

Mechanism of vibrational relaxation and intersystem crossing within excited ion-pair states of I_2

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Abstract. Visible and ultraviolet fluorescence of I_2 , following excitation by ArF/193 nm excimer laser pulses, was recorded for different pressures of argon buffer gas in a flow system. Dispersed fluorescence spectra due to the transitions $D'(2_g) \rightarrow A'(2_u)$ and $D(0_u^+) \rightarrow X(0_g^+)$ were analysed by inversion and spectral simulations. Thus vibrational distributions in the emitting states were obtained as a function of pressure to determine the mechanism of relaxation to populate the lowest quantum levels of the D' state, which are the emitting states in the iodine laser. Fast intersystem crossing is found to occur from initially populated vibrational levels of the D state to other ion-pair states correlating with the ground state ions, followed by rapid relaxation, involving both direct vibrational relaxation within individual states and intersystem crossing between states.

Keywords. Vibrational relaxation; excited ion-pair; vibrational distributions; spectral simulations; intersystem crossing.

1. Introduction

Rates of vibrational relaxation and intersystem crossing in excited states of emitting species in gas lasers and excimer lasers are of great importance, determining the quality and power of laser beams. This has been studied for excimer laser emitters such as KrF and XeCl where vibrational relaxation and mixing of two ion-pair states, $B(\Omega = 1/2)$ and $C(\Omega = 3/2)$ determine the effective pumping rate into the low-lying vibrational levels of the B state which contribute most strongly to the laser transitions (see for example Morgan *et al* 1983, Kvaran *et al* 1988). Some years ago molecular iodine in high pressure buffer gas was found to lase at 342 nm by using electron beam excitation (Bradford *et al* 1975; Ewing and Brau 1975; Hays *et al* 1976), and by ArF laser pumping (Shaw *et al* 1980). The lasing is due to a transition from the lowest state, $D'(2_g)$, in a cluster of 6 ion-pair states ($0_{g,u}^+, 1_{g,u}, 2_{g,u}$) which correlate with $I^+(^3P_2) + I^-(^1S)$ to a weakly bound valence state $A'(2_u)$ (Tellinghuisen 1977; Shaw *et al* 1980). Electron pulse excitation creates states of I_2 on a subnanosecond time scale via a direct interaction of energetic electrons with iodine molecules in their ground electronic state. Collisions of these excited I_2 molecules with buffer gases are found to be necessary to reach the $D'(2_g)$ state (Sauer *et al* 1976). For ArF laser excitation the

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$D(0_u^+)$ ion-pair state is excited, followed by relaxation within the 6 low-lying ion-pair states (Hemmati and Collins 1979; Shaw *et al* 1980; Martin *et al* 1981; O'Grady *et al* 1982; Donovan *et al* 1983) or by reactions (O'Grady *et al* 1982; Donovan *et al* 1983; O'Grady and Donovan 1985). Vibrational deactivation rates and rates of transfer from the D to the D' state, estimated from comparison with lifetime measurements of ion-pair states (Sauer *et al* 1980; Viswanathan and Tellinghuisen 1983) have been found to be very fast, but a detailed mechanism of the relaxation yet is unknown. The spectroscopy of the iodine molecule has been the subject of many published papers and has led to a large amount of spectroscopic information on the states of concern (LeRoy 1983; Mulliken 1971; Tellinghuisen 1974, 1982, 1983, 1984; Tellinghuisen *et al* 1980; Guy *et al* 1980; Chevaleyra *et al* 1982; Lawley *et al* 1982; Viswanathan and Tellinghuisen 1983; Perrot *et al* 1983; Donovan *et al* 1985; Hiraya *et al* 1988; Bartels *et al* 1989; Li and Basasubramanian 1989). In this paper we report a study of the effect of argon pressure on the UV and visible emission spectrum of I_2 following excitation by ArF excimer laser radiation; 193 nm. Spectra were analysed by simulations and the inversion technique (Johnson *et al* 1983) to obtain vibrational populations in ion-pair states. Results are discussed in terms of mechanism of relaxation within the cluster of ion-pair states.

2. Experimental and method of analyses

The fluorescence was created by using about 100 mJ, 10 ns laser pulses of wavelength 193 nm (bandwidth about 50 cm^{-1}) from Lumonics 510 excimer laser with Ar/F₂/He gas mixture. Typically a repetition rate of 10 Hz was used and the unfocused beam was directed into a simple glass fluorescence cell with Suprasil quartz windows for the input and output radiation. The fluorescence cell was fitted with light baffles along the laser beam axes. Argon was flowed over iodine in a trap to give a mixture of iodine vapor of less than 0.3 torr (vapor pressure at room temperature) and variable argon pressure which was pumped through the fluorescence cell. Argon pressure was controlled by an outlet valve to the pump. Fluorescence was dispersed with a monochromator (Minuteman 305 MV 1/2 meter Czerny-Turner) and detected by a photomultiplier (EMI 9789 QB). Signals were fed through a pulse amplifier, integrated and stored on a home made multichannel analyser connected to a PC (XT 286) computer to obtain dispersed fluorescence spectra which were corrected for spectral response, drift and background.

The bandhead, due to the $D' \rightarrow A'$ transition, near 340 nm was analysed by the inversion technique to obtain vibrational population distributions in the D' state for different argon pressures. Population in the D state was estimated from simulation calculations of the McLennan band ($D \rightarrow X$ transition) between 300–335 nm. Franck-Condon factors (FCF) for $D' \rightarrow A$ and $D \rightarrow X$ transitions were calculated for vibrational spectral contributions corresponding to transitions from all levels in the D and the D' state below the threshold energy corresponding to 193 nm excitation. The threshold energy was determined from the transition from $v'' = 1$ in the ground state, but FCF calculation for $D \leftarrow X$ proved transitions from $v'' = 0$ and 1 to be major contributions to the absorption at 193 nm. Relative contributions at room temperature were found to be about $2(v'' = 0):3(v'' = 1)$.

Potential curves used in the FCF calculations were expressed as analytical functions

(in cm^{-1} ; internuclear distance in \AA) derived in the following way: The $D(0_u^+)$ Expression derived by J Tellinghuisen from detailed analyses of the McLennan band was used (Tellinghuisen 1984):

$$U_D(r) = 2.58913 \times 10^5 \exp[-0.227664(r^{2.19767})] + 8.4 \times 10^8/r^{12} - \\ - 1.16141 \times 10^5/r - 4.4 \times 10^4/r^3 - 5.8 \times 10^5/r^4 - \\ - 1.0 \times 10^6/r^6 + 72181,$$

$$r_e = 3.58 \text{ \AA}; \quad T_e = 41025.96 \text{ cm}^{-1}; \quad D_e = 31155 \text{ cm}^{-1};$$

$$\omega_e = 94.49 \text{ cm}^{-1}; \quad \omega_e x_e = 0.147 \text{ cm}^{-1}; \quad \omega_e y_e = 0.79 \times 10^4 \text{ cm}^{-1}.$$

$D'(2_g)$: Spectroscopic parameters for the D' state have been determined from analyses of $D' \rightarrow A'$ emission spectra for transitions from the lowest vibrational levels of D' only (Tellinghuisen 1984). The average internuclear distance and oscillation frequency were found to be close to that for the D state but the minimum potential energy is lower than that of the D state by about 638 cm^{-1} . The D' -state potential, therefore was assumed to have same shape as the D state and was expressed as:

$$U_{D'}(r) = U_D(r) - 637.657.$$

$X(0_g^+)$: The ground state potential of I_2 has been well characterised and RKR potentials are available in the literature over large energy range (LeRoy 1970; Tellinghuisen *et al* 1980). Best *overall* fit of the RKR potentials was sought for the fluorescence simulation while a best fit in the region of the average internuclear distance was sought for the absorption calculations mentioned above. The *overall* potential could not easily be fitted by a Morse potential but was expressed as such for the short range ($r < 3.6 \text{ \AA}$) while a sum of power terms was used to represent the long range region ($3.6 \text{ \AA} \leq r$):

$$U_X(r) = 14289.4 \{1 - \exp[-1.74644(r - 2.64832)]\}^2; \quad (r < 3.6 \text{ \AA}) \\ = -6.810095971 \times 10^9/r^{12} - 3.765176909 \times 10^6/r^6 + 12548; \\ (3.6 \text{ \AA} \leq r).$$

$A'(2_u)$: The RKR potential for $A'(2_u)$ (Tellinghuisen 1982) was fitted by a Morse potential at short range ($r < 3.7 \text{ \AA}$) and by a Lennard-Jones potential at long range ($3.7 \text{ \AA} \leq r$):

$$U_{A'}(r) = 10047.5 + 2286.4 \{1 - \exp[-2.1214(r - 3.0438)]\}^2; \quad (r < 3.7 \text{ \AA}) \\ = 6.064823092 \times 10^8/r^{12} - 3.339531494 \times 10^6/r^6 + 12548 \\ (3.7 \text{ \AA} \leq r).$$

The inversion technique has been described elsewhere (Johnson *et al* 1983). Briefly, vibrational population corresponding to the best fit of experimental and calculated spectra is sought, using multiple linear regression. Relative populations are represented as histograms. The inversion of the $D' \rightarrow A'$ spectrum was limited to a narrow spectral range (330 to 350 nm, at the most) which minimizes the effect of possible change in transition moment with internuclear distance. Possible overlap of other

spectra (see below) was accommodated by subtracting a constant background from the experimental spectrum until optimal self-consistency between the experimental and calculated spectrum was obtained.

3. Results and discussion

Figure 1 shows I_2 spectra for pure iodine (a) and I_2 in 9.5 torr argon buffer gas (b) between 200–500 nm. Figure 1(c) shows the visible region between 470 and 555 nm at 400 torr argon pressure. For pure iodine, spectra due to transitions from high lying vibrational levels ($v' = 145$ and 149 ; corresponding to transitions from $v'' = 0$ and 1 in ground state in absorption) in the $D(0_u^+)$ state, $D(0_u^+) \rightarrow X(0_g^+)$ and $D(0_u^+) \rightarrow a'(0_g^+)$, are observed (Martin *et al* 1981; Lawley *et al* 1982). The $D \rightarrow X$ emission extends from the laser line (193 nm) to about 330 nm showing a discrete emission due to bound to bound transition for wavelengths less than about 254 nm but a structured diffuse emission above 254 nm due to transitions to the continuum of the ground state (McLennan band). The $D \rightarrow a'$ emission is a broad oscillatory structure characteristic for a transition to the steep repulsive state, $a'(0_g^+)$ which correlates with the ground state atoms. The low wavelength limit of the $D \rightarrow a'$ spectrum is near 254 nm and the spectrum extends to about 430 nm, peaking at 403 nm. The structure on the long wavelength side of the $D \rightarrow a'$ spectrum has not yet been resolved but it could be due to a transition to a repulsive state $0_g^+(\lambda - s \text{ state } ^3\pi_g)$, which is predicted to lie slightly above the a' state (Li and Balasubramanian 1989; Kvaran

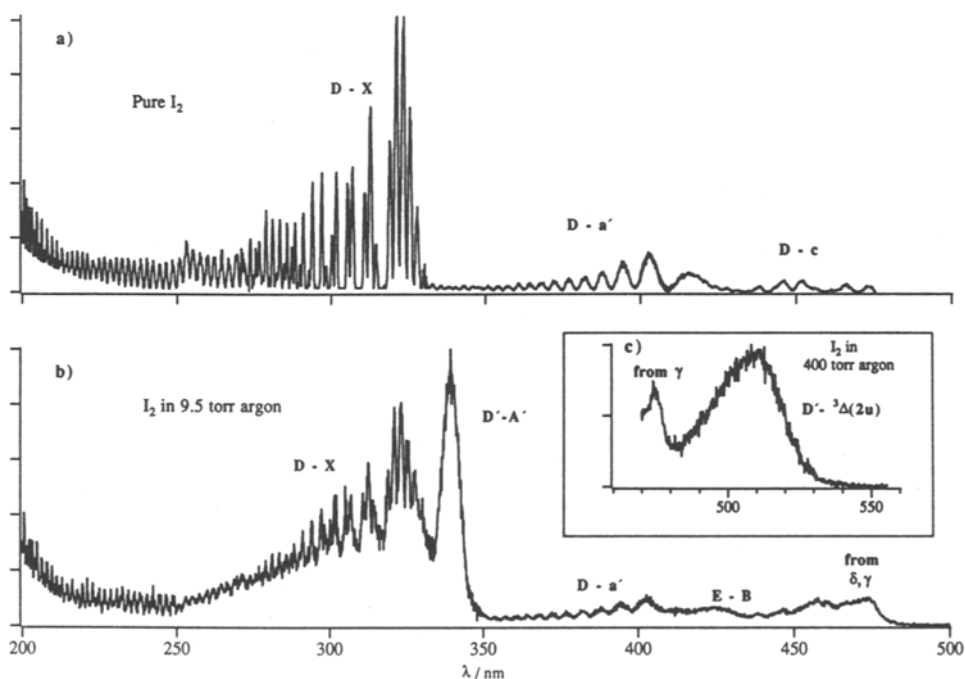


Figure 1. UV and VIS fluorescence spectra of I_2 following excitation by ArF, 193 nm laser pulses, (a) for pure iodine, < 0.3 torr (iodine vapor pressure at room temperature), (b) for iodine in 9.5 torr argon buffer gas, (c) for iodine in 400 torr argon.

et al 1991), here assigned as $c(0_g^+)$. With small increase in argon pressure, emission from the D state is rapidly quenched and new fluorescence systems appear (see figure 1b). The dominant new fluorescence is due to the $D' \rightarrow A'$ transition partly overlapping the $D \rightarrow X$ emission extending from about 250 nm to about 350 nm, peaking near 340 nm. Weaker emission also appears as broad featureless spectra sticking out in the visible region 430 to 480 nm. These are bandheads of spectra due to transitions from the ion-pair states $E(0_g^+)$, $\delta(2_u)$ and $\gamma(1_u)$ (Wieland *et al* 1972; King *et al* 1981) which extend to shorter wavelengths and enhance the baseline for the $D \rightarrow a'$ spectrum below 430 nm. Similarly there is a reason to believe that there is a weak underlying background emission due to the $\beta(1_g) \rightarrow A(1_u)$ transition below 350 nm (Tellinghuisen 1983). As argon buffer gas pressure is increased still further the D emission is quenched rapidly (figure 2) and almost disappears above about 40 torr while other emission is enhanced. The weak fluorescence, due to transitions from the D , δ , and γ states, reaches a maximum at an intermediate pressure while the strong D' emission grows more rapidly and dominates at high pressure. This can be seen in figure 1c where fluorescence at 510 nm, due to the transition $D' \rightarrow 3\Delta(2_u)$ [hardly noticeable at 9.5 torr (figure 1b)], exceeds the emission due to the γ state near 476 nm. See also the region 300–350 nm on figure 2, but notice that the spectra have been normalized to the same height as the strongest peaks.

Since the bandhead of the $D' \rightarrow A'$ spectrum sticks out near 340 nm free of "serious" overlap it could be used to obtain vibrational distributions by inversion. Figure 3 shows vibrational distributions in the D' state on the right side of experimental and recalculated spectra. At lowest argon pressure high vibrational contributions ($v' \approx 110$ –145) dominate while these lower as argon pressure increases and low vibrational contributions ($v' < 60$) grow. Relative population in intermediate vibrational levels ($v' \approx 60$ –110) is never found to be great. The $D - X$ spectrum from pure iodine could easily be simulated by calculated spectrum assuming transitions from less than 6 vibrational levels ($144 < v' < 150$) in the D state. Broader vibrational distribution causes smearing out of the diffuse structure until it disappears for $135 \leq v' \leq 149$ (even population) as shown in figure 4. This contradicts what is observed for the $D \rightarrow X$ emission as argon pressure increases (see figure 2) suggesting that vibrational distribution in the D state is narrow and limited to the highest vibrational levels near those which are initially populated on excitation.

From comparison of calculated and experimental $D \rightarrow X$ and $D' \rightarrow A'$ spectra in the overlapping region the intensity ratios of the two spectra, $I(D - X)$ over $I(D' - A')$, could be estimated as a function of argon pressure. This is shown in figure 5a as well as the fractional vibrational energy in the D' state ($\langle f_{v'} \rangle$) (figure 5b) as a function of argon pressure. $\langle f_{v'} \rangle$ is defined as the fraction of the maximum vibrational energy corresponding to transition to $v' = 149$ in the D state (from $v'' = 1$) after initial excitation by 193 nm.

Comparison of figures 2 and 3 shows that the high vibrational contribution in the D' state is obtained in the pressure region where the $D \rightarrow X$ emission/ D state population is still significant (argon pressure less than about 10 torr) but disappears with $D \rightarrow X$ emission (≈ 40 torr). This effect can also be seen in figure 5 by comparing plots (a) and (b). The greatest drop in the intensity ratio [$I(D - X)/I(D' - A')$] occurs at low argon pressure where the fractional vibrational energy ($\langle f_{v'} \rangle$) is unchanged (< 10 torr) while lowering in vibrational energy occurs as $I(D - X)/I(D' - A')$ vs argon pressure levels off.

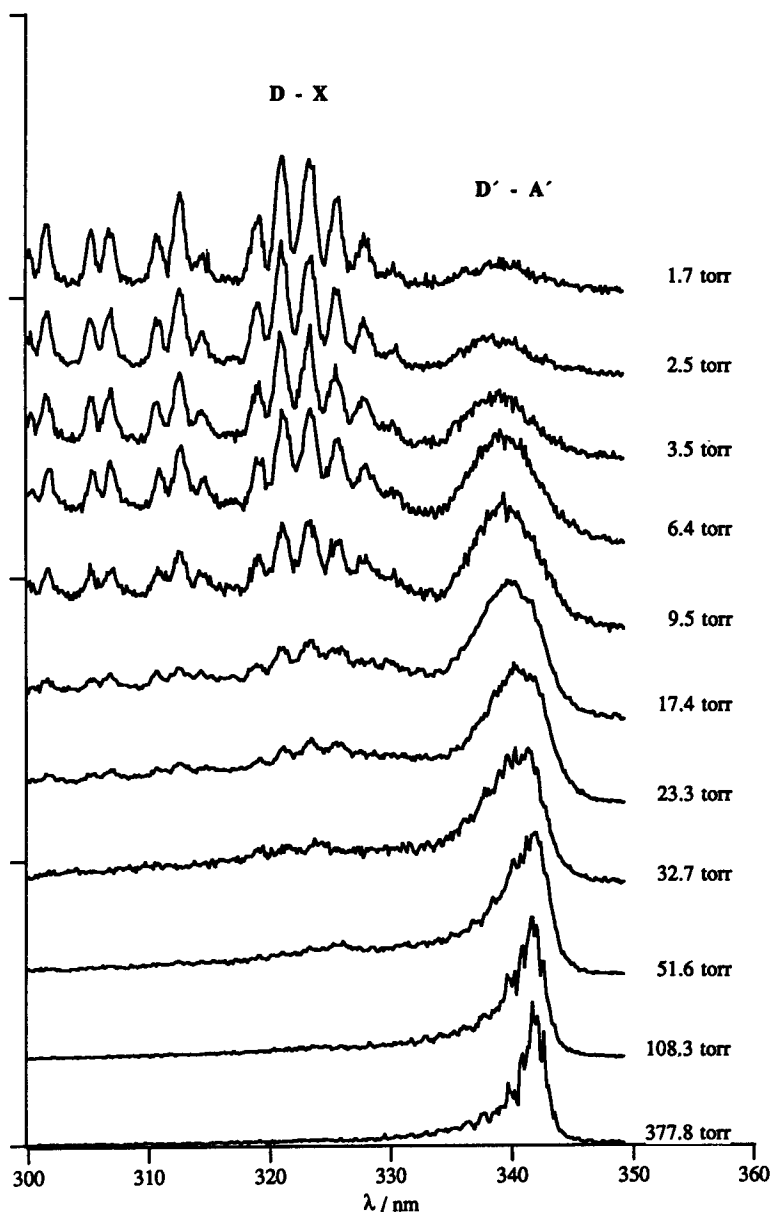


Figure 2. Fluorescence spectra of iodine between 300 and 350 nm showing spectra due to $D \rightarrow D$ and $D' \rightarrow A'$ transitions as a function of argon pressure (pressure is indicated on right side of each spectrum). Spectra have been normalized to the same height as the strongest peak.

This data is consistent with the following proposed mechanism of relaxation (see figure 6). The efficient quenching of the D state emission and appearance of other spectra suggests that rapid collision induced crossing occurs to other states in the lowest cluster of ion-pair states, D' and $\{E, \delta, \gamma, \beta\}$. Limited vibrational distribution observed in the D state and collision into high vibrational levels in the D' state as argon pressure is increased suggests that vibrational relaxation within the D state is

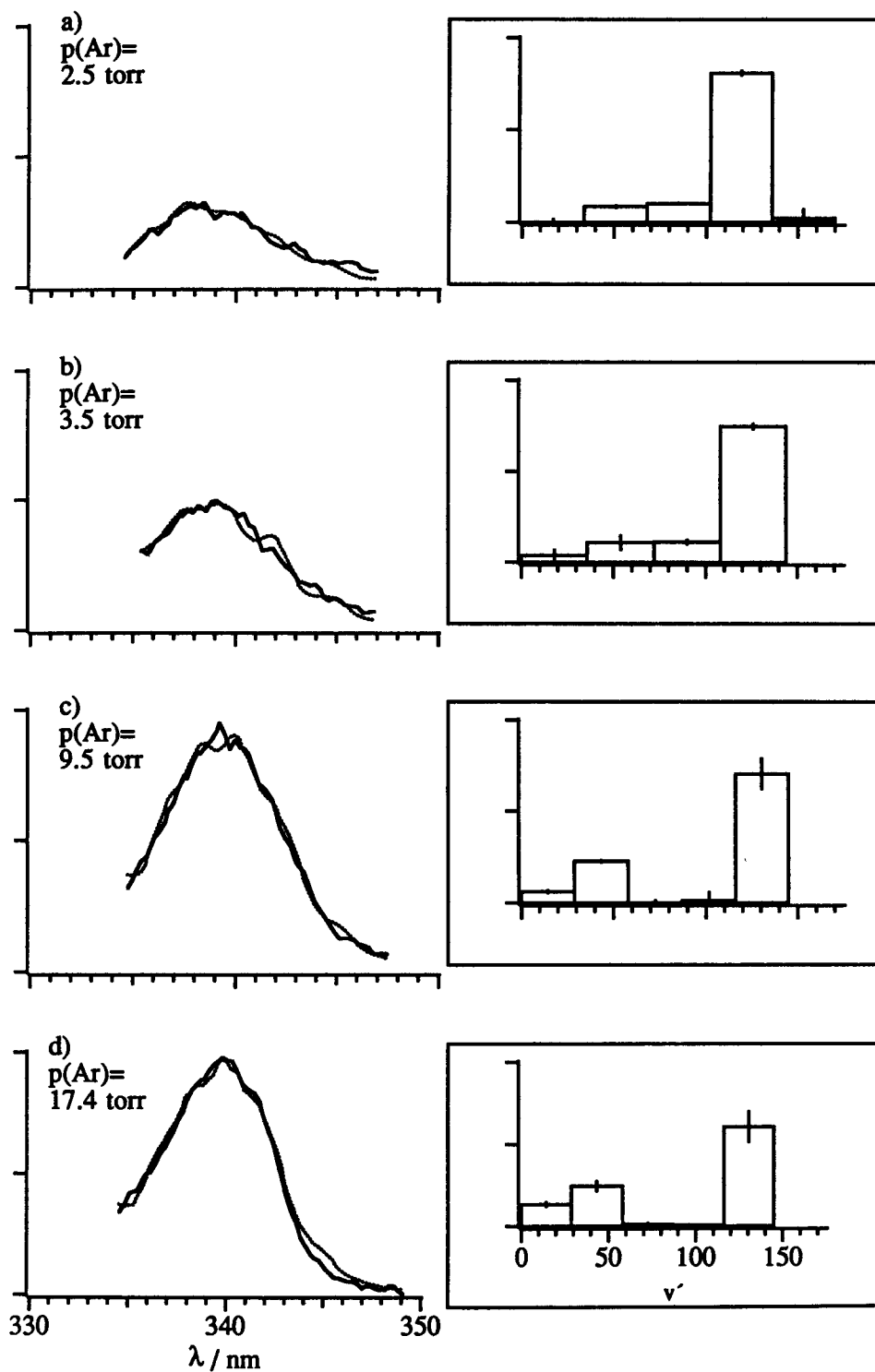


Figure 3(a-d). (Caption on next page.)

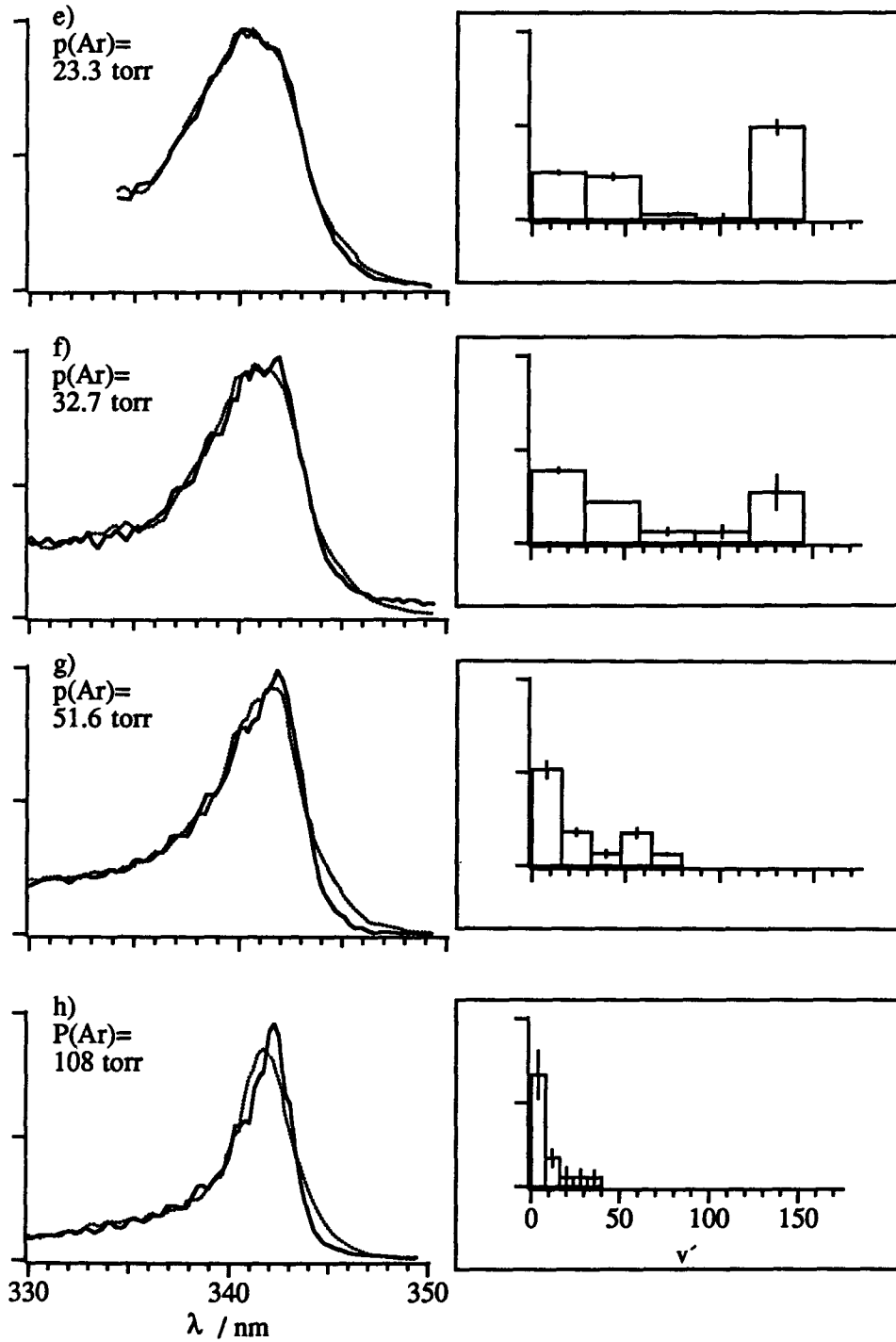


Figure 3(e-h).

Figure 3. Inversion of $D' \rightarrow A'$ spectral bandheads, showing relative vibrational population distributions as histograms (on right) and experimental (solid curves) and recalculated (dotted curves) spectra (on left) as a function of argon pressure ($p(\text{Ar})$).

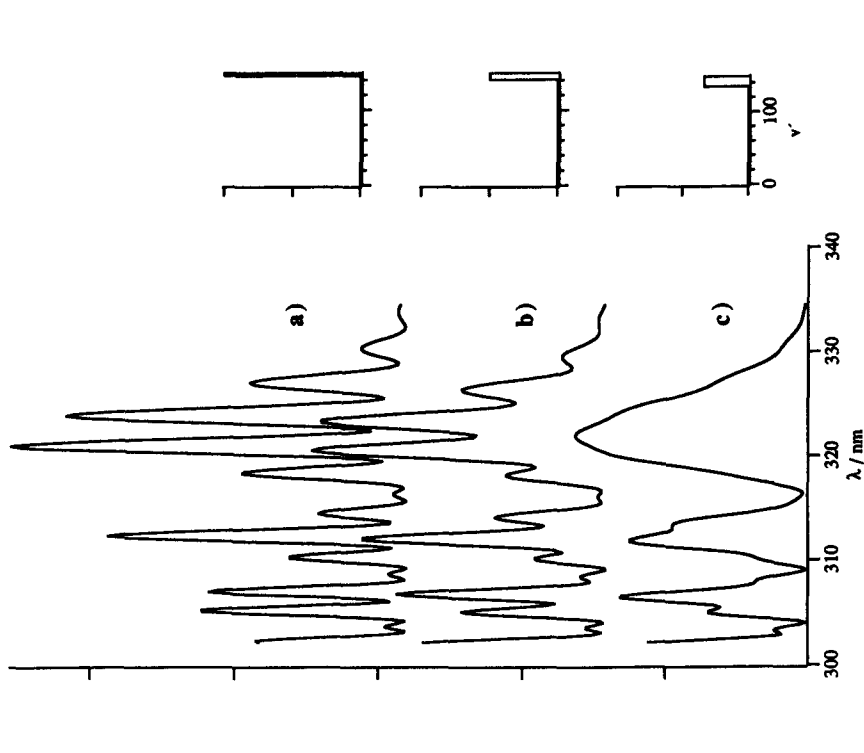


Figure 4. Calculated spectra of $D \rightarrow X$ transitions (left) for different widths of even population distributions shown on right, for population in levels (a) $v' = 145-149$, (b) $v' = 140-149$, (c) $v' = 135-149$.

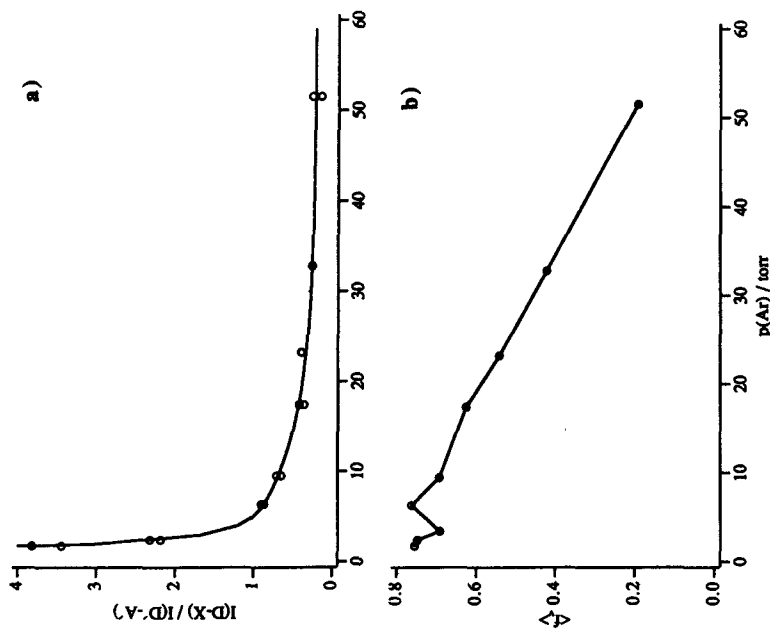


Figure 5. Effect of argon pressure [$p(\text{Ar})$] (a) on intensity ratio of the $D \rightarrow X$ spectrum over the $D' \rightarrow A'$ spectrum [$(I(D-X)/I(D'-A'))$ vs $p(\text{Ar})$] and (b) on fractional vibrational energy in the D' state ($\langle f_v \rangle$ vs $p(\text{Ar})$); see definition in text.

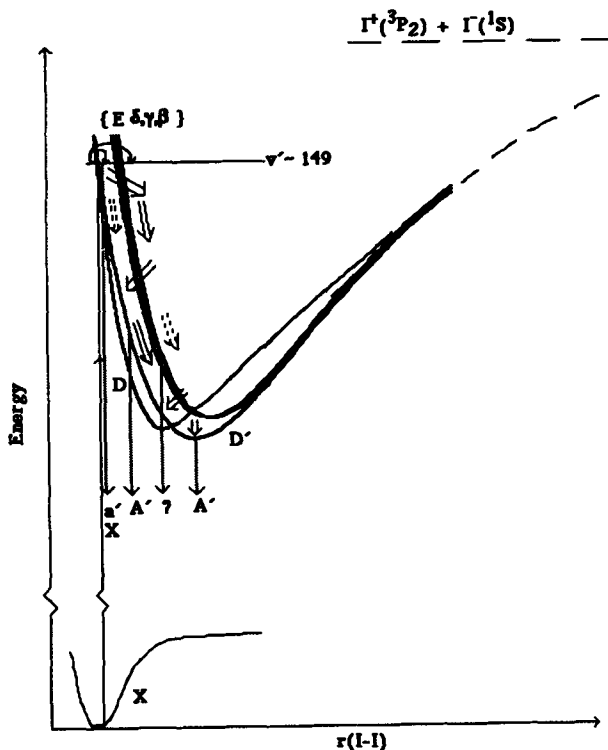


Figure 6. Schematic figure of potential energy curves involved in excitation and relaxation for iodine. Proposed mechanism of relaxation within the lowest cluster of ion-pair states is indicated by arrows (see text for further clarification).

negligible and that the collision induced crossing occurs directly from high lying vibrational levels in D close to those initially populated on excitation ($v' \sim 145, 149$). This could be due to close coupling/crossing between the D state and other state(s) near turning points. The relatively low population found in intermediate v' -levels of the D' state and rise in intensity of spectra due to transitions from other states $\{E, \delta, \gamma, \beta\}$ at low argon pressures suggest that transfer from the D' state to $\{E, \delta, \gamma, \beta\}$ occurs followed by efficient relaxation within $\{E, \delta, \gamma, \beta\}$. Notice however, that relatively low population in intermediate v' levels of the D' state, judging from the histogram in figure 3, can be misleading: While the population distributions shown are normalized it should be remembered that *total* population in the D' state increases with argon pressure. Therefore vibrational relaxation within the D' state can also be of important in this energy/ v' -level region. The drop in emission from $\{E, \delta, \gamma, \beta\}$ as argon pressure increases goes further with increase in population of low v' levels in the D' state suggesting the rapid crossing from $\{E, \delta, \gamma, \beta\}$ to D' occurs in the low vibrational energy range followed by vibrational relaxation within the D' state and to a less extent within the $\{E, \delta, \gamma, \beta\}$ manifold. Finally, crossing from lowest vibrational levels of $\{E, \delta, \gamma, \beta\}$ to the lowest lying ion-pair state, the D' state, occurs followed by vibrational relaxation within D' . The last step only involves radiationless vibrational energy transitions between the lowest vibrational levels in the D' state, where spacing between levels is larger ($\sim \omega_e = 103.95 \text{ cm}^{-1}$) and average internuclear

distance is smaller ($\sim r_e = 3.58 \text{ \AA}$) (Tellinghuisen 1989) than for higher v' levels because of less anharmonicity. According to the "exponential gap" model (Procaccia and Levine 1975) $V-T$ energy transfer probability decreases exponentially with the vibrational energy gap suggesting that relaxation rate slows down in the final step. Also, the smaller size of iodine molecules for the lowest vibrational levels cause a decrease in collision cross section. Therefore there is reason to believe that the final step is a bottleneck in the relaxation to the lowest vibrational levels in the D' state which can affect the lasing capabilities analogous to what has been found for the rare gas halides (Kvaran *et al* 1988).

In the above discussion the group of ion-pair states $\{E, \delta, \gamma, \beta\}$, have been treated as a unit manifold, separate from the D and D' states. Clearly, however, further studies are needed to clarify the importance of individual states in the relaxation process.

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References

- Bradford Jr R S, Ault E R and Bhaumik M L 1975 *Appl. Phys. Lett.* **27** 546
 Bartels M, Donovan R J, Holmes A J, Langridge-Smith P R R, MacDonald M A and Ridley T 1989 *J. Chem. Phys.* **91** 7355
 Chevaleyre J, Perrot J P, Chastan J M, Valignat S and Broyer M 1982 *Chem. Phys.* **67** 59
 Donovan R J, O'Grady B V, Lain L and Fotakis C 1983 *J. Chem. Phys.* **78** 3727
 Donovan R J, O'Grady B V, Shobatake K and Hiraya A 1985 *Chem. Phys. Lett.* **122** 612
 Ewing J J and Brau C A 1975 *Appl. Phys. Lett.* **27** 557
 Guy A L, Viswanathan K S, Sur A and Tellinghuisen J 1980 *Chem. Phys. Lett.* **73** 582
 Hays A K, Hoffman J M and Tisone G C 1976 *Chem. Phys. Lett.* **39** 353
 Hemmati H and Collins G J 1979 *Chem. Phys. Lett.* **67** 5
 Hiraya A, Shobatake K, Donovan R J and Hopkirk A 1988 *J. Chem. Phys.* **88** 52
 Johnson K, Kvaran Á and Simons J P 1983 *Mol. Phys.* **50** 981
 King G W, Littlewood I M and Robins J R 1981 *Chem. Phys.* **56** 145
 Kvaran Á, Shaw M J and Simons J P 1988 *Appl. Phys.* **B46** 95
 Kvaran Á, Thorgeirsson Th E, Jónsdóttir S Ó and Donovan R J 1991 (to be published)
 Lawley K P, MacDonald M A, Donovan R J and Kvaran Á 1982 *Chem. Phys. Lett.* **92** 322
 LeRoy R J 1970 *J. Chem. Phys.* **52** 2683
 Li J and Balasubramanian K 1989 *J. Mol. Spectrosc.* **138** 162
 Mulliken R S 1971 *J. Chem. Phys.* **55** 288
 Martin M, Fotakis C, Donovan R J and Shaw M J 1981 *Il Nuovo Cimento* **63** 300
 Morgan W L, Winter N W and Kulander K C 1983 *J. Appl. Phys.* **54** 4275
 O'Grady B V and Donovan R J 1985 *Chem. Phys. Lett.* **122** 503
 O'Grady B V, Lain L, Donovan R J and Gower M C 1982 *Chem. Phys. Lett.* **91** 491
 Perrot J P, Broyer M, Chevaleyre J and Femelat B 1983 *Mol. Spectrosc.* **98** 161
 Procaccia I and Levine R D 1975 *J. Chem. Phys.* **63** 4261
 Sauer M C Jr, Mulac W A, Cooper R and Grieser F 1976 *J. Chem. Phys.* **64** 4587
 Shaw M J, Edwards C B, O' Neill F, Fotakis C and Donovan R J 1980 *Appl. Phys. Lett.* **37** 346
 Tellinghuisen J 1974 *Chem. Phys. Lett.* **29** 359
 Tellinghuisen J 1977 *Chem. Phys. Lett.* **49** 485

- Tellinghuisen J 1982 *J. Mol. Spectrosc.* **94** 231
Tellinghuisen J 1983 *Chem. Phys. Lett.* **99** 373
Tellinghuisen J 1984 *Can. J. Phys.* **62** 1933
Tellinghuisen J, McKeever M R and Sur A 1980 *J. Mol. Spectrosc.* **2** 225
Viswanathan K S and Tellinghuisen J 1983 *J. Mol. Spectrosc.* **101** 285
Wieland K, Tellinghuisen J and Nobs A 1972 *J. Mol. Spectrosc.* **41** 69