Laser Chem., 1999, Vol. 18, pp. 111–128
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Printed in Singapore.

COLLISION-INDUCED E(0_g^+)–D(0_u^+) STATE-TO-STATE ENERGY TRANSFER IN I_2

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(Received 19 November 1998)

Electronic energy transfer in the E(0_g^+) – D(0_u^+) system of I_2 is investigated in an experiment, where single rovibrational quantum states are prepared, single collision conditions prevail, and the final states have been determined from dispersed fluorescence. In $I_2^*(E) - X$ ($X = Ar, N_2, O_2$) the collisional decay is found to be governed by minimum energy transfer. With ($X = I_2$) an anomalous behaviour is found for the initially prepared E, $v = 8, J = 56$ level, which is tentatively ascribed to vibrational excitation of the collision partner.

Keywords: Energy transfer; iodine; ion-pair state; fluorescence

1. INTRODUCTION

The halogen and interhalogen molecules have provided a testground for innumerous experimental relaxation studies, because of the relative ease with which quantum states of various electronic character and up to large vibrational and rotational quantum numbers may be prepared, by just using visible and sometimes fixed frequency lasers. The $B^3\Pi(0_u^+)$ electronic state of iodine and bromine is often used as a prototype system [1]. Collisional relaxation data were put in a semi-empirical perspective by several authors [2, 3]. In most experimental studies

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the focus has been on rotational relaxation within an electronic configuration and for these cases models based on the energy-gap-law or the statistical-power-gap-law have been devised. The ultimate goal of collisional studies, a comparison of the data with scattering calculations based on ab initio potential energy surfaces, is still far away, because these procedures are difficult to implement for the heavy halogen molecules. Therefore physical insight into collision phenomena for these systems remains limited to the formulation of specific propensity rules.

Molecular iodine has attracted special interest because of the quenching-induced laser transition at 340 nm, that was assigned as belonging to the $D'(2_g)-A'(2_u)$ transition [4, 5]. All six electronic states in the first ion-pair cluster corresponding to the $I^-(^1S)+I^+(^3P_2)$ combination, have been investigated spectroscopically and accurate molecular constants were reported for the $E(0_g^+)$-state [6, 7], the $D'(2_g)$-state [8, 9] and the $D(0_u^+)$-state [10]. Through a number of investigations it was established that a delicate interplay of electronic relaxation occurs between the near-resonant $E(0_g^+)$, $D(0_u^+)$, and $D'(2_g)$ ion-pair states. Several studies have concentrated on relaxation upon single photon excitation of the $D(0_u^+)$ state, either by atomic line pumping [10], flashlamp pumping [5] or laser pumping [11 – 13]. Apart from $D \rightarrow E$ and $D \rightarrow D'$ quenching also reactive transfer was observed [14]. In Figure 1a potential energy diagram is shown, displaying RKR potential curves for E, D and D′ states, their dominant fluorescence relaxation channels and the laser excitation scheme used in the present study.

In a previous study [15] a single $E(0_g^+), v, J$ level was excited and the direct fluorescence channels and the indirect relaxation channels, after collision-induced electronic quenching, were characterized. Similar studies had been performed by Min *et al.* [16] and Koffend *et al.* [8]. Following a two-photon scheme [17] singly resolved quantum states $E(0_g^+), v, J$ were prepared. It was shown that the experimental conditions for $E(0_g^+) - D(0_u^+)$ transfer are easily achieved, due to an extremely large inelastic collision cross section. State-to-state relaxation could be studied under single collision conditions. Dispersed fluorescence measurements with both a tunable and a fixed frequency pulsed laser form a well-suited arrangement for this purpose. The properties of the iodine molecule itself, *i.e.*, the short lifetime of the $E(0_g^+)$-state [18] and the limited number of relaxation channels in $E \rightarrow D$

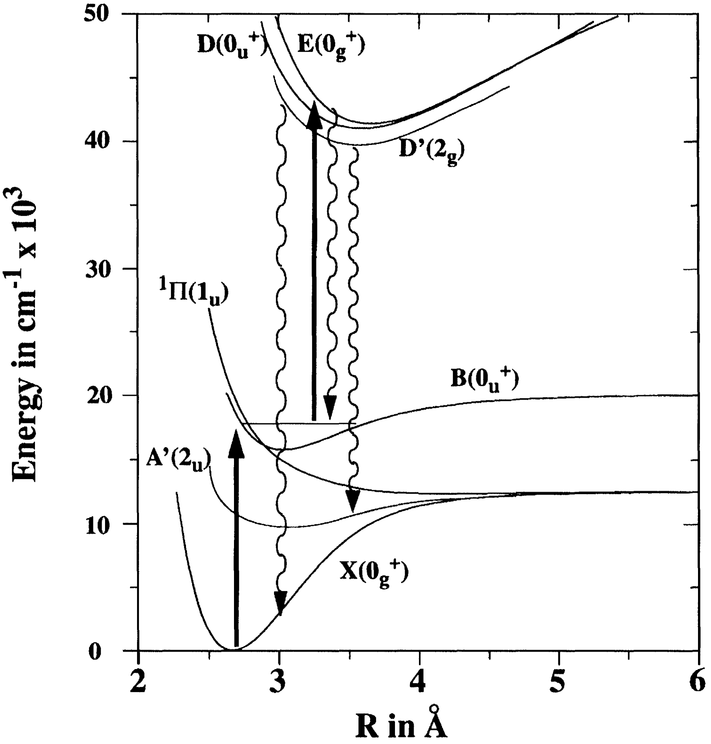

FIGURE 1 Potential energy diagram for I_2, limited to the states relevant to the present collisional study. The two-colour excitation scheme is denoted by the dark arrows. Fluorescence channels originating from the three ion-pair states E, D and D′ are indicated by curly downward arrows. E-B fluorescence occurs in the blue region near 430 nm, D′-A′ fluorescence is found in the near-ultraviolet (330–350 nm) and D-X fluorescence in the UV-region (280–320 nm). E-$^1\Pi$ fluorescence in the range 360–380 nm is not indicated.

quenching, provide these favourable conditions. In extension to the preliminary observations [15], in the present work the state-to-state quenching behaviour of four different rovibrational quantum states in $E(0_g^+)$ was investigated in detail for collisions with $I_2(X0_g^+)$, N_2, O_2 and Ar. The observed phenomena were found to depend on the collision partner and on the specific prepared state. Particularly the self-quenching features differ from effects induced by foreign collision partners. Relative relaxation rates in E → D quenching is qualitatively explained in terms of resonant energy transfer. Some apparent deviations from resonance transfer hint at the exchange of vibrational quanta between collision partners. The main goal of the present paper is to present the experimental results of these collisional relaxation processes in a phenomenological way to stimulate researchers in the field to carry out detailed calculations.

2. EXPERIMENTAL

The experimental setup is schematically displayed in Figure 2. Gaseous molecular iodine was laser-excited in a Pyrex-glass cell, equipped with quartz windows and connected to a rotary pump and a baratron (MKS 170M-26B), allowing for accurate pressure readings in the range 0.1 – 15 torr. After evacuation the cell was filled with I_2 at its room temperature vapour pressure of 0.3 torr. All experiments were performed at room temperature. Buffer gases (Ar, N_2, O_2) were admitted through a gas inlet, varying the total pressures between 0.3 and 10 torr.

The I_2 molecules were excited to rovibrational levels in the $B(0_u^+)$ state using the green output (532 nm) of a Nd:YAG laser (Quantel Yg 585-10). With the aid of an echelle grating monochromator the frequency

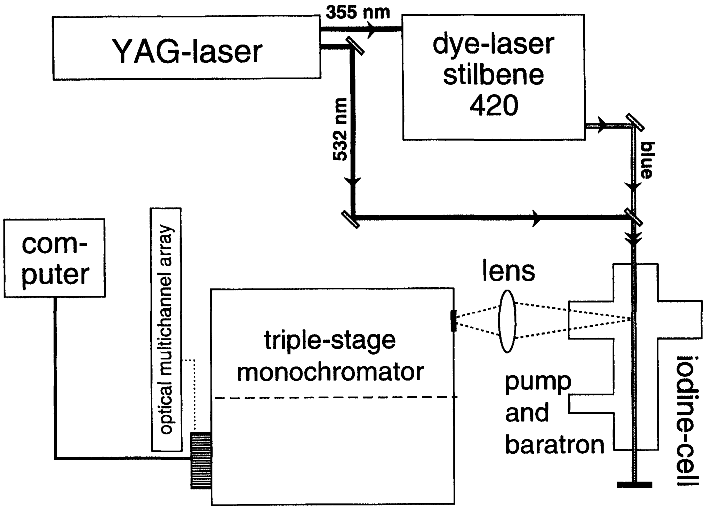

FIGURE 2 Schematic representation of the experimental setup.

was determined to be $18789.1 \pm 0.1\,cm^{-1}$ and the bandwidth was estimated at $1.8\,cm^{-1}$. The Nd : YAG laser operated at 10 Hz and the pulse duration was 5 ns. The UV-output of the same laser was used to pump a stilbene pulsed dye laser (Quantel TDL-50) providing tunable light in the range 415 – 440 nm for the second step of the two-colour absorption process exciting selected $E(0_g^+)$, v, J quantum states. In the dye laser a home-built prism beam expander was installed, yielding a laser bandwidth of $0.15\,cm^{-1}$. The laser bandwidth is reflected in the linewidth of the excitation spectra. The green and blue laser beams were temporally and spatially overlapped in the iodine cell. Both excitation and fluorescence spectra were measured by collecting the fluorescence radiation in a direction perpendicular to the laser beams. The fluorescence was focused on to the entrance slit of a 0.6 m triple stage monochromator (SPEX-1877). Fluorescence radiation was collected during a time averaging period, which was determined by the intensity of the emitted light. Typical averaging times were 1s for the blue E-B spectra and 30 s for the D-X and D′-A′ UV spectra. The dye laser wavelength was initially calibrated with the use of the OMA and reference spectra obtained from gas discharge lamps (Ar, Hg and Xe). As the spectroscopy of the E-B system in I_2 is known to high accuracy, an accurate internal reference was provided by the spectra.

Dispersed fluorescence spectra, recorded with the blue laser fixed to a selected E-state resonance, were obtained with the OMA using a 2400 line grating covering a span of 18 nm. Blue (E-B) and UV (D-X) fluorescence spectra were recorded at several buffer gas pressures. These spectra were wavelength calibrated by interpolation with emission lines from the gas discharge lamps, resulting in an accuracy of $3\,cm^{-1}$ or 0.03 nm. The resolution of the fluorescence spectra was limited by the OMA-instrument; in the UV about $12\,cm^{-1}$.

3. STATE PREPARATION

In a two-colour excitation scheme a fixed frequency Nd : YAG laser and a tunable dye laser, single rovibrational quantum levels in the $E(0_g^+)$ state were prepared *via* a scheme displayed in Figure 1. A typical laser excitation spectrum is presented in Figure 3 for the tuning range 427 – 429 nm of the blue dye laser. The significant difference between this

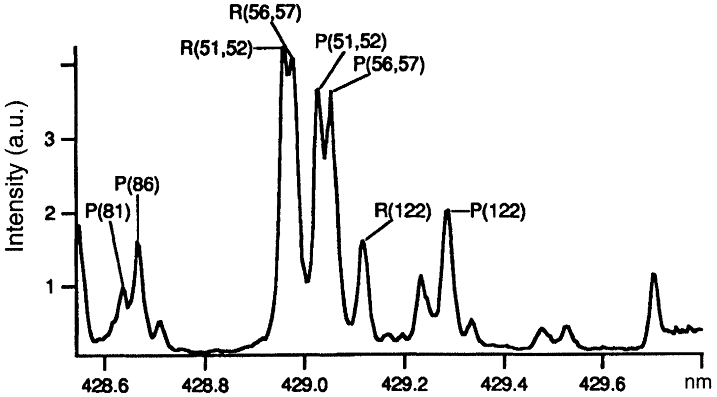

FIGURE 3 Two-colour laser excitation spectrum of I_2 with second laser in the wavelength range 428.5–429.5 nm.

spectrum and the one observed in Ref. [15] is an effect of a relatively broad bandwidth of the tunable laser (0.15 cm^{-1}) and the slightly shifted centre frequency of the Nd : YAG laser. Based on the accurate molecular constants of Luc [19] for the B-X system, the intermediate $B^3\Pi(0_u^+), v', J'$ states excited by the fixed 532 nm output could be identified, similarly as in Ref. [15], and the E-B excitation could be inferred. From a spectral analysis of the E-B excitation spectrum and the calculation of coincident transitions at 18789.1 cm^{-1} in the B-X system it follows that 9 rovibrational states of $B^3\Pi(0_u^+)$ will be excited in the present experiment. The two-colour laser excitation spectrum consists of multiple vibrational sequences of P-R doublets in the $E(0_g^+)$ state originating from each populated B-level. The main features could be assigned to sequences originating from $J' = 51, 52$ (overlapping) and $J' = 56, 57$ of the $B^3\Pi(0_u^+)$, $v' = 32$ level, $J' = 86$ of $B^3\Pi(0_u^+)$, $v' = 33$ and $J' = 122$ of $B^3\Pi(0_u^+), v' = 35$. Level assignments in the $E(0_g^+)$ state were confirmed by analysis of the blue dispersed fluorescence in the E-B system, by making use of calculated E-B Franck-Condon factors [15]. From an analysis of these E-B fluorescence spectra, it was verified that neither broadening effects, nor the appearance of rotational satellite lines, nor the growth of a continuous background occurred in the E-B system for samples with up to 10 torr buffer gas. This proves a clear absence of vibrational and rotational relaxation within the E state under the present experimental conditions.

In our study the UV-fluorescence after two-step excitation of four selected rovibrational levels of the E state has been investigated: E(0_u^+), $v = 8$, $J = 56$, E(0_u^+), $v = 9$, $J = 56$, E(0_u^+), $v = 13$, $J = 56$ and E(0_u^+), $v = 15$, $J = 123$. Figure 4 shows the energies of the relevant E state quantum levels together with the ones that we found to be collisionally excited *via* E → D transfer. The collisional energy transfer for the $v = 8, J = 56$ level has been studied previously [15], however

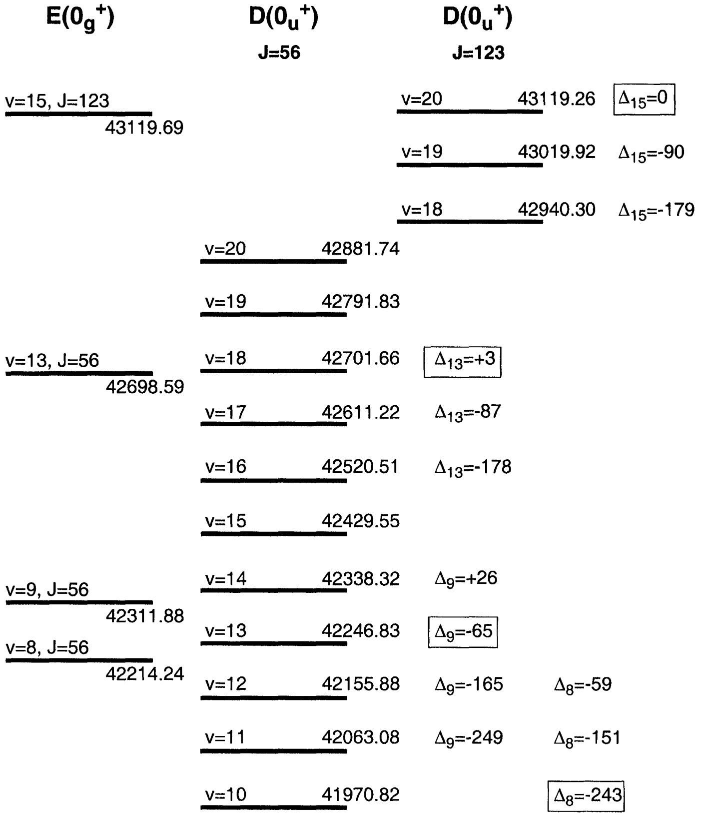

FIGURE 4 Energy level diagram of the relevant levels for the present E → D electronic transfer study. In the left column the laser-excited E levels, in the second and third column the collisionally populated D-levels for $J = 56$ and $J = 123$; note that in fact $J = 55, 57$ and $J = 122, 124$ are populated *via* the $\Delta J = 1$ selection rule. Energies in cm^{-1}. Δ_v represent the energy differences between laser-excited and collisionally populated states , with v the vibrational quantum number of the prepared state; values marked in a box represent the dominant decay channels.

only for $I_2^*-I_2$ collisions. The initial levels, restricted by the fixed frequency of the first laser, access a considerable spread in detuning from the nearest D levels.

Crucial for a straightforward interpretation of collisional relaxation effects in the present experiment is the fact that the conditions ensure that only primary collisions involving the laser-prepared state play a role and that secondary effects may be neglected. The collisional conditions are determined by the lifetimes of the prepared state, the molecular densities and the collisional rates. For the $E(0_g^+)$ state a radiative lifetime was determined at 26.6 ns [18] and we assume here that this value does not depend on rovibrational substates. Furthermore in $I_2^*-N_2$ collisional experiments the electronic state transfer rate was determined at $1.2 \times 10^{-10}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}$ [16]. Where the inelastic energy transfer I_2-I_2 collision rate equals a similar value, the total collision rate, to be associated with the total collision cross section, is calculated to be about a factor of 10 larger [1]. Taking the inelastic value as a typical gas kinetic collision rate, probabilities for single and multiple collisions may be calculated based on the statistical models by Suijker *et al.* [20] and Yamasaki and Leone [21]. It is found that for pressures up to 1 torr the fraction of multiple collisions remains below 10%. We will refer to this regime as that of strictly "single collision condition". For buffer gases up to 8 torr the events of single collision still dominate over the events of multiple collisions.

4. RESULTS ON ELECTRONIC ENERGY TRANSFER

4.1. $I_2^*(E)$–I_2 Collisionally Induced Fluorescence in the D-X System

As pointed out previously [15] fluorescence in the $D(0_u^+)-X(0_g^+)$ system can be observed in a wide wavelength range. While the most intense emission features are near 325 nm, the range 295–315 nm is very suitable for determining excited state population densities. The temporal behaviour of the latter UV-fluorescence shows that it originates in a collisionally populated state. By integrating the blue (E-B system) and UV(D-X) fluorescence we estimate that the collisionally induced UV-fluorescence yield remains less than 10% of the total yield. This yield indicates an upper limit of $10^{-10}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}$ as found in our experiment for the $I_2^*(E - I_2^*(D)$ collisional induced transfer rate. This rate corresponds to an electronic state transfer cross section of about $3 \times 10^{-15}\,\mathrm{cm}^2$, which is in agreement with theory and which is attributed to large impact parameters exceeding the critical value for orbiting [24]. The spectral features originate from certain rovibrational levels in the $D(0_u^+)$ state. Transition frequencies in the D-X system can be accurately calculated from the spectroscopic constants for the $D(0_u^+)$ state [6] and from the $X(0_g^+)$ state [22]. Franck-Condon factors, to be used for an analysis of the intensities in the D-X system, analogously to Ref. [15], were calculated from RKR-potentials reported for both states [6, 23].

In the D-X dispersed fluorescence spectra partly resolved doublets are visible. As an example we show, in Figure 5, D-X fluorescence after

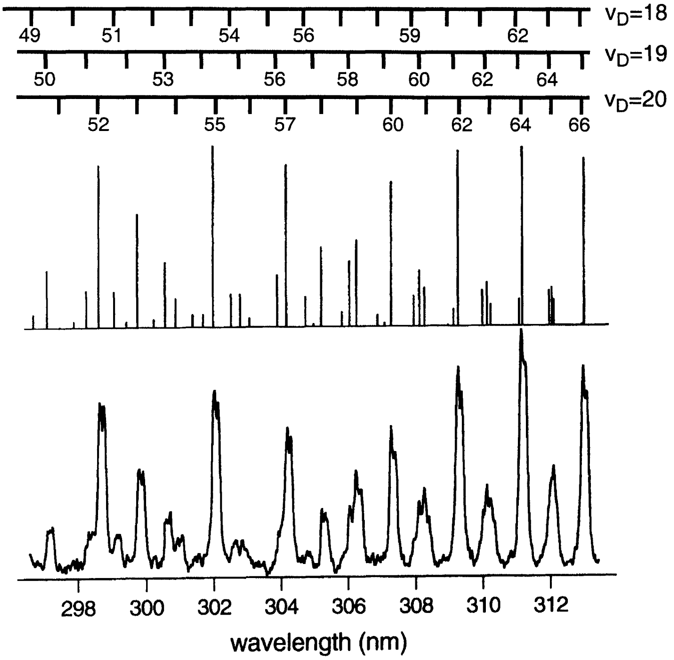

FIGURE 5 Dispersed fluorescence spectrum in D-X system after laser excitation of the E, $v = 15$, $J = 123$ level in pure I_2. Stick spectrum represents the calculated intensity using Franck-Condon factors and relative population densities $N_{v\mathrm{D}}$. The latter values for $N_{v\mathrm{D}}$ were obtained from a fit to the experimental spectrum.

laser excitation of the E, $v = 15, J = 123$ level in pure I_2-gas. The appearance of sharp resonances with doublet structure in D-X indicates that only specific rotational quantum numbers in the $D(0_u^+)$ state are populated in the collisional transfer process. In a previous study [15] it was erroneously assumed that only $\Delta J = 0$ transitions would occur. In view of the distinction between para and ortho species for the homonuclear iodine molecule a transition from a *g*-symmetry state to a *u*-symmetry state must be accompanied by a $\Delta J =$ odd change in rotational quantum number. The calibration accuracy of the dispersed fluorescence spectra is not sufficient to determine the *J*-value within a few *J*'s. From the fact that P-R doublets are visible we deduce that collisional transfer in $E \rightarrow D$ follows predominantly a $\Delta J = \pm 1$ selection rule.

To relate the fluorescence line intensities in the spectrum of Figure 5 to the relative populations of the individual vibrational states, Franck-Condon (FC) factors for D-X (v_D, v_X) were calculated for $v' = 18$, 19 and 20 and all relevant v'' levels. In the FC-calculations the rotational effect was accounted for and *J* was fixed at 123. The intensities in the spectra were analysed using:

$$I_{v_D v_X} \propto N_{v_D} |\langle v_D | v_X \rangle|^2$$

where relative values of N_{vD} were derived by fitting to the observed intensities. As a result it is found that after laser-excitation to E, $v = 15, J = 123$ energy transfer takes place to the D state with a population ratio: $N_{18} : N_{19} : N_{20} = 13\% : 20\% : 67\%$.

Similar analyses were performed for all four excited levels in the E state for pure I_2 gas at room temperature vapour pressure of 0.3 torr. In this way the relaxation channels for the different states were established. Results of the deduced relative relaxation rates are summarized in Table I. In Figure 4, where the energy gaps between prepared E-state levels and decaying channels are displayed also the dominant channels are indicated. Here the energies of the D-levels are taken for $\Delta J = 0$, knowing that in reality decay is *via* $\Delta J = \pm 1$. We note that the spacing to adjacent rotational states is less than 5 cm^{-1} for *J* as high as 123. For several examples it is found that relaxation occurs into the most resonant level, with the exception of the E, $v = 8, J = 56$ level. Here it is found, similarly to Ref. [15], that relaxation occurs dominantly to a level

TABLE I Results for $E(0_g^+, v, J) \rightarrow D(0_u^+, v, J)$ relaxation in $I_2^* - I_2$ collisions as obtained from an analysis of the observed D-X fluorescence. In the first two columns the quantum states before and after collision are given. In the last column the relative population of the D(v) collisional channel is given

Laser prepared state	*Collisionally excited state*	*Decay fraction*
E, $v = 15$, $J = 123$	D, $v = 20$	67%
	D, $v = 19$	20%
	D, $v = 18$	13%
E, $v = 13$, $J = 56$	D, $v = 18$	55%
	D, $v = 17$	28%
	D, $v = 16$	17%
E, $v = 9$, $J = 56$	D, $v = 14$	29%
	D, $v = 13$	34%
	D, $v = 12$	17%
	D, $v = 11$	20%
E, $v = 8$, $J = 56$	D, $v = 12$	16%
	D, $v = 11$	16%
	D, $v = 10$	68%

which is off-resonant by $243\,\mathrm{cm}^{-1}$. In case of E, $v = 9, J = 56$ the dominant channel is exothermic by $65\,\mathrm{cm}^{-1}$, while an almost equally large fraction relaxes endothermically by $+26\,\mathrm{cm}^{-1}$.

4.2. I_2^*(E)-X (X = O_2, N_2, Ar) Collisionally Induced Fluorescence in the D-X System

The E → D collisional energy transfer process was further investigated for various foreign collision partners and for several E-states by monitoring the D-X dispersed fluorescence at different pressures. The $E(0_u^+), v = 8, J = 56, E(0_u^+), v = 13, J = 56$ and $E(0_u^+), v = 15, J = 123$ were chosen as initially prepared states. In all cases the I_2 pressure was kept at the room temperature vapour pressure of 0.3 torr. The buffer gases were argon, nitrogen and oxygen respectively. In Figure 6 an example is displayed for an initially laser-excited E, $v = 8, J = 56$ state for pure I_2 and for increasing N_2 buffer gas pressure.

All UV fluorescence spectra observed after excitation of certain E-state levels showed a significant increase of the background signal at higher buffer gas pressures, already visible at pressures below 1 torr (see also Fig. 6). This suggests that the electronic transfer rate must be higher than previously estimated [16, 24]. The P-R splitting of the individual vibrational lines remained visible, while the background increased, implying that still specific rotational quantum states were

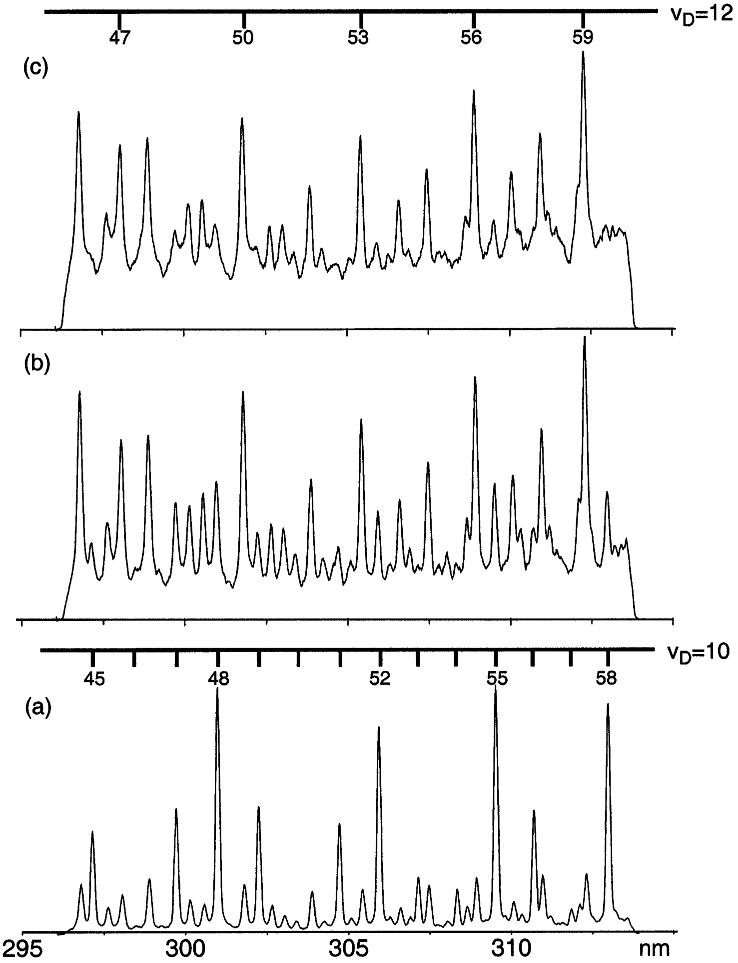

FIGURE 6 Dispersed fluorescence spectrum in D-X system after laser excitation of the E, $v = 8$, $J = 56$ level. (a) in pure I_2, 0.3 torr; (b) total pressure of $I_2 + N_2$ 1 torr; (c) total pressure of $I_2 + N_2$ 2 torr. From the assigned upper state levels D(v) it is clearly seen that in pure I_2 $v_D = 10$ is the dominant channel, while for increased N_2 pressure $V_D = 12$ is dominant. Note that the background increase is a real effect, which is ascribed to rotational relaxation by multiple collisions within the D state.

preferably populated in the collisional transfer process. When the pressures were raised to a maximum of 10 torr, the individual rotational lines became almost invisible as a result of secondary relaxation processes.

TABLE II Results for E → D relaxation in I_2^*–X collisions as obtained from an analysis of the observed D-X fluorescence. In the first two columns the quantum states before and after collision are given. In the last column the relative population of the D(v) collisional channel is given

Laser prepared state	*Transfer state*	*Decay fraction*		
		I_2^*–Ar	*I_2^*–N_2*	*I_2^*–O_2*
E, $v = 15$, $J = 123$	D, $v = 20$	68%	58%	58%
	D, $v = 19$	18%	29%	29%
	D, $v = 18$	18%	13%	13%
E, $v = 13$, $J = 56$	D, $v = 18$	73%	50%	70%
	D, $v = 17$	15%	34%	20%
	D, $v = 16$	12%	16%	10%
E, $v = 8$, $J = 56$	D, $v = 12$	43%	60%	58%
	D, $v = 11$	35%	37%	40%
	D, $v = 10$	20%	< 5%	< 5%

The relative population of the various D(v) levels is expected to vary with the buffer gas pressure, when I_2^*–X (X = Ar, N_2, O_2) collisions lead to different distributions than I_2^*–I_2 collisions. In the single collision regime E → D(v) transfer is induced by either one of these. Hence at a certain pressure it can be calculated which part of the total D(v) population is caused by I_2^*–I_2 collisions assuming that the E → D transfer rate does not (largely) depend on collision partner. Since the relative energy transfer rates to the D(v) levels are known for I_2^*–I_2 collisions (Tab. I) a subdivision can be made to deduce the relative rates pertaining to I_2^*–X collisions. By following this procedure at a number of buffer gas pressures a reasonable accuracy can be obtained on the parameters for the I_2^*–X collisions. The resulting relative rates for decay into D(v) channels are listed in Table II for the three buffer gases used. The errors in the tabulated numbers are estimated to be 5%.

4.3. Collision Induced Fluorescence in the D′(2_g) – A′(2_u) System

In the UV-range 330–350 nm a second fluorescence spectrum was observed which we attribute to the D′(2_g) – A′(2_u) system. This transition, described in earlier studies [8, 12, 13] is important for its use in a chemical laser [25]. A collision-induced D′-A′ spectrum after laser-excitation of the E, $v = 8$, $J = 56$ is displayed in Figure 7 for collisions with N_2 as buffer gas. Also the integrated fluorescence in the D′-A′ channel was monitored as a function of buffer gas and displayed in

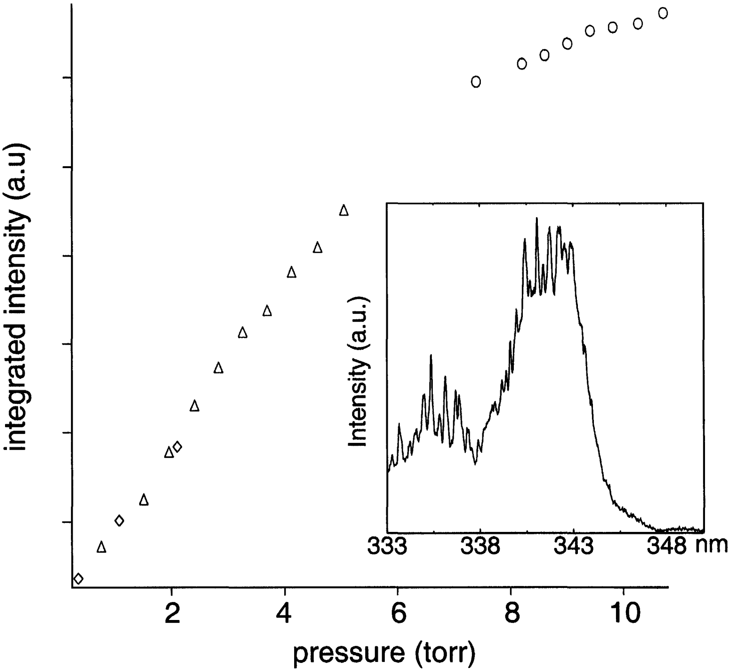

FIGURE 7 Collision induced fluorescence in the D′-A′ system after excitation of E, $v = 56, J = 8$ level. The main graph shows the integrated intensity in the D′-A′ system as a function of buffer gas pressure. In the inset the collisionally induced D′-A′ spectrum is shown at 5 torr N_2 buffer gas pressure.

Figure 7. The fluorescence yield increases linearly with pressure, for pressures up to several torr. This indicates that the D′ state is populated through a single collision $E(v, J) \rightarrow D'(v', J')$ and not *via* indirect relaxation *via* the D state. The latter $D \rightarrow D'$ relaxation was investigated by Koffend *et al.* [8]. In view of the strong congestion in our spectrum no rotational assignments could be made and we did not attempt to further analyze this feature.

5. DISCUSSION

No ab initio scattering calculations have been performed for excited state halogen molecules, so no detailed comparison between theory and experiment is possible. The purpose of this work is primarily to present the observed features on electronic transfer and fit them into a phenomenological framework. In this study no rovibronic relaxation within the $E(0_g^+)$ state was observed for buffer gas pressures of up to 10 torr. Obviously interelectronic $E \rightarrow D$ transfer is faster than rovibronic transfer within the E state. A second feature in this process is that virtually no angular momentum is transferred, except for the single quantum which is necessary because of the para-ortho distinction. This phenomenon was observed previously [15] for I_2^*–I_2 collisions starting from E, $v = 8, J = 56$, but is now confirmed for several other E-states and for foreign collision partners. For a phenomenological explanation of the observed features two hypothetical frameworks might be postulated. A first concept is that of *resonance* in energy transfer. A second concept that might add to understanding is vibrational wave function overlap between laser-excited and transfer states. In the following these hypotheses will be looked at in some detail.

In most cases resonance energy transfer in the $E \rightarrow D$ process seems to prevail. The one notable exception is transfer in I_2^*–I_2 collisions from the E, $v = 8$, $J = 56$ state. Here a strong deviation from the resonance propensity rule is found in that 68% decays into D, $v = 10$, which is off by 243 cm^{-1}. This effect is largely dependent on the collision partner; for Ar only 20% decays into D, $v = 10$ while for N_2 and O_2 this fraction is negligibly small. Within the framework of resonance energy transfer one might postulate that in the case of I_2^*–I_2 collisions vibrational excitation of the ground state I_2 molecule takes place; with a vibrational spacing of 213 cm^{-1} in $I_2(X0_g^+)$ this would result in a nearly resonant transition leaving 30 cm^{-1} to be disposed of in translational energy. This value is much smaller than the 59 cm^{-1} and 151 cm^{-1} that should be disposed in translation after transfer to D, $v = 12$ and $v = 11$ respectively. Since vibrational excitation of the foreign collision partner cannot take place this mechanism might explain the strong difference in behaviour for I_2^*–I_2 collisions. Upon excitation of the E, $v = 9, J = 56$ level a vibrational excitation mechanism does not play a decisive role; only 20% decays to D, $v = 11$ which is off by 249 cm^{-1}. For this E, $v = 9, J = 56$ level most of the decay is into the two near-resonant levels, one endothermic (D, $v = 14$ for 29%) and one exothermic (D, $v = 13$ for 34%). For all foreign collision partners and for all three laser-excited states studied in detail the resonance propensity rule holds; more than half of the transfer goes into the nearest level.

A second concept for explaining the results is the wave function overlap between states before and after collision. In view of the large collisional cross-section the collisions may be considered as long-distance glancing collisions, where the internuclear separation of the molecule is not affected. Based on this assumption one might expect a behaviour with the relative decay rates following the Franck-Condon (FC) overlap between the E and D states:

$$R_{\mathrm{E}\to\mathrm{D}(v)} \propto \left|\langle v_{\mathrm{E}} | v_{\mathrm{D}} \rangle\right|^2$$

Franck-Condon calculations were performed based on the available RKR potentials of E and D states. The results are displayed in Figure 8,

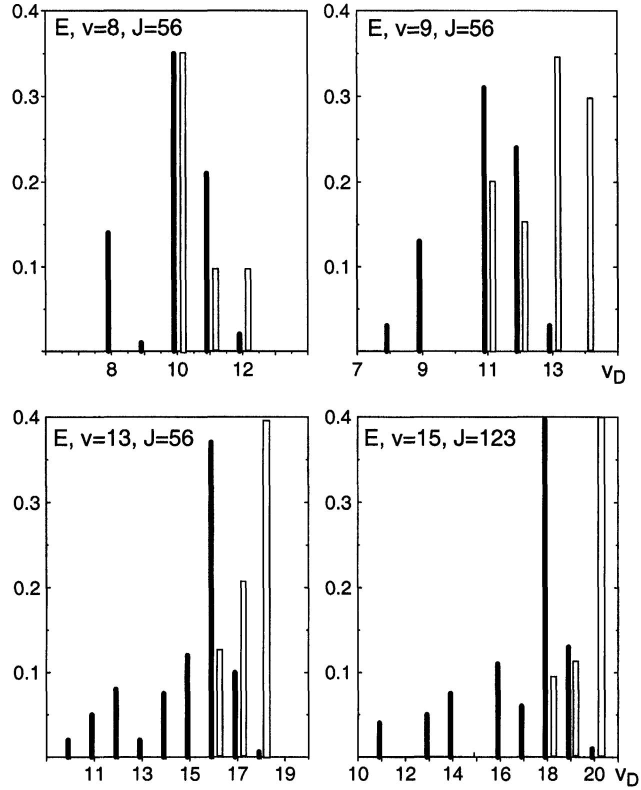

FIGURE 8 Calculated Franck-Condon factors for the overlap between four laser-excited E states and the relevant decay channels D(v) displayed on a relative scale with black sticks. White sticks represent the relative collisional rates into D(v) states as experimentally determined for I_2^*–I_2 collisions.

where they are compared with the observed relative decay rates for I_2^*–I_2 collisions. For the specific case of the E, $v = 8$, $J = 56$ level, where an anomalous behaviour was found, indeed the FC-overlap with the D, $v = 10$ level is very high. Here the concept of vibrational wave function overlap could provide an explanation for the large offset from resonance; the FC-overlap with the most resonant level D, $v = 12$ is very small. The cases of the E, $v = 13, J = 56$ and E, $v = 15, J = 123$ provide a counterexample. Here the population decays predominantly into the near resonant levels, where the FC-factors are very small. At the same time the overlap with $\Delta v = -2$ levels is again high, but only a minor fraction decays into these off-resonant channels. We note however that for these two levels there exists an exact resonance (0 and 3 cm^{-1}) with a D-level.

6. CONCLUSION

Collision induced state-to-state electronic energy transfer is investigated for the $E(0_g^+) - D(0_{u^+})$ system in molecular iodine, with quantum state selective preparation of initial states, single collision conditions and quantum state selectivity in the outgoing channel. By choosing different laser-prepared initial states the effect of resonance in the decay was investigated. For foreign collision partners Ar, N_2 and O_2 indeed the transfer is dominated by resonance. In case of ground state I_2 as collision partner an anomalous case is found which might be explained by the mechanism of vibrational excitation of the collision partner. Alternatively the wave function overlap between initial and final collision states might play a role as well. The $E \rightarrow D$ system is an interesting object for future experimental studies since a variety of initial states can be easily prepared by two-colour laser excitation.

Acknowledgements

The authors wish to thank K. van Gelder for her assistance during the measurements and C. Gooijer and N. Velthorst of the Analytical Chemistry group within Laser Centre VU for lending us their laser system and the setup for measuring dispersed fluorescence.

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