Dynamic polarizability functions of H_2 and N_2 molecules

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We propose an analytical approach to description of the dynamic polarizability functions of H_2 and N_2 molecules. Frequency behavior of the polarization functions of these molecules are defined through the entire range of internuclear distance $R = [0,\infty)$ and correctly describe their asymptotic behavior both at small and large R values. Numerical values of the dynamic polarizability functions of H_2 and N_2 molecules obtained are quite reasonable estimates of their upper bound.

Introduction

In the adiabatic approximation, the polarizability tensor of a molecule is a function of coordinates of the nuclei and of the frequency ω of the external electromagnetic field. The tensor of electron polarizability of a diatomic molecule depends only on two independent coordinates (functions or surfaces of the polarizability), $\alpha_{zz}(\omega, R)$ and $\alpha_{xx}(\omega, R) = \alpha_{yy}(\omega, R)$, where R is the distance between the nuclei and the z-axis coincides with the molecular axis.

At present the polarizability surfaces are known in wide ranges of R and ω only for hydrogen molecule.[1–7] Moreover, most of these studies used high-precision special *ab initio* methods of calculations, which are only applicable to diatomic molecules with one or two electrons. In the case of diatomic molecules with larger numbers of electrons *ab initio* calculations have been performed only within relatively narrow interval of internuclear distances near its equilibrium value R_e (see, for instance, Refs. 8–10). For the case of entire range of internuclear distances only static polarizability functions have been obtained and only for molecular nitrogen[11–15] and oxygen[13–15] and for CH molecule (Ref. 12). Moreover, these functions have been calculated within the framework of a semi-empirical approach. As to the frequency behavior of the polarizability of multielectron molecules, it has been studied only at equilibrium internuclear distance R_e (see, for example, Refs. 16–19).

The aim of this study is to show how the functions of electron polarizability $\alpha_{zz}(\omega, R)$ and $\alpha_{xx}(\omega, R) = \alpha_{yy}(\omega, R)$ of H_2 and N_2 transform at variation of the frequency of the external electromagnetic field.

Analytical representation of the dynamic polarization function

Tensor of the dynamic electron polarizability of a homonuclear diatomic molecule being in its nth energy state can be presented in the following form

$$\alpha_{ii}^{(n)}(\omega,R) = 2\sum_{m \neq n} \frac{\left[E_m(R) - E_n(R)\right]\left|\left\langle n(R)\left|d_i\right|m(R)\right\rangle\right|^2}{\left[E_m(R) - E_n(R)\right]^2 - (\hbar\omega)^2}, \quad (1)$$

where $\left\langle n(R)\left|d_i\right|m(R)\right\rangle$ is the ith component of the dipole moment of the transition between the nth and mth electron energy states having energies $E_n(R)$ and $E_m(R)$. It is obvious that the frequency behavior of the molecular polarizability is fully determined by the structure of the electron energy levels of the molecule as well as by the probabilities of the dipole transitions among these levels. For this reason the view of this frequency behavior is characteristic of a molecule and of particular components of its polarizability tensor.

For a molecule at the ground electron energy level expression (1) can be presented by the product of its static polarizability, $\alpha_{ii}^{(0)}(0,R)$, and a frequency dependent factor $f_i(\omega, R)$:

$$\alpha_{ii}^{(0)}(\omega,R) \approx \alpha_{ii}^{(0)}(0,R)f_i(\omega,R), \quad (2)$$

where

$$f_i(\omega,R) = \frac{\left[E_{1i}(R) - E_0(R)\right]^2}{\left[E_{1i}(R) - E_0(R)\right]^2 - (\hbar\omega)^2}. \quad (3)$$

Here $E_0(R)$ is the energy of the ground electron energy state of the molecule; $E_{1i}(R)$ is the energy of the lowest of the excited electron energy states the transition to which from the ground state is allowed. Note that the energies $E_{1i}(R)$, in the expression (3), are different for different components of the polarizability tensor, $\alpha_{zz}^{(0)}(\omega,R)$ and $\alpha_{xx}^{(0)}(\omega,R) \equiv \alpha_{yy}^{(0)}(\omega,R)$. These energies are determined by the selection rules for Λ value, the eigenvalue of the projection of the electron orbital moment onto the molecular axis. Thus, for $\alpha_{zz}^{(0)}(\omega,R)$ component of the tensor the lowest excited electron energy state ($E_{1i}(R)$ energy) is determined by the selection rule $\Delta\Lambda = 0$,

while for the components $\alpha_{xx}^{(0)}(\omega, R) \equiv \alpha_{yy}^{(0)}(\omega, R)$ the selection rule reads $|\Delta\Lambda| = 1$.

The energy difference $E_{1i}(R) - E_0(R)$ in the expression (3) can be presented by a function, which is finite and continuous within the entire range of internuclear distance variation $R \in [0, \infty)$. As a result the frequency dependent factor $f_i(\omega, R)$ is a continuous function of R. At $\omega = 0$ this factor takes the value $f_i(\omega, R) = 1$ while increasing with the growth of the frequency ω of the electromagnetic field. Note that expression (2) sets the upper boundary for the components of dynamic polarizability of the molecule $\alpha_{ii}^{(0)}(\omega, R)$ in the frequency range $\omega < [E_{1i}(R) - E_0(R)]/\hbar$.

Dynamic polarizability of a hydrogen molecule

The method we propose for calculating $\alpha_{ii}(\omega, R)$ factor (Eqs. (2) and (3)) has been first tested by calculations made for a hydrogen molecule. (Here and in what follows, we omit the superscript denoting the ground electron state of the molecule.) To achieve this task, we have calculated, by formulas (2) and (3) the functions of the H_2 molecule's dynamic polarizability and compared it with the values $\alpha_{ii}(\omega, R)$ from Ref. 6 obtained by use of high-precision *ab initio* calculations. To calculate $\alpha_{ii}(\omega, R)$ values, we have constructed the energy differences $E_{1i}(R) - E_0(R)$. The values $E_0(R)$ of the potential energy of the ground electron energy state $(X^1\Sigma_g^+)$ were taken from Ref. 20, while the energies $E_{1z}(R)$ and $E_{1x}(R)$ of the excited electron states $(B^1\Sigma_u^+$ and $C^1\Pi_u$, respectively) from Ref. 21. In the region of small internuclear distances $(R \leq 0.5 \text{ Å})$ the missing values of the energy differences

$$\Delta E_z(R) = E_{1z}(R) - E_0(R) \text{ and } \Delta E_x(R) = E_{1x}(R) - E_0(R)$$

were determined by interpolation to the value

$$\Delta E_z(0) = \Delta E_x(0) = E(^1P^0) - E(^1S),$$

where $E(^1S)$ and $E(^1P^0)$ are the terms of the ground state (^1S) and of the first, allowed by the selection rules, excited state $(^1P^0)$ of the "united" He atom. Figure 1 presents the functions $\Delta E_z(R)$ and $\Delta E_x(R)$ calculated for the H_2 molecule.

These functions have been used in calculating the frequency dependent factors $f_z(\omega, R)$ and $f_x(\omega, R)$, which then allowed, together with the static polarizability $\alpha_{ii}(0, R)$ taken from Ref. 2, to calculate the relevant functions of the components of the dynamic polarizability tensor, $\alpha_{zz}(\omega, R)$ and $\alpha_{xx}(\omega, R) = \alpha_{yy}(\omega, R)$, as well as its invariants: the mean polarizability

$$\alpha(\omega, R) = \left[\alpha_{zz}(\omega, R) + 2\alpha_{xx}(\omega, R)\right]/3 \tag{4}$$

and the polarizability anisotropy

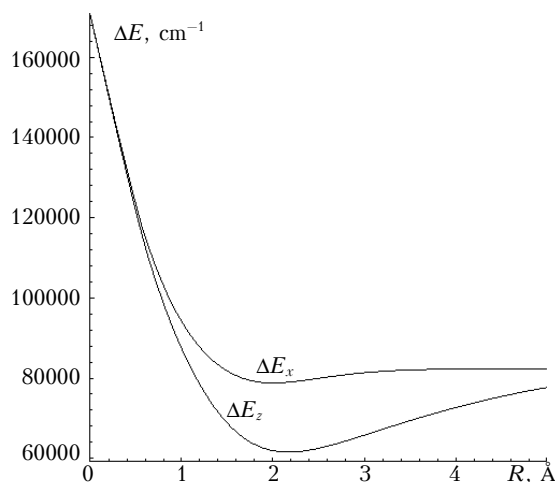$$\gamma(\omega, R) = \alpha_{zz}(\omega, R) - \alpha_{xx}(\omega, R). \tag{5}$$

Fig. 1. The difference between the electron terms of the H_2 molecule.

Thus obtained invariants of the dynamic polarizability tensor of a hydrogen molecule are depicted in Fig. 2, where the results obtained by *ab initio* calculations[6] of these invariants are shown for comparison.
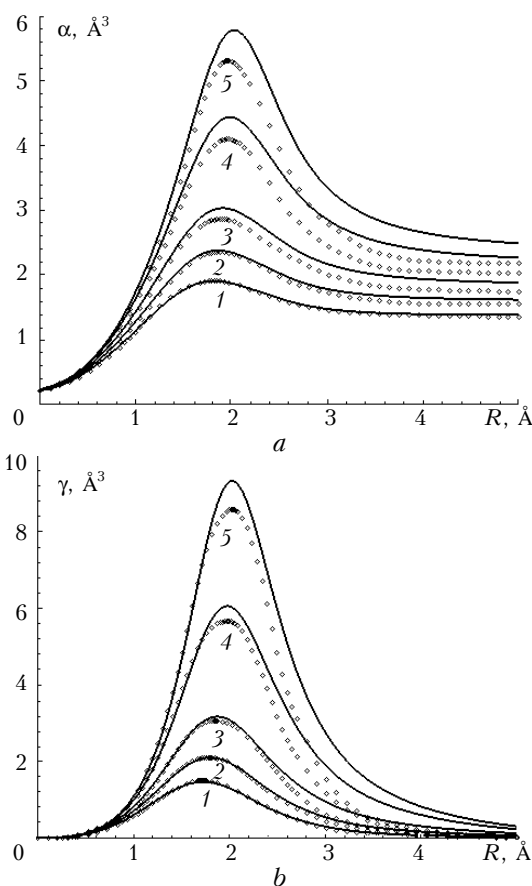

Fig. 2. The mean dynamic polarizability (*a*) and anisotropy of the dynamic polarizability (*b*) of the H_2 molecule: $\omega = 15803 \text{ cm}^{-1}$ (*1*); 33692 cm^{-1} (*2*); 43424 cm^{-1} (*3*); 51658 cm^{-1} (*4*); 54867 cm^{-1} (*5*). Solid lines correspond to our calculations, rhombs present data of *ab initio* calculations.[6]

It is well seen from these data that despite of being quite simple the proposed method adequately describes the invariants of the polarizability tensor of H_2 molecule as functions of the frequency of the external electric field. This conclusion is obviously valid in the case of individual components of the tensor of dynamic polarizability of the hydrogen molecule as well. Comparison of the calculated components of the dynamic polarizability tensor of the hydrogen molecule has also been made with the data available from literature for the characteristic values of the internuclear distance $R = 0$, R_e, ∞.

Figure 3 shows the calculated results on $\alpha_{zz}(\omega, 0) = \alpha_{xx}(\omega, 0)$ and the dynamic polarizability of the ground state of the helium atom taken from Refs. 22 and 23 (Fig. 3a) as well as on the $\alpha_{zz}(\omega, \infty)/2 = \alpha_{xx}(\omega, \infty)/2$ and the dynamic polarizability of the ground state of the hydrogen atom taken from Ref. 24 (Fig. 3b).

The dynamic polarizability of the hydrogen molecule at $R = R_e$ (see Refs. 3 and 7) and the frequency dependences of the polarizability tensor components $\alpha_{zz}(\omega, R_e)$ and $\alpha_{xx}(\omega, R_e)$ are shown in Figs. 3c and d. Analysis of the curves presented shows that though our calculated data exceed the results obtained by *ab initio* calculations the mismatch occurred to be not very large so it does not distort the view of the dynamic polarizability functions essentially. Note that this method yields quite good results for the frequency dependences of the components of the polarizability tensor (see Fig. 4).

$$\left(\alpha'_{ii}\right)_e = R_e \, \partial\alpha_{ii}(\omega, R)/\partial R\big|_{R=R_e}.$$

Therefore, the proposed method of calculating the functions of the dynamic polarizability $\alpha_{zz}(\omega, R)$ and $\alpha_{xx}(\omega, R) = \alpha_{yy}(\omega, R)$ quite well describes their frequency behavior for H_2 molecule and may be applied to description of other diatomic molecules.
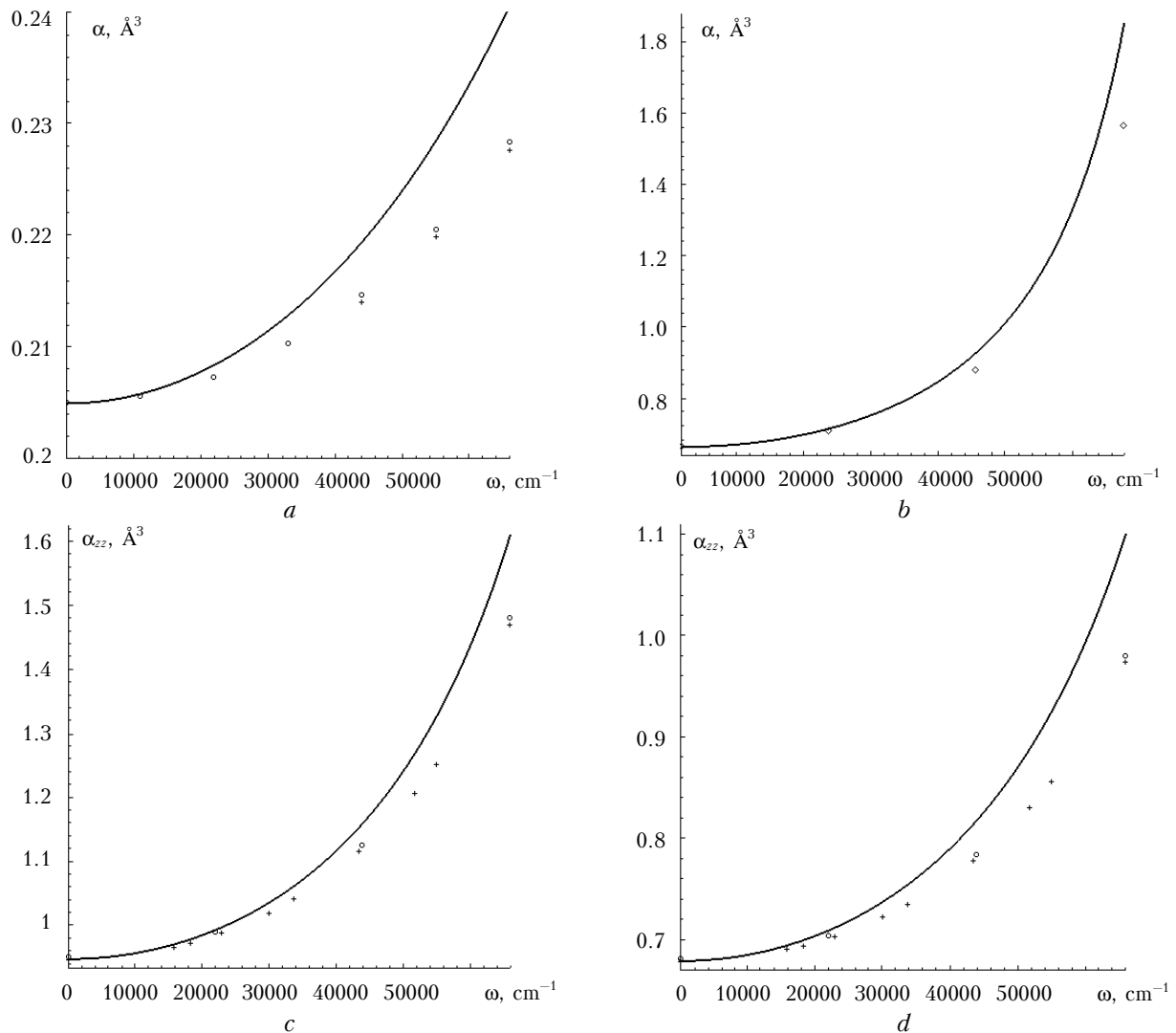

Fig. 3. Dynamic polarizabilities of He and H atoms and of the H_2 molecule at $R = R_e$; helium atom: solid line presents our calculations, open circles are the data of *ab initio* calculations from Ref. 22; crosses show *ab initio* calculations from Ref. 23 (*a*); hydrogen atom: solid line presents our calculations, rhombs show *ab initio* calculations from Ref. 24 (*b*); H_2 molecule: solid line presents our calculations, crosses show *ab initio* calculations from Ref. 3; open circles are the data of *ab initio* calculations from Ref. 7 (*c* and *d*).
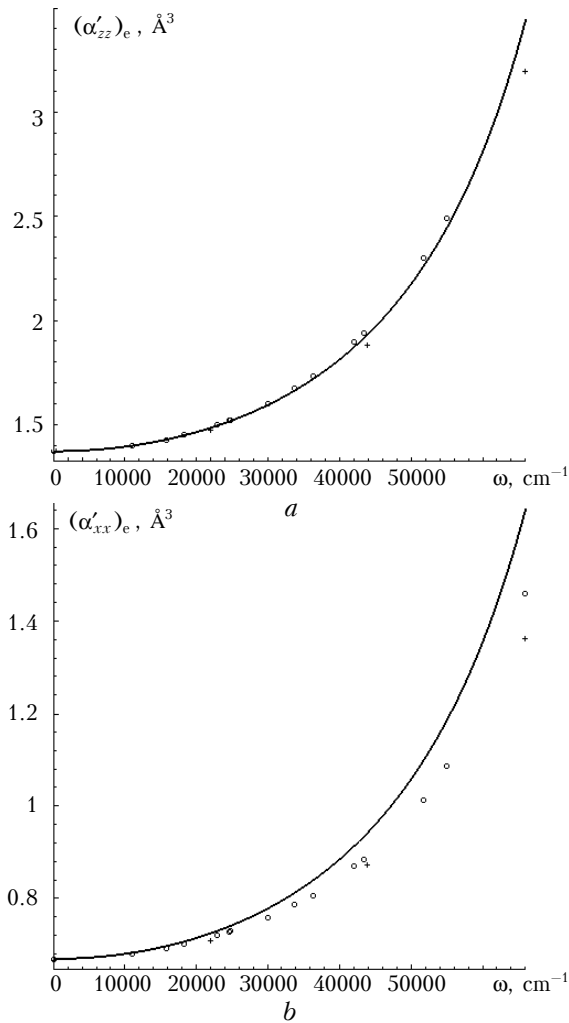
Fig. 4. Frequency dependences of $(\alpha'_{zz})_e$ (*a*) and of $(\alpha'_{xx})_e$ (*b*) of H_2 molecule at $R = R_e$. Solid line presents our calculations, open circles are the data of *ab initio* calculations from Ref. 6; crosses show *ab initio* calculations from Ref. 7.

Dynamic polarizability of the nitrogen molecule

We have applied the above-discussed method to calculation of the dynamic polarizability functions of the nitrogen molecule. Figure 5 shows the functions $\Delta E_z(R)$ and $\Delta E_x(R)$ calculated using numerical values of the energy $E_0(R)$ of the ground electron state $X^1\Sigma_g^+$ taken from Ref. 25 and energies $E_{1z}(R)$ and $E_{1x}(R)$ of the first excited electron states ($^1\Sigma_u^+$ and $^1\Pi_u$, respectively) taken from Ref. 26.

Note that in the range of small internuclear distances ($R \leq 0.85$ Å) the missing energy differences $\Delta E_z(R)$ and $\Delta E_x(R)$ were determined, as in the case with the H_2 molecule, by their interpolation to the value

$$\Delta E_z(0) = \Delta E_x(0) = E(^1P^0) - E(^1D),$$

where $E(^1D)$ and $E(^1P^0)$ are the terms of the excited states ^1D and $^1P^0$ of the "united" Si atom. These terms

are determined following the rules of correlation between the electron states of a diatomic molecule and the states of the "united" atom. Using thus found functions $\Delta E_z(R)$, $\Delta E_x(R)$, and the components of the static polarizability tensor $\alpha_{ii}(0, R)$ from Ref. 15, we have calculated components of the tensor of dynamic polarizability of the nitrogen molecule (see Fig. 6).
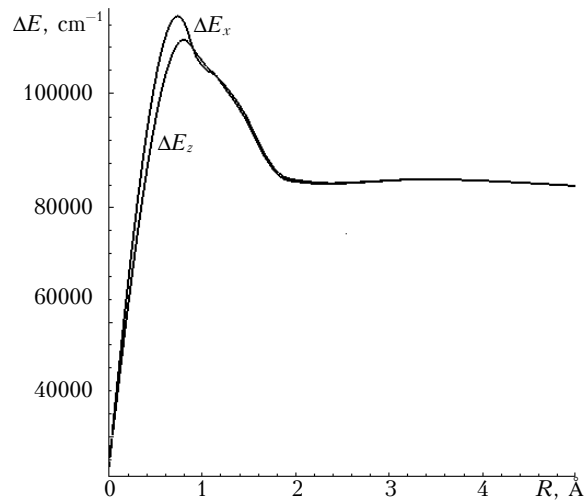

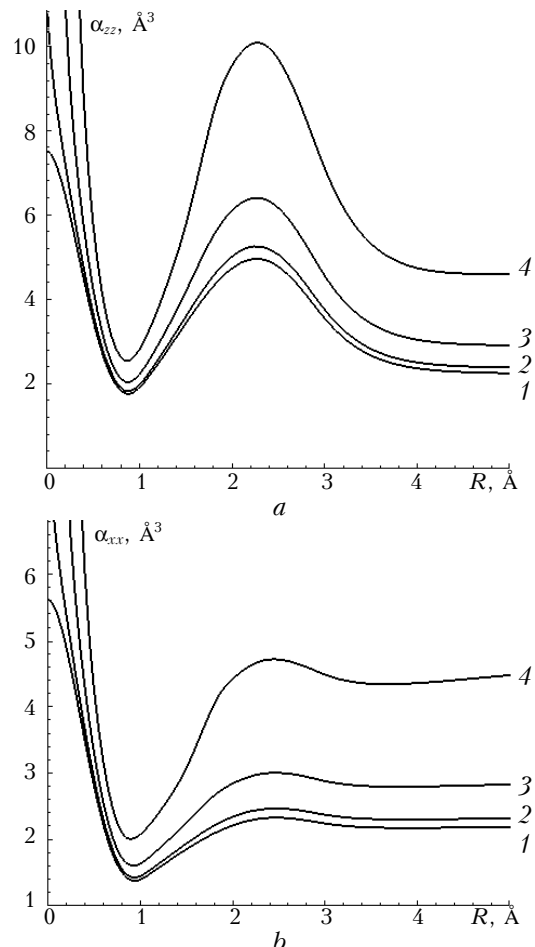**Fig. 5.** Difference of the electron terms of the N_2 molecule.

Fig. 6. Components of the tensor of dynamic polarizability of N_2 molecule $\alpha_{zz}(\omega, R)$ (*a*) and $\alpha_{xx}(\omega, R)$ (*b*): $\omega = 0$ cm^{-1} (*1*); 20000 cm^{-1} (*2*); 40000 cm^{-1} (*3*); 60000 cm^{-1} (*4*).
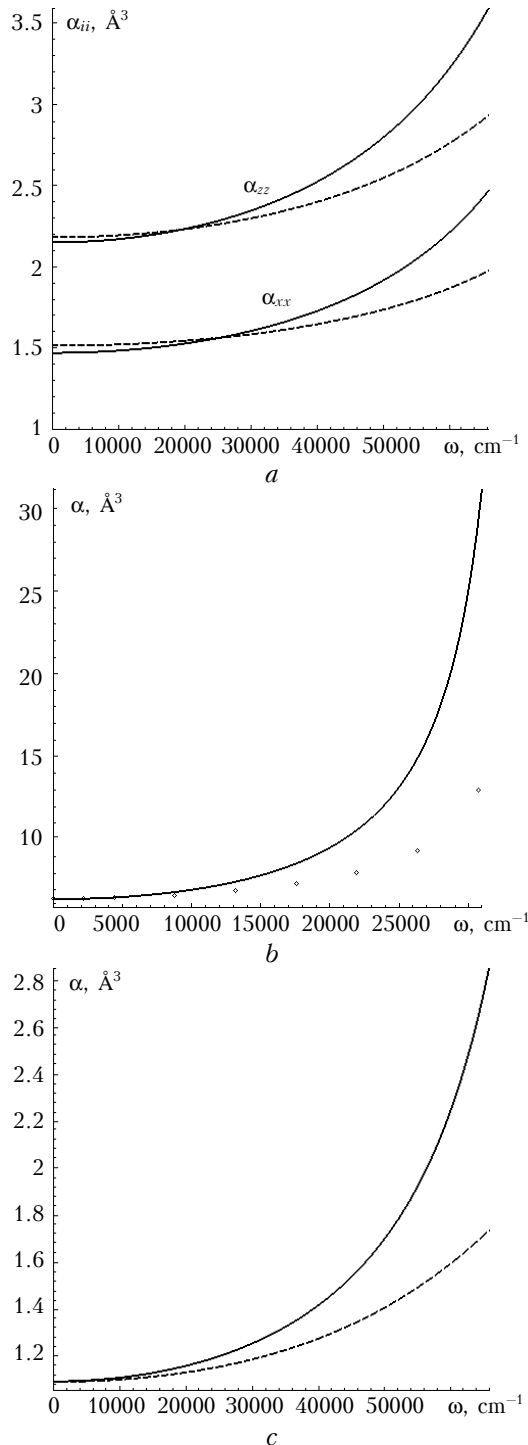
a

b

c

Fig. 7. Dynamic polarizability of Si and N atoms and N_2 molecule at $R = R_e$; N_2 molecule: solid lines present our calculations; dashed lines show data of *ab initio* calculations from Ref. 27 (*a*); atom of Si (^1D): solid line presents our calculations, rhombs show data of *ab initio* calculations from Ref. 28 (*b*); nitrogen atom N (^4S); solid line presents our calculations, dashed line shows data of *ab initio* calculations from Ref. 29 (*c*).

In contrast to H_2 molecule with the most strong frequency dependence of the polarizability tensor components occurring at $R \approx 2$ Å in nitrogen molecule

such a strong dependence occurs at small internuclear distances. At the same time the minimum frequency of the resonance transition in N_2 molecule coincides with the resonance transition in the "united" Si atom (≈ 34700 cm^{-1}). It is for this reason that no values of the components of the polarizability tensor are shown in Fig. 6 for $R \le 0.3$ Å as those are too large or take negative values. The dependences depicted in Fig. 6 can be checked up only at some particular distances between the nuclei. Figure 7*a* shows the curves of the frequency dependences of $\alpha_{zz}(\omega, R_e)$ and $\alpha_{xx}(\omega, R_e)$ components of the polarizability tensor calculated in this study and in Ref. 27.

It is seen that the curves do agree quite well. The approach of the "united" atom allows the comparison with the literature data to be performed only between the mean polarizability $\alpha(\omega, 0)$ values (see Fig. 7*b*). Analysis of the frequency dependences presented in these figures, shows that our results only slightly exceed those from Ref. 28 at the frequencies up to $\omega \le 25\,000$ cm^{-1}, while then the difference between them rapidly grows with the frequency growth. Such a growth is caused by that the increasing frequency approaches the frequency of the resonance transition in the "united" Si atom ($\approx 34\,700$ cm^{-1}).

Figure 7*c* shows the calculated components $\alpha_{zz}(\omega, \infty)/2 = \alpha_{xx}(\omega, \infty)/2$ of the polarizability tensor and tensor of the dynamic polarizability of the nitrogen atom in the ground energy state taken from Ref. 29. It is worth noting here that in Ref. 29 the dynamic polarizability of the nitrogen atom was set in the form of Cauchy expansion

$$\alpha(\omega) = \sum_{n=0}^{\infty} S(-2n - 2)\omega^{2n}, \qquad (6)$$

where Cauchy moments $S(-2n - 2)$ are determined only for $n = 0, 1, 2$. For this reason the dynamic polarizability of the nitrogen atom calculated in Ref. 29 is underestimated at high frequencies. However, the curves in Fig. 7*c* agree well enough. On the whole, it can be stated that the calculated $\alpha_{ii}(\omega, R)$ functions (see Fig. 6) correctly describe the behavior of the N_2 molecule polarizability at variations of the internuclear distance R and frequency ω of the external electromagnetic field.

Conclusion

We believe that, despite its simplicity, the calculation scheme proposed yields physically correct description of the polarizability of a homonuclear diatomic molecule as a function of the internuclear distance and the frequency of the external electromagnetic field. At the same time some remark are pertinent concerning the applicability of such an approach to calculations discussed. First, this calculation technique is restricted to the frequency of the first allowed electron transition of the electric dipole type. Second, such a technique enables one to obtain quite reasonable estimates of the upper bound

of the polarizability function and the overestimation of these values is determined by the structure of the excited electron energy levels of the molecule.

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