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Efficient long-range collisional energy transfer between the $E_0g^+ (3P_2)$ and $D0_u^+ (3P_2)$ ion-pair states of I$_2$, induced by H$_2$O, observed using high-resolution Fourier transform emission spectroscopy

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Using high-resolution Fourier transform emission techniques, we have resolved rotational structure in the $D0_u^+ (3P_2) \rightarrow X0_s^+$ emission following collisional transfer from the $E0_g^+ (3P_2)$ state in I$_2$. The $P:R$ branch ratios in the $E0_g^+ (3P_2) \rightarrow D0_u^+ (3P_2)$ transfer are found to vary enormously with $v_E$ and $v_D$. We show that the observed intensities are all consistent with the transfer being dominated by long-range, near-resonant collisions with residual H$_2$O. Unequal $P:R$ branch ratios in the $E0_g^+ (3P_2) \rightarrow A1_u$ emission have been shown to result from mixing of the $E0_g^+ (3P_2)$ and $\beta1_u (3P_2)$ states via $\Omega$-uncoupling. © 2011 American Institute of Physics. [doi:10.1063/1.3638267]

I. INTRODUCTION

In a recent paper,1 we reported long-range (resonant) energy transfer between $g/u$ ion-pair states of molecular iodine, e.g., $E0_g^+ (3P_2) \rightarrow D0_u^+ (3P_2)$, induced by collisions with H$_2$O via dipole coupling. The large rate constants deduced for collisional transfer between a range of vibrational levels of the two states, up to $5 \times 10^{-5}$ molecules$^{-1}$ cm$^3$ s$^{-1}$, can be two orders of magnitude greater than that for transfer between the same two levels following collisions with I$_2(X)$. Consequently, it was proposed that H$_2$O desorbed from the walls of the sample cell or from solid I$_2$ itself could have significantly affected the results of earlier studies of collisional transfer by supposedly dry I$_2(X)$ previously reported in the literature. The large rate constants required at such low partial pressures of H$_2$O were shown to be possible with long-range, near-resonant interactions that arise when there is close matching of the energy change in the ion-pair states, $\Delta E(I_2)$, with the change in energy that accompanies a rotational transition in the ground state of H$_2$O, $\Delta E(H_2O)$. This dipole-induced electronic transition must be accompanied by $\Delta J = \pm 1$ and a dipole-allowed transition in H$_2$O to fulfil the conditions for rapid energy transfer.

The requirement1 that these energy mismatches, $\Delta E^*$, $(\Delta E(I_2) - \Delta E(H_2O))$, be $\leq 5$ cm$^{-1}$ (and $\leq 2$ cm$^{-1}$ for a detailed rate constant $\geq 10 \times 10^{-9}$ molecules$^{-1}$ cm$^3$ s$^{-1}$) suggests that the intensity of emission from pairs of levels populated by $\Delta J = \pm 1$, for $E0_g^+ (3P_2) \rightarrow D0_u^+ (3P_2)$ collisional transfer should, according to the model, be very unequal. This will become more likely as the branch separation increases at higher $J$ values, and also as the resonant transitions required from H$_2$O move to higher energies where the density of possible transitions (far-IR lines) is less. This energy matching criterion is based on collisions occurring with the most probable relative velocity, $v^*$, at room temperature. Doubling the collision velocity to, say, $2v^*$ would double the value of $\Delta E^*$ to preserve the same value of the Massey parameter, $\Delta E b hv$, at a given impact parameter, $b$. However, $\Delta E^*$ would then be an even smaller fraction of the relative kinetic energy. These collisions in the tail of the Maxwell-Boltzmann distribution would have the effect of slightly reducing inequalities in the $P:R$ branch ratios.

In our earlier work,1 each vibronic band in the $D0_u^+ (3P_2) \rightarrow X0_s^+$ emission was composed of four lines, a $P$ and $R$ branch from each of the two collisionally populated rotational levels. However, it was not possible to resolve these lines and, hence, determine whether the populations of the two collisionally populated levels were different.

However, such data are available in a much earlier study,2 in which Fourier transform (FT) detection was used. Rotational structure was resolved in $D0_u^+ (3P_2) \rightarrow X0_s^+$ emission that was also observed following collisional transfer from the $E0_g^+ (3P_2)$ state which had been selectively excited by optical-optical double resonance (OODR). These spectra were recorded with the specific aim of obtaining molecular constants for the $Cl_u$ valence state (called $B''I_u$ in Ref. 2 and some earlier studies but relabelled to be consistent with the notation used for the other halogens). As it was not possible to record any new spectra with this experimental arrangement, we were restricted to re-examining the original data in the light of our recent study.1 Consequently, the ideal ($v, J$) combinations are not always available.

In the FT experiments,2 considerable effort was made to remove traces of H$_2$O and other impurities (see below), and hence, it was assumed that all H$_2$O would have been removed from the sample cell. Spectra recorded under these conditions will subsequently be described as “dry.” However, many FT spectra were also recorded before these measures were taken to remove H$_2$O and these will be described as “wet.” In

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II. EXPERIMENTAL

The present paper, we will present some of these unpublished spectra and show that the intensities of the rotational lines are very irregular and that these intensities are entirely consistent on a quantitative basis with them being determined by long-range, near-resonant interactions with ground state H2O. In addition, we will propose that the imbalances in rotational line intensities, but no quantitative estimate was given of the electron densities required, or any rotational branch selectivity that might result.

A second imbalance in rotational line intensities was observed in the previous FT study.2 It could be clearly seen that while the P:Q:R branch ratios in the direct E0g+(3P2) → C1u emission were as expected, those in the E0g+(3P2) → A1g emission were not, but this observation was not commented on by the authors. In this case, we will propose that the imbalance is due to Ω-uncoupling between the E0g+(3P2) and β1u(3P2) states, first reported in absorption by Perrot et al.4 Potential energy curves of all of the relevant states2,5–10 are shown in Fig. 1.

II. RESULTS AND DISCUSSION

A. Collisional transfer by H2O

An example of a “dry” low-resolution emission spectrum, recorded by exciting E(v = 8, J = 55), is shown in Fig. 2(a). With the exception of part of the broad band around 325 nm, all the emissions above 320 nm in the spectrum are due to E0g+(3P2) → A1g. Very weak D0u+(3P2) → X0g+ emission resulting from E0g+(3P2) → D0u+(3P2)
collisional transfer is observed down to 275 nm which is the low-wavelength limit of the emission from the vibrational levels populated \((v_D = 10–13)\). Previously,\(^1\) we showed that, under these conditions, the \(E_0 g^+ (3P_2) \rightarrow D_0 u^+ (3P_2)\) transfer is dominated by collisions with \(I_2(X)\). The spectrum in Fig. 2(b) was recorded with 0.03 Torr of \(H_2O\) added. The intensity of the spectra are normalized to the most intense peaks.

Expansions of the 322–332 nm region of the spectra shown in Figs. 2(a) and 2(b) are shown in Figs. 3(a) and 3(c), respectively. The same wavelength region of the “wet,” high-resolution FT emission following excitation of \(E(v = 8, J = 98)\) is shown in Fig. 3(b). The relative intensity distribution observed in the FT emission appears to be intermediate between those observed in the two low-resolution spectra. The two largest peaks in the spectra of “dry” \(I_2\) and \(I_2\) with \(H_2O\) added lie at 330.5 nm, \(E_0 g^+ (3P_2) \rightarrow A_1 u^+\), and 326 nm, \(D_0 u^+ (3P_2) \rightarrow X_0 u^+\), respectively; both peaks are very small in the complementary spectra. In the high-resolution FT spectrum, two sets of bands are observed centred at the same wavelengths but with nearly equal intensities, suggesting that there is residual \(H_2O\) present.

Furthermore, the relative contributions of the \(D_0 u^+ (3P_2)\) state vibrational levels, \(N_v\), observed in the high-resolution spectrum are 0.3, 1, 0.5, and 0 for \(N_{10}, N_{11}, N_{12},\) and \(N_{13}\), in agreement with the distributions that we observed previously for transfer by \(H_2O\). In contrast, the equivalent distributions observed for transfer by \(I_2(X)\) were 0.5, 1, 0.9, and 0.6. Hence, it is concluded that the \(E_0 g^+ (3P_2) \rightarrow D_0 u^+ (3P_2)\) transfer that gives rise to the emission shown in Fig. 3(b) is predominantly induced by collisions with ground state \(H_2O\) and not \(I_2(X)\).

This is not surprising as the measured rate constants for \(E(v = 8, J = 55)\) are \(0.2 \times 10^{-10}\) and \(33 \times 10^{-10}\) molecules\(^{-1}\) cm\(^3\) s\(^{-1}\) for collisional transfer by \(I_2(X)\) and \(H_2O\), respectively.\(^1\)

A further amplification of two segments of the FT spectrum, together with the assignments of the \(D_0 u^+ (3P_2) \rightarrow X_0 u^+\), rovibrionic transitions, determined from published molecular constants,\(^5,9\) is shown in Fig. 4. It can be seen that the intensity of the emission from pairs of levels populated by \(\Delta J = \pm 1\), \(E_0 g^+ (3P_2) \rightarrow D_0 u^+ (3P_2)\), collisional transfer varies enormously. For example, emission is seen almost exclusively from \(J = 97\) of \(D(v = 10)\); for \(D(v = 11)\), emission from \(J = 97\) is approximately three times more intense than from \(J = 99\) and for \(D(v = 12)\), the emissions from \(J = 97\) and \(J = 99\) have approximately the same intensity. The spectra in Figs. 4(a) and 4(b) from the same upper state exhibit the same intensity patterns to adjacent vibrational levels in the ground state.

To a first approximation, the same marked branch imbalance is true for all of the pairs of \(D_0 u^+ (3P_2)\) state rotational levels that we conclude are populated by long-range collisional transfer from all of the other \(E_0 g^+\) state vibrational levels that were excited, namely, \(E(v = 7, 5, 3, 1, 0)\). An example of the \(D_0 u^+ (3P_2) \rightarrow X_0 u^+\) emission following excitation of \(E(v = 7, J = 31)\) is shown in Fig. 5 and the intensity data are summarized in Table I.

The term values of the rotational levels relevant to the high-resolution spectrum are shown in Table I. The energy changes, \(\Delta E(I_2)\), associated with collisional transfer between the ion-pair states are also shown and can be compared with the energy changes, \(\Delta E(H_2O)\) associated with intense rotational transitions in \(H_2O\) at room temperature.\(^1\) Randall et al.\(^1\) tabulated the intensities of the lines, in a scale of 0.1–300, observed between 75 and 550 cm\(^{-1}\) in the absorption spectrum of \(H_2O\). In the present paper, intense transitions are arbitrarily chosen to have intensities \(\geq 50\). The values for \(\Delta E(H_2O)\) of \(\leq 75\) cm\(^{-1}\) are calculated from the

FIG. 2. Low-resolution emission between 270 and 333 nm following the excitation of \(E(v = 8, J = 55)\) recorded (a) immediately after refilling the cell, “dry,” and (b) with 0.03 Torr of \(H_2O\) added. The intensities of the spectra are normalized to the most intense peaks.

FIG. 3. Expansions of the low-resolution emission between 322 and 332 nm following the excitation of \(E(v = 8, J = 55)\); (a) “dry” and (c) with 0.03 Torr of \(H_2O\) added. The “wet,” high-resolution FT emission following excitation of \(E(v = 8, J = 98)\) is shown in (b). The intensities of the spectra are normalized to the most intense peaks.
FIG. 4. Two segments of the FT $D_0 u^+(3 P_2) \rightarrow X_0 g^+$ emission following the excitation of $E(v = 8, J = 98)$. The labels identify vibrational quantum numbers in the $(D,X)$ bands and rotational numbering in the $D_0 u^+(3 P_2)$ state.

rotational energy levels$^{11}$ for $J_\tau' \rightarrow J_\tau''$ transitions where $J_\tau'$ has a rotational energy $\leq 500$ cm$^{-1}$ and only those for which $\Delta J = 0, \pm 1$, $\Delta \tau = 0, \pm 2$ as these characterize the strongest transitions.

The energy mismatches, $\Delta E(I_2) - \Delta E(H_2O)$, explain, at least semi-quantitatively, the observed emission intensities.

FIG. 5. Part of the FT $D_0 u^+(3 P_2) \rightarrow X_0 g^+$ emission following the excitation of $E(v = 7, J = 31)$. The labels identify vibrational quantum numbers in the $(D,X)$ bands and rotational numbering in the $D_0 u^+(3 P_2)$ state.

### Table I

<table>
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<th>$v$</th>
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<th>$\Delta E(H_2O)$/cm$^{-1}$</th>
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<td>1</td>
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(i) $E(v = 8, J = 98; 42 341.0$ cm$^{-1}$); see Fig. 4

(ii) $E(v = 7, J = 31; 42 073.2$ cm$^{-1}$); see Fig. 5

TABLE I. The term values, relative to $X(v = 0, J = 0)$, of rovibronic levels of the $D_0 u^+ (3 P_2)$ state (Ref. 9), the energy change, $\Delta E(I_2)$, associated with collisional transfer from various rovibronic levels of the $E_0 g^+ (3 P_2)$ state (Ref. 10), the relative intensity of the emission from the level populated, $I$, and the energy change, $\Delta E(H_2O)$, associated with the most intense rotational transitions in the ground state of $H_2O$ (Ref. 11). Only $H_2O$ transitions where the energy mismatch, $\Delta E(I_2) - \Delta E(H_2O)$, $\leq 5$ cm$^{-1}$ are included; those where it is $\leq 2$ cm$^{-1}$ are shown in bold type. The values for $\Delta E(H_2O)$ of $\geq 75$ cm$^{-1}$ are taken from the experimental data (Ref. 11), while those of $\leq 75$ cm$^{-1}$ are calculated from the rotational energy levels (Ref. 11) for $J_\tau' \rightarrow J_\tau''$ transitions where $J_\tau'$ has a rotational energy $\leq 500$ cm$^{-1}$ and only those for which $\Delta J = 0, \pm 1$ and $\Delta \tau = 0, \pm 2$, as these characterize the strongest transitions.
For example; following excitation of $E(v = 8, J = 98)$, for $D(v = 10)$, the collisional transfer to $J = 97$ is enhanced by one rotational transition in $\text{H}_2\text{O}$ with an energy mismatch of $<2\text{ cm}^{-1}$ and another of $<5\text{ cm}^{-1}$, but there is no such transition in $\text{H}_2\text{O}$ that can enhance the transfer to $J = 99$. Hence, almost no emission is observed from $J = 99$ in the (10,71) vibronic band in Fig. 4(a). From a similar consideration of the energy mismatches involved, it can be predicted that for $D(v = 11)$, the transfer to $J = 97$ should be enhanced more than to $J = 99$ and for $D(v = 12)$ the two transitions should be equally enhanced. The intensities observed in the (11,71), (11,72) (12,72), and (12,73) vibronic bands are consistent with these predictions. It would be a remarkable coincidence, if the relative intensities of the ten pairs of $P/R$ lines studied could be predicted as accurately as illustrated in Table I in case they were being determined by anything other than resonant collisions with $\text{H}_2\text{O}$. The same criteria can be used to explain the intensities observed in all of the spectra obtained by exciting various $E(v, J)$ levels, including $E(v = 7, J = 31)$, shown in Fig. 5.

On the basis of energy mismatches alone, it is predicted that there should also be effective transfer to $D(v = 13)$ from $E(v = 8)$. However, it was shown that the probability of a particular transition is also dependent on the Franck-Condor (FC) overlap between the initial and final states. The FC overlaps between $E(v = 8)$ and $D(v = 10, 11, 12, 13)$ are 0.344, 0.210, 0.021, and $<$0.001, respectively, and consequently, the transition probability to $D(v = 13)$ is very small.

There is another apparent anomaly in the values for the $E(v = 1) \rightarrow D(v = 2)$ collisional transfer, shown in Table I(v). Although some $\Delta J = +1$ collisional transfer is observed, no $\text{H}_2\text{O}$ transitions lie inside the 5 cm$^{-1}$ window for $\Delta E(\text{I}_2) - \Delta E(\text{H}_2\text{O})$ for the transition. However, there are two $\text{H}_2\text{O}$ transitions with mismatches of 5.2 and 5.4 cm$^{-1}$, just outside the window, and this illustrates that the window is only used as a guide to the rate of the transfer and is not a threshold.
It should be emphasized that none of the six $E_0 g^+ (^3 P_2)$ state vibrational levels excited are in near-resonance with a $D_0 u^+ (^3 P_2)$ state level, and hence, the transfer by $I_2(X)$ will only involve short-range, non-resonant collisions. Under these conditions, the rate constant for transfer by $I_2(X)$ will be two orders of magnitude less than for transfer by H$_2$O.

A further illustration of how difficult it is to eliminate H$_2$O from these $I_2$ experiments is provided by a comparison of spectra recorded before and after the rigorous drying measures described above for the FT experiments were applied. An example of spectra recorded following excitation of $E(v = 1, J = 35)$ is shown in Figs. 6 and 7. The spectra, normalized to the $E_0 g^+ (^3 P_2) \rightarrow A_1 u$ emission, recorded before and after the drying are shown in Figs. 6(a) and 6(b), respectively. Clearly, the relative intensity of the collision-induced $D_0 u^+ (^3 P_2) \rightarrow X_0 g^+$ emission has greatly been reduced by the drying.

An enlargement of one segment of these spectra is shown in Figs. 7(a) and 7(b), the latter being a reproduction of part of Fig. 3c of Ref. 2. Although it might be argued that there is a slight equalization of the intensities of the rotational lines in the “dry” spectrum, they are clearly still irregular, and hence, it has to be concluded that, in this example, collisions with H$_2$O are still having a significant effect on the $E_0 g^+ (^3 P_2) \rightarrow D_0 u^+ (^3 P_2)$ transfer, even after initial attempts at drying. At the time when the experiments were carried out in Lyon, the magnitude of the influence that H$_2$O can have on the spectra was not known and the effectiveness of the removal of “impurities” was judged solely on the minimization of the collision-induced $D_0 u^+ (^3 P_2) \rightarrow X_0 g^+$ emission. In the Edinburgh experiments, we had a second diagnostic for a truly “dry” spectrum (Figs. 2(a) and 3(a)), namely, the relative contributions of the emitting $D_0 u^+ (^3 P_2)$ state vibrational levels as outlined above. It is possible that these conditions were never achieved in Lyon. Were the spectrum in Fig. 7(b), if not that in 7(a), to be caused predominantly by collisions with $I_2(X)$ this would mean that such collisions result in the same irregular intensities of rotational lines that are characteristic of collisions with H$_2$O which would be a remarkable coincidence.

However, as the pressure of H$_2$O decreases, a point will be reached when short range non-resonant collisional transfer by $I_2(X)$ will become competitive with long-range resonant transfer by H$_2$O. If non-resonant collisions with $I_2(X)$ have collision rates for $\Delta J = +1$ transitions that are the same as those for $\Delta J = -1$ transitions, as the conditions become “drier,” the imbalance in the intensities of the emission from the collisionally populated pairs of lines will begin to diminish. This effect may explain any equalization of the intensities observed in Fig. 7(b) and also the rare minor inconsistencies in the intensities shown in Table I, e.g., the intensity of the $E(v = 3, J = 72) \rightarrow D(v = 4, J = 71)$ transfer seems to be larger than expected.
FIG. 8. Part of the FT $E_0 g^+ (3P_2)$ $\rightarrow$ $A_1 u$ emission following excitation of (a), $E(v=7, J=31)$, (b), $E(v=3, J=72)$, and (c), $E(v=8, J=98)$. 

B. $R:Q:P$ branch ratios in $E_0 g^+ (3P_2)$ $\rightarrow$ $A_1 u$ emission

An expansion of part of the $E_0 g^+ (3P_2)$ $\rightarrow$ $A_1 u$ emission following excitation of $E(v=7, J=31)$ is shown in Fig. 8(a). It can be seen that the $R:Q:P$ branch ratios are not 1:2:1 as expected, with the $P$ branch ($J=31 \rightarrow 32$ emission line) being significantly more intense than the $R$ branch. This phenomenon can be observed in the spectra shown by Inard et al. but was not commented on by the authors. In all of the spectra that we recorded, the trend increases with $J$; two examples are shown in Figs. 8(b) and 8(c) to the extent that the $P$ branch is the most intense in the emission from $J=98$. Unfortunately, we do not have a complete series of spectra that shows how the $R:Q:P$ branch ratios vary with $v$ and $J$. In contrast, the $R:Q:P$ branch ratios in the $E_0 g^+ (3P_2)$ $\rightarrow$ $C_1 u$ emission have the expected 1:2:1 values as can be seen from the spectra in Fig. 9.

Similar anomalous line intensities were reported by Perrot et al. in fluorescence excitation spectra recorded by populating the $\beta_1 g (3P_2)$ state via a $\Delta \Omega = 1$ transition from the $B_0 u^+$ state. The spectra also showed inequalities in the $R:P$ branch ratios that increased with $J$ but were almost invariant with $v$.

The observations were explained by vibrationally induced coupling between members of the close-lying $E_0 g^+ (3P_2)$ and $\beta_1 g (3P_2)$ vibrational manifolds. Interference between the parallel and perpendicular transitions depends on the relative phases of the two transition amplitudes. These change between the $P$ and $R$ branches, resulting in a departure of the $R:P$ branch ratio from unity.

In the experiments of Perrot et al. the $\beta_1 g (3P_2)$ state is directly accessed and each $v_\beta$ level contains a small $E_0 g^+ (3P_2)$ state component. In the present work, vibrational levels of the $E_0 g^+ (3P_2)$ state are directly accessed and these contain a small $\beta_1 g (3P_2)$ component. In both cases, the $\Omega$-uncoupling operator,

$$V = -\frac{\hbar^2}{\mu R^2} \mathbf{J} \cdot (\mathbf{L} + \mathbf{S}),$$

is responsible for $E/\beta$ mixing and the treatment of Perrot et al. is unchanged. A key requirement is that the transition dipole between the minor electronic component in the upper (lower) state to the major component in the lower (upper) state is much stronger than the transition dipole between the two major components. In the experiments of Perrot et al., the strong transition was $E_0 g^+ (3P_2) \rightarrow B_0 u^+$ and the weak transition was $\beta_1 g (3P_2) \rightarrow B_0 u^+$; in the present experiments, the strong transition is $\beta_1 g (3P_2) \rightarrow A_1 u$ and the
weak transition is \( E_{0g}^+ (3P_2) \rightarrow A1_u \). The extent of mixing is very small and the term values are not measurably perturbed. In principle, a given vibrational level of the \( E_{0g}^+ (3P_2) \) state, \( v_E \), is mixed with the complete manifold of \( v_\beta \) levels,

\[
|\Omega, v_E\rangle = |0, v_E\rangle + \sum_{v_\beta} \alpha(v_E, v_\beta)|1, v_\beta\rangle,
\]

with mixing coefficients \( \alpha(v_E, v_\beta) \) given in 1st order by

\[
\alpha(v_E, v_\beta) \approx -J_B \langle 0^+_g | L_\pm + S_\pm | 1_g \rangle / E(v) / E(v, J_\beta) (v_E | v_\beta),
\]

where any \( J \)-dependence of the FC factor \( \langle v_E, v_\beta \rangle \) has been ignored and the vibronic levels are assumed to have the same \( B \) value. Then, if the pure precession model is used for the ion-pair states, which must be in the same tier, Perrot et al.\(^5\) find

\[
\langle 0^+_g | L_\pm + S_\pm | 1_g \rangle = 12.\tag{4}
\]

The sign of \( \alpha(v_E, v_\beta) \) depends on the sign of the denominator in Eq. (3). If the parent \( v_\beta \) level lies exactly mid-way between adjacent \( v_\beta \) levels, \( \alpha(v_E, v_\beta - 1) \) and \( \alpha(v_E, v_\beta) \) would have opposite signs (disregarding any difference in FC factors and ignoring sums over more distant vibrational levels). Their contribution to emission from the mixed state to a common lower electronic state would then cancel. In the present case, there is an imbalance in contributions from higher and lower energies to the sum over \( v_\beta \) in Eq. (2) and the effect is seen. For instance, for \( v_E = 8 \), the two adjacent \( v_\beta \) levels lie, respectively, 61 cm\(^{-1}\) below and 38 cm\(^{-1}\) above. Substituting these energy differences into Eq. (3) with \( B = 0.02 \text{ cm}^{-1} \), \( J = 110 \), and \( (v_E, v_\beta) = 0.1 \) gives \( \alpha(8, v_\beta - 1) = 3.9 \times 10^{-2} \) and \( \alpha(8, v_\beta) = 6.3 \times 10^{-2} \). Since the relative intensities of the \( E_{0g}^+ (3P_2) \rightarrow A1_u \) and \( \beta 1_g (3P_2) \rightarrow A1_u \) systems is \( \approx 10^{-2}:1 \),\(^{13} \) the two transition amplitudes from the mixed upper state have comparable strength and appreciable interference results.

The value \( E(v_E) - E(v_\beta) \) only varies slightly over the \( (v, J) \) range studied. The two adjacent \( v_\beta \) rotationless levels lie 70–61 cm\(^{-1}\) below and 32–38 cm\(^{-1}\) above the rotationless levels of \( v_E = 0–8 \), respectively. In addition, the difference between the rotational energy for \( J = 100 \) in the coupled levels only varies by \( \sim 2 \text{ cm}^{-1} \) over the same range of vibrational levels.

For the \( E_{0g}^+ (3P_2) \rightarrow Cl_1 \) system shown in Fig. 9(b), the \( R:Q:P \) branch ratios are 1:2:1 as expected. Here, the transition dipole between the minor electronic component in the upper state to the major component in the lower state, \( \beta 1_g (3P_2) \rightarrow Cl_1 \), is \( \approx 0 \),\(^{13} \) hence no interference results.

It is also possible that the lower state is subject to \( \Omega \)-uncoupling. In the present case, the \( A1_u \) state would have to mix with a valence \( 0_u^+ \) state in order for the minor component to have a large transition dipole to the dominant component of the upper \( E_{0g}^+ (3P_2) \) state. However, the lowest valence \( 0_u^+ \) (the \( B \) state) lies \( \sim 4000 \text{ cm}^{-1} \) above the \( A1_u \) state and the mixing is negligible.

IV. CONCLUSIONS

Using high-resolution FT spectroscopy, we have been able to resolve rotational structure in the \( DO_u^+(3P_2) \rightarrow X0_u^+ \) emission following collisional transfer from the \( E_{0g}^+ (3P_2) \) state of \( I_2 \). The ratio of the intensities of the emission from the two rotational levels populated by \( \Delta J = \pm 1 \) collisional transfer varies enormously as the vibrational numbering in the \( E_{0g}^+ (3P_2) \) and \( DO_u^+(3P_2) \) states changes. By comparing “wet” and “dry” spectra, we have concluded that the observed intensities are consistent with the transfer being dominated by long-range, resonant collisions with residual \( H_2O \) which proves to be unexpectedly difficult to remove from \( I_2 \). Unequal \( R:P \) branch ratios in the direct \( E_{0g}^+ (3P_2) \rightarrow A1_u \) emission have been shown to result from mixing of the \( E_{0g}^+ (3P_2) \) and \( \beta 1_g (3P_2) \) states via \( \Omega \)-uncoupling.

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\(^{3}\)V. A. Alekseev, Opt. Spectrosc. 110, 335 (2011).
\(^{7}\)P. Luc, J. Mol. Spectrosc. 80, 41 (1980).