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# Vibrational excitation of the allene-fluorine reaction in cryogenic matrices: Possible mode selectivity

Arne K. Knudsen and George C. Pimentel

Chemistry Department, University of California, Berkeley, California 94720 (Received 13 December 1982; accepted 24 February 1983)

The infrared induced reaction of allene  $(C_3H_4)$  and fluorine in N<sub>2</sub>, Ar, Kr, and Xe matrices at 12 K has been studied. The reaction is promoted by the selective vibrational excitation of  $C_3H_4 \cdot F_2$  reactive pairs and the course of the reaction followed by infrared spectroscopy. Four products are detected, consistent with the concerted addition of  $F_2$  across the C–C double bond to form vibrationally excited *cis*- and *gauche*-CH<sub>2</sub>CFCH<sub>2</sub>F which may then eliminate HF to yield either CH=CH<sub>2</sub>CFCH<sub>2</sub>F · HF or CH<sub>2</sub> = C = CHF · HF pairs. The relative abundance of each product depends markedly upon the matrix. Selective vibrational photoisomerization of CH<sub>2</sub> = CFCH<sub>2</sub>F was used to distinguish and assign spectral features due to the *cis*- and *gauche*-rotameters as well as to provide evidence about the torsional barrier in the matrix. In a particular matrix, the allene–fluorine reaction product distribution is independent of the exciting frequency, with measurements at 1679, 1953, 1999, and 3076 cm<sup>-1</sup>. However, the relative quantum yield at 3076 cm<sup>-1</sup> is three orders of magnitude higher than observed at the lower frequencies. Furthermore, the quantum yields at 1680, 1953, and 1999 cm<sup>-1</sup> show differences that implicate mode selectivity in the allene–fluorine reaction. The CH<sub>2</sub> rocking overtone  $2\nu_{10}$  at 1679 cm<sup>-1</sup> show a higher reaction propensity than that of the asymmetric skeletal stretching vibration  $\nu_6$  at 1953 cm<sup>-1</sup>.

#### I. INTRODUCTION

The possibility of vibrational mode-selective excitation of bimolecular reactions in cryogenic matrices has been demonstrated for the ethylene-fluorine reaction.<sup>1,2</sup> (Hereafter, Ref. 2 will be called I.) Other examples of mode-selective or nonstatistical effects involving polyatomic molecules are limited to unimolecular reactions, and they are not numerous.<sup>3,4</sup> Indeed, the preponderance of experimental evidence supports the view that vibrational energy is rapidly randomized on the time scale of chemical reaction.<sup>5,6</sup>

Cryogenic matrices of inert gases differ from conventional environments in that rotational degrees of freedom are "frozen out" and they are replaced by phonon modes of the host lattice that are only weakly coupled to the guest molecule. The result is a sparse energy level density, at least in the energy range of the vibrational fundamentals, and relatively slow relaxation of guest molecule excitation into host lattice heating. This slow relaxation has been manifested in a number of infrared-induced isomerizations in cryogenic matrices: HONO, <sup>7,8</sup>  $N_2O_3$ , <sup>9</sup>  $Fe(CO)_4X$ , <sup>10</sup> and haloethanols. <sup>11-16</sup> These conditions, sparse energy level density and slow relaxation, are favorable for mode-selective excitation of bimolecular reactions and presumably they account for the success reported in I. It behooves us to explore other examples that exploit these potentialities.

Cesaro *et al.*<sup>17</sup> has examined the vinyl bromidefluorine reaction but the low product yields did not permit definitive identification of mode-selective behavior. We investigate here the allene-fluorine reaction which had been shown by Hauge and co-workers<sup>18</sup> to be induced by broadband infrared irradiation in cryogenic matrices. Using tuned laser sources for selective excitation, we have found behavior like that reported in I including, we believe, mode selectivity. These experiments are reported here.

#### II. EXPERIMENTAL

The experimental apparatus is described in I. Equal amounts of allene/inert gas and fluorine/inert gas mixtures were simultaneously deposited at a total flow rate of 1.0 mmol/h through separate jets onto a cold CsI window. The window was cooled to 12 K by a Displex CS-202 closed cycle refrigerator. Typically, 0.5 mmol of pure matrix gas was deposited to protect the cold window, then 3.0 mmol of the reaction mixture. Deposition temperatures were as follows: N<sub>2</sub>, 15 K; Ar, 12 K; Kr, 21 K; Xe, 12 K. After deposition, infrared spectra were recorded and sample irradiation conducted with the window at 12 K.

After the first spectrum, the sample was held at 12 K for 50 min protected from globar illumination. Then a second spectrum was recorded. The difference between these two spectra always showed loss of some parent allene and growth of product bands. This evidence of dark reaction was taken as a quantitative measure of the number of reactive allene-fluorine pairs.

The sample was then irradiated with the infrared source of interest for a measured time. Spectra were recorded periodically to derive kinetic parameters. With the CO laser, irradiation periods were 5-90 min; for all other experiments, the irradiation period was 50 min.

Allene (Matheson, 98%) was purified through two bulbto-bulb distillations before dilution in N<sub>2</sub> (Matheson, O<sub>2</sub>free 99.998%), Ar (Liquid Carbonics, 99.995%), Kr (Matheson, 99.995%), or Xe (Matheson, 99.995%) which were used without further purification. Fluorine (Matheson, 98%) mixtures were passed through a liquid nitrogen trap to remove HF and any condensible impurities. Infrared spectra were recorded using a Nicolet 7199 FTIR spectrometer at a resolution of 0.24 cm<sup>-1</sup> (200 scans) and a frequency accuracy of better than 0.1

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Vibration	Gas phase	$N_2 (\Delta \nu)$	Ar (Δν)	Kr (Δν)	Xe (Δν)
$\nu_{10}(CH_2 \text{ wag, } e)$	841	846.6(+1.5)	837.6(+1.6)	836, 4(+1, 2)	834.8(-0.7)
$\nu_{\vartheta}$ (CH <sub>2</sub> rock, e)	999	999.2(-1.9)	996.7(+0.5)	995,2(?)	994(+ 2, 0)
$\nu_7$ (CH <sub>2</sub> scis, $b_2$ )	1398	1392.6(+0.7)	1389.6(-0.2)	1387.3(+1.0)	1385, 5(+ 0, 5)
2ν <sub>10</sub> (B <sub>2</sub> )	1698	1695,8(?)	1679.5(+0.2)	1676.7	1674.8(+1.6)
$\nu_{\rm g}$ (as, $b_2$ )	1957	1954.6(-5.2)	1955, 2(-1,1)	1952.0(-1.2)	1949.3(+3.7)
2v <sub>9</sub> (B <sub>2</sub> )	2004	2002.2(0.0)	1998.4(+0.3)	1995. 0(- 0, 4)	1992.5(+ 2.5)
$\nu_5$ (CH str, $b_2$ )	3007	2998.6(+0.8)	3000.1(-0.6)	2998.6	3009
ν <sub>8</sub> (CH str, <i>e</i> )	3086	3079,3(-0,2)	3076.8(+3.2)	3067.2(+0,1)	3065
$\nu_{\theta} + \nu_{\theta} (\mathbf{B}_2)$	4056	4061, 2(-2, 5)	4062.6(-2.6)	4065	4052

TABLE I. Selected vibrational frequencies of isolated  $C_3H_4$  with shift due to  $F_2$  nearest neighbor  $(\Delta \nu = \nu_{C_3H_4}, F_2 - \nu_{C_3H_4})$ .

cm<sup>-1</sup>. The infrared sources used were as follows: the spectrometer globar with output filtered by the spectrometer optics to expose the sample to the range 5500-400 cm<sup>-1</sup>, laboratory-built  $CO_2$  and liquid-nitrogen cooled CO flowing gas lasers with single-line output in the regions 1090-920 and 2030-1550 cm<sup>-1</sup>, respectively, and a Kr-ion (Coherent, model CR-750K) or an Ar-ion (Coherent, model CR-8) pumped F-center laser (Burleigh model FCL-10) with continuously tunable output from 4350 to 2950 cm<sup>-1</sup>. Infrared laser power was monitored with a Scientech power meter (Model 3600).

Propargyl fluoride was synthesized by the slow addition of  $HgF_2$  (Columbia Organic Chemical Co. Inc., technical grade) to fractionally distilled propargyl chloride (Columbia Organic Chemical Co., Inc.). The product, propargyl fluoride, was collected in a dry ice-acetone trap atop a reflux condenser attached to the reaction vessel. Following dilution in N<sub>2</sub>, its matrix spectrum was obtained.

### **III. RESULTS**

Allene, the prototype cumulene, has  $D_{2d}$  symmetry. Its gas phase infrared spectrum is well known and there is little ambiguity in the vibrational assignment.<sup>19,20</sup> Matrix frequencies are in good agreement with gas-phase values: for the selection of frequencies given in Table I, average shifts are 4, 6, 9, and 11 cm<sup>-1</sup> in the four matrices, respectively, N<sub>2</sub>, Ar, Kr, and Xe.

For each matrix, a series of concentration studies was performed to distinguish absorption frequencies of isolated allene from those of aggregates. Only a few bands showed distinctive dimer shifts. In contrast, absorptions due to  $C_3H_4 \cdot F_2$  pairs were usually quite apparent, as shown by example in Fig. 1. The asymmetric skeletal stretch  $\nu_6$  of isolated  $C_3H_4$  in N<sub>2</sub> is found at 1954.6 cm<sup>-1</sup> (middle spectrum, Fig. 1). With 2% F<sub>2</sub> added, a new absorption appears at 1949.4 cm<sup>-1</sup> (top spectrum, Fig. 1). After exposure to the spectrometer globar for 7 h, this new feature diminishes, as shown in the difference spectrum (bottom spectrum, Fig. 1). This absorption loss is accompanied by the growth of new bands as shown in Fig. 2, so the 1949.4 cm<sup>-1</sup> feature can be assigned to  $C_3H_4 \cdot F_2$  reactive pairs and the new bands to reaction products. Thus, the course of the light-induced reaction can be followed both through growth of products and loss of reactants. Similar studies in Ar, Kr, and Xe matrices led to the  $C_3H_4$  monomer and  $C_3H_4 \cdot F_2$  reactive pair absorption frequencies given in Table I.

#### A. Infrared-induced, dark, and deposition reaction in Ar

When  $C_3H_4/Ar$  and  $F_2/Ar$  samples are codeposited, a number of absorptions appear that are not present in the spectrum of  $C_3H_4$  in argon and are plainly not connected with allene itself. These new absorptions are readily associated with reaction products formed during condensation and subsequently, either in the dark and/



FIG. 1. Absorption due to the asymmetric skeletal stretch  $\nu_6$  of  $C_3H_4 \cdot F_2$  mixtures in  $N_2$  at 12 K: (a)  $C_3H_4/F_2/N_2=1/4/200$ ; (b)  $C_3H_4/N_2=1/100$ ; (c) Difference spectrum after irradiation of mixture (a) with spectrometer globar for 7 h.



FIG. 2. Difference spectrum showing growth of products (above baseline) and disappearance of  $C_3H_4 \cdot F_2$  pairs (below baseline) of  $C_3H_4/F_2/N_2 = 1/4/200$  sample at 12 K irradiated for 7 h with globar.

or through photochemistry caused by the spectrometer globar. The absorptions associated with sample preparation are readily distinguished from those produced during deliberate irradiation through difference spectra as shown in Fig. 2. Since product absorption growth occurred without change in band shapes, peak heights could be used in quantitative growth studies.

The product growth in Ar at 973.9 cm<sup>-1</sup> (which will be assigned to  $\nu_8$  of H<sub>2</sub>CCCHF  $\cdot$  HF pairs) is shown in Fig. 3 plotted vs irradiation time for several different experiments. Each datum has been corrected for growth during spectroscopic study as well as for the very slow growth that continues in the absence of irradiation. Plainly, growth is faster using laser irradiation at 3075.9 (5.3 mW/cm<sup>2</sup>), 1679.3 (111), 1952.9 (888), and 1999.1 cm<sup>-1</sup> (460 mW/cm<sup>2</sup>) than with the globar source.

Each of these laser source frequencies matches an



FIG. 3. Growth of peak at 973, 9 cm<sup>-1</sup> (assigned to  $H_2C=C=CHF \cdot HF$  pairs) in the dark and due to irradiation with the globar, CO laser, and F-center laser in Ar at 12 K ( $C_3H_4/F_2/Ar = 1/4/200$ ). Each absorbance (A) has been normalized to the same initial  $C_3H_4 \cdot F_2$  reactive pair reservoir.



FIG. 4. Difference spectra showing the regions 1325-1100 and 3350-3250 cm<sup>-1</sup> for  $C_2H_4/F_2/M=1/4/200$  samples irradiated with the spectrometer globar at 12 K. The bands at ~1290, 1234, 1145, and 3311 cm<sup>-1</sup> are assigned to c-H<sub>2</sub>CCFCH<sub>2</sub>F, g-H<sub>2</sub>CCFCH<sub>2</sub>F, H<sub>2</sub>CCCHF • HF, and HCCCH<sub>2</sub>F • HF, respectively: (a) M=Ar, 23 h globar; (b) Kr, 20.5 h; (c) Xe, 18 h, (d) N<sub>2</sub>, 7 h.

absorption of  $C_3H_4 \circ F_2$  reactive pairs. If, on the other hand, the laser frequency is shifted to the product band absorption at 970.7 cm<sup>-1</sup> at 401 mW/cm<sup>2</sup> for 2 h, no increase in product bands was observed. This experiment shows that product growth cannot be attributed to bulk heating and/or diffusion.

#### B. Product distribution in Ar matrix

Table II lists, in the second column, the major product features that appear during irradiation of  $C_3H_4/F_2/$ Ar=1/4/200 samples deposited and irradiated at 12 K. (The basis for assignments will be discussed later.) Figure 4(a) displays two portions of the difference spectrum recorded after 23 h of globar irradiation. The regions 3350-3250 and 1325-1100 cm<sup>-1</sup> are expanded to show a characteristic band due to each of the four reaction products, to be compared with the same regions in Kr, Xe, and N<sub>2</sub>. In the high frequency range (not shown) 3700-4000 cm<sup>-1</sup> where HF absorptions are expected there

TABLE II. Intense  $C_3H_4/F_2$  product bands<sup>2</sup> after globar exposure (5500-400 cm<sup>-1</sup>), in M=N<sub>2</sub>, Ar, Kr, and Xe,  $C_3H_4/F_2/M=1/4/200$ .

N <sub>2</sub> <sup>b</sup>	Ar	Kr	Xe	Assignment (Ref. 27)
3805.9 (0.007) 3788.2 (0.043) 3778.8(0.034) 3311.0(0.033)	 3810 3823 3319.1	3796 3851.6 3826 3311	<b>3795</b> ••• 3821.9	HF unidentified $\nu_{HF}$ (P) $\nu_{HF}$ (F) P ( $\nu_1$ , 3338)
2140.7(0.015)	2135	2141.8	2140	P ( $\nu_3$ , 2150)
1696. 3(0. 024) 1687. 2(0. 046) 1676. 5	1693.7 1686.6 1676.5	1692.6 1683.9 c	1691 1685 c	g c c
1444.4(0.007)	1442.2	1439.8	1437.8	F (V4, 1451)
1397.4	1395.5	1393.6	1392.6	с
1321.6	1324.6	1322.6	1320.0	F (v <sub>6</sub> , 1336)
1289.5(0.064) 1267.8(0.011) 1232.6(0.036) 1145.4(0.017)	1289.7 1269.9 1234.8 1148.9	1287.8 1268.6 1233.3 1147.1	1286.7 1269.8 1231.2 1145.6	c P (2v <sub>14</sub> , 1260) g F (v <sub>7</sub> , 1165)
1070.3(0.038)	1080,5	1077.7	1072	g
1028.0	1037.8	1031.6	1029	c, P(v <sub>6</sub> , 1039)
1023.7(0.041)	1025	• • •	1023,2	с
1000.3	1001.5	999.8	999	c
988.1(0.020)	•••	986.9	•••	?
970.7(0.019)	973.9	972.3	970.7	F ( <i>v</i> <sub>8</sub> , 996)
943.8	942.7	941.7	941.5	с
937.9	938.0	937.3	936.4	g
934.3	* * *	933.6	• • •	P (v <sub>7</sub> , 940)
902	900.8	898.9	897	g
883.2	872.5	871.4	872.3	с
858.0	858.8	857.5	859.6	с
461.3	460	460	472	с

<sup>a</sup>Other weaker absorptions in N<sub>2</sub> include: HF: 3850, 3812;  $c = cis - C_3H_4F_2$ : 1682, 1458, 1373, 863;  $g = gauche - C_3H_4F_2$ : 1460, 1407; F = fluoroallene • HF: 3006, 2896, 1982, 1095, 907, 813, 598; P = propargyl fluoride • HF: 1471, 1378, 1310, 1245, 659, 545; unidentified: 1346, 1156. <sup>b</sup>Peak optical densities of the three largest bands due to each product in N<sub>2</sub> are listed parenthetically (Globar exposure, 7 h).

These absorptions overlap a C<sub>3</sub>H<sub>4</sub> absorption.

is an intense absorption at  $3823 \text{ cm}^{-1}$  and a broader side band at  $3810 \text{ cm}^{-1}$ . These absorptions, attributable to HF hydrogen bonded to a cage partner, are shifted, respectively, by 130 and 144 cm<sup>-1</sup> from HF isolated in Ar at 3953.8 cm<sup>-1</sup>. Also quite distinctive are the weak bands at 3319.1 and 2135 cm<sup>-1</sup>. In addition, there are many distinct absorption features between 1700 and 800 cm<sup>-1</sup>, the strongest being 1686.6, 1289.7, 1234.8, 1148.9, 1080.5, 1037.8, 1001.5, 973.9, 942.7, and 872.5 cm<sup>-1</sup>.

#### C. Product distribution in Kr matrix

The Kr matrix samples were deposited at 21 K and then irradiated at 12 K. There is more prereaction than in Ar but parent absorptions are sharper. Figure 4(b) shows a difference spectrum after 20.5 h of globar irradiation. There are five absorptions in the  $3700-4000 \text{ cm}^{-1}$  region, two of which, at 3851.6 and at  $3825.6 \text{ cm}^{-1}$  (shifted, respectively, by 82 and 108 cm<sup>-1</sup> from the HF monomer in Kr) might be associated with the two argon matrix counterparts (see Table II). There are clear absorptions at 3311 and at  $2141.8 \text{ cm}^{-1}$ , the first more intense although weak and the second comparable to the similar argon absorptions. In the  $1700-800 \text{ cm}^{-1}$  region the strongest features, at 1683.9, 1287.8, 1031.6, 999.8, 941.7, and  $871.4 \text{ cm}^{-1}$ , match both in frequency and intensity six of the most prominent features in the argon matrix spectrum.

In contrast, the absorptions at 1233.3 and 1077.7  $\text{cm}^{-1}$  are close in frequency to two of the argon bands but relatively weaker. Still weaker are the two Kr matrix bands at 1147.1 and 972.3  $\text{cm}^{-1}$ . Thus, for each of the



FIG. 5. Difference spectrum after irradiation at 1076.0 cm<sup>-1</sup> (indicated by arrow) for 34 min with 850 mW/cm<sup>2</sup> of a  $C_3H_4/F_2/Ar = 1/3/200$  sample previously irradiated for 4.5 h at 1999.1 cm<sup>-1</sup> and overnight with the globar. Those bands above the base-line increased in intensity while those below decreased in intensity.

ten most intense argon matrix absorptions below 3400 cm<sup>-1</sup> there are close krypton matrix counterparts but with substantially differing relative intensities. These features, then, furnish an initial indication that several products are formed, and in varying amounts.

#### D. Product distribution in Xe matrix

When xenon matrix samples were deposited at 45 K, broad absorption bands characteristic of aggregate spectra were obtained and there was little evidence of induced reaction even after 30 h of globar irradiation. When a  $C_3H_4/F_2/Xe = 1/4/200$  sample was deposited at 12 K, sharp parent spectral features were observed. After 18 h of globar irradiation, there was substantial evidence of reaction as shown in Fig. 4(c). (Again, all product bands are listed in Table II.) Three absorptions appear in the  $3700-4000 \text{ cm}^{-1}$  region, at 3821.9, 3795, and 3777 cm<sup>-1</sup>. Since HF monomer in Xe is found at 3911 cm<sup>-1</sup>, these represent shifts of 89, 116, and 134 cm<sup>-1</sup>. For the xenon matrix, no absorption could be detected near 3300 cm<sup>-1</sup> and the absorption at 2140 cm<sup>-1</sup> is extremely weak. In the 1700-800 cm<sup>-1</sup> region, the most prominent features are at 1437.8, 1145.6, and 970.7  $cm^{-1}$ , the latter two of which correspond to much weaker counterparts in argon and krypton. Present, but relatively weaker, are absorptions at 1286.7, 1029, and 872.3 cm<sup>-1</sup> as well as at 1231.2 and 1072 cm<sup>-1</sup>. Again, the product frequencies match but relative intensities indicate that Xe has a still different product distribution than either Ar or Kr.

#### E. Product distribution in N<sub>2</sub> matrix

Prereaction in nitrogen matrices is more pronounced than in the inert gas matrices. Surprisingly, this effect seemed to be somewhat greater with a sample deposition temperature of 12 K than at 15 K. Also, there is more prereaction product absorption in the HF region  $3700-4000 \text{ cm}^{-1}$  and more at  $3311 \text{ and } 2140.7 \text{ cm}^{-1}$ .

Figure 4(d) shows the expanded portions of the difference spectrum (Fig. 2) associated with product growth after 7 h of globar irradiation of a  $C_3H_4/F_2/N_2 = 1/4/200$ sample at 12 K. Five distinct bands appear at 3851, 3812, 3805.9, 3788.2, and 3778.8 cm<sup>-1</sup> but the intensities of the first three of these decreased as allene concentration was decreased in a series of experiments at  $C_{3}H_{4}/F_{2}/N_{2} = 1/1/100$ , 1/4/200, and 1/20/1000. Thus, the lowest two frequencies, with hydrogen bonding shifts from the monomer frequency (3879.5 cm<sup>-1</sup>) of 91.3 and 100.7 cm<sup>-1</sup>, are of most interest. Most distinctive, perhaps, were the high intensities of the two product features at 3311.0 and 2140.7 cm<sup>-1</sup>, relatively much more intense than in any of the rare gas matrices. Below 1700 cm<sup>-1</sup>, Fig. 2 shows that there are many more product bands discernable than in the other matrices. As in Ar and Kr, the product features at 1687.2, 1289.5, 1028.0, and 883.2  $\rm cm^{-1}~are~among$ the most intense. The two features at 1232.6 and at 1070.3 cm<sup>-1</sup> are also comparable in relative intensity to their argon counterparts, as are the remaining pair of comparison bands at 1145.4 and at 970.7  $cm^{-1}$ .

#### F. Laser-induced product interconversion

To identify products and their substituent infrared bands, various product absorptions accessible to our CO and CO<sub>2</sub> lasers were systematically irradiated with the hope of observing product isomerization or further reaction. Figure 5 shows the results of such an experiment using  $C_3H_4/F_2/Ar = 1/3/200$  sample that had been previously irradiated with the CO laser at 1999.1 cm<sup>-1</sup> and exposed to the globar overnight. The figure shows a difference spectrum following an additional irradiation at 1076.0 cm<sup>-1</sup> for 34 min with a laser power of 850 mW/ cm<sup>2</sup>. Those peaks above the baseline, including the features at 1686.6, 1289.7, 1034.8, and 872.5 cm<sup>-1</sup>, grew in during the irradiation. Those peaks below the baseline, including the band irradiated at 1076.6 cm<sup>-1</sup> and the feature at 1232.4 cm<sup>-1</sup>, decreased during irradiation. Meanwhile, there were no noticeable changes in the features at 1148.9 or at 973.9 cm<sup>-1</sup> as manifested by their absence in the difference spectrum. Also unaffected were the two absorptions at 3319.1 and at 2135 cm<sup>-1</sup>. The simplest interpretation of these experiments is that the product molecules responsible for the irradiation bands at 1076.6 cm<sup>-1</sup> are converted through isomerization into the product molecules whose absorption features grew. The absorption bands of product molecules not involved in the isomerization were unaffected. Thus, the experiment provides a powerful means of identifying those bands that can be classified together and related to a particular product.

To test this interpretation, the same sample was then irradiated at 1686.7 cm<sup>-1</sup> using the CO laser for 30 min with a power of  $1060 \text{ mW/cm}^2$ . This time, the difference spectrum showed that the bands at 1686.6, 1289.7, 1037.8, 1034.8, 1031.9, and 872.5 cm<sup>-1</sup> all decreased

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while the 1076.6 cm<sup>-1</sup> feature increased, as did the features at 1232.4 and 1234.2 cm<sup>-1</sup>. With a return to irradiation at 1076.0 cm<sup>-1</sup>, the previously observed changes were reproduced. Both the 1076.6 and 1232.4 cm<sup>-1</sup> bands belong to a product formed exclusively during prereaction.

Therefore, using a similarly prepared sample, we irradiated the band at 1080.5 cm<sup>-1</sup> with the CO<sub>2</sub> laser at 1081.1 cm<sup>-1</sup> (15 min, 416 mW/cm<sup>2</sup>). We again observe the growth of the bands at 1686.6 and 1289.7 cm<sup>-1</sup> as well as a band at 1031.9 cm<sup>-1</sup> which is a shoulder of the strong band at 1034.8 cm<sup>-1</sup>. Decreasing bands include those at 1693.7, 1234.8, and  $1080.5 \text{ cm}^{-1}$ . Thus, it was possible to classify quite a number of bands as absorptions of two reversibly interconverted isomers present in differing environments, leading to the observed splitting of the bands. One of these isomers has prominent absorptions at 1686.6, 1455.9, 1395.5, 1289.7, 1037.8, 942.7, and  $872.5 \text{ cm}^{-1}$ . The other isomer is present in at least two different environments; one after deposition, and the second resulting from the IR-induced reaction, which has prominent absorptions at 1693.7, 1234.8, and 1080.5 cm<sup>-1</sup>. Of course the interconversion experiments also identified many weaker bands as listed in Table II.

As a further exploration of this interpretation, the experiment was repeated in N<sub>2</sub>, Kr, and Xe. The coincidence between product absorption features and our CO and CO<sub>2</sub> lasers was best in N<sub>2</sub> where we have irradiated each laser accessible band. The results are shown in Table III in which the bands that behave like 1070.3 cm<sup>-1</sup> are labeled "g" and the ones that behave like 1687.2 cm<sup>-1</sup> are labeled "c." The g-c conversion was observed with irradiation at all three of the accessible bands, at 1694.7, 1070.3, and 937.9 cm<sup>-1</sup>. The c + g conversion, however, took place only with irradiation at 1687.2 cm<sup>-1</sup>; no changes were observed if irradiation was carried out at 1028.0 or 943.8 cm<sup>-1</sup>.

As one final test, the  $CO_2$  laser was tuned to its lines

at 934.9 and 970.5 cm<sup>-1</sup>, two frequencies that are absorbed by products not affected when the laser irradiation is at any frequency that induces the c = g interconversion. As expected, even after 52 min of irradiation with 46 mW/cm<sup>2</sup> at 934.9 and 120 min of irradiation with 401 mW/cm<sup>2</sup> at 970.5 cm<sup>-1</sup>, no isomerization or change in any absorption took place.

There is one more characteristic of these interconversion experiments that deserves mention. An expanded, high resolution spectrum of the 1076.6 cm<sup>-1</sup> band after a period of irradiation showed that the depleted absorption was centered about the irradiating laser frequency, i.e., "hole-burning" had taken place. On the other hand, the half-width of the "hole" was about  $0.4 \text{ cm}^{-1}$ , to be compared to our laser linewidth of less than  $0.01 \text{ cm}^{-1}$ .

#### IV. DISCUSSION

#### A. Possible reactions

Apparently the reaction of allene and fluorine has not been studied. Peer<sup>21</sup> and Poutsma<sup>22</sup> have examined the chlorination of allene in the dark at -30 °C in inert, nonpolar solvents. They found three major products in approximately equimolar amounts, 2, 3-dichloropropene H<sub>2</sub>C=CClCH<sub>2</sub>Cl, propargyl chloride HC=CCH<sub>2</sub>Cl, and hydrochloric acid HCl along with minor amounts of C<sub>6</sub> products. No chloroallene H<sub>2</sub>C=C=CHCl was reported. Peer<sup>21</sup> contends that HC=CCH<sub>2</sub>Cl is not formed through elimination of HCl from an H<sub>2</sub>C=CClCH<sub>2</sub>Cl intermediate. Instead, he proposes that HC=CCH<sub>2</sub>Cl is a primary product formed in a separate mechanism involving a six membered ring in an intermediate, bridged structure.

In contrast, the products observed in the infraredinduced matrix reaction of ethylene and fluorine are consistent with a concerted addition of  $F_2$  across the double bond followed by deactivation or HF elimination. If this mechanism were presumed to apply to allene, either 1, 2 or 2, 3 HF elimination could occur.

#### $\Delta H(\text{kcal/mol})^{23}$

$H_2C = C = CH_2 + h\nu - H_2C = C = CH_2^{T}$		
$H_2C = C = CH_2^{\dagger} + F_2 - cis - H_2C = CFCH_2F^{\dagger}$	- 129.0	(1a)
$-gauche-H_2C=CFCH_2F^{\dagger}$	- 128.6	(1b)
c- or $g$ -H <sub>2</sub> C=CF-CH <sub>2</sub> F <sup>†</sup> → H <sub>2</sub> C=C=CHF + HF	- 108.1	(2a)
$\rightarrow HC \equiv C - CH_2F + HF$	- 107.4	(2b)
c - or $g$ - H <sub>2</sub> C=CF-CH <sub>2</sub> F <sup>†</sup> + M - $c$ - or $g$ - H <sub>2</sub> C=CI	$FCH_2F + M$ .	(3)

Г

Reactions (1), (2), and (3) provide a basis for interpretation of the product bands observed here.

#### B. Identification of propargyl fluoride

Propargyl fluoride was suspended in solid  $N_2$  at a mole ratio of 1/100. The most intense absorptions at 3314, 1364, and 1023 cm<sup>-1</sup> with weaker features at 2977, 2139, 1444, 958, 686, 645, and 532 cm<sup>-1</sup> obviously cor-

respond both in intensity and frequency to the gas phase frequencies<sup>24</sup> at 3338  $(\nu_1)$ , 1381  $(\nu_5)$ , 1039  $(\nu_7)$ , 2977  $(\nu_{11})$ , 2150  $(\nu_3)$ , 1465  $(\nu_4)$ , 940  $(\nu_7)$ , 675  $(\nu_8)$ , 635  $(\nu_{14})$ , and 539  $(\nu_9)$  cm<sup>-1</sup>. Two of these frequencies, at 3314 and 2139 cm<sup>-1</sup>, which are especially characteristic, surely can be related to the prominent product absorptions at

Band irradiated	Assignment (Ref. 27)	Laser line <sup>2</sup>	Result
1694.7	g	1694.0	$g \rightarrow c$
1687.2	С	1686.7	$c \rightarrow g$
1070.3	g	1070.4	g→ c
1028.0	С	1027.4	No reaction
970.7	F	970.5	No reaction
943.8	С	944.2	No reaction
937.9	g	936.8	$g \rightarrow c$
934.8	Р	934.9	No reaction

TABLE III. Laser-induced isomerization in  $N_2$ .

<sup>2</sup>Irradiation was typically for 1 h with  $\sim 300 \text{ mW/cm}^2$ .

3311.0 and 2140.7 cm<sup>-1</sup> in the N<sub>2</sub> matrix and to their related absorptions in Ar and Kr. The frequency differences indicate nearest-neighbor shifts due to HF in the N<sub>2</sub> cage of 3 and 1 cm<sup>-1</sup>, respectively. Since these absorption frequencies are especially characteristic of the acetylenic C-H stretch and C=C stretch, there can be no doubt that *propargyl fluoride is an infrared-induced product in the present work*. With this identification, every one of the frequencies listed above has a counterpart in the product spectra, as labeled in Table II.

#### C. Identification of fluoroallene

The infrared spectrum of gaseous fluoroallene has been reported.<sup>25</sup> There is a close correspondence between the most intense gas-phase frequencies at 1165 and 996 cm<sup>-1</sup> and the two comparison product features reported here at 1145.4 and 973.9 cm<sup>-1</sup> in solid N<sub>2</sub>. The implied matrix shifts of 15 and 22 cm<sup>-1</sup> are plausible. Consequently, these two features can be assigned with confidence to show that *fluorallene is a second infrared-induced product* in the present work, presumably formed in reaction (2a). The gas phase spectra permit assignment of several other features attributable to fluoroallene, as listed in Table II.

#### D. Identification of 2,3-difluoropropene

English and co-workers<sup>26</sup> reported infrared absorption frequencies of 2,  $3-H_2C=CFCH_2F$  below 1000 cm<sup>-1</sup>. Though they show no spectra and do not indicate relative intensities, their tabulated frequencies at  $945\pm5$ ,  $865\pm5$ ,  $635\pm2$ , and  $457\pm2$  cm<sup>-1</sup> correspond closely to some of the matrix product absorptions at these longer wavelengths. No counterparts are found for the gas-phase absorptions at 775\pm2 and  $510\pm5$  cm<sup>-1</sup> while some of their frequencies, 389, 328, and 242 cm<sup>-1</sup>, are out of our spectral range. Nevertheless, the four matching frequencies suffice to indicate that 2,  $3-H_2C=CFCH_2F$  is probably formed and stabilized as suggested by reactions (1) and (3).

Equally important, however, is the identification by English *et al.* of two rotational conformers and their deduction of the potential function associated with interconversion. Their far-infrared and microwave spectra indicate that the *cis* species is more stable than the two gauche conformers by  $145 \pm 60 \text{ cm}^{-1}$  and that the cis – gauche barrier is  $1000 \pm 100 \text{ cm}^{-1}$ . This implies that the gauche – cis barrier is smaller,  $855 \text{ cm}^{-1}$ , with an uncertainty near  $120 \text{ cm}^{-1}$ . These observations immediately provide a clear basis for interpreting our interconversion experiments. Plainly the reversible changes indicate that infrared excitation of one difluoropropene conformer converts it into the other. Furthermore, all of the frequencies that decrease in concert can be assigned to the same conformer and all those that increase to the other. The outcome is that almost every feature in the crowded product spectrum is accounted for with confidence by the four products of reactions (1) and (2).

The data in Table III also provide a basis for deciding which conformer is cis and which is gauche. If we presume that the matrix does not substantially change the relative stability of the cis- and gauche-forms, then the barrier to isomerization of gauche into cis must be lower than that for cis into gauche. Our evidence is that one conformer can be converted to the other with excitation at 1694.7, 1070.3, or 937.9 cm<sup>-1</sup> whereas the reverse change occurs with excitation at  $1687.2 \text{ cm}^{-1}$  but not at 1028.0 or 943.8 cm<sup>-1</sup>. If we now add the assumption that the interconversion is primarily limited by whether the exciting photon gives the molecule enough energy to surmount the rotational barrier, then 937.9  $\mathrm{cm}^{-1}$  is enough to convert one conformer to the other form but 1028.0 cm<sup>-1</sup> is not enough to reverse the change. The latter must then, involve the more stable conformer-we label it cis-. By inference, the  $cis \rightarrow gauche$  barrier is at least 90 cm<sup>-1</sup> higher than that of gauche - cis, so cis is at least 90 cm<sup>-1</sup> more stable.

Summarizing, we feel that the identification of the two interconvertible forms of 2, 3-difluoropropene is definite. The labeling of the two conformers, *cis*- and *gauche*-, is somewhat more questionable since it depends upon additional assumptions. We intend to pursue further these assumptions, since the apparent similarity between the gas phase evidence and the matrix evidence about barriers and relative stabilities suggests that we have a new technique for learning quantitatively about relative energies of conformational isomers and about the barriers to their interconversion.

#### E. Matrix effect

It is evident in Fig. 4 that the  $C_3H_4/F_2$  product distribution is dependent upon the matrix material. This conclusion is quantitatively demonstrated in Table IV based upon the integrated intensities of nine well identified and isolated product absorptions in typical globar experiments. The intensities for the nitrogen matrix are given for reference purposes. Each of the other matrix intensities is expressed relative to the intensity of the same band in an  $N_2$  matrix. The quality of the data is probably indicated by the three fluoroallene bands. If the matrix does not perturb the individual band intensities, then the three bands should give the same value of  $R_{N_2}^M$  for a given matrix M. In fact, the three values of  $\tilde{R}_{N_2}^{Ar}$  average at 1.47 with a standard deviation of 12%. The three values of  $R_{N_2}^{K_r}$  average 0.84 with  $\sigma = 25\%$  and  $R_{N_2}^{X_0}$  at 0.78 with  $\sigma = 17\%$ . Whether these standard deviations signal the magnitude of matrix intensity perturbations, the quality of the data, or both, they are small enough to indicate real differences between the amount of fluoroallene in the four matrices.

The intensity measurements for fluoroallene suggest that somewhat more of this product is obtained in an argon matrix than in any of the other three matrices, ranging from about 1.5 times the  $N_2$  amount to almost double the Xe amount. Such modest differences could be entirely due to differences in the concentrations of

TABLE IV. Integrated intensities of product bands in various matrices after globar irradiation.

	N <sub>2</sub>	Ar	Kr	Xe
$\nu (\rm cm^{-1})$	$A_{N_2}(\nu)d\nu$	R <sub>N2</sub> <sup>Ar<sup>a</sup></sup>	R <sub>N2</sub> <sup>Kra</sup>	gN2 a
$cis-H_2C=CFCH_2F(c)$				-
1289	0.155	0.82	1.16	0.12
883	0.120	0.62	1.13	0.10
average	•••	0.72	1.14	0.11
$gauche-H_2C=CFCH_2F(g)^b$				
1332	0.076	0.4	0.4	0.05
1070	0.138	0.7	0.8	0.04
average	•••	0,6	0.6	0.05
fluoroallene(F)				
970	0.064	1.44	0.78	0.93
1145	0.049	1.32	1,07	0.68
1444	0.020	1.66	0.66	0,74
average	•••	1.47	0,84	0,78
propargyl fluoride (P)				
3331	0.089	0.00	0.31	0,00
2140	0.021	0.36	0.41	0.00
average	•••	0.18	0.36	0.00

 ${}^{a}R_{N_{2}}^{M} = (A_{N}^{(\nu)d\nu}/A_{N_{2}}^{(\nu)d\nu}).$ 

<sup>b</sup>g intensity measurements in Ar, Kr, and Xe are low due to the  $g \rightarrow c$  interconversion of  $g-C_3H_4F_2$  present as a result of prereaction.

TABLE V. Branching ratio dependence upon matrix.

	Ar/N <sub>2</sub>	Kr/N <sub>2</sub>	$Xe/N_2$
$\frac{\overline{R}_{N_2}^{M}(F)}{\overline{R}_{N_2}^{M}(c)}$ (Ref. 27)	2.04	0.74	7.1
$\frac{\overline{R}_{N_2}^{M}(\mathbf{P})}{\overline{R}_{M_2}^{M}(c)}$	0.25	0.32	0.0

reactive pairs due to different deposition behaviors. Such a mundane explanation will not, however, account for the contrasts shown by the other products. Propargyl fluoride is found in largest amount in the  $N_2$  matrix, and there is only one-third as much of this product in the Kr matrix. There is even less propargyl fluoride seen in Ar, about one-fifth the  $N_2$  amount, and none at all in Xel

Determination of the amounts of cis- and gauche-2, 3difluoropropene in Ar, Kr, and Xe is complicated by the g - c interconversion of g-species present following deposition. In the difference spectra, all g-bands growing with IR irradiation are obscured by partially overlapping negative absorptions due to this isomerization [e.g., see 1234 cm<sup>-1</sup> in Figs. 4(a)-4(c)]. At the same time, c bands represent species due to both isomerization and IR-induced reaction. Crude analysis of the relative peak heights of c and g bands in each of the four matrices suggests that the relative amounts of the two isomers are not significantly affected by the matrix. There are, however, significant differences in their absolute amounts. Concentrating on  $c-H_2CCFCH_2F$ , we see that in krypton there is somewhat more than in  $N_2$ , which in turn, exceeds that found in argon. Again for this product, the xenon matrix yield is distinctively low  $[e.g., see 1286.7 \text{ cm}^{-1} \text{ in Fig. 4(c)}]$ . We conclude that the product branching ratios are strongly affected by the matrix environment.

The absolute amounts of the various products cannot be decided because the extinction coefficients are not known. These coefficients cancel, however, in the ratios of average values of  $R_{N_2}^{M}$ , so such ratios indicate quantitatively the change in branching ratios going from nitrogen to another matrix. Table V shows these ratios; the first row relates the channels forming fluoroallene and difluoropropene and the second row the channels forming propargyl fluoride and difluoropropene. If the mechanism of Sec. IV A is correct in detailing the successive reactions (1)-(3) leading to each of the four products, we can see that the branching between elimination, reactions (2a) and (2b), and stabilization [reaction (3)], is matrix dependent. In argon, reaction (2a) is twice as important as in nitrogen, whereas reaction (2b) is only one-fourth as important. Thus, in argon matrices, elimination is a significant pathway, with a strong preference for fluoroallene over propargyl fluoride. In krypton, reaction (2a) is only slightly disfavored while reaction (2b) is, as in argon, much less important than in nitrogen. Thus, stabilization of difluoropropene [reaction (3)] is favored over elimination to form fluoro-

Source	Laser intensity (mW/cm <sup>2</sup> )	Irradiation time (h)	$k^{\mathrm{F}}$	k <sup>c</sup>	k <sup>g</sup>
Dark	•••	6	0, 000 <b>36</b>	0.00056	0
Globar (5500-400 cm <sup>-1</sup> )	•••	22.5	0.00193	0, 00 <b>3 5</b> 6	0.00151
CO laser-1679.3 cm <sup>-1</sup>	111	4	0.0120	0.00174	0.0141
CO laser-1958.9 cm <sup>-1</sup>	493	3,3	0.0118	0,00756	0.0119
CO laser-1958, 9 cm <sup>-1</sup>	888	1.6	0.0142	0.0118	0.0207
CO laser-1958.9 cm <sup>-1</sup>	888	2.8	0.0171	0.00801	0.0182
CO laser-1999.1 cm <sup>-1</sup>	230	6.0	0.00167	0.00062	0.00114
CO laser-1999. 1 cm <sup>-1</sup>	460	6.8	0.00322	0.001 04	0.00431
F-center laser 3075. 9 cm <sup>-1</sup>	5.3	5.8	0.00596	0, 005 27	0. 006 57

TABLE VI. Rate constants (min<sup>-1</sup>) for product formation  $-C_3H_4/F_2/Ar = 1/4/200$ .

allene and in particular, propargyl fluoride in krypton matrices. In xenon, the elimination to form fluoroallene is seven times more important than in nitrogen relative to the stabilization of difluoropropene while propargyl fluoride is not detected at all.

#### F. Rate constants

The product growth curves shown in Fig. 3, like those observed in I, can be well fitted to a first order rate law with the rate of product formation proportional to the number of reactive  $C_3H_4 \cdot F_2$  pairs present after deposition. As in the earlier work, such analysis gives a rate constant for product growth  $k_p$  and the product absorbance at infinite time  $A^P_{\infty}$ . These two parameters are determined through optimization of the correlation coefficient in a least-squares fit to the equation

$$\ln \frac{A_{\infty}^P - A_t^P}{A_{\infty}^P - A_0^P} = -k_P \cdot t \quad ,$$

where  $A_t^P$  and  $A_0^P$  represent peak absorbances at time tand at t=0 for a particular product P. Typically, correlation coefficients exceeded 0.999. The results are displayed in Table VI. For the laser experiments, the curves have been corrected for growth due to the dark reaction and during spectroscopy.

Table VI indicates that the globar leads to a five- to sixfold increase in the rate constants for formation of  $c-C_3H_4F_2$ ,  $k_c$ , and of  $CH_2=C=CHF \cdot HF$  pairs,  $k_F$ , over the corresponding dark reactions.<sup>27</sup> With CO laser excitation,  $k_F$  is larger by factors of 8.9 at 1999.1 cm<sup>-1</sup> (460 mW/cm<sup>2</sup>), 33.3 at 1679.3 cm<sup>-1</sup> (111 mW/cm<sup>2</sup>), and 39.4 at 1952.9 cm<sup>-1</sup> (888 mW/cm<sup>2</sup>) whereas F-center laser excitation yields a  $k_F$  larger by a factor of 16. Clearly, selective vibrational excitation of reactive pairs with the high power densities afforded by our tunable infrared lasers results in significant reaction rate enhancements.

Table VI also shows the effect of changing the laser power. Thus, with a change of laser power at 1952.9 cm<sup>-1</sup> from 493 to 888 mW/cm<sup>2</sup>, by a factor of 1.8, the product rate constants change, on the average, by a factor of 1.4 (standard deviation,  $\pm 0.2$ ). We feel that these factors are close enough to indicate a one-photon process. The same conclusion is reached for  $k_{\rm F}$  with laser irradiation at 1999.1 cm<sup>-1</sup>. Here a doubling of laser power (230 to 460 mW/cm<sup>2</sup>) causes a change in  $k_{\rm F}$  by a factor of 1.9. This same change in laser power has rather different effects upon the rate constants  $k_c$ and  $k_f$ . The former rate constant increases by a factor of 1.7 while the latter changes by a factor of 3.8. We attribute these apparently anomalous factors to the fact that the laser-induced reaction rate is no longer much greater than the dark interconversion rate. We shall see in the next section that there are other instances where  $c \rightarrow g$  or  $g \rightarrow c$  conversion during product formation may be complicating interpretation of product growth curves.

#### G. Branching ratios in product distribution

In argon matrix experiments we have sought to determine whether product branching ratios depend upon the irradiation frequency. Table VII tabulates the results expressed as  $c_F$ ,  $g_F$ , and d, defined as follows:

$$c_{\rm F} = \frac{A(c, 1289.7)}{A(F, 973.9)}$$
,  
 $g_{\rm F} = \frac{A(g, 1234.8)}{A(F, 973.9)}$ ,  
Ref. 27

and

$$d = \frac{A(c, 1289.7)}{A(g, 1234.8)}$$

The ratios are calculated using peak absorbances to reflect their integrated intensities. Each ratio was calculated at each spectroscopic measurement so the entries in Table VII are average quantities  $\overline{c}_{\mathbf{F}}$ ,  $\overline{g}_{\mathbf{F}}$ , and  $\overline{d}$ , each involving several measurements and sometimes more than one experiment.

The last three rows show agreement within experimental uncertainty between the branching ratios associated with irradiation at 3075.9, at 1999.1, and at 1952.9 cm<sup>-1</sup>. This cannot be said to be true for irradiation at 1679.3 cm<sup>-1</sup>. The value of d is about one third the average d for the three higher laser frequencies. This can

TABLE VII. Branching ratios  $C_3H_4/F_2/Ar = 1/4/200$ .

Source	$\overline{c}_{\mathbf{F}}$	<u></u> <i>Rr</i>	$\overline{d}$
Dark	$2.13 \pm 0.32$	0	0
Globar	$1.36\pm0.07$	$0.81 \pm 0.04$	$1.69 \pm 0.12$
CO laser at 1679.3 $cm^{-1}$	$0.16 \pm 0.09$	$1.03 \pm 0.03$	$0, 22 \pm 0, 04$
CO laser at 1952. 9 $cm^{-1}$	$0.29 \pm 0.04$	$0.79 \pm 0.07$	$0.37 \pm 0.03$
CO laser at 1999.1 cm <sup>-1</sup>	$0,32\pm0,09$	$0.64 \pm 0.12$	$0.53 \pm 0.22$
F-center laser at 3075. 9 cm <sup>-1</sup>	$0.32 \pm 0.05$	$0.66 \pm 0.01$	$0.48 \pm 0.08$

be interpreted to indicate that the laser frequency 1679.3 cm<sup>-1</sup> is absorbed by the *cis* product, as it is being formed, converting it to the *gauche*.

The second row shows that the globar gives still another behavior. Here the ratio  $\overline{d}$  is almost four times the average obtained at 1952.9, 1999.1, and 3075.9 cm<sup>-1</sup>. This could signal net *gauche* to *cis* conversion. This outcome is consistent with the continuum nature of the source and our earlier observation that the *gauche* rotamer is converted to *cis* more readily than the reverse.

Even more extreme variations are observed in the dark reaction branching ratios. It is conceivable that these values reflect the room temperature radiation impinging on the sample during the so-called dark periods. These longer wavelengths should favor the gauche to cis conversion in accord with our deduction that this conversion has the lower activation energy barrier.

#### H. Quantum yields

The most interesting parameters to be derived from the kinetic analysis are the quantum yields  $\phi_P$ . For optically thin samples,  $\phi_P$  is related to the measured  $k_P$  through the laser intensity I and  $C_3H_4 \cdot F_2$  extinction coefficient  $\epsilon$ :

 $\phi_P = k_P / I \cdot \epsilon$  .

The most uncertain term is  $\epsilon$  because it requires an estimate of the concentration of  $C_3H_4 \cdot F_2$  pairs. An estimate of this concentration can be based upon an assumed random substitutional distribution of guest molecules in a perfect host crystal. This estimate is undoubtedly low, possibly by as much as a factor of 2 or 3 which tends to make our estimate of  $\epsilon$  too high. Thus our values of  $\phi$  are uncertain in an absolute sense and are undoubtedly lower limits.

The relative uncertainties, however, are more important for comparative purposes. Each value of  $\epsilon$  is based upon the *same* concentration so the uncertainty connected with the relative magnitude of two quantum yields is entirely determined by the uncertainties in the measured values of  $k_p$ , I, and absorbance of the  $C_3H_4 \cdot F_2$  pairs.

Table VIII lists the deduced values of  $\phi_P$  for three of the products as measured in the argon matrix results presented in Table VI. The uncertainties listed are our estimates of the *relative* accuracy of each quantum yield. The least certain data are those connected with the 1679.3 and 3075.9 cm<sup>-1</sup> irradiation experiments. In the former case, reactant consumption is difficult to measure because of an overlapping product band due to *cis*-CH<sub>2</sub>CFCH<sub>2</sub>F. The depletion of C<sub>3</sub>H<sub>4</sub> · F<sub>2</sub> pairs in both is below our detection limit. Therefore  $\epsilon$  was estimated in each case by assuming that the peak of the C<sub>3</sub>H<sub>4</sub> · F<sub>2</sub> pair absorption was coincident with the laser frequency and that the ratio between the pair and mono-

INDED VIII, Quantum Vietus and average quantum Vietus IOI Colli/ Po Leagero	TABLE VIII.	Quantum yields and average quantum yiel	lds for C <sub>3</sub> H <sub>4</sub> /F <sub>2</sub> reaction
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C <sub>3</sub> H <sub>4</sub> mode	ν				$\Delta \phi_{\nu,\nu}$ .
excited	(cm <sup>-1</sup> )	$\phi_{ u}^{ ext{observed}}$	$\Delta \phi_{\nu,\nu'}^{a}$	$(1 + \Delta n_{\nu,\nu},)^{b}$	$\overline{(1+\Delta\eta_{\nu,\nu'})}$
ν <sub>8</sub>	3076	0.21 (0.06-0.60) <sup>c</sup>	0.21	106	2.0·10 <sup>-3</sup>
$2\nu_9$	1999	2.4 • 10 <sup>-4</sup> (±0.2 • 10 <sup>-4</sup> ) <sup>c</sup>			
			1.4.10-4	1	1.4.10-4
$ u_6 $	1953	$\frac{1.0 \cdot 10^{-4}}{(\pm 0.2 \cdot 10^{-4})^{c}}$			
			0.3 • 10 <sup>-4</sup> to 0	14	< <b>2.1 •</b> 10 <sup>-6</sup>
$2\nu_{10}$	1679	0.7-7·10 <sup>-4</sup>			
-			$0.7 - 7 \cdot 10^{-4}$	17	$0.4 - 4 \cdot 10^{-5}$

 $^{\mathbf{a}}\Delta\phi_{\nu,\nu'}=\phi_{\nu}-\phi_{\nu'}.$ 

 ${}^{b}\Delta\eta_{\nu,\nu}$ , represents the number of states with energy less than  $\nu'$ .

<sup>c</sup>Error bars denote estimated *relative* accuracy of  $\phi$ .

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FIG. 6. Quantum yield  $\phi$  vs photon energy for excitation of  $C_3H_4 \cdot F_2$  pairs at 1679.3, 1952.9, 1999.1, and 3075.9 cm<sup>-1</sup> in solid argon at 12 K ( $C_3H_4/F_2/Ar = 1/4/200$ ). (Error bars denote estimated *relative* accuracy of  $\phi$ .)

meric  $C_3H_4$  peak heights are equal to the measured value for  $\nu_6$ .

The significance of the quantum yields for the cis and gauche difluoropropenes is beclouded somewhat by their interconversion in the dark and under the influence of the globar and the CO laser at 1679.3 cm<sup>-1</sup>. The fluoroallene production is free of this difficulty, hence it is more readily interpretable. The most obvious feature of the four values of  $\phi$  in Table VIII is that  $\phi_{\rm F}$  (3075.9) is three orders of magnitude higher than any of the quantum yields at the three lower frequencies. This can be seen to be still another manifestation of the general trend for  $\phi$  to increase with photon energy, as observed in I. In Fig. 6, we have displayed  $\phi_F$  vs photon energy on a logarithmic scale and, as in I,  $\phi_{\rm F}$  does not increase in a smooth fashion. The other three values of  $\phi_{\rm F}$  do not so easily lend themselves to this general trend. Despite its rather considerable uncertainty range, the nonzero value of  $\phi_{F}$  (1679.3) assures us that any inhibiting activation energy barrier is well below 1679.3 cm<sup>-1</sup>. This in turn implies that the quite large increase in  $\phi_{F}$ between 1952.9 cm<sup>-1</sup> ( $\nu_{\theta}$ ) and 1999.1 cm<sup>-1</sup> ( $2\nu_{9}$ ) is not simply caused by close proximity to such a barrier. Instead we attribute the factor of 2.4 increase caused by the 46 cm<sup>-1</sup> increase in photon energy to some special advantage of  $2\nu_9$  excitation over  $\nu_8$  excitation.

As in I, we consider that the experimentally measured quantum yield is determined by the quantum yield of the state excited plus the sum of the quantum yields of all of the states involved in the relaxation process. This model leads us to attribute the change in quantum yield  $\Delta \phi_{\nu,\nu'}$ , between any two successive excitation frequencies  $\nu$  and  $\nu'$  to the level excited plus some or all of the intervening levels. The extremum of this model, the "smallest step" relaxation model, is expressed as  $\Delta \phi_{\nu,\nu'}/(1 + \Delta n_{\nu,\nu'})$ , as given in the last column of Table VIII.

As indicated in the next to last column, there are no

intervening energy states between  $2\nu_9$  and  $\nu_6 (\Delta n_{\nu,\nu'} = 0)$ . Hence, if relaxation from  $2\nu_9$  occurred predominantly through  $\nu_6$ , then all of the *change* in quantum yield between these two excitations can be attributed to  $2\nu_9$ .

Table VIII also shows that the average quantum yield associated with the  $\nu_8$  excitation is much lower than the  $2\nu_9$  value. Thus, whether we consider  $\phi_{\nu}^{\text{observed}}$  or  $\Delta \phi_{\nu,\nu'}/(1 + \Delta n_{\nu,\nu'})$ , the  $2\nu_9$  excitation displays an especially high quantum yield relative to that of  $\nu_8$ .

The quantum yield of a particular eigenstate is undoubtedly determined by two factors: the residence time in that state and its specific reaction propensity. Further, we expect that residence time will decrease as energy level density increases. However, the average quantum yield associated with the  $\nu_8 - 2\nu_9$  interval, 2.0  $\cdot$  10<sup>-3</sup>, is even higher than that of  $2\nu_9$  despite level densities at  $\nu_8$  about three times higher (15 levels per 100 cm<sup>-1</sup>) than at  $2\nu_9$ . Again as in I, we conclude that residence time is less important than the effects of photon energy and specific reaction propensity. This deduction is underscored by the fact that both the special arguments that can be made about  $2\nu_{9}$  residence time lead to the expectation that it will be short. First, the energy gap to the next energy level  $\nu_{\rm s}$  is 46 cm<sup>-1</sup>. This matches well the phonon band of a perfect argon crystal which is calculated<sup>28</sup> to extend from 20 to 60 cm<sup>-1</sup>. Second, there is evidence that  $2\nu_9$  and  $\nu_6$  are coupled through Fermi resonance with a 6.7 cm<sup>-1</sup> interaction.<sup>29</sup> This coupling has been proposed by Bondybey and English<sup>30, 31</sup> as a factor that facilitates relaxation in their studies of CNN and NCO in solid argon. Since a short  $2\nu_9$  residence time would act to lower  $\phi_{2\nu_0}$ , its high value must be attributed to another factor. We are led to the conclusion that  $2v_9$  is especially effective in causing reaction between allene and fluorine.

This conclusion, that mode specific behavior accounts for the high quantum yield at 1999.1 cm<sup>-1</sup> relative to that at 1953 cm<sup>-1</sup>, invites inspection of the nature of the vibrational modes involved. The 1999.1 cm<sup>-1</sup> absorption is due to excitation of  $2\nu_9$ , the first overtone of the doubly degenerate CH<sub>2</sub> rocking motion. This type of distortion of the  $sp^2$  geometry of the terminal CH<sub>2</sub> groups in allene seems quite appropriate to the change in molecular geometry as the reaction proceeds to form 2, 3-difluoropropene. This product requires the development of tetrahedral geometry at one terminal carbon atom and a bent molecular skeleton. In contrast, the 1953 cm<sup>-1</sup> absorption is due to  $\nu_8$ , the asymmetric skeletal stretch. This motion retains the linear skeletal geometry and the twofold symmetry around the skeletal axis of the parent molecule. Rather than bend the skeleton towards the product geometry, it shortens one C=C bond while lengthening the other. This is to be contrasted with the need to lengthen both 1.31 Å C=Cbond lengths of allene to the final product bond lengths which, in propene, are 1.35 and 1.49 Å. This vibration is less obviously relevant to the final product geometry with its bent skeletal frame and tetrahedral angles at the CH<sub>2</sub>F end of the molecule. Thus the finding that  $2\nu_9$  has a higher reaction propensity than  $\nu_6$  is

readily interpreted in terms of a plausible reaction coordinate.

The large error bars make it more difficult to interpret the  $2\nu_{10}$  quantum yield. The 1679.5 cm<sup>-1</sup> level is separated from the next lower level  $2\nu_{11} + \nu_4$  by over 100 cm<sup>-1</sup>. Hence we expect this level to have a relatively long residence time. In addition, the  $2\nu_{10}$  vibrational mode is the overtone of a CH<sub>2</sub> wagging motion that distorts the axial symmetry, and thus again seems to be a reasonable candidate for high reaction propensity. We can at least conclude that the residence time and mode specificity seem to favor a relatively high quantum yield for this eigenstate. In fact, even the lowest limit of our assigned error bars is consistent with this expectation.

#### **V. CONCLUSIONS**

There is no doubt that the allene-fluorine reaction is accelerated in cryogenic matrices upon selective excitation of the four allene vibrational modes studied. Also, the reaction leads to four products, *cis*- and *gauche*-H<sub>2</sub>C=CFCH<sub>2</sub>F, H<sub>2</sub>C=C=CHF · HF, and HC=CCH<sub>2</sub>F · HF, consistent with a concerted addition of F<sub>2</sub> across an allene double bond followed by either deactivation or HF elimination.

The characterization of the cis- and gauche-difluoropropenes by selective photoinduced interconversion is of considerable interest in its own right. First, the isomerization indicates that the photon energy can be efficiently channeled into the torsional modes. We estimate that with excitation at 1076 cm<sup>-1</sup>,  $\phi(g-c)$  may be as high as 0.1 while at 1687 cm<sup>-1</sup>  $\phi(c-g)$  may be about 10<sup>-2</sup>. This 1076 cm<sup>-1</sup> behavior is relevant to, and consistent with, our view that relaxation takes place through intramolecular cascading with small energy increments. Second, we find that one rotamer can be converted to the other in solid nitrogen with  $h\nu = 937$  cm<sup>-1</sup>. This behavior is in sufficient agreement with the gas phase rotational barriers, for which the cis-gauche torsional barrier is 1000  $\text{cm}^{-1}$  and the gauche-cis-barrier is 855 cm<sup>-1</sup>, to permit us to infer the identities of the observed rotamers and assign one as the more stable cis and the other as the less stable gauche form. The results suggest, further, that the matrix perturbation of the torsional barrier may be sufficiently small to encourage the use of this technique for the bracketing of torsional barriers in more complex molecules for which gas phase measurements might not be possible.

Another observation not encountered in earlier work<sup>1, 2, 14</sup> is that the matrix has a dramatic influence on the product distribution. In solid N<sub>2</sub>, each of the four products is present in appreciable amounts whereas in Ar, Kr, and Xe the amount of propargyl fluoride is very much reduced. The results for the xenon matrix are the most surprising since this product is undetected while the other elimination product, fluoroallene, is a dominant product. One possible avenue of explanation is suggested by the interpretations of Peer<sup>21</sup> of his solution phase studies of the chlorination and bromination of allene. Peer suggests that the propargyl halide is formed via a different mechanism involving a cyclic intermediate in which a halogen molecule is partially bonded to one of the terminal carbon atoms and to a hydrogen atom at the other end followed by the elimination of HX to form propargyl halide. If this were the origin of propargyl fluoride in the present work, rather than reaction (1) followed by reaction (2b), then the role of the matrix may be mainly a steric one, effectively blocking this mechanism in xenon but encouraging it in nitrogen.

If, however, our simpler interpretation is maintained, reaction (1) followed by reaction (2a) or (2b) in competition, then phonon relaxation rates are probably the important factors. As relaxation becomes more rapid, the difluoropropene product will become more important. At the same time, if the two elimination pathways have different activation energies, then elimination via the lower activation energy will become more favored. The data shown in Table V do not present a consistent picture. For example, the absence of  $HCCCH_2F$  in a xenon matrix would suggest rapid relaxation relative to that in a nitrogen matrix but the yield of difluoropropene is not correspondingly raised.

There is still one more possible explanation. In the ethylene-fluorine reaction, elimination is strongly dis-favored if the reaction takes place in a cage containing another ethylene molecule.<sup>1</sup> This observation raises concern about the differing effectiveness of the various matrices in isolating reactive pairs.

Even though we cannot point to any one of these lines of argument with confidence, our observation that the choice of matrix can have a profound effect on branching ratios must attract interest and warrant further study.

Finally, this new evidence for mode selectivity encourages the search for other bimolecular reactions that can be studied in this fashion and the hope that such studies will increase our ability to determine the types of molecular distortion that contribute to the reaction coordinate.

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