Rovibrational Resonance Effects In Collision-Induced Electronic Energy Transfer: I2(E,v=0-2)+CF4

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Rovibrational resonance effects in collision-induced electronic energy transfer: \( \text{I}_2(\text{E}, \nu=0-2) + \text{CF}_4 \)

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Collisions of \( \text{I}_2 \) in the \( E(0^+_r) \) electronic state with \( \text{CF}_4 \) molecules induce electronic energy transfer to the nearby \( D \), \( \beta \), and \( D' \) ion-pair states. Simulations of dispersed fluorescence spectra reveal collision-induced electronic energy transfer rate constants and final vibrational state distributions within each final electronic state. In comparison with earlier reports on \( \text{I}_2(\nu_r=0-2) \) collisions with He or Ar atoms, we find markedly different dynamics when \( \text{I}_2 \), excited to the same rovibrionic states, collides with \( \text{CF}_4 \). Final vibrational state distributions agree with the associated Franck-Condon factors with the initially prepared state to a greater degree than those found with He or Ar collision partners and suggest that internal degrees of freedom in the \( \text{CF}_4 \) molecule represent a substantial means for accepting the accompanying loss of \( \text{I}_2 \) vibronic energy. Comparison of the \( E \rightarrow D \) transfer of \( \text{I}_2 \) excited to the \( J=23 \) and \( J=55 \) levels of the \( \nu_r=0 \) state reveals the onset of specific, nonstatistical dynamics as the available energy is increased above the threshold for excitation of the low frequency \( \nu_3 \) bending mode of \( \text{CF}_4 \).

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I. INTRODUCTION

Over the past decade a number of studies have demonstrated the rich electronic energy transfer dynamics that accompany collisions of diatomic iodine prepared in an ion-pair electronic state with atomic, diatomic, and polyatomic collision partners.\(^1\)-\(^{13}\) The initial work in this field was reported by Ubachs et al.\(^1\) and Teule et al.,\(^2\) and considered collisions of ion-pair state excited \( \text{I}_2 \) with \( \text{I}_2(X) \). More recently, reports from this laboratory\(^3\)-\(^{5}\) and the experiments of Pravilov and co-workers\(^6\)-\(^9\) have focused on studies involving a variety of collision partners interacting with \( \text{I}_2 \) prepared in the \( E(0^+_r) \) electronic state in one of a range of initial vibrational levels. These studies fall into two general categories: Pravilov and co-workers have examined the collision-induced electronic energy transfer dynamics that result from collisions of \( \text{I}_2 \) prepared in high vibrational levels (\( \nu=8-47 \)) of the \( E \) electronic state\(^6\)-\(^9\) [or most recently, a range of vibrational levels in the higher energy \( f(0^+_r) \) ion-pair state\(^10\)-\(^{11}\)] with the collision partners He, Ar, \( \text{I}_2(X) \), \( \text{N}_2 \), and \( \text{CF}_4 \). In this laboratory, our focus has been on preparing low vibrational levels of the \( E \) electronic state and using a narrower range of collision partners—\( \text{I}_2(X) \) and rare gas atoms.\(^3\)-\(^5\)

In Fig. 1, the potential energy curves for the lowest energy region of the so-called first tier of ion-pair states in \( \text{I}_2 \) are displayed. These states all correlate with the separated ion limit \( \text{I}^+(2P_J) + \text{I}^- (1S_0^-) \) and are characterized by a large dissociation energy (\( \approx 31000 \text{ cm}^{-1} \)).\(^{14}\) Note that a total of six ion-pair states exists with \( T_e \) values that lie within 1500 \text{ cm}^{-1} \) of one another. For these first-tier states, ease of experimental preparation in double resonance experiments \((E \leftarrow B \leftarrow X)\) has focused the previous laboratory experiments exclusively on the collision dynamics that result following excitation of the \( E \) ion-pair state.\(^3\)-\(^9\),\(^12\) All of these previous investigations reveal the importance of \( E \rightarrow D \) collision-induced electronic energy transfer.\(^12\) Experiments in this laboratory have also demonstrated the presence of both \( E \rightarrow D' \) and \( E \rightarrow \beta \) energy transfer following excitation of \( \text{I}_2 \) to low vibrational levels in the \( E \) state when He or Ar is the collision partner.\(^3\),\(^5\) The major focus of all the investigations—at both high and low levels of vibrational excitation in the \( E \) state—has been on gaining a complete understanding of the propensity rules that govern the distribution of vibrational energy in the final electronic state(s).

Comparison of these studies reveals that increasing the vibrational energy in the \( E \) electronic state not only increases the overall cross section for electronic energy transfer but also alters the trends in the propensity rules for collision-induced vibrational populations. For example, for rare gas collision partners, at low vibrational energies \((\nu_r=0-2)\), Franck-Condon factors compete with energy gap effects in determining the \( D \) state vibrational distributions.\(^3\),\(^5\) At higher vibrational levels, the general trend is that energy gap effects are dominant, with the \( D \) state vibrational distributions having an almost symmetric appearance centered at a \( D \) state vibrational level that is nearly resonant with the initially prepared \( E \) state level.\(^5\),\(^8\)-\(^{10}\) This variation in behavior with initial vibrational level is attributed to a significant broadening of the distribution of Franck-Condon factors between \( E \) and \( D \) state vibrational levels at high values of \( \nu_r \).\(^12\) Thus, significant impediments to the population of near resonant levels due to very unfavorable vibrational wave function overlaps are removed at high values of \( \nu_r \).

As noted previously, Pravilov and co-workers extended...
their work on the collision dynamics of high vibrational levels of the \(E\) state by examining collisions with a polyatomic molecule, \(\text{CF}_4\). The distribution of population in the vibrational levels in the \(D\) electronic state that results from electronic energy transfer was found to be multimodal. Significant population was found in the \(D\) state levels that are near resonant with the initially prepared \(E\) state level, just as observed for rare gas collision partners. Unique to the case of \(\text{CF}_4\) collisions, however, was the observation of population in \(D\) state levels with energy gaps that coincided with the vibrational frequencies of ground electronic state \(\text{CF}_4\). These results are consistent with a model in which vibrational excitation of \(\text{CF}_4\) serves to minimize the amount of \(\text{I}_2\) vibrational energy released to relative translation of the recoiling species. A similar mechanism was implicated in early work on electronic energy transfer in collisions of \(\text{I}_2\).

The intriguing observation of nearly resonant energy transfer into the \(\text{CF}_4\) internal degrees of freedom provides the motivation for the work described in this manuscript. Our previous studies have demonstrated that collisions involving \(\text{I}_2\) in the lowest vibrational levels of the \(E\) state result in electronic energy transfer pathways that are distinct from those observed at higher vibrational energies. At the same time, the relative simplicity of the spectroscopy of the ion-pair states for the lowest vibrational levels allows for a somewhat more detailed analysis of the processes observed. In the sections that follow, we present the results of our investigations that strongly suggest that resonant energy transfer into the energetically available vibrational states of \(\text{CF}_4\) is a universal feature of the \(\text{I}_2(E) + \text{CF}_4\) collision dynamics.

II. EXPERIMENT

Our experimental strategy has been used in previous work from our laboratory and is described in detail elsewhere. Briefly, we prepare single rovibrational levels of the \(E\) ion-pair state of iodine through double resonance excitation. For all excitation schemes, a Nd\(^{3+}:\text{YAG}\) (yttrium aluminum garnet) pumped dye laser system (Continuum Lasers YG580/TDL-50, \(\sim 0.15 \text{ cm}^{-1}\) bandwidth) provides light resonant with a \(B \leftrightarrow X\) transition (\(\lambda_1\)), and a \(\text{N}_2\)-pumped dye laser system (Laser Photonics UV24/DL-14P, \(\sim 0.25 \text{ cm}^{-1}\) bandwidth) provides light resonant with the corresponding \(E \leftrightarrow B\) transition (\(\lambda_2\)). We prepare electronically excited iodine with 0, 1, or 2 quanta of vibrational excitation in either the \(J_E=23\) or \(J_E=55\) rotational level. Excitation schemes along with \(\lambda_1\) and \(\lambda_2\) values are shown in Table I.

Excitation of \(\text{I}_2\) vapor occurs in a glass and fused silica cell, equipped with Brewster’s angle laser inlet and exit windows. In the experiments reported, we use 40 mTorr \(\text{I}_2\) vapor (Aldrich, 99.999%) and a variable pressure of \(\text{CF}_4\) (Aldrich, 99.9%), typically 200–1000 mTorr. Double resonance excitation results in intense \(E \leftrightarrow B\) emission between 415 and 435 nm, as well as a number of weaker features, depending on the sample pressure conditions. We measure \(\text{I}_2\) fluorescence after dispersion through a 0.5 m focal length scanning monochromator (Instrumants SA 500M). The exit slit of the monochromator has been replaced with a charge-coupled device (CCD) camera (Princeton Instruments LN/CCD-2500PB); we record a total spectral width of \(\sim 24 \text{ nm}\) in a single exposure.

We simulate the dispersed fluorescence spectra to extract the distribution of electronic and vibrational states populated through collision-induced electronic energy transfer. Spectroscopic constants were taken from the literature for the electronic ground state \(X(0^+_g)^{15}\), excited valence states \(A'(2_u)^{16}\), \(A(1_u)^{17}\), and \(B(0_u)^{18}\), and ion-pair states \(D'(2_u)^{19}\), \(\beta(1_g)^{20}\), \(D(0_u)^{21}\), and \(E(0_u)^{22}\). We calculate Franck-Condon factors through computer code based on the Numerov method,\(^23\) which calculates numerical wave functions for a given one-

<table>
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<th>(E) state (\nu_E)</th>
<th>(J_E)</th>
<th>(\nu_B, \nu_X)</th>
<th>(\Delta J(J_E))</th>
<th>(\lambda_1) (nm)</th>
<th>(\nu_E, \nu_B)</th>
<th>(\Delta J(J_B))</th>
<th>(\lambda_2) (nm)</th>
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<td>(0, 20)</td>
<td>(P(24))</td>
<td>426.29</td>
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<td>(P(56))</td>
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<td>(21, 0)</td>
<td>(R(55))</td>
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<td>(1, 21)</td>
<td>(P(56))</td>
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<td>(2, 21)</td>
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<td>424.53</td>
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</table>
III. RESULTS AND DISCUSSION

Dispersed fluorescence of I$_2$ after excitation to the E ion-pair state shows intense $E \rightarrow B$ transitions along with weaker $E \rightarrow A$ and $E \rightarrow B''(1_u)$ bands. The top half of Fig. 2 shows the region of the fluorescence spectrum from 40 mTorr I$_2$ excited to the state ($v_E=0, J_E=55$) including the $E \rightarrow A$ (332–338 nm) and $E \rightarrow B''$ (345–351 nm) spectral features. There are additional weak features between 300 and 330 nm assigned to $D \rightarrow X$ emission. Here, the $D$ state is populated through collisions with ground state iodine molecules, I$_2$(E)+I$_2$(X). In the following analysis of $E \rightarrow D$ energy transfer through collisions of I$_2$ with CF$_4$, we have subtracted the relatively weak $D \rightarrow X$ emission seen here for a sample of pure I$_2$.

In similar behavior to collisions with He and Ar, collisions with CF$_4$ induce transitions in I$_2$(E) to the lower energy ion-pair states $D'$, $\beta$, and $D$. Upon addition of CF$_4$ gas to our sample cell, fluorescence due to collision-induced energy transfer dominates the emission spectrum between 300 and 350 nm. The bottom half of Fig. 2 shows the fluorescence spectrum from a cell filled with 40 mTorr I$_2$ and 250 mTorr CF$_4$ in which the I$_2$ has been excited to the state ($v_E=0, J_E=55$). As indicated in Fig. 2, the spectral features of interest include $D(0_u^+) \rightarrow X(0_u^+)$ emission between 305 and 330 nm and the overlapping $\beta(1_u^+) \rightarrow A(1_u)$ and $D'(2_u) \rightarrow A'(2_u)$ emissions between 334 and 346 nm. We find the fluorescence intensity from the ion-pair states $D'$, $\beta$, and $D$ to be linear with the pressure of CF$_4$ for all experiments described herein, indicative of single collision conditions.

Collisions of I$_2$ in low vibrational levels of the E state with CF$_4$ molecules induce transitions into a range of vibrational and rotational levels in the $D$, $\beta$, and $D'$ electronic ion-pair states. To extract the distribution of vibrational levels populated through collision-induced energy transfer in a given electronic state, we perform spectral simulations of the fluorescence spectra, where the populations of the $v=0$–7 vibrational levels in the given electronic state are variable parameters.

A. $E \rightarrow D$ transfer

The $D \rightarrow X$ emission recorded after excitation to the ($v_E=0, J_E=23$) level of a 40 mTorr I$_2$ sample with 517 mTorr CF$_4$ is shown in the bottom half of Fig. 3, where each peak in this spectrum corresponds to a particular vibrionic transition. Each peak is slightly asymmetric with a more gradual tail toward the long-wavelength side. We attribute the asymmetry of these peaks to rotational relaxation that accompanies the collision-induced electronic energy transfer process. As we are unable to resolve the rotational fine structure in our fluorescence spectra, our bands appear asymmetric, where fluorescence from states with $J_D$ larger than the initial $J_E$ occurs at longer wavelengths than the peak transition.

To describe the rotational population of the $D$, $\beta$, and $D'$ states in our fluorescence spectrum simulations, we use a statistical exponential-power gap model that is frequently used for collision-induced rotational relaxation:

$$P(J_f) \propto \frac{(2J_f+1)}{(2J_i+1)} \left( \frac{\Delta E_{\text{rot}}}{B_p} \right)^{-\alpha} \exp(-\theta\Delta E_{\text{rot}}).$$

$P(J_f)$ is the probability of transfer to the rotational state $J_f$, $J_i$ is the rotational state populated in the absence of rotational relaxation, $J_{\text{rel}}$ is the smaller of $J_f$ and $J_i$, $B_p$ is the rotational constant for the vibrational state in question, and $\Delta E_{\text{rot}}$ is the difference in energy between the states $J_f$ and $J_i$. The parameters $\alpha$ and $\theta$ are adjusted to best match the experimental spectrum. Because the $E \rightarrow D$ transfer involves a change of inversion symmetry in the electronic wave function, conservation of nuclear spin symmetry dictates that only even values of $J_D$ are populated in the $D$ state when an odd value of $J_E$ is prepared in the $E$ state. Correspondingly, we assume that $J_D=22$ or $J_D=54$ rotational level is popu-
lated in the $D$ state in the absence of rotational relaxation when we prepare $J_D = 23$ or $J_D = 55$, respectively. We find the vibrational distributions in the $D$, $\beta$, and $D'$ states discussed below to be relatively insensitive to the values of $\alpha$ and $\theta$, and use $\alpha = 0.6$ and $\theta = 0.002$ cm for all vibrational levels in all of our simulations. These values are in no way unique—we do not have the resolution to definitively comment on the relative accuracy of this statistical rotational energy redistribution. We simply find this model to be useful in accounting for the innate asymmetry of our spectral bands.

Our simulation of the $D \rightarrow X$ emission following excitation to $(v_\alpha = 0, J_E = 23)$ is shown in the top half of Fig. 3 and faithfully reproduces all spectral features and band shapes. The population distribution of $D$ state vibrational levels, $P(v_D)$, averaged over spectra obtained with six different pressures of CF$_4$, is shown in Table II. These data show a clear preference for the population of $v_D = 0$. Of the collisions with CF$_4$ that induce transfer to the $D$ state, over 75% of them cause transfer to the ground vibrational level. Indeed, the trend in transfer probability for the first eight vibrational levels of the $D$ state reflects the trend in Franck-Condon factors between each $v_D$ and the initially prepared state $(v_\alpha = 0, J_E = 23)$, as listed in Table II. This is a markedly different trend in $P(v_D)$ than that previously reported from our laboratory on collisions of I$_2$(v$_\alpha = 0)$ with He or Ar atoms, and in which the trend was best described as a balance between pathways that maximized Franck-Condon overlap of the initial and final vibrational wave functions and those that also minimized the energy gap.

2. $v_\alpha = 0, J_E = 55$

Following excitation of a 40 mTorr I$_2$ and 1004 mTorr CF$_4$ sample to the state $(v_\alpha = 0, J_E = 55)$, a rotational level $\sim 50$ cm$^{-1}$ higher in energy than $(v_\alpha = 0, J_E = 23)$, we observe a $D \rightarrow X$ emission that is superficially very similar to that shown in Fig. 3. Consistent with this result, the $D$ state vibrational distributions following excitation of $(v_\alpha = 0, J_E = 23)$ and $(v_\alpha = 0, J_E = 55)$ are roughly the same (Table II). We observe, however, that each $D \rightarrow X$ vibronic transition has a substantially increased spectral width following excitation of $(v_\alpha = 0, J_E = 55)$. We attribute this width to a larger distribution of rotational states that accompanies the collision-induced electronic energy transfer.

Our best fit using the statistical exponential-power gap model to simulate this emission spectrum reproduces the overall intensities of the $D \rightarrow X$ transitions, but as shown in Fig. 4(a), the width of each vibronic transition in the experimental spectrum is considerably larger than that produced by our rotational relaxation model. Adjusting the values of $\alpha$, $\beta$, or $J_r$ does not significantly improve the quality of our fit. Here we see that our statistical function for the rotational distribution does a good job of recovering the long-wavelength, or high $J_D$, side of each vibronic transition. It is only those peaks corresponding to emission from $v_D = 0$ that contain additional low $J$ (short-wavelength) emission intensity. We interpret the short-wavelength intensity to be a signature of additional nonstatistical dynamics in the collision-induced electronic energy transfer that specifically populates low $J$ rotational levels of the $v_D = 0$ vibrational level, dynamics that are absent in transfer from $(v_\alpha = 0, J_E = 23)$.

Following the results of I$_2$(v$_\alpha = 8–47$)+CF$_4$ collision-induced electronic energy transfer experiments by Pravilov and co-workers, we interpret our results as a resonant excitation of CF$_4$ vibrational modes to explain these anomalous nonstatistical dynamics. An energy level diagram of the relevant rotational levels of $v_D = 0$ and $v_\alpha = 0$ in I$_2$, including energy differences (cm$^{-1}$), is shown in Fig. 5. Because the rotational constants for the $v = 0$ levels of the $D$ and $E$ states do not differ significantly, the energy gaps for energy transfer pathways that minimize $\Delta(J_I - J_D)$ are relatively independent of $J_E$ and are equal to $\sim 389$ cm$^{-1}$. Conversely, the transitions that involve that largest possible loss in iodine rovibrionic energy, i.e., those terminating at $(v_\alpha = 0, J_D = 0)$, are significantly different: 399.5 cm$^{-1}$ from $(v_\alpha = 0, J_E = 23)$ and 449.8 cm$^{-1}$ from $(v_\alpha = 0, J_E = 55)$.

The lowest energy vibrational frequency of CF$_4$ is the $\nu_2$ bending mode at 435.399 cm$^{-1}$. Therefore, in the $v_\alpha = 0$ state of CF$_4$, the $\nu_2$ mode is a bound state at $0.005$ cm$^{-1}$ and can not contribute to energy transfer.
→ ν2 = 0 energy transfer channel, there is sufficient available energy in the J_E = 55 experiment to selectively excite the ν2 mode of CF4 (assuming a large value of ΔJ), while there is an insufficient amount in the J_E = 23 experiment. As shown in Fig. 5, it is the (ν_E=0, J_E=55) → (ν_E=0, J_D=26) energy transfer channel of I2 that has an energy gap that is closest to the excitation energy of ν2 in CF4, (0, 1, 0, 0) ← (0, 0, 0, 0). Figure 5 shows an energy difference of 434.99 cm⁻¹, corresponding to excitation of CF4 with J = 30, the most populated rotational level at room temperature. The slight shift from the fundamental ν2 energy originates from the difference in rotational constants in the ground and excited ν2 states of CF4.⁵⁶

To test this resonant nonstatistical model, we add additional fluorescence from the state (ν_E=0, J_D=26) in our D → X emission simulation. The results of our best fit are shown in Fig. 4(b). As can be clearly seen, emission from (ν_E=0, J_D=26) exactly matches the rise of the short-wavelength side of each peak corresponding to transitions from ν_E=0. We surmise that this extra intensity is evidence of selective E → D energy transfer that is resonant with excitation of the lowest energy vibrational level in CF4. This channel is absent in energy transfer from (ν_E=0, J_E=23) because of insufficient available energy. Averaged over six different CF4 pressures, the intensity of the emission from (ν_E=0, J_D=26) represents 10±1% of the total emission intensity. The values for P(ν_D) listed in Table II are only for the portion of the D → X emission from rotational states populated through the statistical mechanism.

In the interest of simplicity to our resonant energy transfer model, we have not considered energy transfer to other rotational states near J_D=26 that may also be populated in the nonstatistical energy transfer. This simplification manifests itself in our simulation, as seen in Fig. 4(b). There is a clear gap in the simulation between peaks from (ν_E=0, J_D =26) and peaks from the statistical rotational distribution centered at (ν_E=0, J_D=54) that does not adequately represent the experimental spectrum. A more sophisticated fitting routine could better fit the experimental spectrum by including additional fluorescence from J_D states between 26 and 54 that would fill in this gap. Transitions to such states in the electronic energy transfer process could be resonant, for example, with ν2 transitions in CF4 that are accompanied by a substantial change in CF4 rotational energy. Additionally, due to our limited resolution, the rising edge on the low wavelength side of each ν_E=0 peak can also be fitted by transitions from J_D=22 though J_D=30. However, we still use only J_D=26 to describe this low wavelength side because the (ν_E=0, J_E=55) → (ν_E=0, J_E=26) transition is the closest energy match to the (0, 1, 0, 0)J=30 ← (0, 0, 0, 0)J=30 transition in CF4.

3. ν_E=1–2, J_E=55

In Fig. 6 we show emission spectra from samples of 40 mTorr I2 + 1000 mTorr CF4 excited to the states (ν_E=1, J_E=55) and (ν_E=2, J_E=55). Simulations using only the statistical function to describe the D state rotational distribution are also shown in Fig. 6, with the best fit vibrational state distributions P(ν_D) given in Table III. In a trend similar to the listed Franck-Condon factors and that reported in I2(ν_E=0–2)+He, Ar collisions, the P(ν_D) values for the E → D transfer are broadened and the maximum peaks at larger values of ν_D as the initial level ν_E is increased. However, in contrast to our previous work, the distributions in Table III peak at levels with a smaller ν_D than those observed through collisions with He and Ar, a trend also shown above in transfer from ν_E=0 (Table II).

The P(ν_D) distributions shown in Tables II and III all show a trend that is markedly different than those seen in collisions with He and Ar. The distribution of vibrational levels that are populated in the D state following collision with CF4 is consistent to a greater extent with Franck-Condon factors with the initially prepared level than those observed after collision with He or Ar, the most extreme
example seen in \( v'_E = 0 \). At the low levels of \( v'_E \) investigated in our experiments, the \( v'_E \) levels with the largest Franck-Condon factors with the initially prepared level correspond to energy gaps of 300–400 cm\(^{-1}\). Because this energy difference must necessarily be transferred to translational energy upon collisions with He or Ar, any strong propensity for transfer to vibrational levels with a large vibrational wave function overlap is tempered by the need to transfer large amounts of energy into relative translation. The closer agreement of \( P(v'_D) \) trends with Franck-Condon factors upon collision with \( CF_4 \) indicates that there exists a propensity to populate vibrational levels with large wave function overlap in the \( E \rightarrow D \) transfer and that the vibrational and rotational degrees of freedom in \( CF_4 \) are a more favorable acceptor of available energy than translation.

Comparison of the experimental and simulated \( D \rightarrow X \) emission spectra in Fig. 6 shows similar behavior to that observed in emission after excitation to the state \( (v'_E = 0, J'_E = 55) \). Many peaks corresponding to emission from \( v'_D = 0 \) and \( v'_D = 1 \) have considerable intensity on the low wavelength side that is not reproduced with our statistical rotational distribution function. This effect is most easily seen in the difference in experiment and simulation between 310 and 320 nm, an area where emission from the two lowest energy vibrational states are prominent and well separated from emission from higher vibrational levels. Again, we interpret these wide spectral features to be evidence of specific rotational level energy transfer that is resonant with vibrational frequencies in \( CF_4 \). Unlike collisions with \( I_2 \) in the initial state \( (v'_E = 0, J'_E = 55) \) where there was only a maximum of \( \sim 450 \) cm\(^{-1}\) of available energy in the \( E \rightarrow D \) transfer, there exists much more available energy in transfer from \( v'_E = 1 \) and \( v'_E = 2 \) to low vibrational levels of the \( D \) state. As a result, we are unable to make any unambiguous identifications of a specific \( I_2 \) rovibrionic energy transfer channel that is resonant with a larger number of higher energy rovibrational transitions in \( CF_4 \). Better resolution of the rotational fine structure in the \( D \rightarrow X \) emission could lead to a better understanding of the rotational distribution in the \( D \) state and, hence, a more complete picture of specific \( E \rightarrow D \) channels resonantly enhanced through vibrational excitation of \( CF_4 \).

### Table III. Probability distribution of transfer to specific vibrational levels of the \( D \) ion-pair state, \( P(v'_D) \)

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<th>( P(v'_D) )</th>
<th>FCF</th>
<th>( P(v'_D) )</th>
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### FIG. 7. Vibrational state distributions upon collision-induced electronic energy transfer to the \( \beta \) (top) and \( D' \) (bottom) electronic states from initial states \( (v'_E = 0–2, J'_E = 55) \).

### B. \( E \rightarrow D' \) and \( E \rightarrow \beta \) transfer

Probability distributions for transfer to the lowest eight vibrational levels of the \( D' \) and \( \beta \) states are shown in Fig. 7. Because the \( D' \rightarrow A' \) and \( \beta \rightarrow A \) emissions from these states are overlapped between the wavelengths of 334 and 346 nm, we must fit the vibrational distribution from both states simultaneously.\(^3,5\) In addition, we account for spectral bands due to the \( E \) state emission in the absence of collision-induced energy transfer (see Fig. 2). We find no significant rotational state dependence on the \( E \rightarrow D' \) and \( E \rightarrow \beta \) collision dynamics. Vibrational state distributions in the \( D' \) and \( \beta \) states are equal within our error bars after excitation to the initial states \( (v'_E = 0, J'_E = 23) \) and \( (v'_E = 0, J'_E = 55) \).

For all fits in this region, the statistical function for rotational state distribution adequately reproduces all of the spectral features. Thus, we see no direct evidence of any specific, nonstatistical, resonantly enhanced rovibronic energy transfer. However, given the complexity of this spectral region and our limited resolution, it is not surprising that we are unable to detect any subtle spectral features similar to those seen in the \( D \rightarrow X \) emission after excitation to \( (v'_E = 0–2, J'_E = 55) \). As discussed below, the overall distribution of vibrational levels populated in both the \( D' \) and \( \beta \) states allows us to infer that \( CF_4 \) vibrational modes are a significant pathway to accept vibronic energy lost by \( I_2 \) in the energy transfer dynamics.

Again, the vibrational populations are markedly different than those produced in collisions with He or Ar.\(^3,5\) Figure 7 shows a clear preference for transfer to vibrational levels with large Frank-Condon overlap—transitions that minimize the change in vibrational quantum number. Collisions with He and Ar produce much broader distributions with substantial probability to transfer population to states with a larger number of vibrational quanta than the initial \( v'_E \) level—transitions with lower energy gaps than those with larger Franck-Condon factors. The \( D' \) and \( \beta \) states have signific-
cantly lower $T_e$ values than the $E$ state, and transitions that minimize the change in vibrational quantum number, i.e., have large Franck-Condon factors, correspond to changes of $\sim 600$ and $\sim 1000$ cm$^{-1}$ in vibronic energy to the $\beta$ and $D'$ states, respectively. With He and Ar as the collision partner, transitions with a reduced energy gap are important in the collision dynamics. There is a reduced propensity for the population of states with large Franck-Condon overlap because of the impediment of transferring large amounts of energy into translation.

With CF$_4$ as a collision partner we observe a severe reduction of this impediment, as states with both large Franck-Condon factors and large energy gaps are populated in the electronic energy transfer. It is likely that the rotational and vibrational degrees of freedom in the CF$_4$ collision partner are effective at accepting the excess energy from the I$_2$ vibronic energy change. Because the magnitude of the energy gaps in these channels are on the order of 500–1000 cm$^{-1}$, we suggest that the low frequency bending modes of CF$_4$ at 435 and 631 cm$^{-1}$ may be particularly effective in accepting excess energy at the low $v_F$ levels reported here. The higher frequency stretching modes at 909 and 1284 cm$^{-1}$ may become important in accepting I$_2$ vibronic energy changes at higher values of $v_F$. Indeed, it is the $v_3$ bend at 631 cm$^{-1}$ and $v_4$ antisymmetric stretch at 1284 cm$^{-1}$ that Pravilov and co-workers find to accept energy after collision-induced electronic energy transfer with I$_2$ ($v_F=8-47$).  

C. Kinetic analysis

We use the same kinetic analysis that was used for He and Ar collision partners to calculate collision-induced electronic energy transfer rate constants and hard-sphere collision cross sections. The scheme has been described previously in detail. To determine the rate constant for the $E \rightarrow D$ transfer, for example, we find the ratio of the total intensity of the $D \rightarrow X$ emission to the $E \rightarrow B''$ emission. In previous work, we used the intensity of the $E \rightarrow A$ transitions rather than the $E \rightarrow B''$ intensity in the denominator of this ratio. As both of these transition intensities are linear with I$_2$ pressure and independent of CF$_4$ pressure, the results do not depend on which particular transitions we use to normalize the $D \rightarrow X$ intensities. However, because the $E \rightarrow A$ transitions are strongly overlapped by $D' \rightarrow A'$ and $\beta \rightarrow A$ emissions at high CF$_4$ pressures, we find less error in the ratio when the $E \rightarrow B''$ intensity is used. Confirmation that this ratio is linear with the pressure of CF$_4$ indicates that we are operating with single collision conditions. We use Einstein $A_{n,n'}$ coefficients for the particular electronic transitions and the radiative lifetime of the $E$ electronic state (25.7 ns) from the literature to extract the energy transfer rate constants from the intensity ratio.

The second-order collision-induced electronic energy transfer rate constants and effective hard-sphere cross sections are listed in Table IV. Of particular note is that the rate constants are uniformly an order of magnitude larger than those found when He or Ar is the collision partner with I$_2$ ($v_F=0-2$). The largest cross sections are for transfer to the $\beta$ state, followed by the $D'$ and $D$ states, a trend similar to that found when Ar is the collision partner. The large cross sections for electronic energy transfer are consistent with a model in which the attractive region of the intermolecular potential has a dominant role in determining the collision cross sections. The static electric polarizability of CF$_4$ is more than twice that of Ar, so we expect a significantly enhanced interaction with ion-pair excited I$_2$. Akopyan et al. have explored the role that rare gas–I$_2$ complexes might play in the electronic relaxation of I$_2$ excited to the $f(0)^1$ ion-pair state, while Stephenson et al. explored dissociation induced electronic relaxation in the NeICl van der Waals complex in the $E$ ion-pair state 15 years ago. It is possible that collision complexes of I$_2$ with CF$_4$ play a role in the rovibrational resonance effects that we observe. Formation of such complexes might result in selective excitation of internal degrees of freedom within CF$_4$ via an intramolecular vibrational redistribution (IVR) mechanism and would account for the large effective hard-sphere cross sections. Contradicting this conjecture is the observation of vibrational distributions in agreement with Franck-Condon factors, a result associated with sudden, impulsive interactions. An examination of the dynamics of I$_2$–CF$_4$ van der Waals complexes would shed light on these intriguing issues.

IV. CONCLUSION

In this report we have shown emission spectra and vibrational populations from the three lowest energy ion-pair states of I$_2$ populated through CF$_4$ collision-induced energy transfer from the $E$ ion-pair state. Vibrational populations extracted from our spectral fits show a significant change from those found when either He or Ar was the collision partner. While the relative rate constants for transfer to the $D'$, $\beta$, and $D$ states differed between He and Ar collisions, the vibrational distributions within a particular electronic state are relatively independent of the identity of the collision partner. The data shown here show markedly different vibrational state distributions and significantly increased rate constants. We attribute these differences to the vastly increased number of pathways for CF$_4$ to accept the excess energy that accompanies the iodine electronic energy transfer, namely, rotational and vibrational degrees of freedom.

<table>
<thead>
<tr>
<th>Initial state</th>
<th>Final state</th>
<th>Energy transfer rate constants (10$^{-16}$ m$^3$ s$^{-1}$ molecule$^{-1}$)</th>
<th>Energy transfer rate constants (10$^{-16}$ m$^3$ s$^{-1}$ molecule$^{-1}$)</th>
<th>Energy transfer rate constants (10$^{-16}$ m$^3$ s$^{-1}$ molecule$^{-1}$)</th>
<th>Energy transfer rate constants (10$^{-16}$ m$^3$ s$^{-1}$ molecule$^{-1}$)</th>
<th>Energy transfer rate constants (10$^{-16}$ m$^3$ s$^{-1}$ molecule$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(v_F=0, J_F=23)$</td>
<td>$(v_F=0, J_F=55)$</td>
<td>$(v_F=1, J_F=55)$</td>
<td>$(v_F=2, J_F=55)$</td>
<td>$(v_F=0, J_F=23)$</td>
<td>$(v_F=0, J_F=55)$</td>
<td>$(v_F=1, J_F=55)$</td>
</tr>
<tr>
<td>$D'$</td>
<td>1.56±0.15</td>
<td>2.28±0.17</td>
<td>2.5±0.2</td>
<td>2.5±0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td>2.57±0.17</td>
<td>2.71±0.16</td>
<td>3.1±0.2</td>
<td>3.1±0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D$</td>
<td>0.36±0.03</td>
<td>1.10±0.08</td>
<td>1.28±0.08</td>
<td>1.42±0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hard-sphere collision cross sections (Å$^2$)</td>
<td>50±5</td>
<td>73±5</td>
<td>80±6</td>
<td>80±6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td>83±5</td>
<td>87±5</td>
<td>100±6</td>
<td>100±6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D$</td>
<td>12±1</td>
<td>35±3</td>
<td>41±3</td>
<td>46±4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Collisions with He or Ar most likely induce transitions to vibrational levels with both significant Franck-Condon overlap and small energy gaps with the initially prepared state, a trade-off that often produces a broad distribution in many vibrational levels. In the vibrational distributions shown here, we find that collisions with CF$_4$ are most likely to induce transitions to vibrational levels that maximize Franck-Condon overlap—a trend that tends to minimize the change in vibrational quantum number. We attribute the two low frequency bending modes of CF$_2$ to be particularly effective in accepting excess energy because of the associated energy gaps at the low $\nu_2$ levels accessed here. Hence, the need to transfer large amounts of energy into relative translation with an atomic collision partner is lessened in a collision with CF$_4$, and it is far more likely to induce a transition to a vibrionic level with good Franck-Condon overlap and a relatively large energy gap.

Of particular interest is the $E \rightarrow D$ electronic energy transfer in which we find evidence of specific, rotational level dependent, nonstatistical energy transfer that is resonant with the excitation of the $\nu_2$ bending mode of CF$_4$ at 435 cm$^{-1}$. The excess rotational distribution in emission from the $\nu_2=0$ vibrational level that occurs after excitation to the state ($\nu_2=0, J_2=55$) but not after excitation to the state ($\nu_2=0, J_2=23$) is a strong evidence for such a process. In the former case there is sufficient energy from the ($\nu_2=0, J_2=55$) $\rightarrow$ ($\nu_2=0, J_2=26$) transfer to be resonant with the CF$_4$ ($0,1,0,0)\rightarrow(0,0,0,0)$ energy gap, while from the ($\nu_2=0, J_2=23$) state, there is insufficient energy to be resonant with any vibrational mode of CF$_4$ even when terminating at the state ($\nu_2=0, J_2=0$).

However, regardless of any specific vibrational resonance effect, excitation of CF$_4$ internal degrees of freedom would explain the substantial propensity for populating the $\nu_2=0$ level after excitation to $\nu_2=0$, regardless of the I$_2$ rotational state involved. We find a similar mechanism in the $E \rightarrow D$ electronic energy transfer after excitation the states $\nu_2=1$ and $\nu_2=2$. However, the increased available energy when transferring the lowest two vibrational levels of the $D$ state precludes an unambiguous identification of the specific CF$_4$ vibrational resonance involved.

Our analysis indicates a pronounced $E \rightarrow V$ collision-induced electronic energy transfer in the I$_2$($\nu_2=0-2$)+CF$_4$ system. In the case of $E \rightarrow D'$ and $E \rightarrow \beta$ energy transfer, we only have indirect evidence of such through comparison of the vibrational state distribution in similar experiments in which He or Ar atoms are the collision partners. In comparing the $E \rightarrow D$ transfer from the initial states ($\nu_2=0, J_2=23$) and ($\nu_2=0, J_2=55$), however, we see specific evidence of excitation of the $\nu_2$ bending mode of CF$_4$ as the available energy is increased above the threshold for excitation of this vibration. There exist many examples in the literature of vibrationally excited, electronic ground state, molecules inducing vibrational excitation in molecular collision partners. Our data and that of Pravilov and co-workers suggest that similar dynamics occur with ground state molecular collision partners and highly electronically excited I$_2$.

**ACKNOWLEDGMENTS**

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