Investigation of the Luminescence Spectrum of Atomic Iodine ($^2P_{1/2}$—$^2P_{3/2}$ Laser Transition)

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The luminescence spectrum of atomic iodine ($\lambda = 1.315\ \mu$) is investigated. The hyperfine structure of the spectrum measured is in good agreement with the calculations. Values of the constants specifying the shape of the spectrum are determined with greater accuracy. In particular, the magnetic splitting constant for the $^2P_{1/2}$ level, the Einstein coefficient, the polarizability of atomic iodine in the $^2P_{1/2}$ state, and the broadening due to collisions between argon atoms and C_3F_7I molecules are determined.

SEVERAL papers have been published by now on photodissociation lasers, where the generation is observed in the level system of atomic iodine $^2P_{1/2} - {}^2P_{3/2}$ at a wavelength 1.315 μ[1]. However, there are still no exhaustive experimental data on the hyperfine structure of the luminescence spectrum of this transition. Some data on the luminescence spectrum of atomic iodine are contained in several papers[2-5]. Since information on the luminescence spectrum of atomic iodine may be of interest to researchers who use iodine photodissociation lasers, we have investigated experimentally the luminescence of the $^2P_{1/2} - {}^2P_{3/2}$ transition.

In view of the spin of the I^{127} nucleus[6], its luminescence line has a hyperfine structure, which was calculated by us earlier[5]. We present here the main results of this calculation. The expression for the hyperfine level splitting is[7]

$$\Delta E_F = {}^1/_2 AC + BC(C+1) + \Delta, \qquad (1)$$

where A is the magnetic-interaction constant, B is the quadrupole-interaction constant, C = F(F + 1) − J(J + 1) − I(I + 1); J = L + S, S is the spin of the electron spin, and $\Delta = {}^4/_3 BI(I+1)J(J+1)$ is the level shift and does not depend on F. The level $^2P_{1/2}$ splits into two sublevels (F = 3 and 2) and the level $^2P_{3/2}$ into four (F = 4, 3, 2, and 1), there being no quadrupole interaction for the $^2P_{1/2}$ level. For the $^2P_{3/2}$ level, the constants A and B were obtained experimentally[8]:

$$A_{^3/_2} = 0.0276\,\text{cm}^{-1},\quad B_{^3/_2} = {}^1/_{80}0.0382\ \text{cm}^{-1}.$$

The shifts of the components are then equal to:

$$\Delta E_{F=1} = -0.118\,\text{cm}^{-1},\quad \Delta E_{F=2} = -0.094\ \text{cm}^{-1},$$

$$\Delta E_{F=3} = -0.028\,\text{cm}^{-1},\quad \Delta E_{F=4} = 0.113\ \text{cm}^{-1}.$$

The constant $A_{1/2}$ of the $^2P_{1/2}$ level was calculated from the fine splitting of the term $5p^5\ {}^2P$ of the iodine atom with allowance for the relativistic corrections. It can be expressed in the form (see[7])

$$A = \xi_l \frac{g_I L(L+1) F_r(JZ_i)}{J(J+1) H_r(LZ_i) Z_i} \frac{m}{m_p}, \qquad (2)$$

where ξ_l is the fine-splitting constant, given by $\xi_l = \Delta E/(L + {}^1/_2)$; $g_I = \mu/I$ is the gyromagnetic ratio; $F_r(JZ_i)$ and $H_r(LZ_i)$ are the relativistic corrections; $Z_i = Z - 4$ for p-electrons; m and m_p are the masses of the electron and proton, respectively. Substituting in (2) $\xi = 7603/{}^3/_2$, L = 1, J = $^1/_2$, $Z_i = 49$, $F_r({}^1/_2 Z_i) = 1.932$, $H_r(1Z_i) = 1.060$[7], we obtain for our case $A_{1/2} = 0.212\ \text{cm}^{-1}$[5].

With the aid of (1) we obtain the following shifts of the components of the $^2P_{1/2}$ level:

$$\Delta E_{F=2} = -0.371\ \text{cm}^{-1},\ \Delta E_{F=3} = 0.265\ \text{cm}^{-1}.$$

In accordance with the selection rules $\Delta F = 0, \pm 1$, the luminescence spectrum of the investigated transition should consist of six lines. The relative intensities of the components were calculated from the known formulas[7]. Account was taken of the fact that the level splitting energies of $^2P_{1/2}$ and $^2P_{3/2}$ are small compared with kT, as a result of which the level population of the hyperfine splitting is proportional to the statistical weights of the levels.

For the magnetic-dipole radiative transition between the components of the hyperfine structure, the spontaneous emission probability W^{sp} (the Einstein coefficient A) is equal to[7]

$$W^{sp}(\gamma JIF, \gamma' J' IF') = \frac{4\omega^3}{3\hbar c^3} \frac{2I+1}{2F+1} Q(IJF, IJ'F') S(\gamma J, \gamma' J'),$$

where Q(IJF, IJ′F′) is the relative intensity of the transition; $S(\gamma J, \gamma' J') = S(\gamma SLJ, \gamma SLJ+1) = \left(\frac{e\hbar}{2mc}\right)^2$

$$\times \frac{(L+S+J+2)(L+S-J)(S+J-L+1)(J+L-S+1)}{4(J+1)}$$

is the line strength of the transition γ, J → γ, J + 1. The total probability of the transition J → J + 1 is

$$W^{sp}(\gamma J, \gamma' J+1) = \frac{1}{(2J+1)(2I+1)} \sum_F (2F+1) W$$

or, expressed in terms of the probability and the relative intensity of the component

$$W^{sp}(\gamma J, \gamma' J') = (2F+1) W^{cm}(\gamma JIF, \gamma' J' IF') / (2J+1) \cdot (2I+1) Q(IJF, IJ'F'). \qquad (3)$$

The corresponding calculated transition probabilities are listed below:

1) Transition,	3–4	3–3	3–2	2–3	2–2	2–1	Σ
2) Lifetime, sec^{-1}	5	2.1	0.6	2.4	3.0	2.3	7.7

The overall picture of the hyperfine splitting of the atomic-iodine transition is shown in Fig. 1.

To investigate the luminescence spectrum of atomic iodine we used a system with a scanning Fabry-Perot (FP) interferometer. The experimental setup is shown in Fig. 2. Excitation of atomic iodine in cell 3 was the result of the photolysis of C_3F_7I molecules. The uv

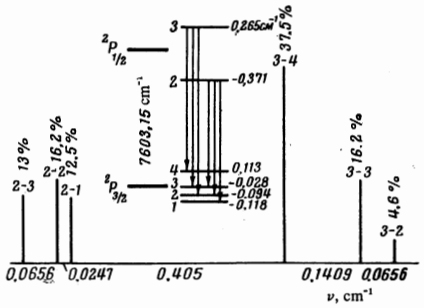

FIG. 1. Calculated hyperfine structure of $^2P_{1/2}-^2P_{3/2}$ transition of atomic iodine.

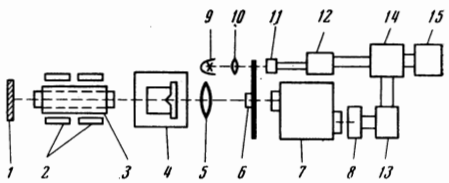

FIG. 2. Experimental setup for the study of the luminescence spectrum of atomic iodine: 1—mirror with R ~ 99%, 2—PRK-2 mercury lamps, 3—cell, 4—pressure chamber, 5—objective, 6—modulator, 7—DMR-4 monochromator, 8—9+-111 germanium photodiode, 9—small lamp, 10—lens, 11—photodiode, 12—V6-4 amplifier, 13—V6-2 narrow-band amplifier, 14—synchronous detector, 15—automatic recorder.

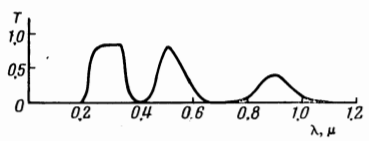

FIG. 3. Transmission curve of liquid filter (25% solution of $NiSO_4 \cdot 6H_2O$ in water).

source consisted of eight PRK-2 mercury lamps. C_3F_7I was made to flow continuously through the cell in order to maintain the useful signal at approximately the same level. To separate the luminescence from the background produced by the infrared part of the mercury-lamp spectrum, a filter constituting a 25% solution of $NiSO_4 \cdot 6H_2O$ in distilled water was poured into the space between the double walls of the cell (Fig. 3), and a DMR-4 monochromator was placed ahead of the radiation receiver. The liquid filter and the monochromator made the ratio of the luminescence over the background due to the lamps larger than 30 : 1. To increase the useful signal, a 100% reflectance mirror was placed behind the cell, and a special test was made to ensure absence of line saturation. To prevent the filter from boiling, it was made to circulate continuously.

We used an FP interferometer with dielectrically coated mirrors having a reflectance R on the order of 97% at $\lambda = 1.315\ \mu$. The luminescence passed through the FP interferometer, objective 5, and entered a diaphragm located at the focus of objective 5. The center of the interference rings was projected on the diaphragm. The FP interferometer was placed in pressure chamber 4 in which the pressure was varied. The radiation receiver was a 9E-111 germanium photodiode (8) cooled to −75° C. The photodiode signal was recorded

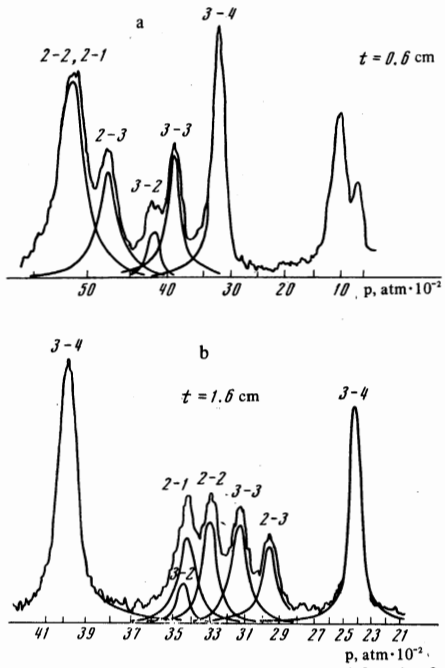

FIG. 4. Luminescence spectrograms obtained for the following FP etalon gaps: t = 0.6 cm (a) and t = 1.6 cm (b), at a C_3F_7I pressure 0.02 atm (the abscissas represent the air pressure in the pressure chamber).

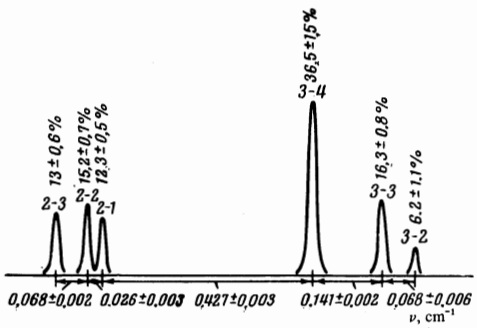

FIG. 5. Experimental luminescence spectrum of atomic iodine at a C_3F_7I pressure 0.02 atm.

automatically after amplification and synchronous detection. The useful light-signal power incident on the photoreceiver was approximately 10^{-12} W.

To interpret the spectrum and to determine the line width, the spectrograms were obtained with three Fabry-Perot etalon gaps, t = 0.6, 1.6, and 3 cm. The true line contours were obtained by reducing the spectrogram by a graphic procedure[9].

Figure 4 shows the reduced spectrograms obtained for different FP etalon gaps (the orders are superimposed). Figure 4b shows, for the purpose of interpretation (t = 1.6 cm), the weak 3—2 component which is not resolved for the given gap. Its position and the relative intensity were transferred from the other spectrogram (t = 0.6 cm). We resolved six hyperfine structure components of the luminescence spectrum of atomic iodine. The positions of the components and their relative intensities are shown in Fig. 5. The luminescence line width is governed by the action of the Doppler and collision broadenings (the natural width can be neglected). To determine the luminescence line width as well

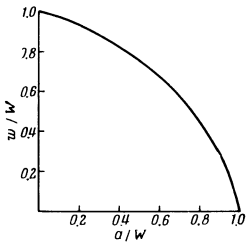

FIG. 6. Plot of w/W vs. a/W, where W is the width of the observed summary contour, w is the width of the component having a Gaussian shape, and a is the width of the component with a Lorentz shape. The plot is valid when the mechanisms that lead to Gaussian and Lorentz broadening are statistically independent.

as the Doppler and collision broadening, we obtained spectrograms with different gaps between the interferometer mirrors and with different C_3F_7I pressures. The results of the measurements of the observed line width W are given in Table I, which lists also the errors, which are the maximal deviations of the individual measurement from their arithmetic mean.

In the reduction of the spectrograms it was assumed that the apparatus function of the Fabry-Perot interferometer has a Lorentz shape,[9] the Doppler width w does not depend on the pressure, and the collision width γ varies in proportion to the pressure. The apparatus and collision parts of the luminescence line form a Lorentz contour of width $a = \gamma + a_1$, where a_1 is the apparatus width. To determine the Doppler width w from the observed and Lorentz parts W and a, we used a plot of w/W against a/W[10] (Fig. 6). Reduction of the data listed in Table I yielded the following values for the widths[1]:

$$w_{Dop} = 0.011 \pm 0.002\,cm^{-1}, \quad \gamma_{col}(0.01_{at}) = 0.0045 \pm 0.0010\,cm^{-1},$$
$$a_i(t = 1.6cm) = 0.010 \pm 0.002\ cm^{-1}.$$

The total true luminescence line width of the atomic iodine at a pressure 0.01 atm turned out to be 0.0140 ± 0.0025 cm^{-1}. The Doppler width 0.011 ± 0.002 cm^{-1} corresponds to the gas temperature averaged over the length of the cell, equal to 530 ± 180°K, which is perfectly reasonable, since the medium becomes heated as a result of the photochemical processes.

In experiments in which a mixture of C_3F_7I with argon was used (1 part of C_3F_7I and 18 parts of argon), with a total pressure 0.40 atm, the luminescence line was due mainly to the collision broadening. In this case the line width turned out to be $\gamma = 0.060 \pm 0.012$ cm^{-1}, and the shift of the luminescence line did not exceed $\delta = 0.005 \pm 0.005$ cm^{-1}.[2)]

A Van-der-Waals interaction of the atomic iodine with the argon was assumed. The expression for the broadening in the case of a Van-der-Waals interaction is[7]

$$\gamma = 8.16 \cdot C_6^{2/5} \bar{v}^{3/5} N, \qquad (4)$$

where N is the concentration of the perturbing particles,

[1)]An attempt was made in[11] to estimate the luminescence line width and the gain cross section from the generation line width of an iodine photodissociation laser. However, the generation line width registered in[11] ($\Delta\nu = 0.023$ cm^{-1}) exceeds by almost one order of magnitude the emission line width of a laser operating under analogous conditions (see[5], $\Delta\nu \leq 0.003$ cm^{-1}). The authors of[11] have apparently registered the apparatus width of their interferometer, and their conclusions seem therefore unfounded to us. Nor was the hyperfine structure of the investigated transition taken into account in[11].

[2)]This apparently makes it possible to use atomic iodine vapor in absorbing cells for gas-laser frequency stabilization.

Table I

Gap between mirrors, cm	p, atm	W, cm^{-1}
3	0.02	0.0196 ± 0.0010
1.6	0.005	0.0179 ± 0.0008
1.6	0.010	0.0193 ± 0.0016
1.6	0.020	0.0244 ± 0.0015
1.6	0.040	0.0320 ± 0.0030

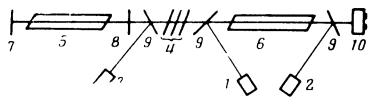

FIG. 7. Schematic diagram of setup for the investigation of the gain cross section: 1–3–photodiodes, 4–attenuating filters, 5–master generator, 6–amplifier, 7, 8–laser mirrors, 9–beam-splitting plates, 10–calorimeter.

and $\bar{v}$ is the average relative velocity of the colliding particles. The constant C_6 is expressed in terms of the polarizabilities of the interacting particles α_1 and α_2:

$$C_6 = \frac{3}{2\hbar} \frac{a_0^{1/2} e^2 \alpha_1 \alpha_2}{(\alpha_1/N_1)^{1/2} + (\alpha_2/N_2)^{1/2}}, \qquad (5)$$

where a_0 is the Bohr radius, e is the electron charge, and N_1 and N_2 are the numbers of the electrons in the atoms. Knowing the polarizability of argon[12], $\alpha_1 = 1.6 \times 10^{-24}$ cm^3, we estimated the polarizability of the iodine atom in the state $^2P_{1/2}$ from the obtained line width. It turned out to be $\alpha_2 = (4 \pm 2.5) \times 10^{-24}$ cm^3.

To determine the Einstein coefficient of the $^2P_{1/2} - {}^2P_{3/2}$ transition, we obtained the gain cross section of the 3–4 transition. The gain cross section was determined with the aid of an amplifier. The theory of such an amplifier and the methods for measuring the gain cross sections were described by us earlier[5]. The apparatus is illustrated in Fig. 7. The master laser 5 and the amplifier 6 were pumped in synchronism by four IFP-20000 lamps each. The current flowed in the lamps in the same direction, as a result of which the magnetic field intensity inside the amplifier and laser cells, as shown by the measurements, did not exceed 20 Oe. The effect of such a magnetic field on the line width in the region of the investigated pressures can be neglected. The polarization of the master signal was so oriented that the radiation passed through the amplifier without loss by reflection from the amplifier windows, which were placed at the Brewster angle. Photodiodes 1, 2, and 3 were used to obtain oscillograms of the parasitic backward radiation from the amplifier and of the amplified and input signals, respectively. The input signal could be varied with the aid of calibrated filters 4. The energy of the amplified output signal was determined both from the areas of the oscillographic pulses and with the aid of calorimeter 10. Precautions were taken during the measurements to make the backward parasitic signal from amplifier negligibly small in comparison with the amplified signal. The partial pressure of the C_3F_7I did not exceed 0.015 atm, so that the working medium in the amplifier was drawn uniformly through the volume. In this scheme, the lasing, meaning also the amplification, was effected on the 3–4 transition. For such an amplifier, the following relation,

Table II

C_3F_7I pressure, atm	Argon pressure, atm	E_+, J	E_0, J	$\ln \frac{P_+}{P_0}$	σ_{3-4}, cm²
0.015	0,280	1.23	0.298	1.55	$10.9 \cdot 10^{-19}$
0.015	0,280	0,18	0.00765	3.97	$10.9 \cdot 10^{-19}$
0.015	0,390	1.06	0.293	1.53	$7.8 \cdot 10^{-19}$
0.015	0,390	0.0722	0.00765	3.13	$7.8 \cdot 10^{-19}$

which follows from the energy conservation law, holds at the instant when the pump stops:

$$\ln \frac{P_+}{P_0} = \sigma_{3-4} \frac{E - E_+ + E_0}{Sh\nu} \left(1 + \frac{g_2}{g_1}\right) \frac{g_{F=3}}{g_{F=2} + g_{F=3}}, \quad (6)$$

where P_+/P_0 is the ratio of the output-signal power to the input-signal power at the instant when the pump stops (it is determined from the oscillograms); E_0 and E_+ are the energies of the input and output signals; S is the area of the amplifier working cross section; g_2/g_1 is the ratio of the statistical weights of the levels $^2P_{1/2}$ and $^2P_{3/2}$; $g_{F=2}$ and $g_{F=3}$ are the statistical weights of the sublevels of the hyperfine structure of the $^2P_{1/2}$ level; σ_{3-4} is the gain cross section of the F = 3 → F = 4 transition; E is the energy pumped into the amplifier during the time of the pump pulse. Relation (6) is valid if the relaxation time between the sublevels of the hyperfine structure is much shorter than the pump-pulse time. Judging from the results of the experiment[5], this condition is satisfied.

If two measurement runs are made with different input signals, then using the relation

$$\sigma_{3-4} = \frac{\ln(P_+''/P_0'') - \ln(P_+'/P_0')}{E_+' - E_0' - E_+'' + E_0''} \frac{Sh\nu}{1 + g_2/g_1} \frac{g_{F=2} + g_{F=3}}{g_{F=3}}, \quad (7)$$

which follows from (6), we can determine the gain cross section of the 3–4 transition from the measurement results. The primed and double-primed quantities in (7) correspond to runs with equal input signals. The experimental results are given in Table II.

The line width, the gain cross section, and the Ein-Einstein coefficient of the 3–4 transition are connected, in the case of a Lorentz line contour, by the relation[7]

$$A_{3-4} = 4\pi^2 c \sigma_{3-4} \Delta\nu / \lambda^2. \quad (8)$$

The measurement results give

$$A_{3-4} = (3.4 \pm 1.1)\ \text{sec}^{-1}.$$

Consequently, the summary Einstein coefficient for the $^2P_{1/2} - {}^2P_{3/2}$ coefficient is, according to (3),

$$A = (5.4 \pm 2.0)\ \text{sec}^{-1}.$$

This agrees well with the data of Dervent and Thrush[4], who obtained a lifetime 0.17 ± 0.04 sec for the $^2P_{1/2}$ level, quite close to the calculated value A = 7.7 sec^{-1}.

On the basis of the experimentally measured distances between the hyperfine structure components, we can determine the magnetic-interaction constant of the $^2P_{1/2}$ level. Experiment yields $\Delta E_{F=3} - \Delta E_{F=2} = 0.662 \pm 0.009\ \text{cm}^{-1}$ and it follows from (1) that

$$A_{1/2} = 0.221 \pm 0.003\ \text{cm}^{-1},$$

which is in good agreement with the calculation.

In conclusion, the authors thank I. S. Sobel'man for useful advice and discussions.

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