(0)}$ are the components of the polarizability tensor of the united atom in the corresponding state, while A_{ii}, B_{ii}, and C_{ii} are the constants for this molecular electronic state, which can be found from the known components of the polarizability tensor $(\alpha_{ii})_e$ and their first $(\alpha'_{ii})_e$ and second $(\alpha''_{ii})_e$ derivatives with respect to $\xi = (R - R_e)/R_e$ at $R = R_e$ (Refs. 1 and 14). The united atom term can be determined following known rules of correlation between the molecular terms and the terms of united atoms.

2. At large R, the molecular polarizability function is specified as

$$\alpha_{zz}(R)=2\alpha_{zz}^0+4\left(\alpha_{zz}^0\right)^2\frac{1}{R^3}+$$
$$+\left(8\left(\alpha_{zz}^0\right)^3+\frac{7\gamma C_6}{9\alpha_0}\right)\frac{1}{R^6}+18\alpha_0^3\left(1+\frac{1}{2\varepsilon+3}\right)\frac{r_0^2}{R^8}+$$
$$+16\left(\alpha_{zz}^0\right)^4\frac{1}{R^9}+32\alpha_0^3\left(1+\frac{2}{3\varepsilon+4}\right)\frac{r_0^4}{R^{10}}, \tag{9}$$

$$\alpha_{xx}(R)=2\alpha_{xx}^0-2\left(\alpha_{xx}^0\right)^2\frac{1}{R^3}+$$
$$+\left(2\left(\alpha_{xx}^0\right)^3+\frac{4\gamma C_6}{9\alpha_0}\right)\frac{1}{R^6}+6\alpha_0^3\left(1+\frac{1}{2\varepsilon+3}\right)\frac{r_0^2}{R^8}-$$

$$-2\left(\alpha^0_{xx}\right)^4 \frac{1}{R^9} + 12\alpha_0^3\left(1+\frac{2}{3\varepsilon+4}\right)\frac{r_0^4}{R^{10}}, \qquad (10)$$

where α^0_{ii} are the components of the polarizability tensor of atoms of the molecule[14] and the sphere polarizability α_0 is equal to the mean polarizability of each of these atoms. The terms in Eqs. (9) and (10) including the Van der Waals interaction coefficient C_6 and the mean second hyperpolarizability γ were introduced by Buckingham in Ref. 6; they reflect the change in the polarizability of atoms as they approach each other due to dispersion interaction.

3. The polarizability functions specified by Eqs. (8)–(10) are joined with the use of fifth-order polynomials, whose coefficients can be found from the conditions of equal values of the polynomials and polarizability functions, as well as their first and second derivatives at joining points (r_1 and r_2). The joining points can be selected with some arbitrariness, but this leads to minor changes in the polarizability functions between the joining points.

Polarizability functions of H_2, N_2, and O_2 molecules

The method described above was tested on the H_2 molecule, for which reliable *ab initio* calculations of the polarizability functions are available.[10] Figure 1 depicts the calculated polarizability functions of the H_2 molecule that differ in the degree, the interactions are taken into account in Eqs. (9) and (10).

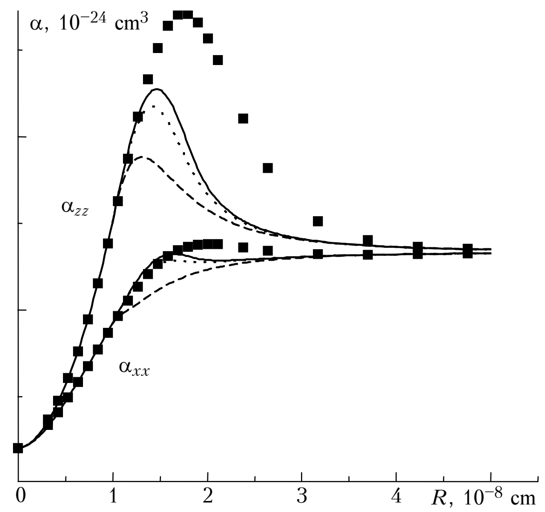

Fig. 1. Polarizability functions of the H_2 molecule: calculated in Ref. 14 (dashed curve); this work at $r_0 = 0$ (dotted curve); this work at $r_0 \neq 0$ (solid curve); *ab initio* calculation of Ref. 10 (squares).

The values of atomic and molecular constants used in calculations are tabulated below.

Table. Parameters for calculation of the polarizability functions of H_2, N_2, and O_2 molecules

Molecule	H_2	N_2	O_2	
Term	$^1\Sigma_g^+$	$^1\Sigma_g^+$	$^3\Sigma_g^-$	
$(\alpha_{xx})_e$, Å^3	0.679 [a]	1.53 (Ref. 2)	1.25 (Ref. 2)	
$(\alpha'_{xx})_e$, Å^3	0.669 [a]	1.12 (Ref. 2)	0.70 (Ref. 2)	
$(\alpha''_{xx})_e$, Å^3	0.121 [a]	0.33 (Ref. 2)	0.80 [b]	
$(\alpha_{zz})_e$, Å^3	0.947 [a]	2.24 (Ref. 2)	2.33 (Ref. 2)	
$(\alpha'_{zz})_e$, Å^3	1.372 [a]	3.35 (Ref. 2)	3.89 (Ref. 2)	
$(\alpha''_{zz})_e$, Å^3	1.221 [a]	2.93 (Ref. 2)	8.60 [b]	
United atom	He	Si	S	
Term	^1S	^1D ($M_L = 0$)	^3P ($M_L = 0$)	
$\alpha^{(0)}_{xx}$, Å^3	0.205 (Ref. 18)	5.62 (Ref. 19)	2.68 (Ref. 19)	
$\alpha^{(0)}_{zz}$, Å^3	0.205 (Ref. 18)	7.50 (Ref. 19)	3.35 (Ref. 19)	
Isolated atom	H	N	O	
Term	^1S	^4S	^3P ($M_L = 0$)	^3P ($M_L = \pm 1$)
α^0_{xx}, Å^3	0.6668 (Ref. 18)	1.101 [c]	0.755 [c]	0.825 [c]
α^0_{zz}, Å^3	0.6668 (Ref. 18)	1.101 [c]	0.895 [c]	0.755 [c]
α_0, Å^3	0.6668	1.101	0.802	
r_0, Å	1.1 (Ref. 20)	1.5 (Ref. 20)	1.4 (Ref. 20)	
ε	4.01 [d]	2.45 [d]	2.24 [d]	
γC_6, Å^{12}	4.18 [e]	10.51 [e]	5.03 [e]	
r_1, Å	1.0	1.1	1.2	
r_2, Å	1.9	2.0	2.0	

[a] Calculated based on data from Ref. 10; [b] values refined in Ref. 2; [c] borrowed from Ref. 14; [d] calculated by Eq. (5); [e] the values of γ and C_6 for H are taken from Ref. 6, γ for N and O are taken from Ref. 21, C_6 for N and O are taken from Ref. 22.

Analysis of the dependences obtained shows that consideration of the dispersion and multipole interactions between the hydrogen atoms markedly improves the polarizability function at medium R as compared with that from Ref. 14 and its values become closer to the accurate *ab initio* values.[10] In this case, the $\alpha_{zz}(R)$ function is more sensitive to consideration of the dispersion and multipole interactions than $\alpha_{xx}(R)$. It should be noted that within this model it is impossible to obtain the coincidence with the *ab initio* calculations because of neglect of the exchange interactions between the atoms.

The method proposed for calculation of the polarizability function was also applied to the N_2 and O_2 molecules (Figs. 2–5), and for the oxygen molecule both channels of its decomposition were considered. The polarizability functions found for these molecules show that the consideration of the dispersion and multipole interactions also leads to the increase of their values at the internuclear separation from 1 to 3 Å.

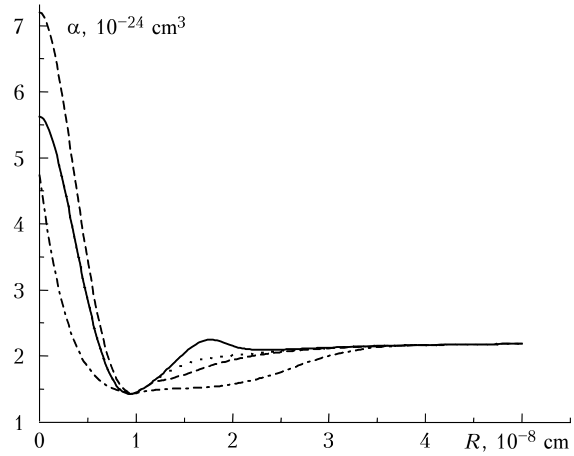

Fig. 2. Polarizability function $\alpha_{xx}(R)$ of the N_2 molecule: calculated in Ref. 14 (dashed curve); this work at $r_0 = 0$ (dotted curve); this work at $r_0 \neq 0$ (solid curve); calculated in Ref. 13 (dot-and-dash curve).

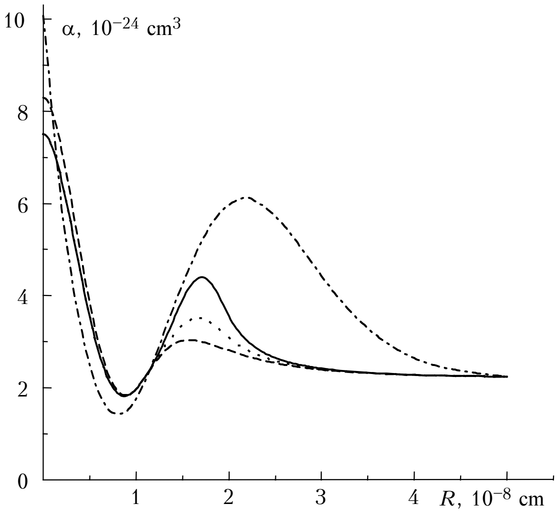

Fig. 3. Polarizability function $\alpha_{zz}(R)$ of the N_2 molecule: calculated in Ref. 14 (dashed curve); this work at $r_0 = 0$ (dotted curve); this work at $r_0 \neq 0$ (solid curve); calculated in Ref. 13 (dot-and-dash curve).

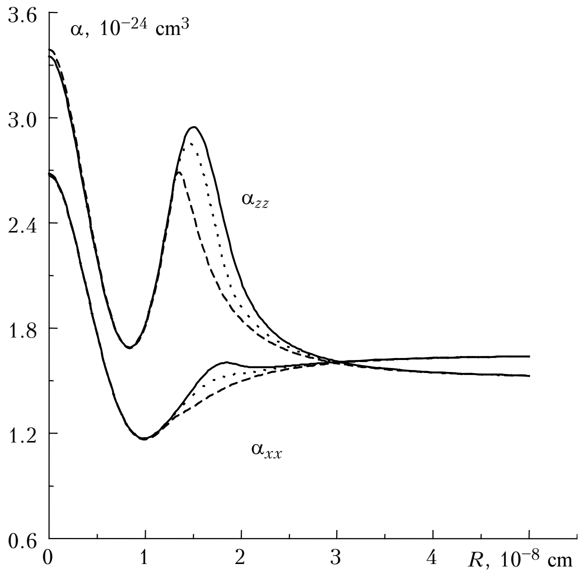

Fig. 4. Polarizability functions of the O_2 molecule (atoms O in the states with $|M_L| = 1$): calculated in Ref. 14 (dashed curve); this work at $r_0 = 0$ (dotted curve); this work at $r_0 \neq 0$ (solid curve).

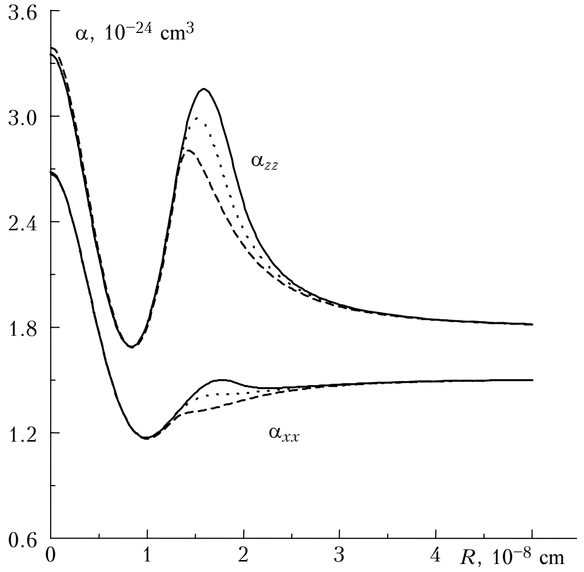

Fig. 5. Polarizability functions of the O_2 molecule (atoms O in the states with $|M_L| = 0$): calculated in Ref. 14 (dashed curve); this work at $r_0 = 0$ (dotted curve); this work at $r_0 \neq 0$ (solid curve).

Based on analysis of the polarizability functions of H_2 molecule, we assume that the polarizability functions obtained for N_2 and O_2 molecules at medium R-values also must be considered as their low boundary values. Some differences between the obtained polarizability functions and those from Ref. 14 at small R are connected with the fact that the polarizabilities of the united atoms Si and S in this paper are different.

It seems interesting to compare the obtained polarizability functions of N_2 molecules with those calculated by an alternative method, in which an attempt was undertaken to take into account the exchange interactions using the found correlations.[13] Apart from some differences in the polarizability functions at small R due to different values of $\alpha_{xx}^{(0)}$ and $\alpha_{zz}^{(0)}$ of the Si atom, to be noted is the unjustified underestimation of $\alpha_{xx}(R)$ for $R \approx 1 - 3$ Å (see Fig. 2). This is caused, in our opinion, by unfounded application of the correlations found for molecules consisting largely of the first-group atoms to the nitrogen atoms. The polarizability functions from Ref. 12 are omitted in Figs. 2 and 3, because they are only of historic interest now.

Conclusion

In this paper it is shown that the refinement of the semiempirical method for calculation of the polarizability functions proposed in Ref. 14 considerably improves the polarizability function at the medium R values. This refinement is in the account for the dispersion and multipole interactions between the atoms. Unfortunately, the use of the model of a pair of dielectric spheres to take into account the multipole interactions between atoms restricts the applicability of this method to only diatomic homonuclear molecules. In spite of the fact that the method proposed is oriented at the molecules decomposing into atoms in the S states, it can give reasonable results for the case of atoms without spherically symmetric charge distribution (for example, the oxygen molecule).

References

1. M.A. Buldakov, N.F. Vasil'ev, and I.I. Matrosov, Opt. Spektrosk. **75**, No. 3, 597–603 (1993).
2. M.A. Buldakov, I.I. Ippolitov, B.V. Korolev, I.I. Matrosov, A.E. Cheglokov, V.N. Cherepanov, Yu.S. Makushkin, and O.N. Ulenikov, Spectrochim. Acta, Part A **52**, No. 8, 995–1007 (1996).
3. L. Silberstein, Phil. Mag. **33**, No. 193, 92–128 (1917).
4. L. Silberstein, Phil. Mag. **33**, No. 198, 521–533 (1917).
5. A.D. Buckingham, Trans. Faraday Soc. **52**, No. 8, 1035–1041 (1956).
6. A.D. Buckingham and K.L. Clarke, Chem. Phys. Lett. **57**, No. 3, 321–325 (1978).
7. S.R. Langhoff, C.W. Bauschlicher, Jr., and D.P. Chong, J. Chem. Phys. **78**, No. 9, 5287–5292 (1983).
8. H. Hettema, S.P.S. Wormer, P. Jorgensen, H.J.Aa. Jensen, and T. Heldaker, J. Chem. Phys. **100**, No. 2, 1297–1302 (1994).
9. W. Kolos and L. Wolniewicz, J. Chem. Phys. **46**, No. 4, 1426–1432 (1967).
10. J. Ruchlewski, Mol. Phys. **41**, No. 4, 833–842 (1980).
11. N. Meinander, G.C. Tabisz, and M. Zoppi, J. Chem. Phys. **84**, No. 6, 3005–3013 (1985).
12. A. Temkin, Phys. Rev. A **17**, No. 3, 1232–1235 (1978).
13. A.J.C. Varandas and S.P.J. Rodrigues, Chem. Phys. Lett. **245**, No. 1, 66–74 (1995).
14. M.A. Buldakov and I.I. Matrosov, Opt. Spektrosk. **78**, No. 1, 26–30 (1995).
15. A. Goyette and A. Navon, Phys. Rev. B **13**, No. 10, 4320–4327 (1976).
16. J.L. Godet and B. Dumon, Phys. Rev. A **46**, No. 9, 5680–5686 (1992).
17. H.B. Levine and D.A. McQuarrie, J. Chem. Phys. **49**, No. 9, 4181–4187 (1968).
18. A.A. Radtsig and B.M. Smirnov, *Reference Book on Atomic and Molecular Physics* (Atomizdat, Moscow, 1980), 240 pp.
19. K. Andersson and A.J. Sadley, Phys. Rev. A **46**, No. 5, 2356–2362 (1992).
20. L. Pauling and P. Pauling, *Chemistry* (WH Freeman and Company, San Francisco, 1975).
21. A.K. Das and A.J. Thakkar, J. Phys. B **31**, No. 10, 2215–2223 (1998).
22. G.D. Zeiss and W.J. Meath, Mol. Phys. **33**, No. 4, 1155–1176 (1977).