

INFLUENCE OF THE COLLISIONAL ENERGY TRANSFER FROM THE I₂ ENERGY LEVELS EXCITED WITH A He-Ne (633 nm) LASER ON ITS FLUORESCENCE IN THE ATMOSPHERE

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We discuss here the influence of the collisional energy transfer from the excited vibrational energy levels of B-state of I₂-127 and I₂-129 isotopes on I₂ fluorescence. A He-Ne (633 nm) laser is used as a source of the fluorescence excitation. The calculations and experimental measurements have shown the process to lead to a change in the population of the excited vibrational levels and, consequently, to changes in I₂ fluorescence spectrum. As a result the ratio between the population of the nearest level and the initially excited one can reach 15–20% under atmospheric pressure, while the populations of more distant levels are much (about two orders of magnitude) lower. The results obtained well explain how one should allow for the influence of the energy collision transfer on the I₂ fluorescence intensity that is of particular importance when detecting I₂ isotopes in the atmosphere.

The following processes can affect the I₂ isotopes fluorescence: self-quenching, quenching of fluorescence, resonance absorption line broadening, and collisional energy transfer from the I₂ excited levels. The processes of self-quenching and quenching have been studied in detail earlier in Refs. 1–6. Thus, in Refs. 1 and 4 I₂ self-quenching cross sections are presented that were obtained using the He-Ne (633 nm) laser as a source of the fluorescence excitation. The I₂-127 fluorescence quenching cross sections for CO₂, O₂, N₂, and Kr have been determined for the case of excitation with a dye-laser (499–640 nm) (Ref. 2). In Refs. 3–6 for determining the coefficients and cross sections of I₂-127 and I₂-129 isotopes fluorescence quenching for a series of buffer gases an Ar (514.5 nm) laser and a He-Ne (633 nm) laser are used. The resonance absorption line broadening has been described in a series of papers.^{6,7} In particular, in Ref. 7 the coefficients and cross sections of collisional line broadening of ¹²⁷I₂ resonance absorption have been determined using a He-Ne (633 nm) laser.

At the same time, the collisional energy transfer from I₂ excited levels is studied much poorer; the investigations of the above energy transfer have been performed mainly under low pressures of buffer gases (≈ 1 Torr) (Refs. 3, 4, 8).

This paper is devoted to investigations of the collisional energy transfer from the ¹²⁷I₂ and ¹²⁹I₂ excited levels. A He-Ne (633 nm) laser is used as an excitation source of fluorescence. Molecular iodine resonantly absorbs the He-Ne laser emission because of transitions from the ground electron X-state to the excited B-state. In this case, the following lines of the resonance absorption iodine

isotopes correspond to the above-mentioned laser wavelength:

– 6–3 P(33) and 11–5 R(127) for ¹²⁷I₂;
 – 6–3 P(33); 8–4 P(54); 8–4 R(60); and 12–6 P(69) for ¹²⁹I₂ (in designations of lines the values are given of the vibrational quantum number for excited and ground electron states of iodine and the value of the rotational quantum number for the ground state, respectively).

For a complete description of the processes of vibration-rotation energy transfer from an excited level it is necessary to solve a set of equations of relaxation for a great number of equations involved in the energy exchange. But the general character of variation of the population of I₂ excited levels, namely, the fluorescence spectrum, can be determined by using simplified models.

Because the rotational energy transfer results only in local “blurring” of the spectral fluorescence lines (within the limits of the vibrational band width), then the overall change of intensity distribution in the fluorescence spectrum may occur only as a result of the vibrational energy transfer. As follows from the consideration of I₂ fluorescence spectra, excited with the He-Ne laser radiation,⁵ the most probable are the single-quantum vibrational transitions, therefore for describing the vibrational energy transfer from the B-state levels excited with a He-Ne laser one can use the model of cascade energy transfer where the successive transfer of vibrational energy from one level to another is taken into account (the levels being spaced by the energy difference ≈ 115 cm⁻¹ (Ref 9)). For simplicity of calculations we shall consider only the downward transitions using the energy

scale, i.e., leading to the initial determination of thermodynamic equilibrium. Such a simplification will only work in the case, when the cascade transitions between the levels do not populate the zero vibrational energy level markedly and, hence, the transitions "from top to bottom" play a decisive role. Based on this condition, we write the set of dynamic equations of populations of the levels participating in the vibrational energy transfer in the form

$$\begin{aligned} \frac{dN_0}{dt} &= \alpha I N_x - \left(\frac{1}{\tau_0} + (R_q^{(0)} + R_v^{(0)})B \right) N_0, \\ \frac{dN_1}{dt} &= R_v^{(0)} B N_0 - \left(\frac{1}{\tau_1} + (R_q^{(1)} + R_v^{(1)})B \right) N_1, \\ &\dots \\ \frac{dN_n}{dt} &= R_v^{(n-1)} B N_{n-1} - \left(\frac{1}{\tau_n} + (R_q^{(n)} + R_v^{(n)})B \right) N_n, \end{aligned} \quad (1)$$

where N_0 is the population of the I_2 B -state level excited with a laser; N_1 in N_n are the populations of B -state levels, successively participating in the vibrational energy transfer; N_x is the population of the ground I_2 X -state, responsible for the laser radiation absorption; α is the I_2 resonance absorption coefficient corresponding to an absorption line; I is the laser radiation intensity; τ_n is the natural lifetime of the n -th level; $R_q^{(n)}$ and $R_v^{(n)}$ are the constants of collisional quenching rate and the vibrational energy transfer velocity, corresponding to the n -th level, B is the buffer concentration.

For stationary conditions the population ratios between the adjacent levels are as follows:

$$\begin{aligned} \frac{N_1}{N_0} &= \frac{R_v^{(0)} B}{\frac{1}{\tau_1} + (R_q^{(1)} + R_v^{(1)})B}, \\ \frac{N_2}{N_1} &= \frac{R_v^{(1)} B}{\frac{1}{\tau_2} + (R_q^{(2)} + R_v^{(2)})B}, \\ &\dots \\ \frac{N_n}{N_{n-1}} &= \frac{R_v^{(n-1)} B}{\frac{1}{\tau_n} + (R_q^{(n)} + R_v^{(n)})B}. \end{aligned} \quad (2)$$

Without any serious effect on the final result the constants τ_n , $R_v^{(n)}$, $R_q^{(n)}$ can be considered to be equal for all the levels and at such a simplification the ratios of equilibrium populations of i -th ($i \neq 0$) and zero levels take the form

$$\begin{aligned} \frac{N_1}{N_0} &= \frac{R_v B}{\frac{1}{\tau} + (R_q + R_v)B}, \\ \frac{N_2}{N_0} &= \frac{N_2}{N_1} \frac{N_1}{N_0} = \left(\frac{R_v B}{\frac{1}{\tau} + (R_q + R_v)B} \right)^2, \end{aligned} \quad (3)$$

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$$\frac{N_n}{N_0} = \frac{N_n}{N_{n-1}} \frac{N_{n-1}}{N_{n-2}} \dots \frac{N_1}{N_0} = \left(\frac{R_v B}{\frac{1}{\tau} + (R_q + R_v)B} \right)^n.$$

As follows from the expressions obtained, relative (with respect to zero level) populations of the levels, participating in the vibrational energy transfer, increase with the buffer gas concentration growth and at $B(R_q + R_v) \gg \frac{1}{\tau}$ the above populations approach asymptotically the limiting values:

$$\begin{aligned} \frac{N_1}{N_0} &= \frac{1}{1 + R_q/R_v}, \\ \frac{N_2}{N_0} &= \left(\frac{1}{1 + R_q/R_v} \right)^2, \\ &\dots \\ \frac{N_n}{N_0} &= \left(\frac{1}{1 + R_q/R_v} \right)^n. \end{aligned} \quad (4)$$

As is evident within the approximation considered the maximum possible relative populations of the energy levels of I_2 B -state closely adjacent to the initially excited one are determined by the ratio of constants of velocity of collisional quenching of fluorescence and vibrational energy transfer R_q/R_v . It should be noted that the theoretical calculations of these constants is rather difficult what is connected with the properties of the molecular system under study. Because the fluorescence quenching and the vibrational energy transfer are the result of inelastic collisions of the I_2 excited molecules with the buffer gas molecules, the consideration of these processes leads to the problem of motion of a particle with the reduced, iodine-buffer, mass in the potential field of the electromagnetic interaction of iodine and buffer gas molecules. One of the most complicated problems in this case is the determination of the type of the interaction potential. Since the colliding particles are electrically neutral, the interaction is of dipole-dipole nature, and at large (as compared with the particle size) distances the potential falls off as r^{-6} (Ref. 10). In the case of the absence of dipole moments of the colliding particles the dipole moments induced by the partner field are of a decisive importance in the interaction. However, if in the course of interaction the particles approach at a distance, comparable with their dimensions, then the dependence of the interaction potential on r changes, and the calculation of interaction cross sections becomes a difficult task. In this case one only manages to determine the order of magnitude of the unknown cross section and some its dependences on the parameters, determining the dipole moment of a buffer gas and its dipole moment.^{3,11,12} In this connection the values of cross sections of quenching and vibrational energy transfer should be determined experimentally.

In this paper we describe the experimental investigations of $^{127}\text{I}_2$ fluorescence and the fluorescence of a mixture of isotopes $^{129}\text{I}_2$: $^{129}\text{I}^{127}\text{I}$: $^{127}\text{I}_2$ in the proportions 0.74:0.24:0.02, obtained from the nuclear fuel wastes. The fluorescence spectra of these isotopes were studied under different atmospheric pressures. The fluorescence was excited with a He–Ne laser radiation in the glass sealed-off cells 10 cm long, containing either isotopically pure $^{127}\text{I}_2$ or a mixture of isotopes. The concentration of saturated iodine vapor was determined by the temperature of the branch, checked by the diode movable-electrode tube and at temperature of 24°C it was $1 \cdot 10^{16}$ mol/cm³. For creating the necessary buffer gas pressure the cell was connected to the vacuum post. The pressure of gas mixture was measured with a vacuum gauge. The fluorescence radiation was focused on the input slit of MDR-23 monochromator with 1 nm resolution and the operation spectral range of 350–1000 nm. To increase the fluorescence intensity we used the multipass cell, formed by the mirrors placed before and after the cell. The laser radiation power was ≈ 15 mW and measured using a photodiode. Recording and processing of the fluorescence spectra were performed using an automated system of data processing based on an IBM PC.

Figure 1 gives the fluorescence spectrum of the iodine isotopes mixture being studied in the range of 580–630 nm (anti-Stokes components) obtained in the absence of a buffer gas. The spectral lines can be observed corresponding to the collisional energy transfer to the adjacent vibrational level (Figure 1 shows the lines 11–2, 11–3, 11–4, 11–5; 5–0, 5–1, 5–2; 7–0, 7–1, 7–2, 7–3).

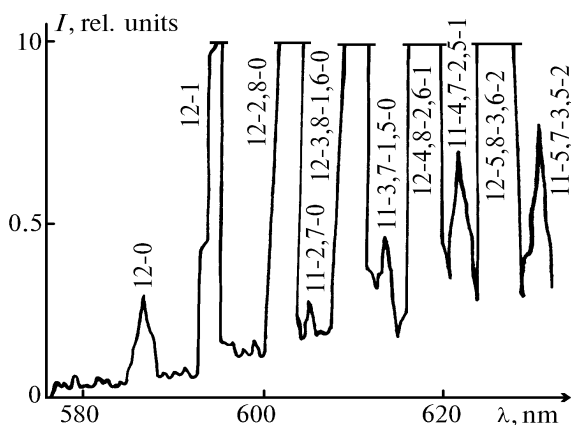


FIG. 1. Fluorescence spectrum of the iodine isotopes mixture in the range from 580 to 630 nm ($n_1 = 1 \cdot 10^{16}$ mol/cm³).

The intensity of these lines is small and does not exceed 0.1% relative to the intensities of spectral lines corresponding to the transitions from the initially excited iodine levels. As to the levels far from the initially excited levels, no corresponding spectral lines were observed.

To analyze the contribution of spectral lines, due to the collisional energy transfer, to the general distribution of fluorescence intensity with the buffer gas in the $^{127}\text{I}_2$ spectrum we have selected the spectral lines 6–7 and 11–9 (corresponding to the initially excited 6-th and 11-th levels). Selection of these spectral lines is caused by the fact that, first, the resonance absorption line 6–3 P(33) makes the main contribution to the $^{127}\text{I}_2$ fluorescence intensity (the contribution of line 11–5 R(127) does not exceed 10% (Ref. 13)) and, secondly, the Franck–Condon coefficient for the spectral line 11–9 is practically zero.¹⁴ These spectral lines, observed in the 660–680 nm range (Stokes components), obtained under different atmospheric pressure are given in Fig. 2. The iodine concentration n_1 was constant during the experiment being approximately 10^{16} mol/cm³ that enabled us to relate the intensity redistribution over iodine fluorescence spectral lines only with the iodine-air collisions. It is evident that with the increasing air pressure additional lines appear in the fluorescence spectrum, due to the transition to the adjacent 5-th vibrational level, in this case the spectral line fluorescence intensity, corresponding to the transition from the initially excited level, exceeds greatly the additional line intensity, and with the increasing air pressure the intensity of the former lines decreases while the latter lines intensity increases.

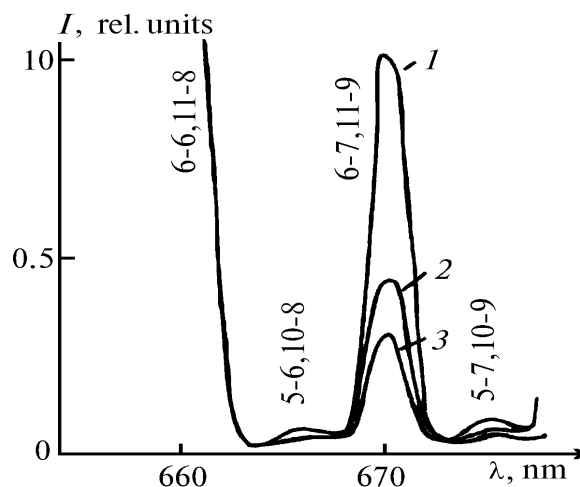


FIG. 2. Fluorescence spectrum of the iodine-127 in the 660–680 nm range at different pressures of air: 2.2 Torr (1), 7.4 Torr (2), 12.3 Torr (3), ($n_1 = 1 \cdot 10^{16}$ mol/cm³).

Figure 3 shows the dependence of the ratio of the fluorescence intensity of spectral lines I_{5-7}/I_{6-7} on the air pressure. It is evident that at pressures ≤ 15 Torr the dependence is close to a linear one. At large pressures its growth slows down, and, in particular, at the pressure of 150 Torr the line intensity, due to the collisional energy transfer, is approximately 15% of the line intensity due to the transition from the initially excited level.

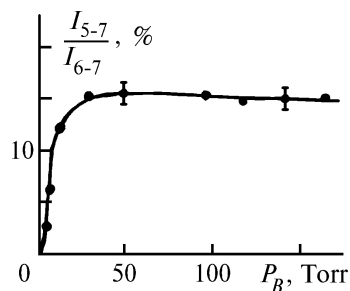


FIG. 3. Dependences of the ratio of the fluorescence intensity I_{5-7}/I_{6-7} of the iodine-127 on pressure ($n_1 = 1 \cdot 10^{16}$ mol/cm³).

From the results obtained the value of R_q/R_v can be determined if we use the following ratio between the fluorescence intensity and the population of an excited level:

$$I = (N/\tau)\eta q, \quad (5)$$

where $\eta = 1/(1 + K_s n_1 + K_B B)$ is the quantum output of the fluorescence (K_s and K_B are the coefficients of self-quenching and quenching of the fluorescence⁶): q is the Franck–Condon coefficient for a corresponding vibrational transition.¹⁴

The value of the ratio R_q/R_v is 5.3 ± 0.2 . From the above it follows that according to Eq. (4) the populations of vibrational levels N_i ($i > 1$) turn out to be more than two orders less than the population of the originally excited level. Thus, the maximum value of the ratio N_2/N_0 does not exceed 2% that is also confirmed by the observed iodine fluorescence spectrum. Since in this case the He–Ne laser radiation excites the vibrational levels of B -state of the iodine-127 and iodine-129 molecules not lower than the sixth level, the population of zeroth vibrational level of B -state due to the vibrational energy transfer is negligible, and, hence, the assumptions proposed earlier in the model under study, are justified.

It should be noted that the results obtained refer to the iodine-127 absorption line 6–3P(33). As to the other absorption lines of iodine-127 and iodine-129, then, based on the available data on the lifetimes, energies of vibrational levels of these iodine isotopes, cross-sections of self-quenching and quenching and the Franck–Condon coefficients, we can draw the conclusion that the redistribution of populations over excited levels and intensities in the fluorescence spectrum for these lines will be similar.

Thus, the above-mentioned investigations have shown that the process of collisional energy transfer from the excited vibrational levels of B -state of the isotopes of iodine-127 and iodine-129 resulted in the

variation of the iodine fluorescence spectrum, manifested both in the occurrence of additional spectral lines due to the radiative relaxation of the levels, populated as a result of this process and in the variation of line intensities, caused by the fluorescence from the initially excited iodine levels. In this case the iodine molecules distribution over the vibrational levels of B -state is not described by the Boltzmann distribution. Thus, the population of the nearest underlying level relative to the initial excited level can reach 15–20% at the atmospheric pressure, and the populations of more distant levels are two or more orders lower. The results obtained enable us to consider the influence of the collisional energy transfer on the iodine fluorescence intensity that is especially important when detecting the iodine isotopes in the atmosphere.

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