

Raman scattering by $(\text{N}_2)_2$ and $(\text{O}_2)_2$ dimers

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Received August 11, 2003

Within the framework of the modified DID theory, the cross sections and the degree of scattered light depolarization have been calculated for the vibrational bands of the N_2 and O_2 molecules in Raman spectra of the $(\text{N}_2)_2$ and $(\text{O}_2)_2$ dimers for different intermolecular distances. The cross sections and the degrees of scattered light depolarization for some equilibrium configurations of the $(\text{N}_2)_2$ and $(\text{O}_2)_2$ dimers have been calculated as well.

Introduction

Weakly bound complexes are present in any molecular gases, in particular, in the Earth's atmosphere, where they take part in all atmospheric processes along with the other atmospheric constituents. Since recent time, various properties of weakly bound molecular complexes have been intensely studied both theoretically and experimentally.^{1,2} One of the important characteristics of the complexes is the polarizability tensor, which determines the contribution of the complexes to the refractive index of gas media and the parameters of Rayleigh and Raman scattering.

Vibrational Raman scattering of light by molecular complexes arises if there occur vibrations of the nuclei in the complexes. The complicated vibrational Raman spectrum of complexes consists of individual vibrational bands caused by either intramolecular vibrations (vibrations of nuclei inside a molecule in the complex) or intermolecular vibrations (relative vibrations and rotations of the component molecules). The intensity and the polarization characteristics of a vibrational band in Raman spectra of a complex are determined by the tensor of the first derivative of the polarizability with respect to the corresponding coordinate.

In particular, for the $(\text{N}_2)_2$ and $(\text{O}_2)_2$ complexes, the band characteristics associated with the intramolecular vibrations in the N_2 and O_2 molecules are determined by the tensors of the first derivative of the polarizability of the complexes with respect to the internuclear separation of these molecules. At present no information on the tensor of the first derivative of the polarizability of the $(\text{N}_2)_2$ and $(\text{O}_2)_2$ dimers with respect to the internuclear separation of the N_2 and O_2 molecules is available in the literature. In this connection, it is of interest to calculate these tensors for different configurations of the nitrogen and oxygen dimers and then determine the cross sections and the degree of depolarization of the corresponding bands in the Raman spectra.

Method of calculation

The nitrogen and oxygen dimers fall in the class of Van der Waals molecular complexes. Since the bond energy of the molecules in the $(\text{N}_2)_2$ and $(\text{O}_2)_2$ dimers is roughly three orders of magnitude lower than the dissociation energy of these molecules,³ the dimers can be considered as pairs of weakly bound molecules that keep their mechanical properties with high accuracy, while having different electric properties. The Raman spectrum of such complexes consists of two groups of vibrational bands: the first group includes two bands caused by the intramolecular vibrations of the nuclei in the dimer molecule, while the second one includes four (or five, in the case of linear dimers) bands associated with relative vibrations and rotations of the molecules in the dimer. In the Raman spectrum, the vibrational bands of the first group are practically the vibrational bands of free molecules. The vibrational bands of the second group have the Raman frequency shifts far different from that of the vibrational bands of the first group and are not considered in this paper.

Consider a dimer free oriented in space. Assume that the exciting laser radiation is linearly polarized, and the scattered light is observed at the angle of 90° with respect to the electric vector of the exciting radiation. Because the vibrational bands of the first group are almost indistinguishable, the differential scattering cross section of the dimer σ is a sum of the differential scattering cross sections σ_i ($i = 1, 2$) for these bands:

$$\sigma = \sigma_1 + \sigma_2. \quad (1)$$

In the harmonic approximation, the differential scattering cross section σ_i can be written as⁴:

$$\sigma_i = 16\pi^4 (\omega_0 - \omega_i)^4 \left[(\alpha'_i)^2 + \frac{7}{45} (\gamma'_i)^2 \right], \quad (2)$$

where ω_0 is the frequency of the exciting radiation, in cm^{-1} , and ω_i is the frequency of the vibrational

Raman transition, in cm^{-1} , of the i th molecule in the dimer. The invariants of the tensor of the first derivative of the dimer polarizability with respect to the vibrational coordinate of the i th molecule in Eq. (2) are expressed through its components $(\alpha'_{km})_i$ in the Cartesian coordinate system as follows:

$$\alpha'_i = \frac{1}{3} [(\alpha'_{xx})_i + (\alpha'_{yy})_i + (\alpha'_{zz})_i] \quad (3)$$

and

$$(\gamma'_i)^2 = \frac{1}{2} \{ [(\alpha'_{zz})_i - (\alpha'_{xx})_i]^2 + [(\alpha'_{zz})_i - (\alpha'_{yy})_i]^2 + [(\alpha'_{yy})_i - (\alpha'_{xx})_i]^2 + 6[(\alpha'_{xz})_i^2 + (\alpha'_{xy})_i^2 + (\alpha'_{yz})_i^2] \}. \quad (4)$$

The degree of depolarization of the scattered light for the dimer can be presented in the form

$$\rho = (\sigma_1^\perp + \sigma_2^\perp) / (\sigma_1^\parallel + \sigma_2^\parallel), \quad (5)$$

where

$$\sigma_i^\perp = 16\pi^4 (\omega_0 - \omega_i)^4 \frac{1}{15} (\gamma'_i)^2 \quad (6)$$

and

$$\sigma_i^\parallel = 16\pi^4 (\omega_0 - \omega_i)^4 \left[(\alpha'_i)^2 + \frac{4}{45} (\gamma'_i)^2 \right]. \quad (7)$$

The invariants α'_i and $(\gamma'_i)^2$ are calculated within the framework of the modified DID theory.⁵ Following this model, each molecule (N_2 or O_2) in the dimer can be presented in the form of two effective atoms, whose polarizability is equal to the half polarizability of the molecule itself. With such a definition, the effective polarizability of the atoms is anisotropic and depends on the internuclear separation in the molecule. As a result, the components of the dimer polarizability tensor take the form

$$\alpha_{km}(r_1, r_2, R) = c_{km}^{(0)}(r_1, r_2) + \frac{c_{km}^{(3)}(r_1, r_2)}{R^3} + \frac{c_{km}^{(5)}(r_1, r_2)}{R^5} + \frac{c_{km}^{(6)}(r_1, r_2)}{R^6} + \frac{c_{km}^{(7)}(r_1, r_2)}{R^7} + \frac{c_{km}^{(8)}(r_1, r_2)}{R^8} + \frac{c_{km}^{(9)}(r_1, r_2)}{R^9} + \dots, \quad (8)$$

where R is the distance between the centers of mass of the interacting molecules, and the coefficients $c_{km}^{(l)}(r_1, r_2)$ depend on the intramolecular internuclear separations r_1 and r_2 and the mutual orientation of the molecules in the dimer. The components of the tensor of the first derivatives of the polarizability can be obtained from Eq. (8) by differentiation with respect to $\xi_i = (r_i - r_i^0)/r_i^0$:

$$\alpha'_{km}(R) = \left[\partial \alpha_{km}(r_1, r_2, R) / \partial \xi_i \right]_{r_1=r_1^0, r_2=r_2^0}, \quad (9)$$

where r_1^0 and r_2^0 are the equilibrium internuclear separations of the first and second molecules.

It is convenient to analyze the Raman scattering parameters of the dimers $\sigma(R)$ and $\rho(R)$ by

comparing them with the analogous Raman parameters of free molecules, σ_0 and ρ_0 . For this purpose, introduce the factor of scattering cross section

$$F_\sigma(R) = \sigma(R) / (2\sigma_0) \quad (10)$$

and the factor of the degree of depolarization of the scattered light

$$F_\rho(R) = \rho(R) / \rho_0. \quad (11)$$

These factors reflect the relative changes of $\sigma(R)$ and $\rho(R)$ of the dimer with respect to the pair of the free molecules forming the dimer.

Calculated results

In this paper, we present the factors $F_\sigma(R)$ and $F_\rho(R)$ calculated for some configurations (Fig. 1) of the interacting molecules in the $(\text{N}_2)_2$ and $(\text{O}_2)_2$ dimers. In these calculations we used the following values of the components of the tensor of the first derivative of polarizability of the effective N and O atoms:

$$\alpha'_{xx}^{(N)} = \alpha'_{yy}^{(N)} = 0.558 \text{ \AA}^3, \quad \alpha'_{zz}^{(N)} = 1.673 \text{ \AA}^3,$$

$$\alpha'_{xx}^{(O)} = \alpha'_{yy}^{(O)} = 0.348 \text{ \AA}^3, \quad \alpha'_{zz}^{(O)} = 1.943 \text{ \AA}^3,$$

which were calculated from the corresponding components of the tensors of first derivatives of polarizability of the N_2 and O_2 molecules⁶ (here x , y , and z are the Cartesian coordinates in the N_2 and O_2 molecules).

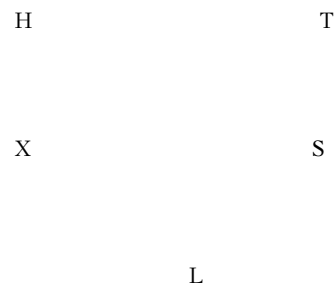


Fig. 1. Some configurations of the dimers of diatomic molecules.

Figure 2 shows the factors $F_\sigma(R)$ and $F_\rho(R)$ at different intermolecular separations R for the configurations H, T, X, S, and L of the interacting molecules in the $(\text{N}_2)_2$ and $(\text{O}_2)_2$ dimers. The results obtained suggest that

– the deviation of the factors $F_\sigma(R)$ and $F_\rho(R)$ from unity usually increases, with the decreasing separation between the molecules in dimers;

– for T and L dimer configurations the factors $F_\sigma(R)$ and $F_\rho(R)$ monotonically increase with the decreasing R , they also increase monotonically for the H and X configurations, while showing a more complicated behavior in the S configuration;

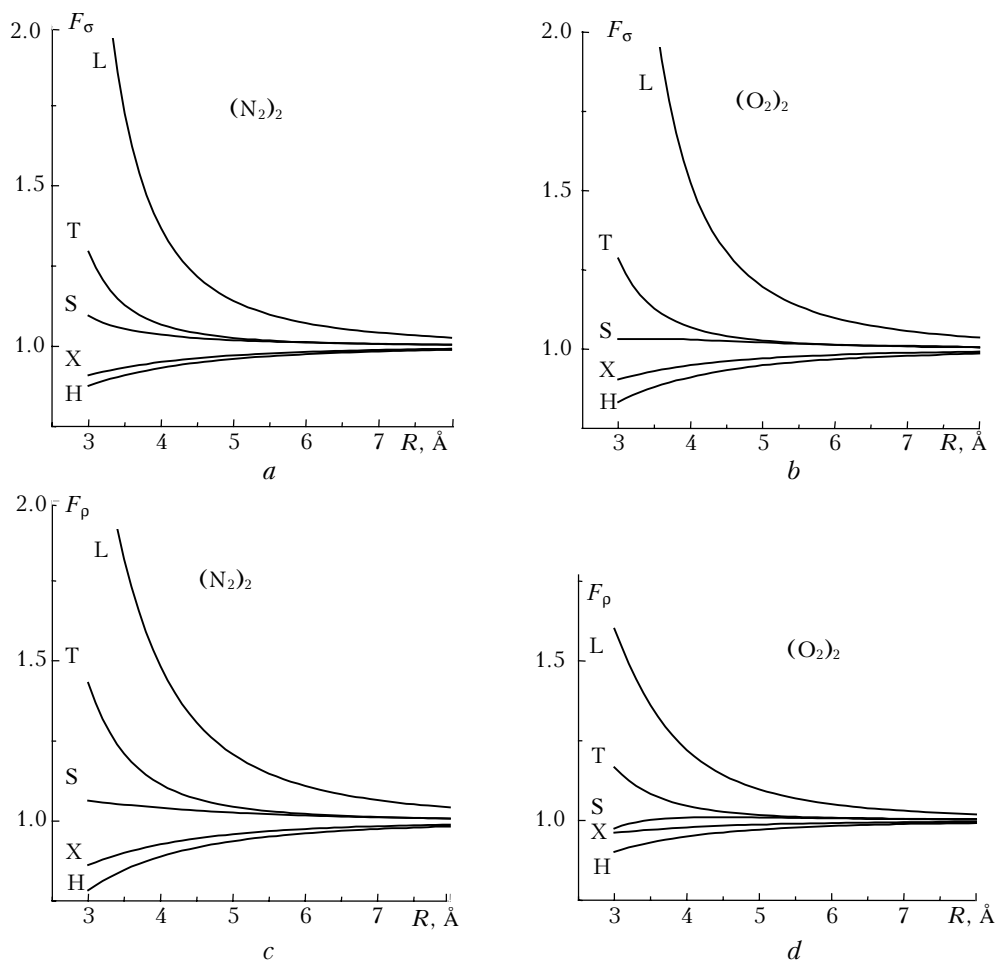


Fig. 2.

– the factors $F_\sigma(R)$ for the $(\text{N}_2)_2$ and $(\text{O}_2)_2$ dimers are close, while the factor $F_\rho(R)$ for the $(\text{O}_2)_2$ dimer is markedly smaller than that for $(\text{N}_2)_2$.

Of greatest interest are the values of the factors $F_\sigma(R_e)$ and $F_\rho(R_e)$ for the equilibrium positions of different configurations of the $(\text{N}_2)_2$ and $(\text{O}_2)_2$ dimers. The Table lists the calculated values of these factors for the H, X, T, S, and L configurations, along with the equilibrium intermolecular separations R_e borrowed from the *ab initio* calculations reported in Refs. 7 and 8. It can be seen that for the configurations considered, the factors $F_\sigma(R_e)$ range within 0.92–1.12 and 0.86–1.29 intervals, while the factor $F_\rho(R_e)$ ranges within 0.86–1.18 and 0.92–1.14 for $(\text{N}_2)_2$ and $(\text{O}_2)_2$, respectively. The values of the factors $F_\sigma(R_e)$ and $F_\rho(R_e)$ for other possible dimer configurations lie within these ranges, since the L and H configurations of the $(\text{N}_2)_2$ and $(\text{O}_2)_2$ dimers are characterized by the limiting values of the factors.

As can be seen from the Table, the dissociation energies of the dimers D_e are low and different for different configurations. Therefore, in real gas media, the dimers exist in different configurations, and only at a very low temperature they are in the most stable configurations: S for $(\text{N}_2)_2$ and H for $(\text{O}_2)_2$. So, as the gas temperature increases, the factors averaged over the

dimer configurations with the allowance for their population acquire the practical significance. The temperature behavior of these factors is analogous to that shown in Ref. 9 for the invariants of the polarizability tensor of the $(\text{N}_2)_2$ and $(\text{O}_2)_2$ dimers, that is at a very low temperature they coincide with the factors $F_\sigma(R_e)$ and $F_\rho(R_e)$ for the most stable dimer configurations, and as the gas temperature increases, they tend to the factors for the dimers, in which the molecules are at some distance \bar{R}_e and practically free oriented.

Factors F_σ and F_ρ for the $(\text{N}_2)_2$ and $(\text{O}_2)_2$ dimers

Configuration	D_e, cm^{-1}	$D_e, \text{\AA}$	$F_\sigma(R_e)$	$F_\rho(R_e)$
	Ref. 7	Ref. 7		
$(\text{N}_2)_2$				
T	75.97	4.15	1.057	1.098
X	52.01	3.63	0.939	0.908
H	44.30	3.70	0.920	0.865
L	6.83	5.22	1.120	1.179
S	80.79	4.09	1.033	1.039
$(\text{O}_2)_2$				
T	61.86	4.02	1.067	1.045
X	123.0	3.28	0.920	0.967
H	128.6	3.33	0.867	0.923
L	45.18	4.55	1.291	1.137
S	37.53	4.39	1.026	1.010

The factors $F_{\sigma}(R)$ and $F_{\rho}(R)$ reported in this paper have been calculated for the entire $0 \rightarrow 1$ vibrational band of the Raman spectrum of the dimers. However, the results obtained are valid, in general, for the Q -branch of this vibrational band.

Conclusions

The method of calculation of the polarizability tensor for a pair of interacting diatomic molecules proposed by us in Ref. 5 has been extended to the calculation of the tensor of the first derivative of the dimer polarizability with respect to the internuclear coordinate of the individual molecule in the dimer. This method has allowed us to follow up the variations of the scattering cross section and the degree of depolarization of the scattered light for the vibrational bands in the spontaneous Raman spectra of N_2 and O_2 molecules as they form dimers. The neglect of the variation of the mechanic properties of the molecules, as they approach each other, can slightly distort the results obtained. In spite of this

fact, we believe that the obtained regularities are valid in the first approximation.

References

1. P.E.S. Wormer and A. van der Avoird, Chem. Rev. **100**, No. 11, 4109–4143 (2000).
2. A. van der Avoird, P.E.S. Wormer, and R. Moszynski, Chem. Rev. **94**, No. 7, 1931–1974 (1994).
3. B.M. Smirnov, Usp. Fiz. Nauk **142**, No. 1, 31–60 (1984).
4. H.W. Schrotter and H.W. Klockner, in: *Raman Spectroscopy of Gases and Liquids*, ed. by A. Weber (Springer, Berlin, 1979), pp. 123–166.
5. M.A. Buldakov, B.V. Korolev, I.I. Matrosov, and V.N. Cherepanov, Opt. Spektrosk. **94**, No. 2, 214–219 (2003).
6. M.A. Buldakov, B.V. Korolev, I.I. Matrosov, and T.N. Popova, Opt. Spektrosk. **62**, No. 3, 519–523 (1987).
7. A. Wada, H. Kanamori, and S. Iwata, J. Chem. Phys. **109**, No. 21, 9434–9438 (1998).
8. B. Bussery and P.E.S. Wormer, J. Chem. Phys. **99**, No. 2, 1230–1239 (1993).
9. M.A. Buldakov, Atmos. Oceanic Opt. **15**, No. 9, 752–756 (2002).