# Radiative and collisional relaxation of a single rovibrational quantum state of I<sub>2</sub>: $E(0_g^+)$ , v=8, J=56

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Dispersed fluorescence from a single quantum state in I<sub>2</sub> is studied. The  $E(0_g^*)$ , v=8, J=56 state is excited via two-colour absorption employing nanosecond lasers. Direct fluorescence in the range 390-455 nm is compared with Franck-Condon calculations for discrete transitions in the  $E(0_g^*)$ -B<sup>3</sup> $\Pi(0_u^*)$  system. A Franck-Condon diffraction pattern in the range 355-375 nm is attributed to the newly identified  $E(0_g^*)$ - $\Pi(1_u)$  system. State-specific inelastic collision processes  $E(0_g^*)$ - $D(0_u^*)$  are observed and secondary fluorescence in the  $D(0_u^*)$ - $X(0_g^*)$  system in the range 300-330 nm is analyzed.

#### 1. Introduction

 $I_2$  is a heavy diatomic molecule with a large number of bound rovibrational states for each electronic configuration. Many thousands of spectral lines in each particular band system are observable. E.g. the  $B^{3}\Pi(0_{u}^{+})-X^{1}\Sigma(0_{e}^{+})$  system is used as a wavelength calibration standard in the range 500-700 nm with a spectral density of several distinct lines per cm<sup>-1</sup> [1,2]. The large number of electrons and the strong spin-orbit interaction in heavy atoms have obstructed detailed ab initio calculations for I2. Nevertheless in a theoretical study Mulliken succeeded some twenty years ago [3] to predict and clarify the electronic structure in terms of valence, ion-pair and Rydberg states. Recently spectroscopic properties and potential energy curves of  $I_2$  were calculated by Li and Balasubramanian [4].

From an experimental point of view the implementation of optical-optical double resonance techniques greatly improved insight in the spectroscopy of I<sub>2</sub> and in particular in the structure of its ion-pair states. Rousseau and Williams [5] were the first to apply a sequential two-photon excitation technique to study the  $E(0_g^+)$  state. Subsequently other groups [6-10] employed this method for detail studies of all six ion-pair states in the first cluster correlating with  $I^-({}^{1}S)$  and  $I^+({}^{3}P_2)$ . Accurate spectroscopic constants as well as reliable potential energy curves, both RKR-type and analytical expressions, are available now. In the present study use is made of the RKR-potential of Brand et al. [8] for the  $E(0_g^+)$  state and of Ishiwata and Tanaka [10] for the  $D(0_u^+)$  state. For the B<sup>3</sup> $\Pi(0_u^+)$  state RKR turning points were derived by Luc [11]. Also for the repulsive  ${}^{1}\Pi(1_u)$  state an empirical potential energy curve was constructed [12]. For the X  ${}^{1}\Sigma(0_g^+)$  ground state an RKR-curve with turning points up to v=108 was reported by Martin et al. [13]. These potential energy curves are plotted in fig. 1.

In the present work the two-colour absorption technique is employed to prepare a single, selected quantum state  $E(0_{g}^{+}), v=8, J=56$ . Attention is focused on the coincidences of the green output of the Nd: YAG laser with transitions in the  $B^{3}\Pi(0_{n}^{+})$ - $X^{1}\Sigma(0_{e}^{+})$  system of I<sub>2</sub>. By observation of dispersed fluorescence radiative as well as collisional relaxation channels have been investigated in the low-pressure regime. The fluorescence intensities in the  $E(0_{g}^{+})-B^{3}\Pi(0_{u}^{+})$  system are compared with calculations of Franck-Condon integrals for a large number of B-state vibrational levels. Also an oscillatory continuum is observed in the wavelength range 355-375 nm. This fluorescence is attributed to the  $E(0_{s}^{+})^{-1}\Pi(1_{u})$  system, observed here for the first time although the states themselves were known.



Fig. 1. Potential energy curves of  $I_2$  for the states relevant in the present work.

 $E(0_g^+)$  to  $D(0_u^+)$  collisional energy transfer into specific rovibrational states is also monitored via dispersed fluorescence measurements. The indirect  $D(0_u^+)-X(0_g^+)$  fluorescence in the range 290-330 nm is separated in wavelength from the direct channels. Remarkably in the collisional process occurring in the low pressure sample the prepared  $E(0_g^+)$ , v=8, J=56 state relaxes mainly into another single quantum state, the  $D(0_u^+)$ , v=10, J=56 state. The intensities obtained in well-resolved and readily assignable spectra of the D-X system are compared with calculations of Franck-Condon factors.

#### 2. Experimental

The green output (532 nm) of a Quanta-Ray GCR3 Nd: YAG laser is used for the first step in a two-colour absorption process. The Nd: YAG laser is equipped with an injection seeder, which narrows the bandwidth of the green output to less than  $0.01 \text{ cm}^{-1}$ . Moreover, by temperature tuning of the seed-laser, it is possible to scan the output frequency over the gain profile of Nd: YAG in a range of  $1 \text{ cm}^{-1}$ . A stilbene dye laser, pumped by the UV-output (355 nm) of the same ND: YAG laser provides the second colour. The frequencies of the lasers are calibrated with a homebuilt echelle-grating monochromator and interpolation between neon lines, resulting in an accuracy of  $0.1 \text{ cm}^{-1}$ . Both laser beams are temporally and spatially overlapped in the excitation zone. Molecular iodine is contained in a pyrex glass cell with a quartz window for the extraction of fluorescence light in a direction perpendicular to the laser beams. The cell is evacuated by a rotary pump to a pressure below 0.05 Torr and measurements are performed on a room-temperature I<sub>2</sub>-vapor pressure sample of 0.3 Torr.

Fluorescence radiation is projected onto the entrance slit of a 0.6 m triple-stage monochromator (SPEX-1877). Laser-excited fluorescence spectra as well as time-resolved fluorescence decays are detected using a fast photomultiplier (Philips XP2020Q). The resolution in the excitation spectra is determined by the bandwidth of the dye laser: 0.07  $cm^{-1}$ . Fluorescence in a range of 10 nm wide is collected onto the cathode of the PMT and selected blue (E-B band system) or ultraviolet (D-X system) fluorescence may be recorded. A 350 MHz storage oscilloscope is used to measure lifetimes of excited states.

Dispersed fluorescence spectra are recorded with the use of a 1024 channel diode array optical multichannel analyzer (OMA). For these measurements the dye laser is kept fixed on a certain resonance. Wavelength calibration in these spectra is performed by comparison with Ne emission lines, measured in various orders of the grating. The spectral accuracy obtained from this procedure is better than 5 cm<sup>-1</sup>. However, the sharp fluorescence lines corresponding to bound-bound transitions, once assigned, provide an intrinsic wavelength standard as accurate as 0.05 cm<sup>-1</sup>. The resolution in the fluorescence experiments is determined by the pixel width of the diode array and the order at which the grating is used. For most of the measurements the resolution is 3.5 cm<sup>-1</sup>.

#### 3. Laser excitation spectra

# 3.1. Coincidences of the Nd: YAG laser in the $I_2 B-X$ system

The green output of the Nd: YAG laser at 532 nm is known to be in resonance with absorptions in the

B-X system [14-16] and indeed strong yellow fluorescence is observed during all experiments. For the identification of the two-photon excited states it is crucial to assign the exact coincidences of the first step. For this purpose transition frequencies in the B  ${}^{3}\Pi(0_{u}^{+})-X {}^{1}\Sigma(0_{g}^{+})$  (v', v") bands near 532 nm were calculated on the basis of accurate spectroscopic constants [11]. The frequency of the centre of the gain profile of the green output of the Nd: YAG laser was determined in a separate experiment [17] at  $18788.39 \pm 0.02$  cm<sup>-1</sup>. Detunings from the specified resonance frequency are calculated for all transitions originating in  $X^{1}\Sigma(0_{g}^{+}), v''=0-2, J=0-140$ states. The result of these calculations, performed with an accuracy of 0.01 cm<sup>-1</sup>, are given in fig. 2. The greyshaded areas, corresponding to a width of  $1.5 \text{ cm}^{-1}$ , represent the resonance frequency with the bandwidth of an unseeded Nd: YAG laser. Zero detuning coincides with  $18788.39 \text{ cm}^{-1}$ . All the points that fall in the grey-shaded area relate to transitions that can be excited. Even in the case of a narrow-band injection seeded Nd: YAG laser transitions with detunings in the order of a few  $0.1 \text{ cm}^{-1}$  may still occur because of saturation effects. The excitation probabilities of particular resonances are governed by the population density of the ground states, the linestrength factors as well as the detuning.

Relative population densities, assuming a Boltzmann distribution at T=293 K, are calculated for X  ${}^{1}\Sigma(0_{g}^{+})$ , v''=0-2, J=0-500 states and plotted in fig. 3 for J up to 140. In table 1 the relevant parameters determining the excitation probability are listed for all transitions close to resonance. Apart form a dependence on the detuning, the excitation probability S<sub>1</sub> is proportional to

 $S_{\rm I} = S_{\rm HL} \, {\rm FCF} \, N_{\rm pop}$ ,

where  $N_{pop}$  is the population density, FCF the Franck-Condon factor and  $S_{HL}$  the Hohnl-London rotational linestrength factor. The latter quantity is proportional to (J+1)/(2J+1) in the R branch and J/(2J+1) in the P branch of an  $\Omega=0\rightarrow\Omega=0$  electronic transition. All resonances are found for J>30, where the  $S_{HL}$  factor is close to 1/2, independent of the specific rotational line. Therefore the  $S_{HL}$  factor is not further taken into account. The FCFs are obtained from Tellinghuisen [18]. The rotational dependence of 5%-10% in the FCF for B-X (v', v''=0) and B-X (v', v''=2) bands is neglected. For B-X (v', v''=1) the rotational dependence is stronger but the FCF values are so small that B-X (v', v''=1) bands are not excited. From table 1 it is concluded that the P(53) and R(56) lines of the B-X(32, 0) band and the P(103) line of B-X(34, 0) band have a large excitation probability and a detuning less than 0.1 cm<sup>-1</sup>. The P(83) line of the B-X(33, 0) band also has a large excitation probability, but the detuning is larger: 0.58 cm<sup>-1</sup>. All other transitions have larger detunings or a low excitation probability, and it is therefore expected that only the four transitions mentioned will be excited by the Nd: YAG laser.

### 3.2. Excitation of the $E(0_g^+)$ state

In fig. 4 recordings of two-colour laser-induced fluorescence spectra of the  $E(0_s^+)$  state are shown. The tunable laser is scanned over the wavelength range 427-439 nm and either blue (around 435 nm) or UV fluorescence (around 300 nm) is collected on a photomultiplier. Similar to the observations of Danyluk and King [19] the spectra do not display a rotational band structure but show characteristic doublets. These are related to the coincidences of the first transition excited by the fixed-frequency Nd: YAG laser. Thus vibrational sequences of P-R doublets, excited in the  $E(0_{g}^{+})$  state, and originating from the coincidentally excited B  ${}^{3}\Pi(0_{u}^{+})$  states are expected. Indeed, the spectral features in fig. 4 can be assigned as related to these states. The main spectral features can be explained in terms of probing of excited B-state population for J=52 and 57 (v'=32), J=102 (v'=34), and to a lesser extent J=82 (v'=33). The identification of E-B transitions is given in the figure. We note that the laser excitation spectra, recorded by detection of either blue or UV fluorescence are similar. The frequency positions of the assigned resonances in both spectra precisely coincide.

#### 4. Dispersed fluorescence measurements

During all experiments described in this section the blue laser was fixed at  $\lambda_2 = 429.06$  nm probing the P(57) line of the E-B (8, 32) band. The radiative and collisional relaxation process of the single quantum state  $E(0_g^+)$ , v=8, J=56 are studied from mea-



Fig. 2. Transition frequencies for the band system B  ${}^{3}\Pi(0_{u}^{+}), v-X {}^{1}\Sigma(0_{g}^{+}), v''$  for v''=0-2 and the relevant values of v. (•) represents R(J) lines and (•) refers to P(J) lines. Frequencies are given in terms of a detuning from the centre of the green output of the Nd: YAG laser; zero detuning corresponds to 18788.39 cm<sup>-1</sup>. The grey bar represents the band width of an unseeded Nd: YAG laser; the frequency of an injection seeded Nd: YAG laser may vary within this range.



Fig. 3. Population distribution of  $I_2$  molecules over states X  ${}^{1}\Sigma(0_{s}^{*})$ ,  $v^{*}=0-2$ , J assuming a Boltzmann distribution at T=293 K. Values on the vertical axis are calculated, assuming a partition sum of unity for states  $v^{*}=0-2$  and J=0-500. Fractions of 0.677, 0.238 and 0.084 are in  $v^{*}=0$ , 1 and 2 states respectively. The alternating population density ratio of 7:5 for odd and even rotational states is an effect of nuclear spin statistics.

surements of dispersed fluorescence. This state lies at a calculated energy 42214.24 cm<sup>-1</sup> above X  ${}^{1}\Sigma(0_{g}^{+})$ , v=0, J=0 [8].

### 4.1. The $E(0_{g}^{+})-B^{3}\Pi(0_{u}^{+})$ system

With the combined use of the monochromator and OMA system strong dispersed fluorescence signals, appearing in doublets of sharp lines, are recorded in the range 392-454 nm. These spectra are assigned to belong to the  $E(0_g^+)-B(0_u^+)$  band system. Moreover at the long-wavelength side of the blue E-B system, in the range 454-480 nm, typical oscillating fluorescence patterns corresponding to bound-free transitions are observed. This E-B structured continuum has been discussed extensively in the literature [5,20,21] as the first experimental evidence of a "Franck-Condon diffraction pattern" and will not be further discussed here.

Bound-bound transitions to vibrational levels v=6-68 of B  ${}^{3}\Pi(0_{u}^{+})$  are distinguishable in the spectra shown in part in fig. 5. The individual lines are split into P-R doublets, typical for a  $\Delta\Omega=0$  transition. Partly resolved doublets for  $v_{B}=20$  and 21 are shown in the inset of fig. 5. The calculated splitting between the P-R components is 5.7 cm<sup>-1</sup>. From the partial overlap the resolution of these dispersed fluorescence measurements is estimated to be 3.5 cm<sup>-1</sup>.

For a quantitative interpretation Franck-Condon overlap integrals have been calculated for the E-B (8, v) bands. An appropriate wavefunction is calculated for the  $E(0_{e}^{+})$ , v=8, J=56 level from the RKR potential of Brand et al. [8]. The B state wavefunctions are calculated from the RKR potential of Luc [11]. Franck-Condon overlap integrals  $q_{\nu''\nu'}$  are then calculated with standard numerical procedures. The effect of rotational energy (J=56) is accounted for in the calculations. The obtained Franck-Condon factors are multiplied by  $\nu^3$  ( $\nu$  being the transition frequency) and the results are plotted in the form of a synthetic spectrum in fig. 5. The PR-doublet structure is not reproduced in the synthetic spectrum. The agreement between calculated and observed intensities is satisfactory in the wide range of fluorescence into discrete levels B(v) with  $v_B = 6-63$ . The range of levels  $v_{\rm B} > 40$  is not included in fig. 5, but the intensities are also in close agreement with calculations. Based on the constants of Barrow and Yee [22] it follows that for rotational quanta J = 55 and 57 bound vibrational levels exist up to  $v_{\rm B} = 71$  assuming a dissociation limit of  $20043.122 \pm 0.020$  cm<sup>-1</sup> [23]. In the observed fluorescence spectra transitions up to  $B(v_B=68)$  are clearly distinguishable. For  $v_B=69$  the energy splitting between P and R lines  $(2 \text{ cm}^{-1})$ gradually converges to the vibrational splitting (4  $cm^{-1}$ ) so that with the resolution of the fluorescence

Table 1

Resonances of the green output of the Nd: YAG laser in the B  ${}^{3}\Pi(0_{u}^{*})-X {}^{1}\Sigma(0_{s}^{*})$  system of I<sub>2</sub>. The resonance frequency is chosen at 18788.39 cm<sup>-1</sup>. FCF denotes the Franck-Condon factor for the band. The expected line intensity S<sub>I</sub> is normalized to the R(56) line of the B-X(32, 0) band; S<sub>I</sub> is only specified if it is at least 0.01

Band	Transition	Frequency (cm <sup>-1</sup> )	Detuning (cm <sup>-1</sup> )	Population	FCF	SI
(32,0)	R(56)	18788.34	-0.05	0.65×10 <sup>-2</sup>	3.1×10 <sup>-2</sup>	1.00
(32,0)	P(53)	18788.45	0.06	$0.92 \times 10^{-2}$	$3.1 \times 10^{-2}$	1.42
(33, 0)	R(85)	18789.91	1.52	$0.65 \times 10^{-2}$	$3.0 \times 10^{-2}$	0.98
(33,0)	R(86)	18787.29	-1.10	$0.45 \times 10^{-2}$	$3.0 \times 10^{-2}$	0.68
(33, 0)	P(83)	18787.81	-0.58	$0.67 \times 10^{-2}$	$3.0 \times 10^{-2}$	1.00
(34,0)	R(106)	18787.34	-1.04	$0.28 \times 10^{-2}$	2.9×10 <sup>-2</sup>	0.41
(34, 0)	P(103)	18788.44	0.05	$0.42 \times 10^{-2}$	2.9×10 <sup>-2</sup>	0.61
(35,0)	R(121)	18789.28	0.89	$0.24 \times 10^{-2}$	$2.8 \times 10^{-2}$	0.34
(35,0)	P(119)	18787.13	-1.26	$0.25 \times 10^{-2}$	$2.8 \times 10^{-2}$	0.35
(36,0)	R(134)	18787.78	-0.61	$0.10 \times 10^{-2}$	2.7×10 <sup>-2</sup>	0.13
(36,0)	P(131)	18790.38	1.99	0.16×10 <sup>-2</sup>	$2.7 \times 10^{-2}$	0.21
(35, 1)	R(37)	18788.55	0.16	0.29×10 <sup>-2</sup>	4.2×10 <sup>-5</sup>	
(35, 1)	P(34)	18788.90	0.51	$0.29 \times 10^{-2}$	$4.2 \times 10^{-5}$	
(36, 1)	<b>R</b> (71)	18788.04	-0.35	0.29×10 <sup>-2</sup>	$2.7 \times 10^{-5}$	
(36, 1)	P(68)	18789.02	0.63	$0.21 \times 10^{-2}$	2.7×10 <sup>-5</sup>	
(37, 1)	R(91)	18789.41	1.02	$0.20 \times 10^{-2}$	2.5×10 <sup>-4</sup>	
(37, 1)	P(89)	18788.07	-0.32	$0.21 \times 10^{-2}$	2.5×10-4	
(38, 1)	R(107)	18787.21	-1.18	$0.13 \times 10^{-2}$	6.5×10-4	
(38, 1)	P(104)	18789.66	1.27	$0.10 \times 10^{-2}$	6.5×10 <sup>-4</sup>	
(38, 1)	P(105)	18786.02	-2.37	$0.14 \times 10^{-2}$	6.5×10 <sup>-4</sup>	
(39, 1)	R(119)	18788.17	-0.22	$0.90 \times 10^{-3}$	$1.1 \times 10^{-3}$	
(39, 1)	P(117)	18787.30	-1.09	$0.96 \times 10^{-3}$	$1.1 \times 10^{-3}$	
(40, 1)	R(129)	18788.83	0.44	$0.62 \times 10^{-3}$	$1.7 \times 10^{-3}$	
(40, 1)	P(127)	18788.39	0.00	$0.67 \times 10^{-3}$	$1.7 \times 10^{-3}$	
(39, 2)	R(43)	18788.75	0.36	$0.11 \times 10^{-2}$	$1.0 \times 10^{-2}$	0.06
(39, 2)	P(41)	18788.24	-0.15	$0.11 \times 10^{-2}$	$1.0 \times 10^{-2}$	0.06
(40, 2)	R(69)	18788.21	-0.18	$0.10 \times 10^{-2}$	$9.7 \times 10^{-3}$	0.05
(40, 2)	P(67)	18787.64	-0.75	$0.11 \times 10^{-2}$	$9.7 \times 10^{-3}$	0.05
(41, 2)	R(86)	18787.98	-0.41	$0.57 \times 10^{-3}$	$8.5 \times 10^{-3}$	0.02
(41, 2)	P(84)	18787.59	-0.80	$0.59 \times 10^{-3}$	$8.5 \times 10^{-3}$	0.02
(42, 2)	R(99)	18787.59	-0.80	$0.59 \times 10^{-3}$	$7.3 \times 10^{-3}$	0.01
(42, 2)	P(97)	18787.52	-0.87	$0.62 \times 10^{-3}$	$7.3 \times 10^{-3}$	0.01
(43, 2)	R(109)	18789.12	-0.73	$0.44 \times 10^{-3}$	$6.1 \times 10^{-3}$	
(43, 2)	P(107)	18789.48	1.09	$0.47 \times 10^{-3}$	$6.1 \times 10^{-3}$	
(44, 2)	R(118)	18787.46	-0.93	$0.24 \times 10^{-3}$	$5.1 \times 10^{-3}$	
(44, 2)	P(116)	18788.33	-0.06	$0.25 \times 10^{-3}$	$5.1 \times 10^{-3}$	
(45.2)	R(125)	18788.22	-0.17	$0.26 \times 10^{-3}$	$4.2 \times 10^{-3}$	
(45.2)	P(123)	18789.68	1.29	$0.28 \times 10^{-3}$	$4.2 \times 10^{-3}$	
(46, 2)	R(131)	18789.54	1.15	$0.20 \times 10^{-3}$	$3.4 \times 10^{-3}$	
(46, 2)	P(130)	18786.26	-2.13	$0.15 \times 10^{-3}$	3.4×10 <sup>-3</sup>	

detection setup  $(3.5 \text{ cm}^{-1})$  the levels  $v_{\rm B} > 68$  start to overlap. Moreover there is a Franck-Condon intensity gap precisely at  $v_{\rm B} = 71$  prohibiting the observation of levels at the dissociation limit.

It is concluded that the dispersed fluorescence in the full range 392-480 nm can be explained as originating from a single excited state  $E(0_g^+)$ , v=8, J=56. This implies that under the present experimental conditions no evidence is found for vibrational or rotational relaxation in the E state.

## 4.2. The $E(0_{g}^{+}) - {}^{1}\Pi(1_{u})$ system

In the near-UV range, 355-375 nm, another fluorescence spectrum has been observed with the typical



Fig. 4. Two-colour laser excitation spectrum of the E-B system in I<sub>2</sub> with one laser set at  $\lambda_1 = 532.24$  nm and a second laser tuned in the range 427-429 nm. (a) Detection of blue fluorescence (E  $\rightarrow$  B); (b) detection of UV fluorescence (D  $\rightarrow$  X).

signature of a bound-free transition. This spectrum is more than an order of magnitude weaker than the E-B system and signal was collected from 1500 laser pulses. The major part of the spectrum is shown in fig. 6. At  $\lambda < 355$  nm the oscillations turn very weak; actually at 355 nm stray light from the third harmonic of the Nd: YAG laser hampers recording. In between 375 and 392 nm one more oscillation is observed, however it overlaps with the E-B (8,  $v_B$ ) bands for the lowest  $v_B$ .

In the experimental setup with the fast photomultiplier the time-dependent decay of this near-UV fluorescence has been registrated. It is found that the intensity decays exponentially, indicating that the near-UV light stems from direct radiative relaxation of the  $E(0_g^+)$ , v=8, J=56 state. The observed decay time is found to be in agreement with the accurately measured lifetime of the  $E(0_g^+)$  state of 26.6 ns [24].

The near-UV fluorescence is attributed to the  $E(v=8, J=56)^{-1}\Pi(1_u)$  system. Wavelength-dependent intensities for this Franck-Condon diffraction pattern have been calculated, by making use of a potential for the  ${}^{1}\Pi(1_u)$  state empirically derived by Tellinghuisen [12]. He analyzed the bound-free  $f(0_g^+), v'=1^{-1}\Pi(1_u)$  fluorescence spectrum, as ob-

tained by Heemann et al. [25] in the wavelength range 288-294 nm. The same functional form is now used for a calculation of intensities of the  $E^{-1}\Pi(1_u)$ system. The results are also included in fig. 6. The expression for V(R) is rather intricate and is represented by [12]

$$V(R) = G[F(U_{-} - U_{+}) + U_{+}],$$

with

$$U_{-} = 8.61 \times 10^{7} R,$$
  

$$U_{+} = 180(1 - e^{-1.43(R-4.2)})^{2},$$
  

$$F = (1 + e^{16(R-3.32)})^{-1},$$
  

$$G = 1 - 0.09 \exp[-40(R-3.34)^{2}].$$

This potential for  ${}^{1}\Pi(1_{u})$  produces reasonably good agreement with the present fluorescence data. The functional form for the potential curve does not represent an entirely repulsive state. For internuclear distances R > 3.7 Å it is weakly bound with a minimum of  $D_{e}=180$  cm<sup>-1</sup> at R=4.2 Å. Because the  $f(0_{g}^{+})$ , v'=1 state has an outer well RKR-turning point at R=3.68 Å [26] only the repulsive part of the  ${}^{1}\Pi(1_{u})$  state was used in the analysis of Telling-



Fig. 5. Dispersed fluorescence in the E-B system from  $E(0_g^+)$ , v=8, J=56 in the wavelength range 393-432 nm at an I<sub>2</sub> pressure of 0.3 Torr. The assignment  $v_B$  refers to E-B (8,  $v_B$ ) transitions. The inset shows a blow-up of the spectrum for  $v_B=20$  and 21. Lower part: calculated intensities from Franck-Condon factors.

huisen [12]. Since the outer RKR-turning point of E(v=8) is at R=4.0 Å the larger internuclear distances do play a role in the present analysis. However the vibrational overlap function derives its major contribution from the inner side of the potential curve.

# 4.3. Indirect fluorescence in the $D(0_u^+) - X^{-1}\Sigma(0_g^+)$ system

A third fluorescence spectrum has been observed at wavelengths  $\lambda < 335$  nm. The temporal response of this fluorescence indicates that it originates from a secondary relaxation channel. This UV intensity shows a maximum about 5–10 ns later in time than the blue fluorescence. This behaviour is characteristic for a fluorescence channel originating from a collisionally-populated excited state. A dispersed UV fluorescence spectrum of the most intense range (318-330 nm) is reproduced in fig. 7. Spectra of somewhat weaker intensity, as observed in the range 299–320 nm are presented in fig. 8.

The assignment of the features in figs. 7 and 8 is based on the assumption that population of the prepared  $E(0_g^+)$ , v=8, J=56 state is transferred to particular rovibrational states of  $D(0_u^+)$ , which subsequently decay to high vibrational levels of the  $X(0_{g}^{+})$  ground state. Similar to the E-B bound system, also in the D-X system sharp line doublets are observed, indicating that in the collisional energy transfer from  $E(0_s^+)$  to  $D(0_u^+)$  only specific rotational quantum states are populated. The transition frequencies of the D-X system are calculated from the most accurate spectroscopic constants reported in the literature, for the  $D(0_u^+)$  state by Ishiwata and Tanaka [10] and for  $X(0_g^+)$  by Martin et al. [13]. The observed features can be consistently assigned as originating from J = 56 levels of  $D(0_{u}^{+})$ , v = 10, 11 and 12. The calculated splitting in the P(57)-R(55)emission doublet in e.g. the D-X (10, 55) band is 6.5  $cm^{-1}$ . With a resolution in the UV-fluorescence spectra of 4.5  $cm^{-1}$ , a resolved doublet may be observable if just a single J state is excited in each D(v')state. In principle  $\Delta J \neq 0$  transitions may occur in the E-D collisional energy transfer as well. This type of rotational relaxation is ruled out by the present experiment as it would wash out the resolved doublet structure. It is concluded that only J=56 levels of  $D(0_u^+)$ , v=10, 11 and 12 are populated.

For an interpretation of line intensities calculations of Franck-Condon factors have been performed, with reported RKR-potentials for the  $D(0_u^+)$  and  $X(0_g^+)$  states [10,14]. In the spectra of fig. 8 fluorescence channels originating from D(v=10), D(v=11) and D(v=12) levels are indicated, while in fig. 7 only the D-X ( $v=10, v_X$ ) channels are specified. Intensities are calculated from Franck-Condon factors, and multiplied by  $\nu^3$ . Population densities  $N_v$  of the D(v) levels are then derived from a fit to the observed data. The calculated relative intensities, displayed also in figs. 7 and 8, show that good quantitative agreement with observations is obtained with population ratios  $N_{10}: N_{11}: N_{12} = 1.0: 0.15: 0.08.$ **Obviously** the D(v=10) state is predominantly populated in collisional energy transfer at pressures of  $p(I_2) = 0.3$  Torr.



Fig. 6. Bound-free emission in  $E^{-1}\Pi(1_u)$  system from  $E(0_s^*)$ , v=8, J=56: (a) observed spectrum; (b) calculation.

### 5. Discussion

The main result of the present investigation is that under the experimental conditions of 0.3 Torr pure I<sub>2</sub> gas no ro-vibrational collisional relaxation within the  $E(0_{F}^{+})$  state is found. However, collisionally induced electronic relaxation is observed, with a transition to the  $D(0_{s}^{+})$  state. Population of the laserprepared  $E(0_g^+)$ , v=8, J=65 state relaxes almost entirely into the  $D(0_n^+)$ , v=10, J=56 state under the influence of collisions with ground state I2 molecules. In a preliminary extension of the present work it is found that in collisions with  $N_2$  and/or  $O_2$  molecules the  $D(0_u^+)$ , v=11 and 12, J=56 states are populated as well, but a remarkable selection rule  $\Delta J=0$  prevails. Further collisional relaxation studies with various collision partners in the E-D transfer process in  $I_2$  are being prepared.

We note that the measurements are performed under single-collision conditions. Collision rates of the I<sub>2</sub> ion pair states are on the order of  $10^{-10}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup>. Specifically for the I<sub>2</sub>D(0<sup>+</sup><sub>u</sub>) state in collisions with O<sub>2</sub> it was found that  $k=0.96 \times 10^{-10}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> [27], while for the I<sub>2</sub> E(0<sup>+</sup><sub>g</sub>) state in collisions with N<sub>2</sub>  $k=1.19 \times 10^{-10}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> [15] has been reported. Assuming that the rate

for  $I_2$  collisions is of the same order of magnitude, then in view of the lifetimes, 13.3 and 26.6 ns for  $D(0_u^+)$  and  $E(0_g^+)$ , respectively, at pressures of up to 10 Torr single-collision conditions will prevail [28,29].

Another important result of the present work is the identification of the  $E(0_g^+)^{-1}\Pi(1_u)$  system. If the  ${}^{1}\Pi(1_u)$  potential indeed has a minimum, some discrete transitions resulting in narrow lines might be expected in the fluorescence data. Unfortunately the FCF vibrational overlap at 4.0 Å is small so that the intensity of these lines, if existing, will be low. At the expected wavelength of 330 nm the strong D-X system interferes and collision-free circumstances will be required for a search of the bound minimum of the  ${}^{1}\Pi(1_u)$  state.

The resonances of the green output of the Nd: YAG laser in the B-X system of  $I_2$  have been discussed extensively. The motivation is that these coincidences are frequently used for non-linear optical studies [14,16,17,30,31] and in collisional relaxation studies like the present one. In a recent study [15] a twophoton excitation process was studied as well, also employing the Nd: YAG laser for the first step. Min et al. assumed that the R(106) line of the B-X (36, 0) band coincides with the Nd: YAG laser. However,



Fig. 7. D-X fluorescence in the interval 318-330 nm, measured in a 0.3 Torr I<sub>2</sub> sample. Lower part: calculated Franck-Condon intensities for D-X(10,  $v_X$ ) bands for  $v_X$ =63-76.

the present calculations show that this is not correct. Table 1 reveals that the R(106) line of the B-X (34, 0) band is a possible, although unlikely coincidence. For this reason the claim that a new electronic state, denoted  $E_2$ , was observed is questionable. In the work of Buntine et al. [16] on laser-induced grating spectroscopy B-X (32, 0) P(51) and B-X (34, 0) P(102) lines were identified as resonances. Both lines lie 3  $cm^{-1}$  outside the gain profile of the Nd: YAG laser. However, the conclusions of Buntine et al. would not be affected, replacing their assignment by B-X (32,0) P(53) and B-X(34,0) P(103), respectively. The present identification not only relies on the fluorescence study, but it is also in agreement with a series of CARS experiments [14,17,31], where careful calibration procedures have been followed. The frequency of the Nd: YAG laser was determined with a monochromator at  $18788.4 \pm 0.2$  cm<sup>-1</sup>. From



Fig. 8. D-X fluorescence spectra in the interval 300-320 nm measured in a nearly pure  $I_2$  sample. The calculated stick spectrum is based on Franck-Condon factors for the D-X system and population ratios D(10):D(11):D(12)=1.0:0.15:0.08.

the resonance CARS [14,17,30,31] measurements a more accurate value has been deduced. Also the calculations on the spectroscopy of the B-X system of  $I_2$ were carefully checked. In ref. [14] a complete assignment of the absorption spectrum of  $I_2$  B-X near the Nd: YAG resonance, based on these calculations, was given. Finally, it is left as an open question whether the precise frequency of a Nd: YAG laser depends on its design, and in particular, on the Nd-doping percentage of the gain material.

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