The excitation of IF($B^3\Pi_{0^+}$) by N$_2$(A$^3\Sigma_{u}^+$)

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Experiments in a discharge-flow reactor show that the energy-transfer reaction between N$_2$(A$^3\Sigma_{u}^+$) and IF($X^3\Sigma^+$) is extremely rapid ($k_{\text{thermal}} = 2.0 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) with 40% of the quenching collisions resulting in fluorescence from IF($B^3\Pi_{0^+}$). The reaction populates IF($B^3\Pi_{0^+}$) vibrational levels up through $v' = 9$ and produces $v' = 0-6$ with about equal probability at low pressure. The vibrational distribution relaxes rapidly in collisions with the reactor bath gas even at pressures of a few Torr. The vibrational relaxation rate coefficients for levels 3–6 of IF($B^3\Pi_{0^+}$) in a mixture of 80% Ar/20% N$_2$ are about $3 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, with levels 1 and 2 being a little slower. Differences in IF excitation between N$_2$(A$^3\Pi$) $v' = 1$ and $v' = 0$ are small ($k_{v' = 1}/k_{v' = 0} \approx 1.2$). Electronic quenching of the IF($B^3\Pi_{0^+}$) is sufficiently slow that even at higher reactor pressures radiative decay is the dominant loss. Rate coefficients for quenching by CF$_4$, CF$_3$I, and NF$_3$, and for vibrational relaxation of N$_2$(A$^3\Pi$) by CF$_4$, CF$_3$I, CH$_4$, and SF$_6$ also are reported.

I. INTRODUCTION

The molecule IF and other interhalogens have been the subject of considerable interest in recent years because their compressed electronic energy manifold and intense radiative transitions cause these molecules to exhibit visible lasing action. The "blue-green" emission, $D^1(P_2)\rightarrow A^3(P_2)$, of IF has been studied extensively for application in short-wavelength, gas-discharge chemical lasers.\textsuperscript{1}

Recently, interest has also focused on the $(B^3\Pi_{0^+}, \rightarrow X^3\Sigma^+)$ bands of the interhalogens. In an elegant series of papers, Clyne and co-workers studied the radiative and collisional properties of IF and BrF. They showed that these species were highly suitable for forming an electronic transition laser operating on the $B \rightarrow X$ transition because the upper states have short radiative and long quenching lifetimes. In parallel with this work, Davis and Hancox\textsuperscript{8} using a pulsed dye laser to excite the ground-state IF formed in an I$_2$/F$_2$ flame, demonstrated optically pumped lasing action on the IF($B \rightarrow X$) transition. Optimal chemical (kinetic) means for pumping the IF($B^3\Pi_{0^+}$) state remain to be determined.

More than a decade ago, Clyne et al.\textsuperscript{9} studied the three-body recombination of I with F, and noted extensive enhancement of the IF($B \rightarrow X$) emission upon adding O$_2$(A$^3\Delta$, $^1\Sigma$) to the reacting mixture. Recently, Davis and co-workers\textsuperscript{10} demonstrated and examined the enhancement of IF($B^3\Pi_{0^+}$) emission from the I$_2$/F$_2$ system upon introducing O$_2$(A$^3\Delta$) and O$_2$(A$^1\Sigma$). In these experiments, O$_2$(A$^3\Delta$) appeared to be responsible for the IF($B^3\Pi_{0^+}$) enhancement. In the absence of O$_2$, IF($B^3\Pi_{0^+}$) distributions were relatively cold, extending only to about $v' = 4-5$. Adding O$_2$ greatly enhanced the $B \rightarrow X$ emission intensity, with up to ten vibrational quanta excited in the $B$ state. Subsequent work by Davis and co-workers\textsuperscript{11} shows even stronger IF($B$) excitation when the effluents of microwave discharges in He/N$_2$ mixtures interact with the I$_2$/F$_2$ mixing zone of their reactor. They did not identify which species in their active nitrogen was responsible for the IF excitation, but speculated that it might be N$_2$(A$^3\Sigma_{u}^+$).

The present study examines the excitation of IF($B \rightarrow X$) emission in the electronic energy-transfer reaction between N$_2$(A$^3\Pi$) and ground-state IF. Three types of measurements characterize fully the excitation of IF($B^3\Pi_{0^+}$) by N$_2$(A$^3\Sigma_{u}^+$). Spectral scans under a variety of conditions characterized the distribution of IF($B^3\Pi_{0^+}$) vibrational levels excited in the energy-transfer reaction. Measurements of IF($B^3\Pi_{0^+}$) intensities as a function of IF number density in the presence of known number densities of N$_2$(A$^3\Pi$) determine the rate coefficient for the excitation of IF($B^3\Pi_{0^+}$) by N$_2$(A$^3\Pi$). Finally the rate coefficient for N$_2$(A$^3\Pi$) removal by IF was determined by monitoring the disappearance of N$_2$(A$^3\Pi$) as a function of added IF number density. The following sections describe these measurements in detail.

II. EXPERIMENTAL

The apparatus used in these measurements is a 2 in. flow tube pumped by a Leybold–Heraeus roots blower/forepump combination capable of producing linear velocities up to $5 \times 10^4$ cm s$^{-1}$ at pressures of 1 Torr. The flow-tube design is modular (see Fig. 1), with separate source, reaction, and detection sections which are clamped together with O-ring joints. We have described it in various configurations previously.\textsuperscript{12–14} The detection region is a rectangular stainless-steel block bored out internally to a 2 in. circular cross section and coated with Teflon\textsuperscript{®} (Dupont Poly TFE #852-201) to retard surface recombination of atoms.\textsuperscript{15,17} Use of a black primer prior to the Teflon\textsuperscript{®} coating reduces scattered light inside the block significantly. The block has two sets of viewing positions each consisting of four circular ports on the four faces of the block. These circular ports accommodate vacuum-ultraviolet resonance lamps, VUV and visible monochromator interfaces, laser delivery side-arms, and a spatially filtered photomultiplier/interference filter combination.

The downstream observation position contains baffled side arms to allow entry and exit of a laser beam, and at right angles to these a filtered photomultiplier and a UV/visible monochromator interface. The filtered photomultiplier is for detecting laser-induced fluorescence (LIF), while the
monochromator is used in the bulk of these studies to detect fluorescence between 180 and 850 nm. A suprasil lens collects light from the center of the flow tube and focuses it on the entrance slit of a 0.5 m Minuteman monochromator outfitted with a 1200 groove mm$^{-1}$ grating blazed at 250 nm. A thermoelectrically cooled photomultiplier detects photons with the aid of an SSR 1105 photon-counting rate meter and strip-chart recorder. Initial experiments used an EMI 9659QA photomultiplier (S-20 response), but for the last sets of measurements this was replaced by an HTV R943-02 photomultiplier (GaAs photocathode). This change resulted in significant improvements in red sensitivity, particularly beyond 650 nm.

The entire spectral detection network was calibrated for relative response as a function of wavelength using standard quartz-halogen (300 to 900 nm) and D$_2$ (180 to 400 nm) lamps. Absolute response calibrations were made in situ by observing the O/NO air afterglow under carefully controlled conditions using techniques we have documented previously.$^{12,18}$

The reaction between metastable Ar($^2P_{0,2}$) and molecular nitrogen produces the metastable nitrogen molecules, N$_2$(A $^{3}Σ_u^+$).$^{19,20}$ This transfer excites ground state N$_2$ to the C $^{3}Π_u$ state which quickly cascades radiatively to the metastable (A $^{3}Σ_u^+$) via the B $^{3}Π_u$ state. An aluminum-hollow-cathode discharge source operating at 240 V and 3 mA produced the argon metastables. Molecular nitrogen was mixed with the argon metastables just downstream of the discharge and observations of Vegard–Kaplan emission, N$_2$(A $^{3}Σ_u^+$ $→$ X $^{1}Σ_g^+$), are used to monitor the number density of the metastable nitrogen molecules. Figure 2 shows a spectrum of the Vegard–Kaplan bands in our reactor.

Reagents enter the flow tube through hook-shaped injectors whose outlet orifices are coaxial with the main flow tube. For some studies, reagents entered through a 1 in. diameter loop injector seated on the end of a 1/4 in diameter tube which slides along the bottom of the flow tube, parallel to its axis, thus allowing a variety of reaction distances to be achieved allowing accurate kinetic studies. The hook injectors facilitate introduction of unstable species produced in a secondary discharge. These injectors have relatively large diameters (10 mm) and are Teflon® coated to inhibit wall recombination of these unstable species. IF is produced in one of these injectors by the reaction between CF$_3$I and F atoms, the F atoms having been produced in a microwave discharge of He/CF$_4$ mixtures further upstream in the injector.

Because IF is known to be somewhat unstable with re-
spect to wall reactions, we studied its production and loss in our flow system using a laser-induced fluorescence diagnostic for measuring IF number densities. Studies relating the production of F atoms to the residence time of CF$_4$ in the microwave discharge indicated a yield of about 0.3 F atoms per CF$_4$ molecule under typical operating conditions. We determined experimentally conditions that produce complete reaction of CF$_4$,I in the injector and showed that a negligible amount of IF is destroyed in the injector under these conditions. At low flow velocities wall collisions do destroy some of the IF molecules in the main flow tube, presumably on the non-Teflon coated windows. This loss appears to be negligible at higher velocities, however, and permits us to operate in a regime where IF number densities may be related directly to the amount of CF$_4$,I flowing into the injector when F atoms are in excess. This is fortunate because operating the injector using excess CF$_4$,I results in the deposition of an optically opaque thin film on the reactor walls.

Mass flow meters or rotameters monitor the flow rates of most gases. All flow meters were calibrated by measuring rates of increase of pressure with time into 6.5 or 12 2-flasks, using appropriate differential pressure transducers (Valdyne DP-15) which themselves have been calibrated with silicon oil or mercury manometers. Typical flow rates for argon, nitrogen, and helium through the injector are 2000–5000, 100–500, and 200–500 $\mu$mol s$^{-1}$, while CF$_4$, and CF$_4$,I flow rates range between 0 and 1 $\mu$mol s$^{-1}$, respectively.

Total pressures, as measured by a Baratron® capacitance manometer, range from 0.4 to 9 Torr, and flow velocities vary from 500 to 5000 cm s$^{-1}$ as controlled by a variable-conductance butterfly valve.

Tetrafluoromethane (CF$_4$) was obtained 99.5% pure from Matheson, and, due to the small amount employed, was used without further purification. Trifluoriodomethane (CF$_3$I) was obtained 99% pure from PCR Research Chemicals. The major impurity, I$_2$, was removed by distilling CF$_3$I from a trap at $-115^\circ$C followed by storage in a dark bulb. The other gases, Ar, N$_2$, and He, were taken directly from their cylinders but flowed through molecular sieve traps before entering the reactor.

FIG. 2. Vegard–Kaplan emission in flow reactor 9 ms downstream from the discharge.

FIG. 3. Experimental (top) and computed (bottom) IF(\beta) spectra from N$_2$(A$^3\Pi_u^-$) excitation of IF at 0.5 Torr.
III. RESULTS AND ANALYSIS

A. Vibrational distributions from N₂(A) excitation

When IF is added to a flow of N₂(A) metastables, the IF(B^3Π_g, X^1Σ^+) system radiates prominently in the spectral region between 440 and 640 nm. Figure 3 shows a typical spectrum. Relative populations of the B-state vibrational levels were determined by dividing the response-corrected, wavelength-integrated intensity of a given band by the appropriate Einstein emission-rate coefficient. The band intensities were determined either by planimetry or by a least squares spectral fitting analysis. The spectral analysis consists of a linear least squares fit between the observed spectrum and a computed spectrum to determine number densities of the emitting states. The computed spectra are determined from the appropriate spectroscopic constants by calculating the line-by-line, intensity-weighted spectral distributions for each transition at an assumed rotational temperature (usually ambient), convolving with the experimental scanning function, and solving for the set of upper-state populations which permit the best least squares fit to the experimental observations. This procedure allows us to account quantitatively for unresolved overlap between adjacent spectral features. The integrated band transition probabilities were determined from a complete reanalysis of the RKR potentials, Franck-Condon factors, and the transition moment function as described elsewhere. The values thus derived are consistent with those obtained from the data of Trautman et al. The lower portion of Fig. 3 shows a typical synthetic fit. Figure 4 shows how the vibrational population distribution varies with pressure over the range of 0.5 to 9 Torr. The increase in population of the lower vibrational levels and the concomitant decrease in population of the upper vibrational levels demonstrates graphically the extent of vibrational relaxation.

A modified Stern-Volmer analysis of the data in Fig. 4 allows us to estimate vibrational relaxation coefficients. The analysis assumes that vibrational relaxation proceeds only a single quantum at a time and that the gas composition is constant. Our mixture is approximately 80% argon and 20% helium and nitrogen, with minor amounts of CF₄ added for this series of experiments. The CF₄ rapidly relaxes the N₂(A) vibrational distribution to v' = 0. Wolf et al. have shown that electronic quenching of IF(B) by Ar, N₂, and He is negligible.

Because its radiative decay rate is rapid compared to the rate of removal of species from the field of view by physical transport, the IF* is in steady state in the observation region. Thus in the absence of vibrational relaxation we have

\[ R_v = N_v^0 A_v, \]

where \( R_v \) is the rate of formation of IF(B) in vibrational level \( v \), \( N_v^0 \) is the population of that level, and \( A_v \) is the radiative decay rate. When vibrational relaxation is included, Eq. (1) becomes

\[ R_v + k_{v+1,v} N_{v+1} \frac{P N_v^0}{R T} = (A_v + k_{v,v-1} \frac{P N_v^0}{R T}) N_v, \]

where \( k_{v,v-1} \) represents the vibrational relaxation rate out of level \( v \), \( k_{v+1,v} \) the vibrational relaxation rate coefficient into level \( v \), \( P \) the gas pressure, \( N_0 \) Avogadro’s number, \( R \) the gas constant, and \( T \) the temperature. Summing Eqs. (1) and (2) over all levels above level \( v \), subtracting the resultant sums of Eq. (1) from Eq. (2), and dividing through by the quantity \( N_v A_v \) gives the working equation for the vibrational-relaxation analysis:

\[ \frac{N_v^0}{N_v} + \sum_{m=1}^{m_{\text{max}}} \frac{N_{v+m} - N_{v+m}}{N_v} = 1 + \frac{k_{v,v-1} N_0}{A_v \frac{P}{R T}}. \]

Figure 5 shows some typical plots of the data analyzed according to Eq. (3). Least-squares fits to the data for each
vibrational level estimate that the vibrational relaxation rate coefficients range from 2.6 to $4 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for vibrational levels 3-8. Levels 1 and 2 relax a bit more slowly with rate coefficients of 0.6 and $1.6 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. Table I summarizes the vibrational-relaxation-rate measurements. Experiments at the Air Force Weapons Laboratories have indicated that the rate coefficients for vibrational relaxation of IF($B_{1}^0 \Pi_0^-$) by helium, nitrogen, and argon are 5.7, 3.9, and $1.2 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. From these data we calculate a vibrational relaxation rate coefficient for an 80/20 Ar/N$_2$-He mixture (with an average rate coefficient for the He-N$_2$ component of $5 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) of $2.0 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ which agrees well with our measured value of $2.6 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ given the 30% to 40% uncertainty in the AFWL data, and our own experimental uncertainties which must be of comparable size. The AFWL experiments also indicate that the rate coefficients for relaxation of vibrational level 1 by He, Ne, and N$_2$ are about a factor of 3 smaller than the corresponding rate coefficients for vibrational level 3. This agrees well with the factor of 4 reduction observed in our experiments.

**B. Rate coefficients for the excitation of IF($B^0 \Pi_0^-$) by N$_2$(A $^2 \Sigma_+^-$)**

Knowledge of the vibrational distribution of the B-state emission, and measurements of the change in intensity of various bands as a function of IF number density, for otherwise constant conditions, determines the rate coefficient for excitation of IF by collisions with N$_2$(A). The differential equation describing the rate of change of the IF($B$) number density with time is

$$\frac{d[IF^*]}{dt} = k_{ex}[IF][N_2(A)] - k_{rad}[IF^*],$$

where $k_{ex}$ is the rate coefficient for IF($B$) excitation by N$_2$(A) and $k_{rad}$ is the radiative decay rate of IF*. We have ignored electronic quenching of the IF($B$) state by the various species in the reactor. Because the IF($B$) radiative-decay rate is quite large, the IF($B$) is in steady state in the observation volume. Thus its intensity is

$$I_{IF^*} = k_{rad}[IF^*] = k_{ex}[IF][N_2(A)] = \frac{I_{IF^*}}{A_{IF^*}}.$$
The ratio of total IF fluorescence intensity to $N_2(A)$ number density in the presence of 2% CF$_4$ added to the bath gas just downstream of the metastable discharge indicated a roughly 20% decrease in the IF fluorescence from the intensities observed in the absence of CF$_4$. The CF$_4$ relaxes the $N_2(A)$ vibrational levels, so that in its presence, only $N_2(A)\nu^\prime = 0$ is in the reactor. Thus the implication of this observation is that the excitation-rate coefficient is slightly smaller for $N_2(A)\nu^\prime = 0$ than it is for higher levels of $N_2(A)$. We do not feel confident in this assertion, however, because adding the CF$_4$ also causes the IF($B$) distribution to be vibrationally relaxed and any error in relative monochromator response function or IF($B$) transition probabilities will be reflected in the total IF fluorescence intensity measurement. Thus we can state with confidence only that no dramatic changes occur when the $N_2(A)$ is vibrationally relaxed compared to conditions under which it is not. The rate coefficients for $N_2(A)$ removal by IF do not show any dependence on $N_2(A)$ vibrational energy (see below).

C. Rate coefficients for $N_2(A)$ removal by IF and other molecules

For these experiments the important kinetic processes in our reactor which involve $N_2(A)$ are:

$$N_2(A) + IF \rightarrow N_2(X) + IF^*$$  \hspace{2cm} (7a)
$$\text{other products,}$$ \hspace{2cm} (7b)
$$N_2(A) + Q \rightarrow N_2(X) + Q^*,$$ \hspace{2cm} (8)
$$N_2(A) + \text{wall} \rightarrow N_2(X),$$ \hspace{2cm} (9)

where Q represents other quenchers. Given these reactions, the differential equation describing the variation in the $N_2(A)$ number density with time is

$$\frac{d}{dt}[N_2(A)] = - \{k_7[IF] + k_8[Q] + k_9[N_2(A)]\}. \hspace{2cm} (10)$$

Because IF any other significant quenchers in the reactor will be at much greater number densities than $N_2(A)$, they can be considered to be constant (the pseudo-first-order approximation) and the differential equation can be solved to give

$$\ln \frac{[N_2(A)]_t}{[N_2(A)]_0} = - \{k_7[IF] + k_8[Q] + k_9t\}, \hspace{2cm} (11)$$

where the reaction time $t$ in the flow reactor is given by the ratio of the distance between the injector and the detection region $z$ and the bulk flow velocity $v$. For fixed $z$ and $v$ (fixed-injection-port analysis), measurements of the change in $N_2(A)$ number density as a function of reagent number density give a decay coefficient $\Gamma$,

$$\Gamma = - \frac{d \ln I_{N_2(A)}}{d [Q]} = k_8[Q]z/v, \hspace{2cm} (12)$$

given that the $N_2(A)$ number density is directly proportional to the Vegard–Kaplan emission intensity. The desired rate coefficient then is the ratio of the slope of a plot of $\ln I_{N_2(A)}$ vs $[Q]$, i.e., $\Gamma$, to the reaction time $z/v$.

The above analysis assumes perfect mixing at the injector, and neglects the fluid dynamic effects of the coupling of the radial density gradient of the $N_2(A)$ (it is destroyed with unit efficiency in collisions with the walls) with a radial velocity profile. This latter effect has been thoroughly discussed in the literature$^{36-33}$ with the result that under appropriate conditions $d \ln I_{VK}/d [IF] = -0.62 \ k_7 z/v$. These conditions are generally obtained in our experiments.

The correction for imperfect mixing must be made empirically by doing experiments at several different values of $z$. Then the effective mixing length, $z_{eff} = z - z_0$ is deduced by plotting decay coefficients $\Gamma$ as a function of reaction time and extrapolating to zero reaction time.

We observed the decays in the log of the Vegard–Kaplan intensity as a function of the number densities of IF, CF$_3$I, CF$_4$, and NF$_3$ for both vibrational levels 0 and 1 of $N_2(A)$ and CF$_3$H, CH$_4$, and SF$_6$ for vibrational level 1. We made careful measurements of the CF$_3$I quenching rate coefficient at three different mixing distances, and applied the mixing correction so obtained to the results of the other systems.

Figure 7 shows the decay in the (0,6) Vegard–Kaplan intensity as a function of CF$_3$I number density for three different reaction times. The slopes of the decays in Fig. 7 are

![FIG. 7. The decay of the Vegard–Kaplan bands as a function of CF$_3$I number density for three different reaction times.](image)

![FIG. 8. Variation in Vegard–Kaplan decay rates with CF$_3$I as a function of reaction time.](image)
NF₃, and SF₆ were survey measurements of potential vibrational relaxation partners for N₂(A ν' > 0), and are therefore only accurate to a factor of 2.

IV. DISCUSSION

The rate coefficients for vibrational relaxation of N₂(A ν' = 1) by CF₄ and CH₄ agree reasonably well with the results of the more detailed studies of Jeffries et al.²⁴ (k_{CF₄} = 4.7 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹, k_{CH₄} = 13 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹) and of Clark and Setser²⁵ (k_{CH₄} = 11 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹). To our knowledge, our measurements are the first reports of any of the other rate coefficients in Table II. In their laser-induced fluorescence studies on N₂(A ν' = 0), Heidner et al.²⁶ inferred that SF₆ relaxed N₂(A) vibrational energy. Our experiments indicate that this is true, but that the efficiency for relaxation by SF₆ is extremely low.

Cao and Setser²⁷ have studied the quenching of N₂(A) by the halogen molecules Cl₂, Br₂, I₂, ICl, and IBr. Like IF, they all quench N₂(A) very rapidly with rate coefficients between 1 and 2 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹. IF appears to be the only halogen species, however, that fluoresces strongly when excited by N₂(A) molecules. Cao and Setser did observe some weak fluorescence when I₂ was excited by N₂(A), (< 1% of total quenching). Coombe and Lam²⁸ observed weak Br₂[D'’^2Π(2_2)→A’’^2Π(2_0))] fluorescence which they attributed to arise from the interaction of N₂(A) with Br₂, again < 1% of total quenching. Cao and Setser failed to observe any fluorescence from Br₂ when they mixed it with N₂(A).

The very strong excitation of IF by N₂(A), in the absence of any significant excitation of other halogens by N₂(A) is somewhat surprising. If the coupling of entrance to exit channels is direct, then the energy defect will be approximately 3.5 eV, enough to leave the product ground-electronic-state nitrogen with 14 quanta of vibrational energy. Large energy defects in efficient N₂(A) transfer reactions are not at all unusual, the energy defect for O(3S) excitation in the N₂(A) + O reaction being 2 eV, for example.²⁹ The efficiency of such reactions is aided, presumably, by the large Franck-Condon overlap appears to be one of the contributing features in an efficient intermolecular electronic energy-trans-

**TABLE II N₂(A) Rate coefficient determinations.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient (cm² molecule⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂(A ν' = 0,1) + IF→IF(3Ππᵣᵥ) + N₂(X)</td>
<td>0.83 × 10⁻¹⁰</td>
</tr>
<tr>
<td>N₂(A) + IF→products</td>
<td>1.9 × 10⁻¹⁰ ν' = 0</td>
</tr>
<tr>
<td>N₂(A) + CF₃I→products</td>
<td>2.0 × 10⁻¹⁰ ν' = 1</td>
</tr>
<tr>
<td>N₂(A ν' = 0) + CF₃H→N₂CF₃ + N₂H</td>
<td>2.1 × 10⁻¹⁰ ν' = 1</td>
</tr>
<tr>
<td>N₂(A ν' = 1) + CH₄→N₂(A ν' = 0) + CH₄</td>
<td>3 × 10⁻¹⁰</td>
</tr>
<tr>
<td>N₂(A) + NF₃→products</td>
<td>3 × 10⁻¹³ ν' = 1</td>
</tr>
<tr>
<td>N₂(A ν' = 1) + SF₆→N₂(A ν' = 0) + SF₆</td>
<td>9 × 10⁻¹⁴ ν' = 1</td>
</tr>
</tbody>
</table>

fer reaction. The even larger energy-defect transition in the N₂(A) + IF interaction occurs, however, with a rather small Franck–Condon overlap, so that one might not expect direct energy transfer in to the B –Π₉⁻ state of IF to be important. The Franck–Condon factors for IF(B) excitation are large, however, and the Franck–Condon factors of both the donor and acceptor species are important in Deperasinska et al. formalism. Furthermore, the long-lived complex indicated by the broad distribution of product states and the polar nature of IF may distort the N₂(A) wave function thereby enhancing the larger energy-defect Franck–Condon factors.

An alternative scheme is that the direct energy transfer is into an intermediate IF state which is coupled radiatively to the Π₉⁻ state. We saw no emission in our reactor between 200 and 850 nm that could be attributed to either N₂(A) or IF(B). If the acceptor state of IF were to lie around 4.5 eV however, its radiative transition to the B state would lie too far into the red to be observed by our detection system.

The D' -Π₉⁻ state of IF lies about 4.7 eV above the ground state and the strong D' – A transition falls in the region between 450 and 500 nm. We saw no features in this spectral region that could be ascribed to this transition, and conclude that any excitation of the D' state of IF by N₂(A) must be at least two orders of magnitude less efficient than the excitation of the B state. This is consistent with Coombe and Lam's report of Br₂ D' excitation by N₂(A) which they said proceeded with a rate coefficient of only 1 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹.

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