

THE THREE-PHOTON ABSORPTION SPECTRUM OF THE IODINE MOLECULE

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The three-photon absorption spectrum of iodine has been recorded under high resolution, using both a single tunable dye laser (3P1C) and independently tunable pump and probe lasers (3P2C). Rotational analysis of the 3P2C spectrum confirms the presence of the $F(0_u^+)$ state and gives improved spectroscopic constants. A separate set of vibrational levels in the 51500–54700 cm^{-1} energy region, with a spacing of 78 cm^{-1} , has also been identified.

1. Introduction

Two-photon sequential absorption spectroscopy has proved a useful tool for analysing the lower g ion-pair states of iodine. These lower states correlate with the $I^+(^3P) + I^-(^1S)$ dissociation products and lie in the 40000–47000 cm^{-1} energy region (see references and summaries in refs. [1,2]). High-gain rhodamine and coumarin dyes which lase in the visible can be used in both the pump dye laser, which excites the $B\ ^1\Sigma_u^+ - X\ ^1\Sigma_g^+$ transition, and in the probe laser which accesses these ion-pair states from the pumped levels of the intermediate B state. The same laser dyes should be capable of accessing higher ion-pair states (which are collectively called "F" for discussion purposes) through three-photon absorption processes.

For convenience, we distinguish between three-photon absorption from a single color laser beam (3P1C), where all three absorbed photons have the same frequency, and three-photon absorption from two laser beams (3P2C), where the pump and probe dye lasers are independently tunable.

Several groups have reported 3P1C absorption in I_2 [3–8], and agree that one of the photons resonantly induces a B–X absorption transition. However there is considerable disagreement about the absorption mechanisms for the other two photons. The most popular candidates for the terminal electronic states in the "F" region which are accessed have been the 1441 D(0_u^+) state, which has now been fully

characterised by classical spectroscopy [9], and the 2332 F(0_u^+) state [10]. Ishiwata et al. [8] observed eight partly resolved rotational 3P1C transitions to an "F" state from which they obtained the dispersed fluorescence. With the aid of Franck–Condon calculations, they concluded that it was the $F'(0_u^+)$ ion-pair state correlating with $I^+(^1D)$, accessed from the B state by a virtual two-photon absorption. Such 3P1C spectra are difficult to analyse spectroscopically because the only observed transitions are those obeying the resonance conditions $\sigma("F"-B) = 2\sigma(B-X)$. This gives the rotational lines in the spectrum an extremely irregular appearance which is quite unlike a classical one-photon absorption spectrum. Conventional analytical techniques which use combination differences cannot be applied.

We have recorded the three-photon spectrum of $^{127}I_2$ in the region accessible with visible laser dyes, and have obtained both the 3P1C and 3P2C spectra under high resolution. Both types of spectra could be satisfactorily analysed as due to one-photon B–X resonance absorption followed by two-photon "F"–X virtual absorption. At the power levels it was necessary to use, the strong lines of the 3P1C spectrum appeared also in the 3P2C spectra. However once the 3P1C lines had been identified and subtracted, the analysis of the 3P2C spectra was comparatively straightforward, and provided a guide to the analysis of the complex 3P1C spectrum.

2. Experimental

The laser spectrometer was a more powerful version of that previously used for 2P2C studies [11]. The 20 mJ pulses, 15 ns long, produced by a XeCl excimer laser were used to excite simultaneously two grazing incidence dye lasers. The pump and probe bandwidths were 0.7 and 0.1 cm^{-1} , respectively. When recording 3P1C spectra, all the excimer power was sent to the probe laser. For 3P2C spectra, 20% of the power was sent to the pump laser, this being just sufficient to saturate strong rotational B-X transitions. The remaining 80% was sent to the probe laser. Probe power levels were extremely critical in the 3P2C experiments: the insertion of Fresnel rhombs in the probe beam produced too much attenuation for polarization measurements to be made, so the 3P2C spectra could only be recorded for the natural linear polarization of the beam.

The "F"-B resonances were detected by monitoring the undispersed fluorescence emitted from the "F" states at 310 nm [8] as the probe laser was scanned. The spectra were calibrated against rotational lines in the single-photon B-X iodine spectrum [12,13].

3. Results

Under the high-power and high-resolution conditions used here, iodine shows a very rich 3P1C spectrum. About 160 rotational lines have been found in the 16400-18300 cm^{-1} region, which represents the experimental limits of observation to date. Five of the eight lines which Ishiwata et al. [8] observed have been found as strong lines. Their other lines at 17138.6, 17135.3 and 17220.6 cm^{-1} could not be detected.

The 3P2C spectrum in the same spectral region was obtained by pumping individual rotational lines in the ($\nu_B=0$) vibrational bands of the B-X transition, where $\nu_B = 14-20$, and scanning the probe laser. Useful survey spectra could be obtained by pumping these bands near their heads, which for the B-X transition of iodine, are at low J and within 0.1 cm^{-1} the respective band origins. The high density of rotational lines in the heads means that several lines are pumped simultaneously, so that the corresponding observed 3P2C spectral features also have a broad head-like ap-

pearance, which can usually be recognized among the sharper lines originating from pump lines with higher J which coincide with the pumped bandheads. The frequencies σ_H of the 3P2C "heads" also enabled the vibrational origins of the F-B transitions to be estimated as $2\sigma_H + T_0(\nu_B)$.

Twelve of these "heads" which were clearly identified across the complete spectral region could be assigned as members of a single progression with regularly decreasing separations to higher frequency of about 40 cm^{-1} . The corresponding upper state vibrational separations in the F region will be twice this, at about 80 cm^{-1} . The calculated upper state vibrational terms for the observed bands can be fitted to within 0.5 cm^{-1} to the formula:

$$T_0(n) = 51596.0 + 77.93n - 0.0924n^2 \\ - 0.186 \times 10^{-3} n^3 \text{ cm}^{-1},$$

where the arbitrary numbering $n = \nu + 0.5$ ranges between 1 and 45. From their separations, it is very likely that these are high vibrational levels with $\nu \approx 50-90$ of one of the $u\text{I}^+(^3\text{P})$ lower ion-pair states. A similar series was observed using multiphoton ionization spectroscopy at higher energies in the 58000-61000 cm^{-1} region by Williamson and Compton [5], who assigned its upper state as $F(0_u^+)$ [10].

An additional series of heads also appears in these 3P2C survey spectra starting at 17174 cm^{-1} when the 14-0, B-X bandhead is pumped, and extending to the blue with a decreasing separation of 65 cm^{-1} . The corresponding upper state vibrational interval must therefore be about 130 cm^{-1} . Detailed rotational analysis confirms this, and establishes the presence of an additional electronic state, which, following [8], we call the F' state.

In order to obtain spectroscopic constants for this state, a total of 171 resolved rotational lines have been analyzed so far for the F'-B transitions of $^{127}\text{I}_2$ to levels with $\nu_{F'} = 0-4$. The B state levels which were pumped had ν_B values in the range 14-16 and J_B ranging from 4 to 126. The F'-B transitions appear in groups of three for each pump transition, obeying the selection rule $\Delta J = 0, \pm 2$, with the Q line usually stronger than the O and S lines. The strongest F'-B transitions were observed for the $\nu_{F'} = 0$ band, whose origin is at 17174 cm^{-1} in the 3P2C spectrum, when pumping on lines of the B-X 14-0 band. Tran-

Table 1
Spectroscopic constants (cm^{-1}) obtained for the F' state from 3P2C spectral analysis

ν_{F}	N	J_{min}	J_{max}	$T_0(\nu, J=0)$ ^{a)}	$10^2 B_\nu$
0	78	2	84	51664.6(2)	2.193(6)
1	36	2	128	51794.5(3)	2.181(4)
2	27	2	100	51922.8(5)	2.184(9)
3	18	15	41	52051.6(4)	2.181(10)
4	12	10	53	52179.1(6)	2.186(20)

a) Relative to $\nu'' = 0, J'' = 0$ in the X state.

sitions to higher ν_{F} levels were progressively weaker, and were more strongly overlapped by 3P1C lines induced by the probe laser. Transitions to levels with $\nu_{\text{F}} > 4$ are also present, as well as transitions to levels of the other state mentioned above, but these are presently too weak and too few to analyse.

The results are summarized in table 1. Here N is the number of analyzed rotational transitions with J_{B} ranging from J_{min} to J_{max} . The spectroscopic constants were obtained from $T(\nu, J) = B_\nu J(J+1)$ by linear regression, with D_ν held at the theoretical value of $0.6 \times 10^{-8} \text{ cm}^{-1}$ [14]. The uncertainties increase with ν_{F} , since fewer lines over a smaller range of J values were available for analysis.

A completely independent analysis of the corresponding 3P1C spectrum using just the observed lines was not feasible: but once approximate constants for the F' state had been obtained from the 3P2C spectral analysis, it was possible to locate and analyse some of the resonance lines due to transitions to this state in the 3P1C spectrum. The 3P1C analysis is not complete, but preliminary results are shown for comparison in table 2. Note that the range of J values for the 3P1C spectrum is considerably higher than for the 3P2C

Table 2
Spectroscopic constants (cm^{-1}) obtained for the F' state from 3P1C spectral analysis

ν_{F}	N	J_{min}	J_{max}	$T_0(\nu, J=0)$ ^{a)}	$10^2 B_\nu$
0	6	38	176	51664.2(2)	2.196(1)
1	13	36	155	51794.2(5)	2.183(4)
2	16	33	131	51923.2(5)	2.186(6)
3	12	58	110	52051.3(9)	2.164(9)
4	14	60	174	52178.1(1.5)	2.165(9)

a) Relative to $\nu'' = 0, J'' = 0$ in the X state.

spectrum, with resonances observed for J up to 176: but both sets of results give the same values of the constants to within acceptable limits.

4. Conclusions

For the sets of pump and probe frequencies investigated so far, we have identified transitions to two electronic states accessed by three-photon absorption from the ground state. The F' state appears to be the same one to which Ishiwata et al. [8] observed eight 3P1C transitions under low resolution. Because only O, Q and S lines are observed for the two-photon transition from the $B(0_u^+)$ state, it follows from the selection rules [15] that the F' state must have O_u^+ symmetry. Our preliminary constants for this state are given in table 3, and agree very well with [8]. The lower ion-pair states of iodine which correlate with $I^+(^3P)$ have vibrational frequencies close to 100 cm^{-1} , bond lengths $r_e \approx 3.6 \text{ \AA}$, and, because of the predominance of the $1/r^2$ term in their potential functions, have very similar dissociation energies $D_e = 32000 \text{ cm}^{-1}$ [1,2]. On the other hand, the F' state has a higher vibrational frequency $\omega_e = 130 \text{ cm}^{-1}$ and a shorter equilibrium bond length $r_e = 3.47 \text{ \AA}$. The method given in ref. [1] for calculating purely ionic dissociation limits predicts $D_e = 37800 \text{ cm}^{-1}$ and $D = 89500 \text{ cm}^{-1}$ for the F' state, which is higher than the predicted limit $D = 85930 \text{ cm}^{-1}$ for dissociation into $I^+(^1D) + I^-(^1S)$. If the F' state does dissociate ionically, then $I^+(^1D)$ is the only reasonable possibility, since the next highest product would be $I^+(^1S)$ at 104830 cm^{-1} . However, the F' state must have more covalent bonding character at short internuclear distances than the ion-pair states which correlate with $I^+(^3P)$.

Table 3
Molecular constants (cm^{-1}) for the F' state of $^{127}\text{I}_2$

T_e	51706.3(3)
ω_e	130.5(3)
$\omega_e x_e$	0.375(70)
B_e	$2.1991(18) \times 10^{-2}$
α_e	$8.42(14) \times 10^{-5}$

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