

EFFECT OF AIR ON THE FLUORESCENCE OF NO₂ EXCITED BY A HE-NE LASER

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The collisional quenching due to air of the NO₂ fluorescence excited by a He-Ne laser (633 nm) has been investigated for the air pressures varying from 0.1 to 750 mm Hg. It has been found that at the air pressures of the order of magnitude of 100 mm Hg or more the quenching efficiency increases due to triple collisions of the excited NO₂ molecules with the air molecules. The constants for quenching NO₂ fluorescence in the process of double and triple collisions with the molecules of air, molecular oxygen, and neon have been found. The dependence of the coefficient of resonance absorption due to NO₂ (at the laser frequency) on the pressure of air has been measured.

1. Nitrogen dioxide is one of a few molecular components of air, which resonantly absorbs the radiation in the visible. The NO₂ fluorescence excited by the light contains a large amount of information about the internal properties of the NO₂ molecule and, in addition, makes it possible to detect the impurities of nitrogen dioxide in air.

The collisional quenching of NO₂ fluorescence due to buffer gases (N₂, O₂, CO₂, Ar, H₂O, etc.),¹⁻⁴ the self-quenching of the fluorescence¹⁻⁹ as well as the mechanisms of energy transfer from the excited levels ²B₂ and states ²B₁ of the NO₂ molecule^{1-4,6-9} were studied previously.

In view of the complexity of the NO₂ absorption spectrum, the laser excitation of the fluorescence was, as a rule, used (argon- and krypton-ion lasers,⁵ a ruby laser,² the dye lasers,^{4,8,9} and a neodymium laser with frequency doubling³). The investigations were carried out at low pressures of gases down to 1 mm Hg. The region of higher pressures is of interest, in particular, for detection of the NO₂ impurities in air and other gases. The attenuation coefficient of the NO₂ fluorescence excited by an argon-ion laser (488 nm) has been obtained in Ref. 10. The optimal conditions for detecting the nitrogen dioxide impurities in air, nitrogen, argon, and helium in the case, in which the NO₂ fluorescence was excited by a neodymium laser (532 nm) were determined in Ref. 11. The effect of buffer gases on the NO₂ fluorescence under conditions of high pressures requires subsequent consideration.

In this paper we examine the collisional quenching of the NO₂ fluorescence due to air for pressures of air varying from 0.1 to 750 mm Hg as well as the effect of the collisional broadening of the NO₂ absorption line on the recorded fluorescence signal. The advantage of the source of excitation of the fluorescence, which we used, is high monochromaticity of the radiation (the lasing linewidth of the helium-neon laser is less than 0.04 cm⁻¹), which makes it possible to excite an individual vibrational-rotational level of the state \tilde{A}^2B_2 of NO₂ (see Ref. 12).

2. The NO₂ fluorescence was excited by an LGN-III commercial multimode ($c/2l = 150$ MHz) laser with a power of 25 mW. The laser radiation was modulated with a

low-frequency (~230 Hz) mechanical chopper and was directed into an analytical chamber, which contained a mixture of NO₂ and air (or other buffer gases) under study. A fluorescence chamber 41 cm long and 3.5 cm in diameter made of stainless steel was connected with a vacuum station, in which the required mixture of gases was formed and the pressure of the mixture was monitored. The pressure of the gases was measured by a diode mechanotron and a reference vacuum meter. The nitrogen dioxide produced as a result of oxidation of NO, prior to filling the system, was subjected to an additional purification by means of freezing out the N₂O₄ crystals with simultaneous evacuation of the gaseous impurities. The air intake into the fluorescence chamber was made directly in the laboratory. The air temperature was (24 ± 1)°C and the relative humidity was ~70%.

The NO₂ fluorescence was recorded by a PMT (FEU-51), whose signal was amplified by a narrow band amplifier and fed into a digital voltmeter and oscillograph. In order to distinguish the fluorescence signal from the background of scattered laser radiation, a KS-17 glass absorptive filter was employed. With an account of the spectral characteristic of the photocathode of the PMT, the NO₂ fluorescence was recorded in the spectral range 670–820 nm. The scattered laser light was additionally bounded by diaphragms with different apertures placed inside and outside the fluorescence chamber. In order to suppress the nonresonance emission of the gas discharge tube of the laser in the spectral range of the recorded fluorescence, a special-purpose interference light filter inserted between the laser and the analytical chamber was employed. Since, the Stokes components of the Raman scattering of laser radiation by N₂ and O₂ molecules shifted by 2331 cm⁻¹ and 1556 cm⁻¹ from the laser frequency fell within the spectral range of recording of the NO₂ fluorescence, the fluorescence signal of nitrogen dioxide in the presence of air was determined as the difference between the total signal and the background (without NO₂). The value of the background signal under normal atmospheric pressure of air was approximately equal to the value of the NO₂ fluorescence signal in the atmosphere with the NO₂ partial pressure ~3 mm Hg.

The power of laser radiation was recorded both prior entering into the fluorescence chamber and after it by two

photodiodes connected with digital microamperimeters. In the presence of air the background attenuation of the transmitted power due to scattering on the molecules and microparticles of air was taken into account.

3. In order to elucidate the experimental results obtained below, let us briefly consider the schematical model of the effect of buffer gases on the NO₂ fluorescence. The de-excitation of the vibrational-rotational levels of the state A²B₂ of NO₂ is determined by perturbations of these levels due to the upper energy levels of the ground state X²A₂ of NO₂ (see Refs. 1-9, 13, and 14). The de-excitation occurs due to the conversion to the levels of the ground state and the fluorescence and as a result of the vibrational-rotational cascade transfer of energy, in which many energy levels of both states take part. As a consequence, both the energy level directly populated by the laser contributes to the recorded fluorescence signal and the lower levels being populated in the course of the cascade energy transfer (see Fig. 1).

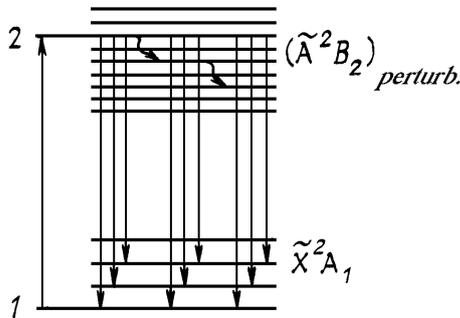
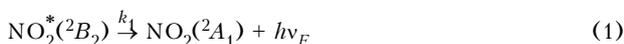
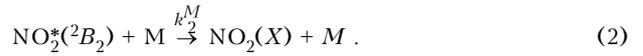


FIG. 1. The scheme of optical pumping and subsequent relaxation in the system $\tilde{A}^2B_2 - \tilde{X}^2A_2$ of NO₂: 1) the energy level of state \tilde{X}^2A_2 responsible for the absorption of the laser radiation (as a rule, one of the rotational sublevels of the ground vibrational level¹²); 2) the level of the excited state \tilde{A}^2B_2 being populated by the laser. The rotational structure of the optical transitions as well as the processes of interconversion between the levels of state \tilde{A}^2B_2 and upper levels of the state \tilde{X}^2A_2 (Ref. 4) are not shown in the scheme.

Such a system of energy levels of the excited state of NO₂ can be treated as a model system of individual levels separated from each other by a definite energy step E_v, which is accepted as the mean value of the vibrational energy transferred in the process of collisions.^{6,7} In so doing, as shown in Ref. 7, this system of levels can be reduced to a simpler Stern-Volmer model describing the de excitation process of the individual level, in which the effective constants describing the de-excitation of the investigated system of levels as a whole are treated as the de excitation constants. After determining these effective constants, the de-excitation constants of the individual energy levels can also be found (with definite simplifications). On the basis of the model, we describe the de-excitation of the system of energy levels of the state \tilde{A}^2B_2 of NO₂, which contribute to the recorded fluorescence signal by the following scheme:



and



Here, NO₂(²B₂) are the NO₂ molecules in the excited state contributing to the recorded fluorescence signal, NO₂(²A₁) are the NO₂ molecules in the ground state, ν_F is the effective frequency of the fluorescence, NO₂(X) are the NO₂ molecules located at the energy levels, which do not contribute to the fluorescence signal (the levels of the ground state and lower levels of the state ²B₂), M are the buffer molecules, and k₁ and k₂^M are the constants of the rate of processes (1) and (2).

The recorded fluorescence signal F is proportional to the intensity of laser radiation I₁ in the geometric region, from which the fluorescence signal is collected, to the coefficient of the resonance absorption α due to NO₂ (at laser frequency), to the density NO₂ [NO₂], and to the quantum yield of the fluorescence η, i.e., F = CI₁α[NO₂]η. The proportionality coefficient C characterizes the efficiency of collection of the fluorescent radiation and of its conversion to the electric signal. On account of the scheme (1)-(2),

$$\eta = \frac{k_1}{k_1 + \sum_i (k_2^{M_i} [M_i])} = \frac{1}{1 + \sum_i (a_{M_i} [M_i])},$$

where a_{M_i} = k₂^{M_i} / k₁ is the constant of collisional quenching of the NO₂ fluorescence due to buffer gas M_i with the density [M_i]. In the absence of foreign gases

$$F_0([NO_2]) = C I_1 \alpha_0 \frac{[NO_2]}{1 + a_{NO_2}[NO_2]},$$

where F₀ and α₀ are the fluorescence signal and the resonance absorption coefficient under these conditions, a_{NO₂} is the constant of self-quenching of the NO₂ fluorescence.

The addition of air into the fluorescence chamber, which contains NO₂ with the prescribed density [NO₂] results in the attenuation of the recorded fluorescence signal by a factor of D

$$D([NO_2], [A]) = \frac{F_0([NO_2])}{F([NO_2], [A])} = \frac{\alpha_0}{\alpha([A])} \left(1 + \frac{a_{air}[A]}{1 + a_{NO_2}[NO_2]} \right) \quad (3)$$

Here, a_{air} is the effective constant of collisional quenching of the NO₂ fluorescence due to air and [A] is the air density. Simultaneous measurement of the dependences D([A]) and α([A]) allows one to determine the values of the constant a_{air}. The value of a_{NO₂} can be obtained from the Stern-Volmer plot

$$\frac{[NO_2]}{F_0([NO_2])} = (C I_1 \alpha_0)^{-1} (1 + a_{NO_2}[NO_2]) \quad (4)$$

In this paper with the purpose of determining the constants a_{NO_2} and a_{air} , we measured the NO_2 -fluorescence signals as functions of the pressures of nitrogen dioxide and air in the analytical chamber as well as the dependences of the attenuation of the intensity of laser radiation transmitted through the analytical chamber on the pressures of NO_2 and air.

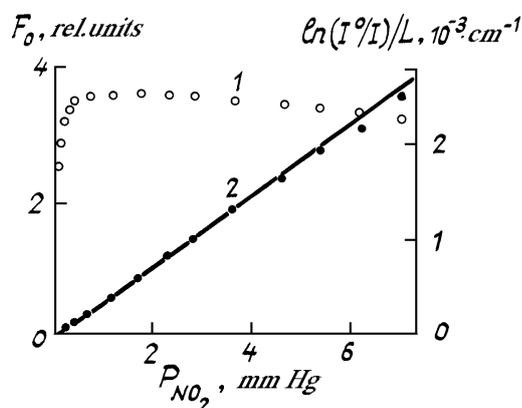


FIG. 2. The fluorescence signal F_0 (1) and the value $(\ln(I^0/I)/L)$ (2) as functions of the NO_2 pressure.

4. Figure 2 shows the plots of the recorded fluorescence signal and the attenuation of the intensity of laser beam when it passes through the analytical chamber versus the NO_2 pressure in the chamber. As can be seen, as the NO_2 pressure rises from 0.1 to 1 mm Hg, the fluorescence signal saturates, what is associated with the fluorescence self quenching. At the NO_2 pressures higher than 3 mm Hg, the fluorescence signal decreases because of the significant absorption of the laser radiation due to nitrogen dioxide and also because of the decrease of the coefficient of the resonance absorption due to NO_2 as a result of the collisional broadening of the absorption line. The latter also affects the linearity of the dependence $(\ln(I^0/I)/L)(P_{\text{NO}_2})$, where I^0 is the intensity of the laser beam transmitted through the fluorescence chamber without NO_2 , I is the corresponding value when NO_2 fills the chamber at the pressure P_{NO_2} , and L is the absorption length which is equal to 41 cm. From the slope of this dependence in its linear part, we determined the coefficient α_0 . Its value was equal to $(3.5 \pm 0.4) \cdot 10^{-4} \text{ cm}^{-1}(\text{mm Hg})^{-1}$. The deviation from the linearity as the pressure rises may be also caused by the dimerization of NO_2 , i.e., $(\text{NO}_2)_2$ does not absorb the laser radiation. According to our estimates, the influence of this effect at the NO_2 pressures varying from 0.1 to 5 mm Hg did not exceed 5% of the quantities being measured: the fluorescence signal and the attenuation of the laser radiation transmitted through the fluorescence chamber. Note also that the obtained value α_0 and the

general pattern of the absorption spectrum of NO_2 in the spectral range under consideration¹⁴ indicates that the absorption of fluorescence of NO_2 due to the proper gas can be neglected for the NO_2 pressures in the employed analytical chamber up to ~ 5 mm Hg; here, the decrease of the fluorescence signal due to the self-absorption does not exceed $\approx 1\%$.

Based on the experimental dependence $F_0(P_{\text{NO}_2})$ the Stern-Volmer curve (4) has been plotted and the constant of self-quenching of the NO_2 fluorescence a_{NO_2} has been determined, whose value was equal to $(1.50 \pm 0.25) \cdot 10^{-15} \text{ cm}^3/\text{mol}$.

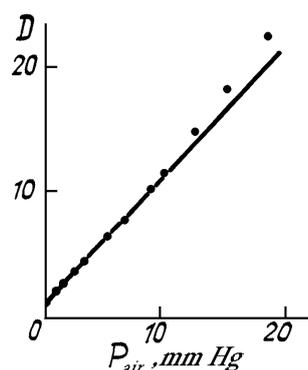


FIG. 3. The fluorescence attenuation coefficient D vs the pressure of air ($P_{\text{NO}_2} = 0.6$ mm Hg).

Figure 3 displays a typical dependence of the value of the fluorescence signal attenuation versus the air pressure. The attenuation coefficient depends linearly on the pressure at $P_{\text{air}} \leq 5$ mm Hg. At higher pressures of air, a faster increase in $D(P_{\text{air}})$ is observed due to the collisional broadening of the absorption line of NO_2 .

Figure 4a shows the plots of the absorption coefficient due to NO_2 and the values $(D \frac{\alpha}{\alpha_0})$ versus the pressure of air. As can be seen, the absorption coefficient decreases by a factor of ~ 1.8 as the pressure rises up to 100 mm Hg. At the same time, the quantity $(D \frac{\alpha}{\alpha_0})$ depends linearly on the pressure of air at $P_{\text{air}} \geq 70$ mm Hg. The constant of collisional quenching of the NO_2 fluorescence due to air calculated based on the slope of this dependence (with the help of Eq. (3)) coincides within the measurement error with the value obtained at low pressures of air (see Fig. 3). We have found that $a_{\text{air}} = (0.74 \pm 0.15) \cdot 10^{-15} \text{ cm}^3/\text{mol}$. At the pressures of air of the order of magnitude 100 mm Hg or higher, the absorption coefficient due to NO_2 continue to decrease (Fig. 4b) and its value is equal to $(1.1 \pm 0.2) \cdot 10^{-4} \text{ cm}^{-1}(\text{mm Hg})^{-1}$ at atmospheric pressure.

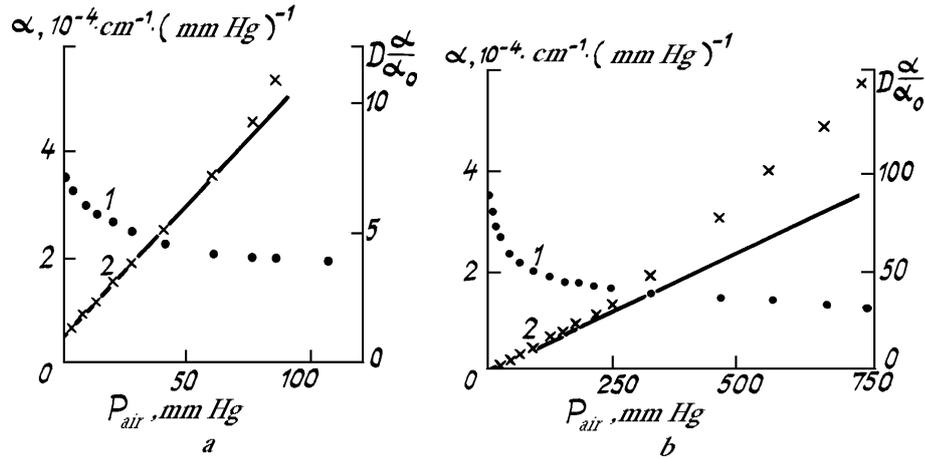
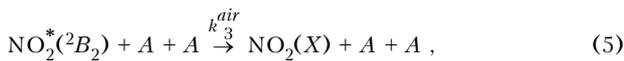


FIG. 4. The coefficient of resonance absorption due to NO₂ α at the laser frequency (1) and the value $(D-\alpha/\alpha_0)$ vs the air pressure (2) ($P_{NO_2} = 4.3$ mm Hg).

The behavior of $(D \frac{\alpha}{\alpha_0})$ for these pressures substantially changes, i. e. , in addition to the linear dependence $(D \frac{\alpha}{\alpha_0})(P_{air})$ characteristic of $P_{air} \lesssim 70$ mm Hg, a component of the attenuation of the fluorescence signal arises, which increases in proportion to a squared pressure. Figure 5 shows the dependence of $(D \frac{\alpha}{\alpha_0} - 1)P_{air}^{-1}$ as a function of air pressures. The analysis of this dependence and relation (3) shows that for pressures of the order of magnitude of 100 mm Hg or higher, along with the above-considered process (2) of the collisional de-excitation of the systems of energy levels of the excited state \tilde{A}^2B_2 of NO₂ in the process of double collisions with the air molecules, the de-excitation becomes substantial which proceeds according to the triple-collision scheme:



where we imply A to stand for "averaged" molecule of air, which represents the air as a whole and k_3^{air} is the rate constant of the process. With account of relation (5), the formula for the attenuation coefficient D can be written down in the following form:

$$D([NO_2], [A]) = \frac{\alpha_0}{\alpha([A])} \left(1 + \frac{a_{air}[A] + b_{air}[A]^2}{1 + a_{NO_2}[NO_2]} \right), \quad (6)$$

where $b_{air} = k_3^{air}/k_1$ is the constant of quenching of the NO₂ fluorescence due to air in the process of triple collisions. Based on the experimental data (Fig. 5) and using formula (6) we found that $b_{air} = (3.1 \pm 0.7) \cdot 10^{-35} \text{ (cm}^{-3}/\text{mol)}^2$.

Since air consists of many gases with various physical and chemical properties, the contribution of each of them to the total process (5) will be, beyond doubt, different. In order to determine the corresponding contributions, two atmospheric gases substantially different in their properties were chosen i.e. , the molecular oxygen and neon. The former possesses the atmospheric absorption bands, whose maxima (7590–7650 Å and 6870–6920 Å, according to

Ref. 15) are correlated with the position of the levels of the state \tilde{A}^2B_2 of NO₂ on the energy base. This absorption bands make the maximum contribution to the recorded fluorescence signal. Since forbidden electron transition $^1\Sigma_g^+ \leftarrow ^3\Sigma_g^-$ of O₂ is partially allowed as a result of the perturbations in the process of collisions, the presence of molecular oxygen at high pressures could cause the intensification of electron quenching of the NO₂ fluorescence according to the triple-collision scheme. On the other hand, neon is an atomic gas, which does not possess the vibrational-rotational degrees of freedom, and as a quenching agent of the NO₂ fluorescence, makes it possible to determine the relative efficiency of the conversion of the vibrational energy of an excited NO₂ molecule to the energy of translational motion of the buffer.

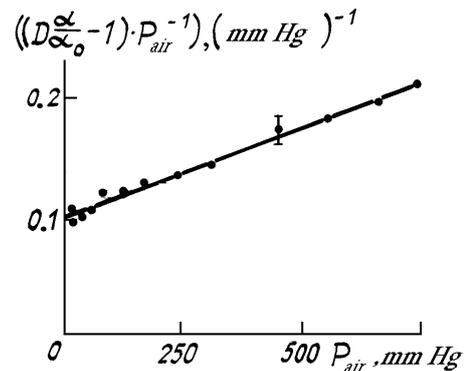


FIG. 5. The value $((D \frac{\alpha}{\alpha_0} - 1) \cdot P_{air}^{-1})$ vs the pressure of air ($P_{NO_2} = 4.3$ mm Hg).

The dependences analogous to those shown in Figs. 3–5 were measured for O₂ (90% ¹⁶O and 10% ¹⁸O) and Ne (90% ²²Ne and 10% ²⁰Ne). Using relation (6), the constants of collisional quenching of the NO₂ fluorescence excited by the He-Ne laser (633 nm) for these gases were found (the spectral range of the fluorescence recording was 670–820 nm; the results are given in Table I).

TABLE I.

Gas	NO ₂	Air	¹⁶ O ₂	²² Ne
$a, 10^{-15}$ cm ³ /mol	1.50 ± 0.25	0.74 ± 0.15	0.79 ± 0.15	0.34 ± 0.007
$a, 10^{-35}$ (cm ³ /mol) ²	—	3.1 ± 0.7	3.9 ± 0.7	1.6 ± 0.3

Using the model of Ref. 7 as well as the values $E_v^{\text{NO}_2} \sim 1000 \text{ cm}^{-1}$ and $E_v^{\text{air}} \sim E_v^{\text{O}_2} \sim 750 \text{ cm}^{-1}$ (see Ref. 3), we obtain that the constants of quenching for the individual vibrational–rotational levels of the state \tilde{A}^2B_2 of NO₂, which contribute to the fluorescence signal, on the average, exceed the corresponding values of the effective quenching constants a_{NO_2} , a_{air} , and a_{O_2} for NO₂, air, and O₂, given in the table, by a factor of ~4–5.

The determined values a_{NO_2} , a_{air} , and b_{air} made it possible to calculate the coefficient of attenuation of the fluorescence of the impurities of NO₂ ($a_{\text{NO}_2} \cdot [\text{NO}_2] \ll 1$) by air. Its value was equal to $(1.2 \pm 0.4) \cdot 10^5$ and agreed with the value $5 \cdot 10^4$ determined in Ref. 10 when exciting the NO₂ fluorescence by an argon–ion laser (488 nm), taking into account the difference between the separation of the exciting frequencies and those of the fluorescence recording in Ref. 10 and this paper.

It follows from the comparison of the quenching constants for NO₂, air, O₂, and Ne that the energy of an excited NO₂ molecule is converted to both vibrational–rotational energy and translational energy of buffer. In addition, the process of energy transfer is of nonresonant nature, therefore, the degree of quenching the NO₂ fluorescence due to air is determined by the basic atmospheric gases, namely, nitrogen, oxygen, and water vapor. As can be seen, the relations between the quenching constants a for different gases remain approximately true for the quenching constants b as well. This indicates that process (5) is not a new channel of quenching the NO₂ fluorescence, which is due to, say, an electron quenching of the fluorescence due to the molecular oxygen, but solely reflects an increase in the efficiency of vibrational transfer of the energy from an excited

NO₂ molecule to a buffer molecule in the presence of a third particle. The comparison of the quenching constants a_{air} and b_{air} for air shows that as a result of the effect of a third particle (a molecule of air) in the process of collision of the NO₂ molecules with air molecules the efficiency of the collisional quenching of the NO₂ fluorescence in the atmosphere increases by a factor of ~2 in comparison with the quenching of air at low pressures ($\leq 70 \text{ mm Hg}$).

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REFERENCES

1. G.H. Myers, D.M. Silver, and F. Kaufman, *J. Chem. Phys.* **44**, No. 2, 718–723 (1966).
2. D.F. Hakala and R.R. Reeves, *Chem. Phys. Lett.* **38**, No. 3, 510–515 (1976).
3. V.M. Donnelly, D.G. Keil, and F. Kaufman, *J. Chem. Phys.* **71**, No. 2, 659–673 (1979).
4. P.J. Brucat and R.N. Zare, *ibid.* **81**, No. 6, 2562–2570 (1984).
5. K. Sakurai and H.P. Broida, *ibid.* **50**, No. 6, 2404–2410 (1969).
6. S.E. Schwartz and H.S. Johnston, *ibid.* **51**, No. 4, 1286–1302 (1969).
7. L.F. Keyser, S.Z. Levine, and F. Kaufman, *ibid.* **54**, No. 1, 355–363 (1971).
8. V.M. Donnelly and F. Kaufman, *ibid.* **66**, No. 9, 4100–4110 (1977).
9. V.M. Donnelly and F. Kaufman, *ibid.* **69**, No. 4, 1456–1460 (1978).
10. J.A. Gelbwachs, M. Birnbaum, A.W. Tucker, and C.L. Fincher, *Opto electronics* **4**, 155–160 (1972).
11. N.V. Golovenkov, S.V. Oshemkov, and A.A. Petrov, *Zh. Prikl. Spektrosk.* **47**, No. 5, 753–757 (1987).
12. K. Abe, F. Myers, T.K. McCubbin, and S.R. Polo, *J. Mol. Spectr.* **50**, 413–423 (1974).
13. A.E. Douglas, *J. Chem. Phys.* **45**, No. 3, 1007–1015 (1966).
14. G.D. Gillispie and A.U. Khan, *ibid.* **65**, No. 5, 1624–1633 (1976).
15. J.G. Calvert and J.N. Pitts, *Photochemistry* (Wiley, New York, 1966).