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B. S. Agrawalla, J. P. Singh, and D. W. Setser

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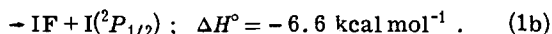
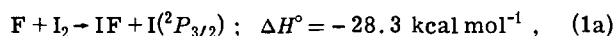
## NOTES

## Branching fraction for $I(^2P_{1/2})$ formation by the $F+I_2$ reaction

B. S. Agrawalla, J. P. Singh, and D. W. Setser

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506  
(Received 19 August 1983; accepted 7 September 1983)

Finding chemical reactions which yield electronically excited state products with high branching fractions so as to provide candidates for chemical lasers has been an elusive goal. Recently Trickl and Wanner<sup>1</sup> suggested that  $F+I_2$  has a high branching fraction for  $I(^2P_{1/2})$ , hereafter denoted as  $I^*$ , from the observation of a bimodal vibrational distribution for the IF product:



The branching ratio for the pathway that gave the low IF vibrational component was about eight times larger than the pathway leading to the high IF vibrational component. Studies at thermal energies have shown that reaction (1) has a total rate coefficient<sup>2</sup> of  $4.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Hence, reaction (1) could be an important chemical source of  $I^*$  and it could supplement the photodissociation of molecules,<sup>3,4</sup> such as  $CF_3I$ , or excitation transfer<sup>5</sup> from  $O_2(a) + I$  as a source for  $I^*$ .

We have investigated the branching fraction for  $I^*$  formation by comparing reaction (1) with  $F+CH_4$  in a flowing afterglow apparatus with interferometric detection of the  $I(^2P_{1/2}-^2P_{3/2})$  and the  $HF(\Delta v=2)$  transitions. Several  $P$  lines of the  $HF(2-0)$  band fall in the same region as the  $I^*$  transition and the Einstein coefficients are similar. Hence, comparison of the  $I^* \rightarrow I$  emission intensity from  $F+I_2$  with the  $HF(\Delta v=2)$  intensity from the well-studied  $F+CH_4$  reaction,<sup>6</sup> which has a rate coefficient of  $7.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and an established  $HF(v)$  distribution,<sup>7</sup> with the same  $[F]$  can provide a measure of the rate constant for  $I^*$  formation.

The infrared emission flowing-afterglow reactor<sup>8</sup> has been described elsewhere for study of  $HF(v)$  chemiluminescence from  $F$  atom reactions.<sup>9</sup> The  $F$  atoms were produced in Ar carrier gas from a microwave discharge in an Ar and  $CF_4$  mixture. The  $CH_4$  was diluted with Ar and metered to the flow reactor. The  $I_2$  was metered to the reactor by passing Ar over a heated reservoir containing  $I_2$  crystals. The flow of  $I_2$  was controlled by changing the flow of the Ar gas and by changing the temperature of the  $I_2$  reservoir; the  $I_2$  flow was measured by condensing the  $I_2$  and weighing it. We were able to vary the  $[I_2]$  and  $[CH_4]$  from  $10^{12}$  to  $10^{14}$

molecules/ $\text{cm}^3$ . The flow speed was  $80 \text{ m s}^{-1}$ , which corresponds to a reaction time of 0.15 ms for traversal of the 1.2 cm distance from  $CH_4/I_2$  inlet to the center of the observation window. The emission was observed through a NaCl window attached to the flow reactor. The Fourier transform interferometer (Digilab FTS-20) was equipped with a calibrated, liquid  $N_2$  cooled, InSb detector. The spectra was collected over the  $15800-0 \text{ cm}^{-1}$  region; a resolution of  $4 \text{ cm}^{-1}$  with 1024 scans was used in collecting the spectra.

Figure 1 shows a typical  $HF(\Delta v=2)$  spectrum from the  $F+CH_4$  reaction; the  $[CF_4]$  and  $[CH_4]$  were  $1.4 \times 10^{13}$  and  $1.3 \times 10^{13} \text{ molecules cm}^{-3}$ , respectively. The absence of  $I^*$  emission from the  $F+I_2$  reaction spectrum recorded

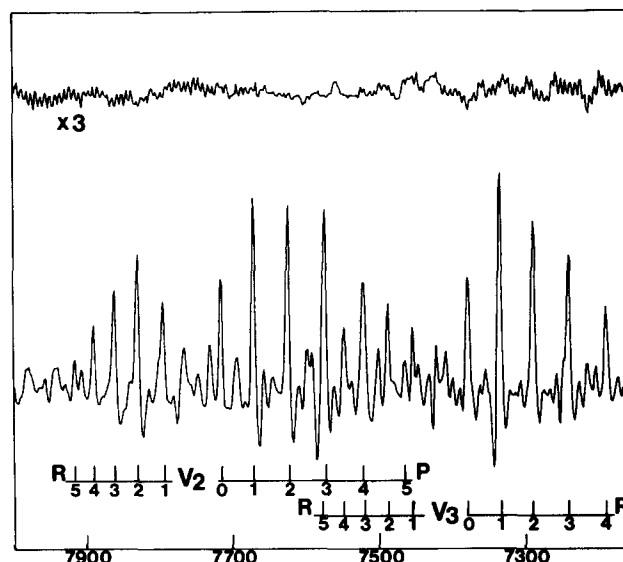


FIG. 1. Spectrum of the HF first overtone at  $4 \text{ cm}^{-1}$  resolution, from the  $F+CH_4$  reaction with  $[CH_4]=1.3 \times 10^{13}$  and  $[CF_4]=1.4 \times 10^{13} \text{ molecules cm}^{-3}$ , respectively, for a reaction time of 0.15 ms. The  $I_{HF}$  varied linearly with  $[CF_4]$  for a range of  $(1-8) \times 10^{12} \text{ molecules cm}^{-3}$  and with  $[CH_4]$  for a range of  $(1-10) \times 10^{12} \text{ molecules cm}^{-3}$ . However, concentrations were increased above the strict first order regime to record stronger spectra of HF and  $I^*$ . The upper spectrum shows that only the noise level is observed from the  $F+I_2$  reaction for  $[CF_4]=1.4 \times 10^{13}$  and  $[I_2]=1.3 \times 10^{13} \text{ molecules cm}^{-3}$ .

TABLE I. Comparison of I\* and HF(2-0) relative intensities.

Reagent	Concentration (molecules cm <sup>-3</sup> )	Transitions of I* and HF	Relative intensity	Einstein coefficient (s <sup>-1</sup> )	Rate constant (cm <sup>3</sup> molecules <sup>-1</sup> s <sup>-1</sup> )
CH <sub>4</sub>	1.3×10 <sup>13</sup>	2P <sub>1</sub>	33.4	16.00 <sup>a</sup>	0.97×10 <sup>-11</sup> b
		2P <sub>2</sub>	32.0	14.47 <sup>a</sup>	1.10×10 <sup>-11</sup> b
I <sub>2</sub>	1.4×10 <sup>13</sup>	<sup>2</sup> P <sub>1/2</sub> - <sup>2</sup> P <sub>3/2</sub>	0.0±1.3 <sup>c</sup>	35.7 <sup>d</sup>	<1.8×10 <sup>-13</sup> e

<sup>a</sup>From Ref. 11. The ratios of Einstein coefficients  $A(\Delta v=2)/A(\Delta v=1)$  were compared with the ratio of HF intensities, corrected for detector response of the first overtone spectrum and the much stronger fundamental spectrum, and were found to be in good agreement. For example for the P<sub>2</sub> line of 2→1 and 2→0 bands, the ratio of intensities give  $I_{2-1}/I_{2-0}=16.1$ ; whereas the ratio of Einstein coefficients give  $A_{2-1}/A_{2-0}=14.4$ .

<sup>b</sup>The  $k_{\text{HF}}(v, J)$  values were calculated using  $k_{\text{HF}}=(7.2\pm1.2)\times10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Ref. 6) and a P<sub>1</sub>:P<sub>2</sub>:P<sub>3</sub> distribution of 0.22:0.61:0.17, as observed in this work with a 300 K Boltzmann rotational distribution.

<sup>c</sup>The noise level in the 7603 cm<sup>-1</sup> region of the F+I<sub>2</sub> spectrum of Fig. 1.

<sup>d</sup>From Ref. 10.

<sup>e</sup> $k_{\text{I}^*}$  was calculated by dividing the noise level by the Einstein coefficient for I\* and comparing the result with the rate constants for the HF(J=1) and HF(J=2) cases;  $k_{\text{I}^*}<(1.3/35.7)*(A_{\text{HF}}/I_{\text{HF}})*k_{\text{HF}}$ .

with the same CF<sub>4</sub> concentration and an I<sub>2</sub> concentration of  $1.3\times10^{13}$  molecules cm<sup>-3</sup> is also shown in Fig. 1. Reaction (1) was studied at [I<sub>2</sub>] from 10<sup>12</sup> to 10<sup>14</sup> molecules cm<sup>-3</sup> and with [CF<sub>4</sub>] as high as 10<sup>14</sup> molecules cm<sup>-3</sup>, but, no I\* signal was ever recorded. In summary, there was no detectable I\* signal at 7603 cm<sup>-1</sup> for any of our reaction conditions.

The upper limit of the rate constant for channel (1b) was assigned from the data of Fig. 1. The noise level corresponding to the wavelength of the I\* emission line was compared with the intensity of 2P<sub>1</sub> and 2P<sub>2</sub> HF lines in Table I. These lines lie in the same spectral region as the I\* transition and no correction for detector response is necessary. The ratio of the HF rotational line intensities and their Einstein coefficient was compared to the ratio of the noise level and the I\* Einstein coefficient. Assigning rate constants to the individual J level of HF(v=2) establishes a rate constant for channel (1b) of the F+I<sub>2</sub> reaction as  $\leq 1.8\times10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Taking into account the quenching rate of I\* by I<sub>2</sub><sup>12</sup> raises the limiting value only to  $\leq 1.84\times10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The comparison of our estimated rate constant for channel (1b) with the total rate constant for reaction F+I<sub>2</sub> gives a branching fraction of  $\leq 0.0004$ .

The I(<sup>2</sup>P<sub>1/2</sub>) and IF(<sup>1</sup>Σ<sup>+</sup>) channel could correlate with F(<sup>2</sup>P<sub>1/2</sub>) and I<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) via an excited state potential. Since the 300 K Boltzmann fraction for F(<sup>2</sup>P<sub>1/2</sub>) is 0.07, one might anticipate that, at least, 7% of I(<sup>2</sup>P<sub>1/2</sub>) would have been observed. Our  $\leq 0.04\%$  limit indicates (i) that the reaction may not be fully adiabatic, i.e., partial collisional mixing of the trajectories on the upper surface with the lower surface may occur or (ii) the reactive cross section of F(<sup>2</sup>P<sub>1/2</sub>) is much lower than for F(<sup>2</sup>P<sub>3/2</sub>) as indicated by a theoretical study<sup>13</sup> of the F+H<sub>2</sub> reaction and experimental work on Br(<sup>2</sup>P<sub>1/2</sub>)+HI.<sup>14</sup>

Our limit for I\* formation is more than three orders of magnitude smaller than that suggested by Trickl and Wanner<sup>1</sup> based on their observation of the low v level component of the IF vibrational distribution. Since trajectory studies of Fletcher and Whitehead<sup>15</sup> on various LEPS surfaces for F+I<sub>2</sub> could not reproduce the low IF

vibrational component, it was suggested that the low vibrational component involves a reaction pathway on a different surface, possibly involving the production of I(<sup>2</sup>P<sub>1/2</sub>), for which the cross section could be larger than the pathway populating high vibrational states of IF and ground state I atoms. It is clear from our results that the channel leading to I\* atoms is unimportant. Alternative explanations for the two component IF vibrational distribution must be sought. Since two component IF vibrational distributions also were observed<sup>1</sup> for F+ICl and F+IBr, a general explanation is needed. Although the ground state (A') I<sub>2</sub>-F surface is bound, the lifetime of the triatomic system is quite short, and the energy disposal may depend on the part of the potential that is sampled by a given trajectory. Alternatively two channels may exist corresponding to trajectories passing over the ground state surface (A') and the first excited surface (A''), both correlate to ground state halogen atoms and molecules.

The F+Br<sub>2</sub> reaction also has been mentioned as a likely secondary process contributing to the high [Br\*] observed in H+BrF reaction.<sup>16</sup> In unpublished work we have observed that F+Br<sub>2</sub> gave no Br\* emission. The Br\* transition occurs near the HF(2-1) band and comparison can be made to the HF(Δv=1) emission from F+CH<sub>4</sub>. Since the Br(<sup>2</sup>P<sub>1/2</sub>-<sup>2</sup>P<sub>3/2</sub>) Einstein coefficient<sup>17</sup> is smaller than for I\* ( $A_{\text{Br}^*}=0.89$  s<sup>-1</sup>), the limit to Br\* formation is only  $\leq 1\%$  of the total reactive cross section. Our results suggest that the source of the Br\* emission is some reaction other than F+Br<sub>2</sub>.

*Note added in proof:* Bersohn and co-workers<sup>18</sup> also have investigated reaction (1) using the laser-induced vacuum ultraviolet fluorescence technique<sup>3</sup> to monitor I\*. They find that I\* is below their detection limit for reaction (1).

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## <sup>2</sup>H solid state NMR of the butane/graphite system

B. Boddenberg, G. Neue, and R. Grosse

*Lehrstuhl für Physikalische Chemie II, Department of Chemistry, University of Dortmund, 4600 Dortmund 50, West Germany*

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Recently,<sup>1</sup> we have studied the two dimensional (2D) fluid-solid phase transition of a one monolayer butane film on the graphitized carbon black Graphon (Cabot Corp., Boston, Mass.). It was found that this transition takes place continuously over the temperature range 113 to 125 K. The bulk (3D) melting point of butane is 134.7 K.<sup>2</sup> The width at half-height of the 2D solid state deuteron spectrum (100 to 112 K) was obtained as  $40 \pm 3$  kHz indicating rapid methyl group rotation. For the 3D solid methyl group rotation has been reported<sup>3</sup> to be slow as compared to the line width for temperatures in the range 63 to 88 K. To have a better basis for the examination of differences of the butane molecule mo-

tional behavior in the 2D and 3D solid states we have decided to measure the 3D deuteron spectra for temperatures greater than 88 K.

In order to achieve good quality polycrystallinity of the solid approximately 0.6 g of thoroughly degassed and heat treated Graphon was loaded with a certain amount of butane C<sub>4</sub>D<sub>10</sub> (Merck, Sharp, and Dohme, Canada) corresponding to ten statistical monolayers or about  $2 \times 10^{20}$  molecules. The deuteron spectra were obtained with the aid of a pulsed NMR spectrometer (CXP 100, Bruker Physik, Karlsruhe, Germany) operated at 13.7 MHz in the quadrature detection mode by Fourier trans-

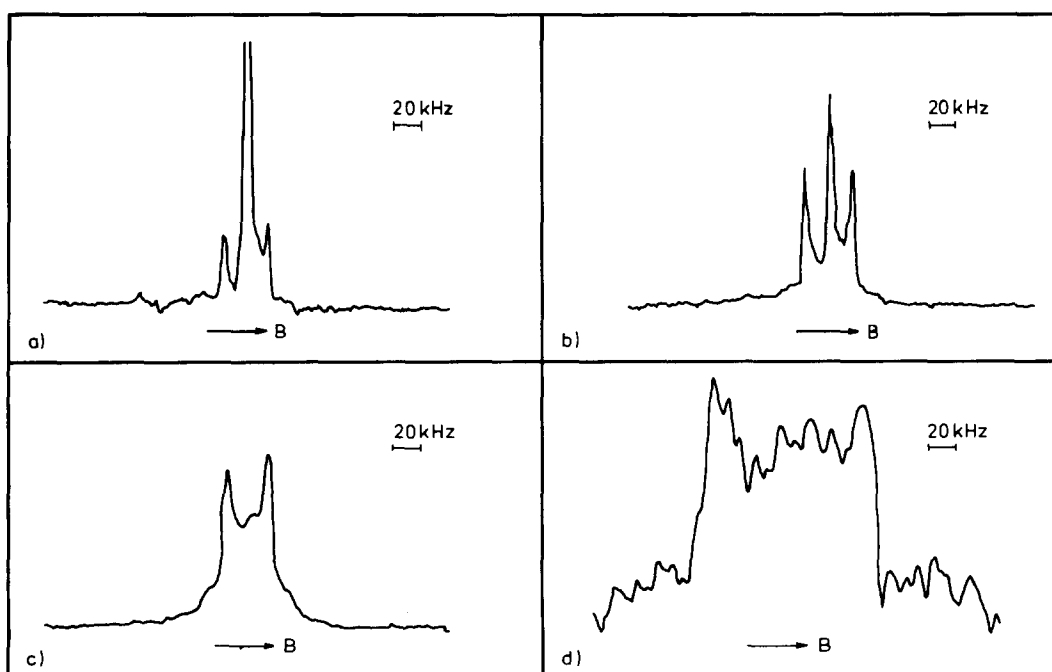


FIG. 1. Deuteron spectra of butane C<sub>4</sub>D<sub>10</sub>/graphitized carbon black. (a) 128 K; (b) 117.5 K; (c) 100 K; (d) 84 K.