Investigation of electron-vibrational relaxation in iodine molecule by means of two-colour laser excitation

M.E. ABRAMENKO, N.K. BIBINOV, A.M. IZMAILOV and D.B. KOCH

Physical Research Institute, 198904 St. Petersburg, Russia

One of the problems appearing at the spectroscopic investigation of iodine molecule is to study mechanisms and efficiency of electron-vibrational energy relaxation. This investigation may be interesting both from scientific and applied points of view: it can help in content optimizing of gaseous mixture used as an active medium of iodine lasers, for example. As a result of specific features of the iodine molecule's potential curves only high vibrational levels of $\text{D}\Omega_u^+$ state ($v' = 100 + 200$) can be populated (and consequently investigated) by one photon excitation [1]. The aim of this paper is investigation of mechanisms and efficiency of electron-vibrational energy relaxation in iodine molecule with aid of two-colour laser photoexcitation.

For this problem decision a polychromatic dye laser was developed which is emitting simultaneously two wavelengths independently tunable inside the broad spectral region demanded for this experiment. The active medium is pumped by commercial nitrogen laser. Radiation of both wavelengths is focused inside the cell with pure iodine vapour or its mixture with buffer gas.

Luminescence spectra of I_2 molecules is recorded being excited by the radiation of various sets of wavelengths (i.e. for different levels initial for relaxation) and for various pressure of buffer gas (i.e. for different efficiency of excited levels decay). Registered luminescence spectra were compared with computer simulated ones. Recorded luminescence spectrum of iodine vapour excited by the light of $\lambda_1 = 560 \text{ nm}$ and $\lambda_2 = 420 \text{ nm}$ simultaneously (1), (2) is shown in fig.1.

Fig.1. Luminescence spectrum of iodine molecules at two-colour excitation ($\lambda_1 = 560 \text{ nm}$, $\lambda_2 = 420 \text{ nm}$).

A strong transition at $\lambda \sim 326 \text{ nm}$ is observed. According to selection rules for dipole transitions only $I_2(DO_2^+ \rightarrow XO_2^+)$ transition is permitted in this spectral region. Excitation of DO_2^+ state from BO_2^+ is forbidden as known. So it is interesting to find out the reason of mentioned band appearance in the iodine vapour luminescence spectrum at the conditions of our experiment. We discussed three possibilities:

- i) luminescence from DO_2^+ state, being populated by two step photoexcitation through another state, formed as a result of iodine atoms recombination;
- ii) luminescence from DO_2^+ state, populated by two step photoexcitation through BO_2^+ state perturbed by the state of other symmetry;
- iii) luminescence from DO_2^+ state, populated by collisionally induced transitions from EO_2^+ state.

Polychromatic laser used in our experiments permits to vary independently the intensity of each lasing line. This gives an ability to measure the dependence of luminescence intensity of iodine vapour ($\lambda \sim 326 \text{ nm}$) on the intensity of excited light ($\lambda_1 = 560 \text{ nm}$ and $\lambda_2 = 420 \text{ nm}$). Experimental data show, that the intensity of luminescence I_L ($\lambda \sim 326 \text{ nm}$) is a linear function of the excited light intensity (of both lines). Supposition that process (i) is responsible for this luminescence appearance contradicts to this experimental result because both dissociation of iodine molecule and excitation from the intermediate state would be forced by the light $\lambda = 420 \text{ nm}$. It should lead, at first, to square dependence of the luminescence intensity from D state on the intensity of the laser beam $\lambda = 420 \text{ nm}$; at second - to the independence of I_L ($\lambda \sim 326 \text{ nm}$) the intensity of the second laser beam $\lambda = 560 \text{ nm}$.

Populating of DO_2^+ state, stimulated by collisions with iodine molecules in process (ii) is unlikely probable reason of I_2 luminescence ($\lambda \sim 326 \text{ nm}$). The pressure of iodine vapour in the experiment was $P(I_2) = 0.2 \text{ Torr}$, so estimated probability of this process is not higher than $3 \cdot 10^6 \text{ s}^{-1}$. This value is ten times less than the least probability of radiative transition from ion-pair states. More than that, according to the literature data, the lowest ion-pair state $D'2g$ is populated most effectively in the interconversion process even for very small pressure of relaxator. The radiative transition from this state is situated at $\lambda \sim 342 \text{ nm}$. In our experiments the luminescence of iodine vapour in this spectral region is weak (see fig.1).

So the most probable reason of the luminescence at 326 nm appearance is two-step photoexcitation of DO_2^+ -state of iodine molecule through BO_2^+ -state, mixed with the state of the other symmetry (a_{1g} or $a'0_{1g}^+$). These states can couple through the hyperfine nuclear magnetic interaction.

When two-step photoexcitation is used of the iodine vapour in mixture with helium an intensive band $I_2(D'2g \rightarrow A'2u)$ appears with $\lambda \sim 342 \text{ nm}$ (see fig.2). Increase of $D \rightarrow X$ luminescence intensity ($\lambda \sim 326 \text{ nm}$) is observed also, which is forced by processes of electron relaxation from the upper states. But with the increase of noble gas pressure the decrease of $D \rightarrow X$ luminescence is observed. It is connected with collisionally induced relaxation from D-state.

Consider main processes, connected with energy relaxation of the excited iodine molecule at the two-step population of EO_2^+ , DO_2^+ , $\beta 1g$ states.

Fig.2. Luminescence spectrum of I_2 in mixture with helium at two-colour photoexcitation ($\lambda_1=560$ nm, $\lambda_2=420$ nm, $P_{He}=40$ Torr): solid line is a measured spectrum, dashed line is a calculated spectrum.

According to literature data it is possible to neglect the processes of nonradiational decay of ion-pair states in collisions with helium. Luminescence intensities for corresponding transitions can be written in the following form:

$$I_{D \rightarrow X} = (N_D + [E] \tilde{\nu}_{EK_4}[He]) K_7 / (K_7 + (K_8 + K_9)[He])$$

$$I_{D' \rightarrow A'} = [He] ([\beta] \tilde{\nu}_{\beta K_{11}} + [D] \tilde{\nu}_{DK_9} + [E] \tilde{\nu}_{EK_9})$$

Comparing the intensities $I_2(D \rightarrow X)$ and $I_2(D' \rightarrow A')$ extrapolated to zero helium pressure, (see fig.3) we find out, that not more than 20% of the energy of excitation pass through D-state. The rate constant of collisionally induced excitation energy decay from E-state can be measured if the radiative lifetime of this state is known. It is known from [2,3] that $K_3 = (3.6 \pm 0.3) \cdot 10^7 \text{ s}^{-1}$. The value of $K_4 + K_5 + K_6$ measured in our work is $(1.9 \pm 0.5) \cdot 10^{-11} \text{ s}^{-1} \text{ cm}^3 \text{ mol}^{-1}$. The rate constant of interconversion from D-state ($K_8 + K_9$) measured with account of radiative lifetime of D state $K_7 = 7.7 \cdot 10^7 \text{ s}^{-1}$ equals $(1.4 \pm 0.1) \cdot 10^{-12} \text{ s}^{-1} \text{ cm}^3 \text{ mol}^{-1}$. The value of interconversion constant

Fig.3. Intensity of $I_2(D' \rightarrow A')$ and $I_2(D \rightarrow A)$ luminescence as a function of He pressure ($\lambda_1 = 560$ nm, $\lambda_2 = 420$ nm).

$K_s + K_e$ measured at two-colour photoexcitation $\lambda_1 = 585$ nm, $\lambda_2 = 420$ nm is equal to $(6 \pm 1) \cdot 10^{-12} \text{ s}^{-1} \text{ cm}^3 \text{ mol}^{-1}$. This is approximately 4 times higher than in the case of iodine molecule excitation through E state.

Different electron-vibrational levels of ion-pair states were selectively populated with aid of polychromatic dye laser. Population of DO_2^+ -state is observed at two-colour photoexcitation through BO_2^+ -state, which is connected with mixing of the last state of other symmetry. Rate constants of electron-vibrational relaxation from D- and E-states are measured in mixture of iodine vapour with helium.

Authors express acknowledgement to Russian foundation of Basic Research for the support of this work.

Literature

1. Mulliken R.S., J.Chem.Phys., 1971, v.55, p.288-309.
2. J.P.Perrot, B.Femelat, J.L.Subtil, M.Broyer, J.Chevaleyre, Mol.Phys., 1987, v.61, n.1, p.85-95.
3. P.I.Jensbury, K.P.Lawley, T.Ridley et al, Chem.Phys., 1991, 151, p.103-109.