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SELECTIVE VIBRATIONAL EXCITATION OF THE ETHYLENE-FLUORINE REACTION IN A NITROGEN MATRIX. II

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## CHEMICAL BIODYNAMICS DIVISION

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Heinz Frei

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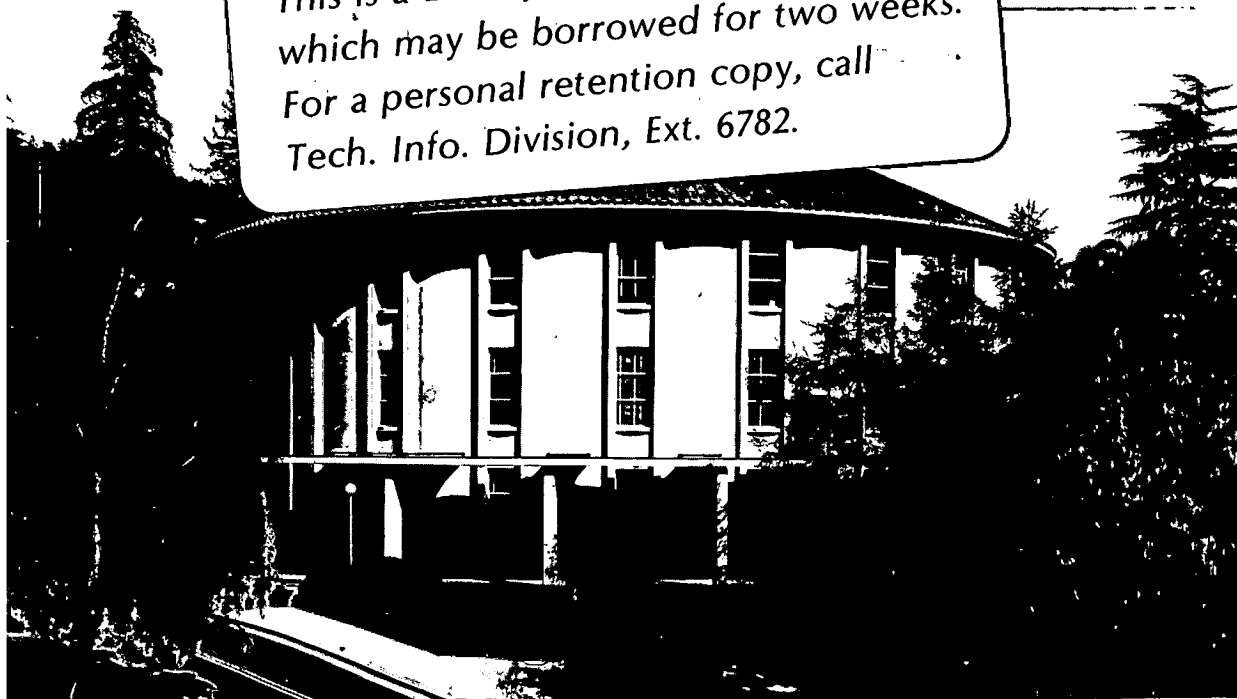
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SELECTIVE VIBRATIONAL EXCITATION OF THE ETHYLENE-FLUORINE REACTION  
IN A NITROGEN MATRIX. II

by

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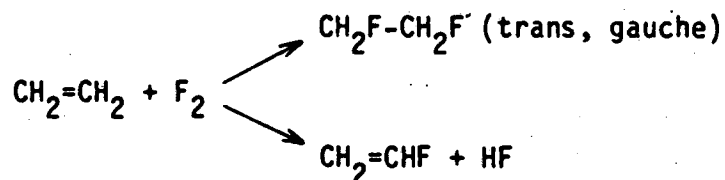
## Abstract

The product branching between 1,2-difluoroethane and vinyl fluoride (plus HF) of the selective vibrationally stimulated reaction of molecular fluorine with  $C_2H_4$  has been studied in a nitrogen matrix at 12 K and found to be the same for five different vibrational transitions of  $C_2H_4$  between 1896 and 4209  $cm^{-1}$ . The HF/DF branching ratio of the reaction of  $F_2$  with  $CH_2CD_2$ , trans-CHDCHD and cis-CHDCHD was determined to be 1.1, independent of precursor  $C_2H_2D_2$  isomer and particular mode which excited the reaction. These results, as well as the analysis of the mixtures of partially deuterated vinyl fluoride molecules produced by each  $C_2H_2D_2$  isomer indicate that the product branching occurs by  $\alpha\beta$  elimination of HF(DF) from a vibrationally excited, electronic ground state 1,2-difluoroethane intermediate. A change of the branching between stabilization of the intermediate and elimination of HF by a factor of two, observed upon increase of the temperature during the condensation of the matrix from 12 to 15.5 K manifests remarkable sensitivity of the deactivation kinetics of the hot 1,2-difluoroethane molecule to changes in the matrix environment. Selective vibrational excitation of fluorine reactions in isotopically mixed matrices t-CHDCHD/ $C_2H_4$ / $F_2$ / $N_2$  and  $CH_2CD_2$ / $C_2H_4$ / $F_2$ / $N_2$ , and in matrices  $C_2H_2$ / $C_2H_4$ / $F_2$ / $N_2$  revealed a high degree of isotopic and molecular selectivity. The extent to which intermolecular energy transfer occurred is qualitatively explained in terms of dipole coupled vibrational energy transfer. A study of the loss of absorbance of the  $C_2H_4 \cdot F_2$  pairs in case of  $\nu_9$  as a function of both the laser irradiation frequency within the absorption profile, and the ethylene concentration showed that the  $C_2H_4 \cdot F_2$  absorption is inhomogeneously broadened at the concentrations  $C_2H_4/F_2/N_2 \sim 1/1/100$  and  $1/6/600$ .

At these concentrations, substantial depletion of reactive pairs occurred which did not absorb laser light. These observations, as well as the sharpening of the absorption of the depleted  $C_2H_4 \cdot F_2$  pairs with decreasing ethylene concentration, are interpreted in terms of Forster transfer among isolated  $C_2H_4$  molecules, and between those and the reactive pairs.

## I. Introduction

In a previous paper [1] (hereafter, reference 1 will be called I), we have reported the frequency dependence of the quantum efficiency of the selective vibrationally stimulated reaction



in nitrogen matrices at 12K, including a study of this reaction with all three dideutero ethylenes. We observed a general increase of the quantum efficiency to reaction with the energy per infrared photon, which we interpreted as a manifestation of the competition between chemical reaction of the vibrationally excited ethylene, and phonon-assisted relaxation. Deviations from a smooth rise of the quantum yield with energy were attributed, in part, to mode selectivity.

The presence of an intermode vibrational cascading process raised the question to what extent intermolecular vibrational energy transfer between ethylene molecules, isolated or part of a reactive pair, may play a role at the concentrations used in our experiments. We present in this paper the results of two series of experiments which aimed at answering this question: A study of the absorption profile of the ethylene-fluorine pairs, depleted by chemical reaction, as a function of the laser irradiation frequency and reactant concentration, and a series of laser stimulated reactions of fluorine with mixtures of ethylene isotopes, and a mixture of ethylene and acetylene. A second important mechanistic aspect of this vibrationally induced reaction, the reaction pathway in the cryogenic

environment, will be discussed in the light of the observed isotopic selectivity, and product branching ratios of the  $C_2H_4+F_2$  and  $C_2H_2D_2+F_2$  reactions.

## II. Experimental

Apparatus and experimental techniques have been described in I. Briefly, separate  $C_2H_4/N_2$  and  $F_2/N_2$  mixtures were simultaneously deposited from dual jets onto a 12K cooled CsI window at a total deposition rate of 1 mmol per hour. Deposition times were 4-11 hours. Reactant depletion and product growth was followed by infrared spectroscopy, using a Nicolet FT-IR spectrometer (model 7199) at  $0.24\text{ cm}^{-1}$  resolution. In most experiments, spectra were recorded over a period of 10 minutes once every 60 minutes. For photolysis, the cold window was rotated by  $90^\circ$  and exposed to laser radiation entering the cryostat through a NaCl window, as shown in Fig. 1 of reference 2. Homemade cw  $CO_2$  and cw CO lasers, and a continuously tunable cw F-center laser (Burleigh, model FCL-10) was used for irradiation. The F-center laser had output between  $2950$  and  $4350\text{ cm}^{-1}$  at intensities between  $5$  and  $80\text{ mW cm}^{-2}$ , and was pumped with  $800$ - $1000\text{ mW}$  of the two red emission lines of a Kr ion laser (Coherent, model CR750K), or  $3.5\text{ W}$  of the  $514.5\text{ nm}$  green emission line of an Ar ion laser (Coherent, model CR8), depending on which F center crystal was being used. Irradiation times were 4-6 hrs for kinetic measurements.

Fluorine (Matheson, 98%) was used without purification, except that the fluorine-matrix gas mixture was passed through a stainless steel coil immersed in liquid nitrogen placed in front of the cryostat. Ethylene (Matheson, 99.98%), 1,1-dideutero ethylene (Merck, Sharp and Dohme, 98%), cis-1,2-dideutero ethylene (Merck, Sharp and Dohme, 98%) and



trans-1,2-dideutero ethylene (Merck, Sharp and Dohme, 98%) and nitrogen (Matheson, oxygen free) were used without further purification. Acetylene (Matheson, 99.6%) was purified by two trap-to-trap distillations.

### III. Results

#### 1. $\nu_9$ profile study

In a series of experiments summarized in Table I, the loss of absorbance of  $C_2H_4 \cdot F_2$  pairs in case of the CH stretching mode  $\nu_9$  was determined as a function of both the laser irradiation frequency within the absorption profile, and the ethylene concentration. Fig. 1 shows the erosion of  $\nu_9$  after irradiation of matrices  $C_2H_4/F_2/N_2 \sim 1/1/100$ ,  $1/6/600$ , and  $1/12/1200$  at two different positions,  $3110 \text{ cm}^{-1}$  and  $3105 \text{ cm}^{-1}$ , for 4.2-5 hours. Each irradiation experiment was done with a separate matrix. Clearly, the absorbance profiles of those  $C_2H_4 \cdot F_2$  pairs and  $(C_2H_4)_2 \cdot F_2$  clusters which were used up by chemical reaction upon irradiation at  $3110 \text{ cm}^{-1}$ , obtained from computer calculated differences of the spectra before and after laser irradiation, sharpen with decreasing ethylene concentration. Among the 3 different spectra of the first column in Fig. 1, only the one obtained from the matrix with the lowest ethylene concentration,  $C_2H_4/F_2/N_2 \sim 1/12/1200$ , shows coincidence of the peak of the reactive pair absorption with the laser irradiation frequency at  $3110 \text{ cm}^{-1}$ . Comparison of the difference spectra of the same row discloses distinctly different profiles or peak frequencies for the absorption of the reactive pairs depleted upon irradiation at the two laser frequencies,  $3110$  and  $3105 \text{ cm}^{-1}$ . These observations suggest that the absorption of the depleted ethylene fluorine pairs is inhomogeneously broadened in case of matrices  $C_2H_4/F_2/N_2 \sim 1/1/100$  and  $1/6/600$ . Because the reactive pair absorption of  $\nu_9$

overlaps considerably with the absorption of ethylene monomers and dimers, it is not evident from Fig. 1 alone that only reactive pairs were used up, and no local diffusion of  $C_2H_4$  or  $F_2$  molecules took place during chemical reaction. Convincing evidence is obtained, however, from the effect of irradiation of  $\nu_9$  at  $3110\text{ cm}^{-1}$  upon the absorption  $\nu_{12}$  in case of the matrix  $C_2H_4/F_2/N_2 \sim 1/12/1200$ , displayed in Fig. 2. The intense peak at  $1437.7\text{ cm}^{-1}$  is assigned to isolated  $C_2H_4$ , whereas the absorptions at  $1439.8\text{ cm}^{-1}$  and  $1440.7\text{ cm}^{-1}$  are mainly due to reactive pairs. The difference spectrum shows that 5 hours of irradiation at  $3110\text{ cm}^{-1}$  eroded only the reactive pair absorption, but no loss of absorbance of isolated ethylene occurred, hence no diffusion of reactants was taking place during laser irradiation.

## 2. Isotopic selectivity

In a second series of experiments described in Table II, isotopic selectivity of the ethylene-fluorine reaction in  $N_2$  matrices was studied for mixtures of  $C_2H_4$  with various deuterio ethylenes. In addition, acetylene was vibrationally excited in a matrix containing  $C_2H_4 \cdot F_2$  pairs. In each experiment, one reactant was selective vibrationally excited at a frequency well separated from an absorption of a second (isotope) molecule present in the matrix, and then a search was made for infrared product absorptions due to reaction between  $F_2$  and the polyatomic which was not optically excited by the laser.

### A. $HC\equiv CH/C_2H_4/F_2$ System

Infrared spectra of matrices  $HC\equiv CH/N_2 \sim 1/50$  and  $1/400$ , and  $HC\equiv CH/F_2/N_2 \sim 1/1/100$  were taken in order to determine absorptions of isolated and aggregated acetylene, and of  $HC\equiv CH \cdot F_2$  pairs, in particular in the asymmetric CH stretching region around  $3300\text{ cm}^{-1}$ . Isolated acetylene

molecules were found to absorb at  $3282.4 \text{ cm}^{-1}$ , whereas shoulders at  $3281.0$ ,  $3269.0$  and  $3257.9 \text{ cm}^{-1}$  were assigned to  $\text{HC}\equiv\text{CH}$  dimers and possibly polymers. No distinct  $\nu_3$  absorption band of  $\text{HC}\equiv\text{CH}\cdot\text{F}_2$  pairs could be found, but the shape of the absorption profile of  $\nu_3$  in matrices  $\text{HC}\equiv\text{CH}/\text{F}_2/\text{N}_2\sim 1/1/100$  indicated that the pairs absorb around  $3278 \text{ cm}^{-1}$ .  $\nu_3$  of acetylene in matrices  $\text{HC}\equiv\text{CH}/\text{F}_2/\text{N}_2\sim 1/1/100$  was irradiated for periods of 30 minutes at  $3280.1$ ,  $3279.0$  and  $3278.1 \text{ cm}^{-1}$ , respectively, in order to check whether reaction between acetylene and fluorine could be induced by infrared laser light. No new absorption could be found after irradiation despite careful search in the spectral regions where possible products, cis and trans  $\text{CHF}=\text{CHF}$ ,  $\text{FC}\equiv\text{CH}$  and  $\text{HF}$  are expected to absorb. In this experiment,  $2.1\text{-}2.3 \times 10^{17} \text{ photons s}^{-1} \text{ cm}^{-2}$  were absorbed by acetylene molecules.  $\nu_3$  of  $\text{HC}\equiv\text{CH}$  in matrices  $\text{HC}\equiv\text{CH}/\text{C}_2\text{H}_4/\text{F}_2/\text{N}_2\sim 0.1/1/1/100$  and  $0.5/0.5/1/100$  was then irradiated with the F-center laser under conditions specified in Table II, and evidence for vibrational energy transfer to nearest neighbor or distant  $\text{C}_2\text{H}_4\cdot\text{F}_2$  reactive pairs was sought by following the growth of gauche and trans 1,2-difluoroethane, vinyl fluoride and  $\text{HF}$  product absorptions. No growth of these products upon irradiation of acetylene was observed. Irradiation of  $\nu_3$  of acetylene was followed in both experiments by an equal period of irradiation of  $\nu_9$  of  $\text{C}_2\text{H}_4$  at  $3106 \text{ cm}^{-1}$  in order to put a limit on the relative effectiveness of direct excitation of  $\nu_9$  of  $\text{C}_2\text{H}_4$ , and energy transfer from  $\nu_3$  of  $\text{HC}\equiv\text{CH}$  to  $\text{C}_2\text{H}_4$  in promoting reaction. Considering power levels, absorbances and exposure times at each frequency in case of the experiment  $\text{HC}\equiv\text{CH}/\text{C}_2\text{H}_4/\text{F}_2/\text{N}_2\sim 0.5/0.5/1/100$ , we find no product absorption after the sample had absorbed 3.4 times as many  $3280 \text{ cm}^{-1}$  photons as were

needed at  $3106\text{ cm}^{-1}$  to produce absorbances\*:  $1139.4\text{ cm}^{-1}$  (VF·E·HF): 0.0241;  $1119.1\text{ cm}^{-1}$  (VF·HF): 0.0588;  $1041.2\text{ cm}^{-1}$  (DFE·E): 0.0319. With a detection limit of 0.001 absorbance units, we conclude that in matrices  $\text{HC}\equiv\text{CH}/\text{C}_2\text{H}_4/\text{F}_2/\text{N}_2 \sim 0.5/0.5/1/100$ , direct excitation of  $\text{C}_2\text{H}_4$  at  $3106\text{ cm}^{-1}$  is at least 200 times more effective in inducing reaction of  $\text{C}_2\text{H}_4\cdot\text{F}_2$  pairs, and at least 110 times more effective in promoting reaction of  $(\text{C}_2\text{H}_4)_2\cdot\text{F}_2$  clusters, than excitation of  $\nu_3$  of acetylene.

#### B. $\text{CH}_2=\text{CD}_2/\text{C}_2\text{H}_4/\text{F}_2$ System

The first overtone of the C=C stretching vibration  $\nu_2$  of  $\text{CH}_2=\text{CD}_2$  at  $3169\text{ cm}^{-1}$  was selectively excited in a matrix  $\text{CH}_2\text{CD}_2/\text{C}_2\text{H}_4/\text{F}_2/\text{N}_2 \sim 0.5/0.5/1/100$  in order to investigate possible vibration to vibration energy transfer from  $2\nu_2$  of  $\text{CH}_2=\text{CD}_2$  to  $\text{C}_2\text{H}_4\cdot\text{F}_2$  reactive pairs. After 2 hours of irradiation with the F-center laser at various frequencies between  $3169$  and  $3163\text{ cm}^{-1}$  (see Table II), no evidence for reaction of  $\text{C}_2\text{H}_4\cdot\text{F}_2$  pairs, isolated or next to a  $\text{CH}_2=\text{CD}_2$  molecule, could be observed. However, subsequent direct excitation of  $\nu_9$  at  $3105\text{ cm}^{-1}$  for 2 hours led to vigorous reaction of  $\text{C}_2\text{H}_4$  with fluorine. Considering again power levels and absorbances at  $3169\text{--}3163\text{ cm}^{-1}$  and at  $3105\text{ cm}^{-1}$ , we find no product absorption after the sample had absorbed at  $3169\text{--}3163\text{ cm}^{-1}$  6.2 percent of the number of photons which were needed at  $3105\text{ cm}^{-1}$  to produce absorbances:  $1139.4\text{ cm}^{-1}$  (VF·E·HF): 0.0282;  $1119.1\text{ cm}^{-1}$  (VF·HF): 0.0528;  $1041.2\text{ cm}^{-1}$  (DFE·E): 0.0250. This implies that in a matrix  $\text{CH}_2=\text{CD}_2/\text{C}_2\text{H}_4/\text{F}_2/\text{N}_2 \sim 0.5/0.5/1/100$ , direct excitation of  $\text{C}_2\text{H}_4$  at  $3105\text{ cm}^{-1}$  is at least 3.3 times more effective in inducing reaction of  $\text{C}_2\text{H}_4$  pairs than excitation of  $2\nu_2$  of  $\text{CH}_2=\text{CD}_2$ , whereas it is at least 1.7 times more effective for  $\text{CH}_2=\text{CD}_2\cdot\text{C}_2\text{H}_4\cdot\text{F}_2$  clusters. Moreover, no reaction of  $\text{CH}_2=\text{CD}_2$

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\*Abbreviations: VF = vinyl fluoride, E = ethylene, DFE = 1,2-difluoroethane

with  $F_2$  was induced upon excitation of  $CH_2=CH_2$  at  $3105\text{ cm}^{-1}$ , which would easily have been detected by growth of C=C stretching absorptions of  $CH_2=CDF$  at  $1625.2\text{ cm}^{-1}$  and  $CD_2=CHF$  at  $1612.2\text{ cm}^{-1}$  (see Fig. 2 of reference 1).

C. t-CHD=CHD/C<sub>2</sub>H<sub>4</sub>/F<sub>2</sub> System

In contrast to the preceding two systems, excitation of  $\nu_9$  of  $C_2H_4$  at  $3106\text{ cm}^{-1}$  in a matrix t-CHD=CHD/C<sub>2</sub>H<sub>4</sub>/F<sub>2</sub>/N<sub>2</sub>~0.6/0.4/1/100 led to slight chemical reaction of the second isotope present in the matrix, t-CHD=CHD. Fig. 3 displays the growth of the C=C stretching absorptions of the vinyl fluoride product molecules in this isotopically mixed matrix in two separate experiments. The upper spectrum (a) shows that irradiation at  $3106\text{ cm}^{-1}$  produced mostly  $CH_2=CHF$  absorbing at  $1652.9$  and  $1649.2\text{ cm}^{-1}$ , but, in addition, also some partially deuterated vinyl fluorides absorbing at  $1633.4$ ,  $1625.1$ ,  $1607.1$ , and  $1597.0\text{ cm}^{-1}$  indicating slight t-CHD=CHD +  $F_2$  reaction. Fig 3b reveals that irradiation of  $\nu_9$  of t-CHD=CHD at  $3066.6\text{ cm}^{-1}$  in a similar matrix led predominantly to growth of the four partially deuterated vinyl fluorides, and only slight  $C_2H_4+F_2$  reaction, as indicated by some growth at  $1652.9\text{ cm}^{-1}$ . However, the infrared spectrum of this mixed isotope matrix in the spectral range  $3120\text{-}3050\text{ cm}^{-1}$ , shown in Fig. 4, suggests that  $C_2H_4 + F_2$  reaction observed upon excitation at  $3066.6\text{ cm}^{-1}$  might be due to direct excitation of  $C_2H_4 \cdot F_2$  pairs, rather than energy transfer, because the irradiation frequency lies only  $10\text{ cm}^{-1}$  below the peak of the absorption  $\nu_2 + \nu_{12}$  of  $C_2H_4$  at  $3076.7\text{ cm}^{-1}$ . On the other hand, no t-CHD=CHD absorption overlaps with the laser line at  $3106\text{ cm}^{-1}$ . Taking into account power levels, absorbances and exposure times at  $3106.0$  and  $3066.6\text{ cm}^{-1}$  (Table II), we find t-CHD=CHD +  $F_2$  product absorbances:  $1633.4\text{ cm}^{-1}$  (c-CHD=CHF): 0.0008;  $1625.1\text{ cm}^{-1}$  (t-CHD=CHF): 0.0007;  $1607.1\text{ cm}^{-1}$

(c-CHD=CHF): 0.0009; 1597.0  $\text{cm}^{-1}$  (t-CHD=CHF): 0.0010, after the sample had absorbed at 3106.0  $\text{cm}^{-1}$  0.82 times as many photons as were needed at 3066.6  $\text{cm}^{-1}$  to produce absorbances: 1633.4  $\text{cm}^{-1}$ : 0.0103; 1625.1  $\text{cm}^{-1}$ : 0.0093; 1607.1  $\text{cm}^{-1}$ : 0.0185; 1597.0  $\text{cm}^{-1}$ : 0.0191. This implies that in a matrix t-CHD=CHD/ $\text{C}_2\text{H}_4/\text{F}_2/\text{N}_2 \sim 0.6/0.4/1/100$ , excitation of  $\text{C}_2\text{H}_4$  at 3106.0  $\text{cm}^{-1}$  is  $10 \pm 2$  times less effective in inducing reaction of t-CHD=CHD $\cdot\text{F}_2$  pairs than direct excitation of  $\nu_9$  of t-CHD=CHD at 3066.6  $\text{cm}^{-1}$ .

### 3. Product branching

#### A. $\text{C}_2\text{H}_4/\text{F}_2$ system:

In each laser irradiation experiment, reaction of  $\text{C}_2\text{H}_4 \cdot \text{F}_2$  pairs and  $(\text{C}_2\text{H}_4)_2 \cdot \text{F}_2$  clusters could be monitored separately, because the products of the former reaction, isolated gauche and trans 1,2-difluoroethane and vinyl fluoride-hydrogen fluoride complexes showed infrared absorptions which could clearly be resolved from those of the  $(\text{C}_2\text{H}_4)_2 + \text{F}_2$  reaction, namely, g-DFE $\cdot\text{E}$ , t-DFE $\cdot\text{E}$ , and VF $\cdot\text{E} \cdot \text{HF}$  aggregates [2]. Quantitative estimates of the product branching ratios for each reaction were attempted, based on the magnitude of the appropriate extinction coefficient determined in our earlier work [2]. Unfortunately, the ratios of the integrated absorbances of g-DFE (t-DFE) and VF

$$\beta_g = \frac{\int \Delta A^{g\text{-DFE}}(\tilde{\nu}) d\tilde{\nu}}{\int \Delta A^{\text{VF}}(\tilde{\nu}) d\tilde{\nu}}, \quad \beta_t = \frac{\int \Delta A^{t\text{-DFE}}(\tilde{\nu}) d\tilde{\nu}}{\int \Delta A^{\text{VF}}(\tilde{\nu}) d\tilde{\nu}}$$

were very small at all laser frequencies in case of the reaction of  $C_2H_4 \cdot F_2$  pairs, and the minute growth of isolated g-DFE and t-DFE absorptions made an accurate estimate of  $\beta_g$  and  $\beta_t$  impossible. On the other hand, comparable growth of addition and elimination products was observed in case of the  $(C_2H_4)_2 + F_2$  reaction in matrices  $C_2H_4/F_2/N_2 \sim 1/1/100$ , allowing accurate determination of  $\beta_g$  and  $\beta_t$ , and hence of the branching ratios

$$b_t = \beta_t \frac{\int E^{VF}(\tilde{\nu}) d\tilde{\nu}}{\int E^{t-DFE}(\tilde{\nu}) d\tilde{\nu}}, \quad b_g = \beta_g \frac{\int E^{VF}(\tilde{\nu}) d\tilde{\nu}}{\int E^{g-DFE}(\tilde{\nu}) d\tilde{\nu}}$$

upon irradiation at a number of different frequencies, shown in Table III.

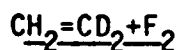
All experiments were done under identical conditions, in particular the matrix temperature during laser irradiation was always kept at 12K.

However, in some experiments the temperature of the cold CsI window was held at 15.5K during deposition of the matrix. Two photolysis experiments done at  $3105 \text{ cm}^{-1}$ , one with a matrix deposited at 12K, the other one at 15.5K, gave branching ratios  $b_g$  and  $b_t$  which differed by approximately a factor of two. On the other hand, Table III shows that for fixed deposition temperature, the branching ratios are the same within the experimental uncertainty, for all irradiation frequencies. These findings

suggest that neither the nature of the excited vibrational transition, nor the energy per infrared photon affects the branching ratio between stabilization of the ethylene-fluorine addition product, and elimination of HF. However, it appears that the product branching is significantly influenced by the temperature of the matrix during the condensation process.

### B. C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>/F<sub>2</sub> systems

Table II of reference I lists the possible products of the reaction of CH<sub>2</sub>=CD<sub>2</sub>, t-CHD=CHD, and c-CHD=CHD with F<sub>2</sub>, if we assume that both αα and αβ elimination can occur. In contrast to the reaction of the parent ethylene molecule, only incomplete assignment of the observed product bands could be made in case of the C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>+F<sub>2</sub> reactions, because no reference infrared spectra were available for any of the expected partially deuterated 1,2-difluoroethane products. Therefore, our quantitative study of product branching was limited to the elimination pathways, and comparison of intensities of elimination product absorptions was made in the HF, DF, and in the C=C stretching region, i.e. in spectral ranges free of possible difluoroethane absorptions.



Frequencies and integrated absorbances for HF and DF, and for product absorptions in the C=C stretching region are listed in Table IV. The two absorptions at 1612.2 and 1625.2 cm<sup>-1</sup> are most probably due to the expected αβ elimination products CD<sub>2</sub>=CHF and CH<sub>2</sub>=CDF, which absorb in the gas phase at 1620 and 1628 cm<sup>-1</sup>, respectively [3]. The ratio of the integrated intensities of HF and DF absorptions at 3796 and 2784 cm<sup>-1</sup>,  $I_{\text{HF}}/I_{\text{DF}}=2.1\pm 0.2$ , is not affected by the laser irradiation frequency as the values are the same within the experimental uncertainty, at 1900 and 3096 cm<sup>-1</sup>. The



ratios of the intensities of the C=C stretching absorptions of  $\text{CD}_2=\text{CHF}$  and  $\text{CH}_2=\text{CDF}$  at the two laser frequencies were found to be  $0.73 \pm 0.02$  and  $0.59 \pm 0.02$ , respectively.

cis, trans -  $\text{CHD}=\text{CHD}+\text{F}_2$

Table V shows frequencies and intensities of HF, DF, and of product absorptions observed in the C=C stretching region. As indicated in Table II of reference I, cis and trans  $\text{CHD}=\text{CHD}$  are expected to lead to the same  $\alpha\beta$  or  $\alpha\alpha$  elimination products, and Fig. 2 of reference I shows that this is indeed the case. Observation of four vinyl fluoride C=C stretching bands (not six) strongly suggests that HF(DF) elimination occurs via the  $\alpha\beta$  mechanism. Comparison of the product absorptions at 1633.4, 1625.1, 1607.1, and 1597.0  $\text{cm}^{-1}$  in  $\text{N}_2$  matrices with gas phase absorptions at 1635, 1630, 1615, and 1603  $\text{cm}^{-1}$  [3] supports assignment of these bands to the expected  $\alpha\beta$  elimination products c- $\text{CHD}=\text{CHF}$ , t- $\text{CHD}=\text{CHF}$ , c- $\text{CHD}=\text{CDF}$ , and t- $\text{CHD}=\text{CDF}$ , respectively. The coincidence of the t- $\text{CHD}=\text{CHF}$  band at 1625.1  $\text{cm}^{-1}$  with the  $\text{CH}_2=\text{CDF}$  absorption at 1625.2  $\text{cm}^{-1}$  observed in the case of the  $\text{CH}_2=\text{CD}_2+\text{F}_2$  reaction, is most likely accidental, because the two gas phase absorptions are also close together (1630 and 1628  $\text{cm}^{-1}$ , respectively). The ratio of the integrated intensities of HF and DF absorptions at 3796 and 2784  $\text{cm}^{-1}$  is independent, within the experimental uncertainty, of laser irradiation frequency and precursor  $\text{CHD}=\text{CHD}$  isomer, namely  $2.3 \pm 0.1$  for trans- $\text{C}_2\text{H}_2\text{D}_2+\text{F}_2$ , and  $2.1 \pm 0.2$  for cis- $\text{C}_2\text{H}_2\text{D}_2+\text{F}_2$ . Table V also displays various intensity ratios for vinyl fluoride C=C stretching absorptions. The ratio  $\frac{\text{CHD}=\text{CDF}}{\text{CHD}=\text{CHF}}$  of the sums of the integrated intensities of the cis and trans isomers of  $\text{CHD}=\text{CDF}$  and  $\text{CHD}=\text{CHF}$  is the same, within 10%, for irradiation at 3066.7  $\text{cm}^{-1}$  (1.47) and 1854.9  $\text{cm}^{-1}$  (1.31), as it is for cis- $\text{CHD}=\text{CHD}+\text{F}_2$  when irradiating at the three frequencies, 3061.0, 3057.7,

and  $1827.2 \text{ cm}^{-1}$ . The last two columns of the Table display the intensity ratios for cis and trans isomers of  $\text{CHD}=\text{CHF}$  and  $\text{CHD}=\text{CDF}$ . The ratio  $\beta_{c/t}$  of  $\text{CHD}=\text{CDF}$  is independent, within 10%, of precursor  $\text{CHD}=\text{CHD}$  and irradiation frequency. However, significant variation of the ratio  $\beta_{c/t}$  in the case of  $\text{CHD}=\text{CHF}$ , both as a function of precursor molecule and irradiation frequency is observed: 0.84 and 1.19 for irradiation at  $3066.7$  and  $1854.9 \text{ cm}^{-1}$  in the case of  $t\text{-CHD}=\text{CHD} + \text{F}_2$ , and 0.64, 0.65, and 0.44 for irradiation at  $3061.0$ ,  $3057.7$ , and  $1827.2 \text{ cm}^{-1}$  in the case of  $c\text{-CHD}=\text{CHD}+\text{F}_2$ .

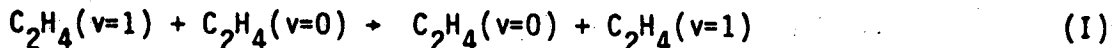
#### IV. Discussion

##### 1. Energy transfer in $\text{C}_2\text{H}_4/\text{F}_2/\text{N}_2$ matrices

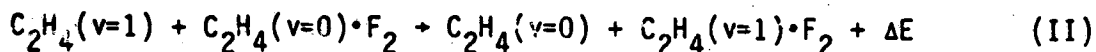
The substantial loss of absorbance  $5\text{-}10 \text{ cm}^{-1}$  below the laser irradiation frequency at  $3110 \text{ cm}^{-1}$ , which was observed at the two concentrations  $\text{C}_2\text{H}_4/\text{F}_2/\text{N}_2 \sim 1/1/100$  and  $1/6/600$ , but not at  $1/12/1200$ , implies that significant depletion of  $\text{C}_2\text{H}_4 \cdot \text{F}_2$  pairs which did not absorb laser light, occurred at the two higher ethylene concentrations. The same conclusion is reached when comparing the shapes of the two curves displayed in Fig. 5. The lower curve depicts the inhomogeneous profile of the reactive  $\text{C}_2\text{H}_4 \cdot \text{F}_2$  pairs in matrices  $\text{C}_2\text{H}_4/\text{F}_2/\text{N}_2 \sim 1/1/100$ , determined from the observed absorbance loss upon irradiation at  $3110$ ,  $3105$ ,  $3100$ , and  $3096 \text{ cm}^{-1}$ . The upper curve shows the asymptotic limit of the absorbance growth of the  $1119 \text{ cm}^{-1}$   $\text{CH}_2=\text{CHF} \cdot \text{HF}$  band upon irradiation at the four laser frequencies. This product growth profile indicates the relative magnitude of the reservoirs of ethylene-fluorine pairs depleted in each irradiation experiment, hence its shape is expected to resemble that of the  $\text{C}_2\text{H}_4 \cdot \text{F}_2$  absorbance curve, if in each experiment only those pairs would have reacted which absorbed at the laser frequency. This appears to be by and large the

case upon irradiation in the range 3105-3096  $\text{cm}^{-1}$ . However, the high value of the product absorbance at 3110  $\text{cm}^{-1}$  indicates that the number of  $\text{C}_2\text{H}_4 \cdot \text{F}_2$  pairs which did react but not absorb laser radiation, is approximately twice as high as the number of pairs which did absorb light at that frequency. The observed depletion of reactive pairs which did not absorb infrared light appears not to be caused by a thermal effect, because at 3110  $\text{cm}^{-1}$  only half as many photons were absorbed by ethylene than in the case of irradiation at 3105  $\text{cm}^{-1}$  (see Table I).

The observation of depletion of reactive pairs not absorbing infrared light indicates vibrational energy transfer among ethylene molecules. At 3110  $\text{cm}^{-1}$ , most photons are absorbed by isolated  $\text{C}_2\text{H}_4$  molecules, hence the dominant energy transfer processes are expected to be resonant transfer among isolated ethylene molecules (energy migration)



and resonant as well as non-resonant, phonon assisted energy transfer from isolated  $\text{C}_2\text{H}_4$  to reactive  $\text{C}_2\text{H}_4 \cdot \text{F}_2$  pairs



Both processes can be described by the Forster-Dexter theory for long range intermolecular energy transfer, induced by multipolar interactions [4,5]. According to this theory, the rate for resonant energy transfer by coupled

dipole-dipole transitions between isolated ethylene molecules (E) in random orientation is (process I)

$$k_{E,E} = \frac{C_{EF}}{R_{E,E}^6} \quad (1)$$

where

$$C_{E,E} = \frac{3}{512 \cdot \pi^6 \cdot c \cdot n^4 \cdot \tau_E^2} \int f_E^2(\tilde{\nu}) d\tilde{\nu} \quad (2)$$

$R_{E,E}$ : distance between isolated ethylene molecules

$n$ : refractive index of the matrix

$\tilde{\nu}$ : vibrational transition frequency

$\tau_E$ : radiative lifetime in vacuum

$f_E$ : normalized lineshape function

Due to the strong distance dependence of eq. (1), ethylene molecules at the closest distance  $R_{E,E}^0$  to a particular excited ethylene dominate the resonant hopping of excitation from molecule to molecule.  $R_{E,E}^0$  is larger than one nearest neighbor distance, since two ethylene molecules in adjacent sites form a dimer which is not considered to participate in energy migration. Assuming a random distribution of ethylene molecules for separations larger than  $R_{E,E}^0$ , the average number of hops of excitation among isolated ethylene molecules during a period of time  $t$  is [6]

$$N \approx \frac{4 \cdot \pi \cdot \rho \cdot x_E \cdot C_{E,E} \cdot t}{3 \cdot R_{E,E}^3} \quad (3)$$

$\rho$ : density of lattice sites

$x_E$ : mole fraction of isolated  $C_2H_4$  molecules

These equations allow an estimate of the number of resonant hops of excitation among isolated  $C_2H_4$  molecules. We calculate a value of  $2.1 \times 10^{-35} \text{ cm}^6 \text{ s}^{-1}$  for the constant  $C_{E,E}$ , eq. (2), based on a radiative lifetime  $\tau_E$  for  $C_2H_4(\nu_9, v=1)$  of 33 msec, calculated from a previously reported integrated absorbance for the gas phase absorption [7], and  $\int f_E(\tilde{\nu}) d\tilde{\nu} = \sqrt{\frac{2 \ln 2}{\pi}} \cdot \frac{1}{\Delta \tilde{\nu}} = 0.22 \text{ cm}$ , assuming a gaussian lineshape with an inhomogeneous linewidth of  $\Delta \tilde{\nu} = 3 \text{ cm}^{-1}$  for  $\nu_9$  of matrix isolated  $C_2H_4$ . Considering two  $C_2H_4$  molecules as being isolated if they are separated by one second nearest neighbor distance, we obtain  $R_{E,E}^0 = 5.64 \text{ \AA}$  in case of  $\alpha\text{-}N_2$  [8]. With a density of substitutional sites of  $2.5 \times 10^{22} \text{ cm}^{-3}$ , and an assumed lifetime of one  $\mu\text{sec}$  for  $\nu_9, v=1$  excitation, eq. (3) gives 97 hops for  $C_2H_4/F_2/N_2 \sim 1/1/100$ , 18 hops in case of  $1/6/600$ , and 9 hops for  $C_2H_4/F_2/N_2 \sim 1/12/1200$ . The product of the number of hops\* and the fraction of the sites at distance  $R^0$ , occupied by a  $C_2H_4 \cdot F_2$  pair, gives a clue as to whether averaging of the  $\nu_9$  excitation among isolated  $C_2H_4$  molecules is complete or not at a given ethylene concentration. At the highest concentration,  $C_2H_4/F_2/N_2 \sim 1/1/100$ , the calculated number of hops suggests that every migrating quantum samples the shortest and least probable, but

\*  $N$ , rather than  $\sqrt{N}$  is more appropriate in this case because the average distance between isolated  $C_2H_4$  molecules is larger than the diameter of second nearest neighbor shells.

for energy transfer most important  $C_2H_4-C_2H_4 \cdot F_2$  interaction  $R = 5.64\text{\AA}$  at least once during the time  $t$ , because this product is much larger than one. In contrast, at  $C_2H_4/F_2/N_2 \sim 1/12/1200$ , energy diffusion is almost certainly not fast enough to ensure that each migrating  $\nu_9$  quantum encounters the shortest possible separation to a  $C_2H_4 \cdot F_2$  pair at least once during its lifetime, because now the product is considerably smaller than one. Although the assumption of 1  $\mu\text{sec}$  for the excitation of  $\nu_9$  is somewhat arbitrary, this calculation suggests that a transition occurs from the fast migration regime at the concentration  $C_2H_4/F_2/N_2 \sim 1/1/100$  to incomplete averaging of the  $\nu_9$  excitation among isolated  $C_2H_4$  molecules at  $1/12/1200$ . This is consistent with the observed sharp decrease of depletion of  $C_2H_4 \cdot F_2$  reactive pairs which did not absorb laser radiation upon a twelvefold decrease of the ethylene concentration.

## 2. Energy transfer in $C_2H_2D_2/C_2H_4/F_2/N_2$ and $C_2H_2/C_2H_4/F_2/N_2$ matrices

Non-resonant vibrational energy transfer through dipole-dipole coupling between  $C_2H_4$  and  $C_2H_2D_2$ , either isolated or part of a reactive pair, occurs under simultaneous creation of lattice phonons, hence a description of Forster transfer has to take into account the phonon density of states [9] ( $d_0$ :  $C_2H_4$ ,  $t-d_2$ : trans-CHD=CHD)

$$k_{d_0, t-d_2} = \frac{C_{d_0, t-d_2}}{R_{d_0, t-d_2}^6} \quad (1')$$

$$C_{d_0, t-d_2} \approx \frac{3}{256 \cdot \pi^6 \cdot c \cdot n^4 \cdot \bar{\nu}^6} \left\{ \frac{1}{\tau_{d_0}^P} \cdot \frac{1}{\tau_{t-d_2}^P} \int f_{d_0}^P(\bar{\nu}) \cdot f_{t-d_2}^P(\bar{\nu}) d\bar{\nu} + \frac{1}{\tau_{d_0}^P} \cdot \frac{1}{\tau_{t-d_2}^P} \int f_{d_0}^P(\bar{\nu}) \cdot f_{t-d_2}^P(\bar{\nu}) d\bar{\nu} \right\} \quad (2')$$

$\tau_{d_0}^P, \tau_{t-d_2}^P$  : radiative lifetime of the transition corresponding to the phonon side band of  $d_0$  and  $t-d_2$ , respectively

$f_{d_0}^P, f_{t-d_2}^P$  : normalized lineshape factors of the phonon side bands.

We did not have the necessary spectral information on phonon side bands to estimate the coupling coefficient  $C_{d_0, t-d_2}$ , but the fact that the energy difference  $\nu_{g, d_0} - \nu_{g, t-d_2} = 39 \text{ cm}^{-1}$  falls into a dense region of the phonon spectrum of solid nitrogen [10] suggests sizable overlap of phonon side bands and zero phonon lines of  $\nu_g$  of the two isotopes. Therefore, we expect  $C_{d_0, t-d_2}$  in case of the two  $\nu_g$  transitions to be large enough to account for  $t\text{-C}_2\text{H}_2\text{D}_2 + \text{F}_2$  reaction observed upon excitation of  $\text{C}_2\text{H}_4$  at  $3106 \text{ cm}^{-1}$ . However, it is conceivable that, in addition, some reaction of  $t\text{-C}_2\text{H}_2\text{D}_2 \cdot \text{F}_2$  pairs is induced by Forster transfer invoking other, lower lying vibrational levels of  $\text{C}_2\text{H}_4$  which are populated by intramolecular cascading. For instance, relaxation of  $\text{C}_2\text{H}_4$  to  $\nu_2 + \nu_{12}$  at  $3076 \text{ cm}^{-1}$  might result in efficient, in part resonant energy transfer to  $t\text{-C}_2\text{H}_2\text{D}_2$  because of the closeness of the  $\nu_2 + \nu_{12}$  absorption with  $\nu_g$  of  $t\text{-C}_2\text{H}_2\text{D}_2$  (Fig. 4).

The energy discrepancy of  $62 \text{ cm}^{-1}$  between  $2\nu_2$  of  $\text{CH}_2\text{CD}_2$  at  $3168 \text{ cm}^{-1}$ , and the next lower infrared active transition of  $\text{C}_2\text{H}_4$ ,  $\nu_g$ , lies also in the spectral range in which the phonon density of states of solid nitrogen is large ( $25\text{-}70 \text{ cm}^{-1}$ , [10]), hence we expect again noticeable transfer between the two isotopes upon excitation of  $2\nu_2$  of  $\text{CH}_2\text{CD}_2$ . The failure to observe any  $\text{C}_2\text{H}_4 + \text{F}_2$  reaction in a matrix  $\text{CH}_2\text{CD}_2/\text{C}_2\text{H}_4/\text{F}_2/\text{N}_2 \sim 0.5/0.5/1/100$  when exciting  $\text{CH}_2\text{CD}_2$  at  $3169\text{-}3163 \text{ cm}^{-1}$  does not contradict this expectation, because not nearly enough photons were absorbed by  $\text{CH}_2\text{CD}_2$  which would have been needed to detect energy transfer as efficient as observed in case of the  $t\text{-C}_2\text{H}_2\text{D}_2/\text{C}_2\text{H}_4/\text{F}_2/\text{N}_2$  system.

Our finding that energy transfer between  $\nu_3$  of  $\text{HC}\equiv\text{CH}$  at  $3280 \text{ cm}^{-1}$  and  $\text{C}_2\text{H}_4$  with its closest infrared active band at  $3106 \text{ cm}^{-1}$  is at least two orders of magnitude less effective than direct excitation of  $\nu_g$  of  $\text{C}_2\text{H}_4$  in a matrix  $\text{HC}\equiv\text{CH}/\text{C}_2\text{H}_4/\text{F}_2/\text{N}_2 \sim 0.5/0.5/1/100$  is consistent with the fact that

the energy gap of  $175\text{cm}^{-1}$  falls well outside the phonon spectrum of  $\text{N}_2$ . At least 3 bulk phonons (or 2-3 local phonons) are needed to match this energy difference, implying a drastic decrease of the rate of non-resonant energy transfer in comparison with the  $\text{C}_2\text{H}_4/\text{C}_2\text{H}_2\text{D}_2/\text{F}_2/\text{N}_2$  systems. It is interesting to note that even energy exchange between nearest neighbor  $\text{HC}\equiv\text{CH}$  and  $\text{C}_2\text{H}_4$  molecules did not occur detectably, since no growth of products due to reaction of  $\text{HC}\equiv\text{CH}\cdot\text{C}_2\text{H}_4\cdot\text{F}_2$  clusters could be observed.

### 3. Product distribution and reaction mechanism

The observation that the particular  $\text{C}_2\text{H}_4$  vibrational which induces the reaction has no influence on the branching between vinyl fluoride and HF, and gauche and trans 1,2-difluoroethane, is consistent with our earlier conclusion that the product branching occurs by elimination of HF from a vibrationally excited, electronic ground state 1,2-difluoroethane molecule [2]. With a  $\Delta H^0(298)$  of  $-115.5$  kcal/mol for the reaction  $\text{C}_2\text{H}_4 + \text{F}_2 \rightarrow \text{trans-CH}_2\text{F-CH}_2\text{F}$ , and  $-116.1$  kcal/mol for gauche- $\text{CH}_2\text{F-CH}_2\text{F}$  [2], and an activation energy for the  $\text{C}_2\text{H}_4 + \text{F}_2$  matrix reaction of about 5 kcal/mol [1], we calculate a minimum energy for the chemically activated 1,2-difluoroethane intermediate of 120 kcal/mol. Because of the very high density of vibrational states of this polyatomic at  $40000\text{ cm}^{-1}$  above the zero point energy level, any initial, non-statistical vibrational energy distribution reflecting the particular ethylene vibrational mode which promoted the reaction is expected to be randomized within a few picoseconds or less [11]. This is at least two orders of magnitude faster than elimination of HF, which was found by Chang and Setzer to occur on the nanosecond time scale for 1,2-difluoroethane chemically activated 40 kcal/mol above the critical energy to elimination of 62 kcal/mol [12]. The latter was



determined by a fit of RRKM calculations, based on a four centered HF elimination activated complex model, to the measured decomposition rates [12]. Therefore, we do not expect the specific ethylene mode which excites the reaction to affect the product branching, in agreement with our observation. On the other hand, the decrease of the branching ratios  $b_t$  and  $b_g$  by a factor of two upon increase of the deposition temperature by only 3.5 K suggests that the local matrix environment strongly influences the deactivation kinetics of the hot 1,2-difluoroethane molecule.

Deposition of the matrix at 15.5 K results in a better annealed cage for the reactive pairs, and consequently for the hot difluoroethane, than deposition at 12 K. This might lead to less effective coupling of the 1,2-difluoroethane vibrational modes to the local phonon modes of the surrounding matrix, resulting in a longer lifetime of the excited molecule, and therefore higher probability for HF elimination in case of the matrix prepared at 15.5 K. It is important to add, however, that the deposition temperature did not appear to affect noticeably the lifetime of the vibrationally excited ethylene, since the quantum efficiency to reaction was the same, within the experimental error, for matrices deposited at 15.5 and 12 K.

The branching between HF and DF elimination observed in the case of the reaction of dideutero ethylenes with fluorine gives additional evidence for our view that the product branching originates in the competition between decomposition and stabilization of a vibrationally excited difluoroethane intermediate. The ratios  $\beta_{\text{HF/DF}}$  of the integrated absorbances of HF and DF fundamentals are independent of laser irradiation frequency and, within the experimental uncertainty, the same for all three  $\text{C}_2\text{H}_2\text{D}_2$  isomers, 2.2. The frequency independence of this ratio indicates

again that vibrational redistribution is complete before product branching occurs. Assuming a ratio of two for the extinction coefficients of HF and DF fundamentals, we obtain an HF/DF branching ratio of 1.1. This intramolecular H/D isotope ratio close to one is expected for a molecule activated more than 50 kcal/mol above the critical energy to decomposition [11]. In fact, our measured ratio is within 10%, the same as the intramolecular H/D isotope ratio (per H and D atom) calculated with RRKM, based on a four centered model, for  $C_2H_4DCl$  (1.24) and  $C_2D_4HCl$  (1.2) activated 35 kcal/mol above the critical energy to HCl elimination [13].

The ratios of the integrated intensities of the C=C stretching absorptions of the various partially deuterated vinyl fluoride molecules displayed in Tables IV and V corroborate the result obtained from the analysis of the relative intensities of HF and DF absorptions. For instance, the ratio of the intensities of HF and DF elimination products in case of  $trans\text{-}CHD=CHD+F_2$  and  $cis\text{-}CHD=CHD+F_2$ ,  $\beta_{CHD=CDF}/CHD=CHF$ , is independent of the particular vibrational mode which excites the reaction. However, the ratio  $\beta_{CD=CHF}/CH=CDF$  of the reaction  $CH_2=CD_2+F_2$  is 20% higher when irradiating at  $1900\text{ cm}^{-1}$  than when exciting the reaction at  $3096\text{ cm}^{-1}$ , a difference which is beyond experimental error. We attribute the higher yield of the HF elimination product in the case of the CO laser irradiation to a closer coincidence of the laser line with the absorption of  $(C_2H_2D_2)_2 \cdot F_2$  clusters at  $1900\text{ cm}^{-1}$  than at  $3096\text{ cm}^{-1}$ . Our earlier finding that an ethylene molecule in the matrix cage adds efficient relaxation channels to the vibrationally excited 1,2-difluoroethane adduct implies more rapid deactivation of the hot intermediate in the case of the reaction of  $(C_2H_2D_2)_2 \cdot F_2$  aggregates than in case the  $C_2H_2D_2 \cdot F_2$  pair reaction [2]. Therefore, we expect for  $(C_2H_2D_2)_2 + F_2$  a heavier contribution

to elimination from less excited vibrational levels of  $\text{CH}_2\text{F}-\text{CH}_2\text{F}$  with intrinsically higher HF/DF ratios, and hence a more intense  $\text{CD}_2=\text{CHF}$  absorption in case of the experiment with the closer coincidence of the laser frequency with the  $(\text{C}_2\text{H}_2\text{D}_2)_2\cdot\text{F}_2$  absorption. This change in branching between HF and DF elimination is only affecting the relative intensities of the C=C stretching absorptions at  $1625.2$  and  $1612.2\text{ cm}^{-1}$ , because here the absorptions due to  $\text{VF}\cdot\text{HF}(\text{DF})$  pairs and  $\text{VF}\cdot\text{E}\cdot\text{HF}(\text{DF})$  aggregates coincide. It is not reflected, however, in the ratio of the HF and DF absorptions at  $3796$  and  $2784\text{ cm}^{-1}$ , because these are exclusively due to  $\text{VF}\cdot\text{HF}(\text{DF})$  pairs ( $\text{VF}\cdot\text{E}\cdot\text{HF}$  and  $\text{VF}\cdot\text{E}\cdot\text{DF}$  have very broad absorptions at  $3682$  and  $2696\text{ cm}^{-1}$ , respectively). We have no explanation so far for the up to 30% variation of the ratio of intensities of cis and trans  $\text{CHD}=\text{CHF}$  as a function of laser frequency and precursor isomer in the case of the  $\text{CHD}=\text{CHD}+\text{F}_2$  reactions.

The lack of product reference infrared spectra in the case of the reactions of the dideutero ethylenes with fluorine did not allow us to verify the appearance of the particular stereoisomers of dideutero-1,2-difluoroethane molecules predicted in Table II of reference I on the basis of a stereospecific four center cis addition of  $\text{F}_2$  across the ethylene double bond. Cis addition of  $\text{F}_2$  in the case of cis- $\text{CHD}=\text{CHD}$  is expected to lead to two conformational isomers of  $\text{CHDF}-\text{CHDF}$ , whereas for trans- $\text{CHD}=\text{CHD}$  three different stereoisomers are predicted, each again displaying a separate infrared spectrum. This suggests that even without assignment we ought to be able to recognize stereospecificity, in principle, by looking for differences in frequencies and intensities of product absorptions of t- $\text{CHD}=\text{CHD}+\text{F}_2$  and c- $\text{CHD}=\text{CHD}+\text{F}_2$  between  $1500$  and  $400\text{ cm}^{-1}$ , the spectral range where  $\text{CHDF}-\text{CHDF}$  deformation and skeletal stretching modes are expected to absorb. Unfortunately, no growth of the sharp absorption bands of

isolated CHDF-CHDF which would have most readily allowed detection of differences could be observed in matrices t-CHD=CHD/F<sub>2</sub>/N<sub>2</sub> and c-CHD=CHD/F<sub>2</sub>/N<sub>2</sub> ~ 1/1/100, indicating very small branching ratios b<sub>t</sub> and b<sub>g</sub> in case of the reaction of CHD=CHD•F<sub>2</sub> pairs. Only broad bands (FWHM=5-10 cm<sup>-1</sup>) appeared between 1200 and 700 cm<sup>-1</sup> which are characteristic for absorptions of aggregates DFE•E, VF•HF(DF), and VF•E•HF(DF) of the various partially deuterated products. Comparison of these bands for matrices t-CHD=CHD/F<sub>2</sub>/N<sub>2</sub> and c-CHD=CHD/F<sub>2</sub>/N<sub>2</sub> revealed slight differences, but no decisive conclusion about the stereospecificity of the reaction of F<sub>2</sub> with cis and trans CHD=CHD can be drawn from these observations.

#### V. Conclusions

This study shows that the vibrationally stimulated reaction of ethylene with fluorine in a nitrogen matrix proceeds with a high degree of molecular and isotopic selectivity. The extent to which intermolecular energy transfer occurs, as revealed by the C<sub>2</sub>H<sub>4</sub> v<sub>9</sub> profile study and the experiments with isotopic mixtures of ethylene, can be explained, at least qualitatively, by dipole induced energy transfer according to the Forster mechanism.

The measured branching ratios are consistent with our assumption that the reaction involves a vibrationally hot 1,2 difluoroethane intermediate whose fate, stabilization or αβ elimination of HF, determines the product branching. In particular, the observed HF/DF branching ratio rules out the possibility that vinyl fluoride and HF(DF) are formed by F atom attack on a CH(CD) bond of a fluoroethyl radical, produced by an initial step C<sub>2</sub>H<sub>4</sub>+F<sub>2</sub>→CH<sub>2</sub>CH<sub>2</sub>F+F. In such a case, we would not expect any DF to be produced since at 12K, the critical energy

difference between CH and CD bond rupture is about 50 times larger than  $kT$ . We have less decisive clues, however, as to whether the hot 1,2-difluoroethane intermediate is formed in a direct molecular, four center addition of  $F_2$  to the C=C bond, or a rapid sequence  $C_2H_4 + F_2 \rightarrow CH_2CH_2F + F \rightarrow CH_2F-CH_2F^\dagger$  within the same cage. Our strongest evidence thus far against an initial radical formation are the findings that (a) reaction of  $(C_2H_4)_2 \cdot F_2$  clusters does not lead to any products expected upon formation of two fluoroethyl radicals in the same matrix cage, namely the gas phase reaction products  $CH_2FCH_2CH_2CH_2F$ ,  $CH_2=CHF$  and  $CH_3CH_2F$  [2], and (b) excitation of  $C_2H_4$  of an aggregate  $C_2H_4 \cdot CH_2CD_2 \cdot F_2$  does not result in any partially deuterated product molecules. Both observations speak against the radical forming step since we would expect from it a noticeable product yield due to attack of the fluorine atom on the nearest neighbor ethylene molecule, particularly because the F atom is formed with excess energy [2].

The change of the product branching ratio by a factor of two upon increase of the deposition temperature by only a few K manifests a remarkable sensitivity of the lifetime of the vibrationally excited 1,2-difluoroethane intermediate to changes in the matrix environment. Our earlier finding that addition of one ethylene molecule in the matrix cage alters the competition between stabilization and elimination 100 fold in favor of stabilization is an even more dramatic illustration of the influence of the local environment of the hot 1,2-difluoroethane molecule on the product branching [2].

### Acknowledgments

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## References

1. H. Frei and G.C. Pimentel, *J. Chem. Phys.* 78, No. 1 (1983).
2. H. Frei, L. Fredin, and G.C. Pimentel, *J. Chem. Phys.* 74, 397 (1981).
3. R. Elst, W. Rogge, and A. Oskam, *Rec. Trav. Chim.* 92, 427 (1973).
4. Th. Forster, *Ann. Physik.* 2, 55 (1948).
5. D.L. Dexter, *J. Chem. Phys.* 21, 836 (1953).
6. J.M. Wiesenfeld and C. B. Moore, *J. Chem. Phys.* 70, 930 (1979).
7. R.C. Golike, I. M. Mills, W.B. Person, and B. Crawford, Jr., *J. Chem. Phys.* 25, 1266 (1956).
8. L.H. Bolz, M.E. Boyd, F.A. Mauer, and H.S. Peiser, *Acta Cryst.* 12, 247 (1959).
9. F. Legay, in: *Chemical and Biological Applications of Lasers*, Vol. II, C.B. Moore (Editor), Academic Press, New York (1977), pg 43.
10. O. Schnepf and A. Ron, *Disc. Farad. Soc.* 48, 26 (1969).
11. P.J. Robinson and K. A. Holbrook, "Unimolecular Reactions" (Wiley, New York, 1972).
12. H.W. Chang and D.W. Setzer, *J. Amer. Chem. Soc.* 91, 7648 (1969).
13. K. Dees and D. W. Setzer, *J. Chem. Phys.* 49, 1193 (1968).

Table I.  $C_2H_4+F_2$  laser irradiation of  $\nu_9$  at 12K

$C_2H_4/F_2/N_2$	Laser frequency ( $cm^{-1}$ )	Power ( $mWcm^{-2}$ )	Photons absorbed ( $s^{-1}cm^{-2}$ )	Irrad. time (hrs)
1/1/100	3110.0	8.2	$3.0 \times 10^{16}$	5.8
	3105.0	7.6	$5.9 \times 10^{16}$	4.2
	3100.0 <sup>a</sup>	5.8	$1.2 \times 10^{16}$	4.2
	3096.0	8.8	$6.9 \times 10^{15}$	4.2
	3095.0	7.0	$1.5 \times 10^{15}$	0.8
1/6/600	3110.0	9.1	$2.1 \times 10^{16}$	5.0
1/12/1200	3110.0	7.6	$1.4 \times 10^{16}$	5.0
	3105.0	8.1	$2.0 \times 10^{16}$	5.0

<sup>a</sup>In addition: 4.2 hrs.,  $6.0 mWcm^{-2}$ ,  $C_2H_4/F_2/N_2 \sim 1/1/100$



Table II. Energy transfer studies

Matrix	Irradiated Molecule	Mode	Laser frequency (cm <sup>-1</sup> )	Power (mW/cm <sup>2</sup> )	Photons Absorbed (s <sup>-1</sup> cm <sup>-2</sup> )	Irrad. time (min)	Donor-Acceptor Energy Difference	Reaction
HC≡CH/CH <sub>2</sub> =CH <sub>2</sub> /F <sub>2</sub> /N <sub>2</sub> ~0.1/1/1/100	HC≡CH	ν <sub>3</sub> (Σ <sub>u</sub> <sup>+</sup> ) 3282.4cm <sup>-1</sup>	3281.9	13.7	1.1x10 <sup>17</sup>	60	ν <sub>3</sub> , C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub> +F <sub>2</sub> : no
			3280.5 3278.4 3276.2 3274.1 3271.9 3269.8 3267.7 3265.5	15.2	2.2x10 <sup>17</sup> 2.1x10 <sup>17</sup> 1.5x10 <sup>17</sup> 1.2x10 <sup>17</sup> 1.0x10 <sup>17</sup> 1.0x10 <sup>16</sup> 9.5x10 <sup>16</sup> 7.7x10 <sup>16</sup>	30 15 15 15 15 10 10 10		C <sub>2</sub> H <sub>4</sub> +F <sub>2</sub> : no
CH <sub>2</sub> =CD <sub>2</sub> /CH <sub>2</sub> =CH <sub>2</sub> /F <sub>2</sub> /N <sub>2</sub> ~0.5/0.5/1/100	CH <sub>2</sub> =CD <sub>2</sub>	2ν <sub>2</sub> (A <sub>1</sub> ) 3168.6cm <sup>-1</sup>	3169.0	9.1	2.0x10 <sup>15</sup>	20	2ν <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>	C <sub>2</sub> H <sub>4</sub> +F <sub>2</sub> : no
			3168.0 3167.0 3166.0 3165.0 3164.0 3163.0		3.5x10 <sup>15</sup> 3.3x10 <sup>15</sup> 2.5x10 <sup>15</sup> 1.3x10 <sup>15</sup> 1.3x10 <sup>15</sup> 8.7x10 <sup>14</sup>	20 20 15 15 15 15	-ν <sub>9</sub> , C <sub>2</sub> H <sub>4</sub> =62cm <sup>-1</sup>	
t-CHD=CHD/CH <sub>2</sub> =CH <sub>2</sub> /F <sub>2</sub> /N <sub>2</sub> ~0.6/0.4/1/100	CH <sub>2</sub> =CH <sub>2</sub>	ν <sub>9</sub> (b <sub>2u</sub> ) 3107.1cm <sup>-1</sup>	3106.0	15.2	4.5x10 <sup>16</sup>	90	ν <sub>9</sub> , C <sub>2</sub> H <sub>4</sub>	t-C <sub>2</sub> H <sub>2</sub> D <sub>2</sub> +F <sub>2</sub> : slight
			3066.6	7.6	5.5x10 <sup>16</sup>	120	-ν <sub>9</sub> , t-C <sub>2</sub> H <sub>2</sub> D <sub>2</sub> =39cm <sup>-1</sup>	C <sub>2</sub> H <sub>4</sub> +F <sub>2</sub> : slight <sup>a</sup>

<sup>a</sup> probably due to direct excitation of ν<sub>2</sub>+ν<sub>12</sub> of C<sub>2</sub>H<sub>4</sub>.

Table III. Estimated branching ratios for  $(C_2H_4)_2 + F_2$  in matrices  
 $C_2H_4/F_2/N_2 \sim 1/1/100$  at 12K<sup>a</sup>

Photolysis	T <sub>dep</sub> 'n	b <sub>t</sub>	b <sub>g</sub>	b <sub>g</sub> /b <sub>t</sub>
4208.9cm <sup>-1</sup> <sup>b</sup>	15.5K	1.5±0.2	2.8±0.6	1.9±0.5
3110.0cm <sup>-1</sup>	12K	3.0±0.4	6.8±0.8	2.3±0.4
3105.0cm <sup>-1</sup>	12K	2.7±0.4	5.5±0.8	2.0±0.4
	15.5K <sup>c</sup>	1.4±0.2 <sup>c</sup>	2.7±0.7 <sup>c</sup>	1.9±0.4
3100.0cm <sup>-1</sup>	12K	3.1±0.4	6.6±0.8	2.1±0.4
3096.0cm <sup>-1</sup>	12K	2.9±0.4	6.3±0.8	2.1±0.4
3076.1cm <sup>-1</sup>	12K	2.8±0.4	6.1±0.8	2.2±0.4
2989.0cm <sup>-1</sup>	15.5K	1.3±0.2	2.6±0.6	2.0±0.5
1896.2cm <sup>-1</sup>	15.5K	1.5±0.2	3.2±0.6	2.2±0.5

<sup>a</sup>Estimates made on basis of integrated absorbances of the following bands, determined from computer calculated difference spectra: VF·E·HF: 1139.4cm<sup>-1</sup>; t-DFE·E: 1041.2cm<sup>-1</sup>; g-DFE·E: 1088.0cm<sup>-1</sup> (see reference 2). Details of each laser irradiation experiment are described in Table I of this paper, and in Table I of reference 1.

<sup>b</sup>This transition is assigned to  $\nu_6 + \nu_{11}(B_{2u})$ , not  $\nu_3 + 2\nu_7 + \nu_{10}(B_{2u})$ , as erroneously assigned in reference 1.

<sup>c</sup>Measured in a matrix  $C_2H_4/CH_2CD_2/F_2/N_2 \sim 0.5/0.5/1/100$ .

Table IV. Growth of integrated absorbances of elimination products of the reaction  $\text{CH}_2=\text{CD}_2+\text{F}_2$  in matrices  $\text{CH}_2=\text{CD}_2/\text{F}_2/\text{N}_2 \sim 1/1/100$  at 12K

Photolysis <sup>a</sup>	Irrad. time (hrs.)	$\Delta A_{\text{HF}}$ <sup>b</sup>	$\Delta A_{\text{DF}}$	$\Delta A_{\text{CD}_2=\text{CHF}}$	$\Delta A_{\text{CH}_2=\text{CDF}}$	$\beta_{\text{HF/DF}}$ <sup>c</sup>	$\beta_{\text{CD}_2=\text{CHF/CH}_2=\text{CDF}}$
3096.0cm <sup>-1</sup>	5.2	0.2997	0.1386	1612.2cm <sup>-1</sup>	1625.2cm <sup>-1</sup>	2.2±0.2	0.59±0.02
1900.0cm <sup>-1</sup>	4.2	0.1404	0.0716	0.0584	0.0817	2.1±0.2	0.73±0.02

<sup>a</sup> Experimental details are described in Table I of reference I.

<sup>b</sup> Integrated absorbances, determined from computer calculated difference of the spectra after and before laser irradiation.

<sup>c</sup>  $\beta_{\text{HF/DF}} = \frac{\Delta A_{\text{HF}}}{\Delta A_{\text{DF}}}$ ,  $\beta_{\text{CD}_2=\text{CHF/CH}_2=\text{CDF}} = \frac{\Delta A_{\text{CD}_2=\text{CHF}}}{\Delta A_{\text{CH}_2=\text{CDF}}}$ : relative growth of elimination products, determined after every 50 minute irradiation period (constant with time within the indicated standard deviation).

Table V. Growth of integrated absorbances of elimination products of the reactions t-CHD=CHD+F<sub>2</sub> and c-CHD=CHD+F<sub>2</sub> in matrices CHD=CHD/F<sub>2</sub>(M<sub>2</sub>)<sup>1/1</sup>/100 at 12K

Reaction	Photolysis <sup>a</sup>	Irrad. Time (hrs)	<sup>b</sup>					<sup>c</sup> R <sub>HF</sub> /DF	R <sub>CHD=CDF</sub> CHD=CHF	R <sub>CHD=CHF</sub> R <sub>c/t</sub>	R <sub>CHD=CDF</sub> R <sub>c/t</sub>
			ΔA <sub>c-CHD=CDF</sub> 1607.1cm <sup>-1</sup>	ΔA <sub>t-CHD=CDF</sub> 1597.0cm <sup>-1</sup>	ΔA <sub>c-CHD=CHF</sub> 1633.4cm <sup>-1</sup>	ΔA <sub>t-CHD=CHF</sub> 1625.1cm <sup>-1</sup>	ΔA <sub>c-CHD=CDF</sub> +ΔA <sub>t-CHD=CHF</sub>				
t-CHD=CHD+F <sub>2</sub>	3066.7cm <sup>-1</sup>	4.4	0.1297	0.1625	0.0920	0.1083	2.4±0.1	1.47±0.03	0.84±0.04	0.80±0.01	
	1854.9cm <sup>-1</sup>	5.0	0.0986	0.1236	0.0888	0.0771	2.3±0.1	1.31±0.03	1.19±0.03	0.82±0.02	
c-CHD=CHD+F <sub>2</sub>	3061.0cm <sup>-1</sup>	5.3	0.0474	0.0505	0.0293	0.0452	2.2±0.2	1.31±0.04	0.64±0.02	0.91±0.03	
	3057.7cm <sup>-1</sup>	5.3	0.0372	0.0467	0.0271	0.0419	2.0±0.3	1.18±0.04	0.65±0.04	0.82±0.02	
	1827.2cm <sup>-1</sup>	5.1	0.0451	0.0570	0.0231	0.0580	--	1.7±0.05	0.44±0.07	0.82±0.02	

<sup>3</sup> Details of each laser irradiation experiment are described in Table I of reference I.

<sup>b</sup> Integrated absorbances, determined from computer calculated difference of the spectra after and before laser irradiation. HF: 3796cm<sup>-1</sup>; DF: 2704cm<sup>-1</sup>

<sup>c</sup> R<sub>HF</sub>/DF =  $\frac{\Delta A_{HF}}{\Delta A_{DF}} \cdot \frac{R_{CHD=CDF}}{R_{CHD=CHF}} = \frac{\Delta A_{c-CHD=CDF} + \Delta A_{t-CHD=CHF}}{\Delta A_{c-CHD=CHF} + \Delta A_{t-CHD=CDF}}$ , etc.; relative growth of elimination products, determined after every 50 minute irradiation period (constant with time within the indicated standard deviation).

### Figure Captions

Figure 1: Loss of  $C_2H_4$ ,  $\nu_9$  absorption after 4.2-5.0 hours laser irradiation at  $3110\text{ cm}^{-1}$  (left column) and  $3105\text{ cm}^{-1}$  (right column) at concentrations  $C_2H_4/F_2/N_2 \sim 1/1/100$ ,  $1/6/600$ , and  $1/12/1200$ . Top spectrum:  $\nu_9$  before laser irradiation. All other spectra are computer calculated differences of the spectra before and after irradiation.

Figure 2: Loss of absorbance of  $\nu_{12}$ ,  $C_2H_4$  after 5.0 hours irradiation with the laser at  $3110\text{ cm}^{-1}$ ,  $C_2H_4/F_2/N_2 \sim 1/12/1200$ . The peak at  $1437.7\text{ cm}^{-1}$  is due to isolated  $C_2H_4$ , the absorptions at  $1439.8$  and  $1440.7\text{ cm}^{-1}$  are due to  $C_2H_4 \cdot F_2$  pairs. Top spectrum: before irradiation. Bottom spectrum: computer calculated difference of the spectra before and after irradiation.

Figure 3: Growth of C=C stretching absorptions of vinyl fluoride product molecules in a matrix  $t\text{-CHDCHD}/C_2H_4/F_2/N_2 \sim 0.6/0.4/1/100$ . (a) Difference of the spectra after and before 1.5 hours irradiation of  $\nu_9$  of  $C_2H_4$  at  $3106.0\text{ cm}^{-1}$ . (b) Difference spectrum after 2.0 hours irradiation of  $\nu_9$  of  $t\text{-CHDCHD}$  at  $3066.6\text{ cm}^{-1}$ .

Figure 4: CH stretching spectral region  $3120\text{-}3050\text{ cm}^{-1}$  of a matrix  $t\text{-CHDCHD}/C_2H_4/F_2/N_2 \sim 0.6/0.4/1/100$  at 12 K.

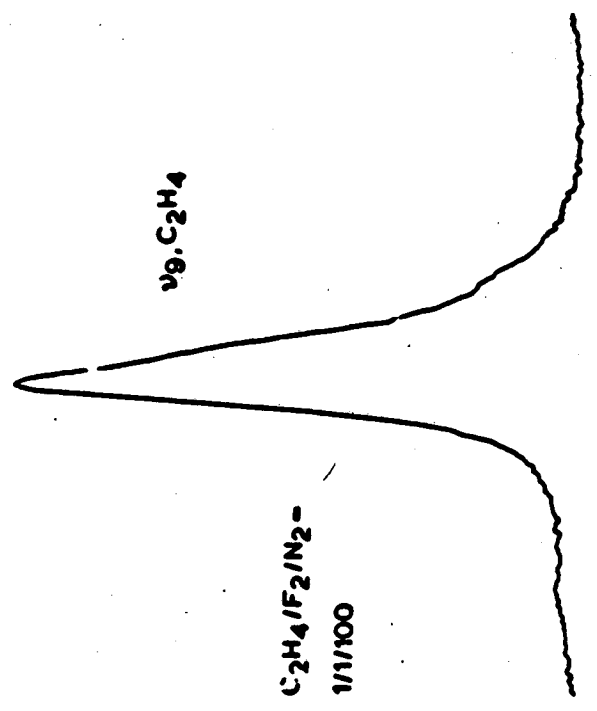
Figure 5: Irradiation of  $\nu_9$  in a matrix  $C_2H_4/F_2/N_2 \sim 1/1/100$ . Lower curve  $A^{E \cdot F_2}$ : absorbance loss, measured at the irradiation frequency, upon irradiation at 3110, 3105, 3100, and 3096  $cm^{-1}$ . Upper curve  $A_{\infty}^{VF}$ : asymptotic limit of the absorbance growth of the 1119  $cm^{-1}$   $CH_2=CHF \cdot HF$  band upon irradiation at the four frequencies 3110, 3105, 3100, and 3096  $cm^{-1}$ .

Absorbance

$\nu_9$ . C<sub>2</sub>H<sub>4</sub>

C<sub>2</sub>H<sub>4</sub>/F<sub>2</sub>/N<sub>2</sub> =  
1/1/100

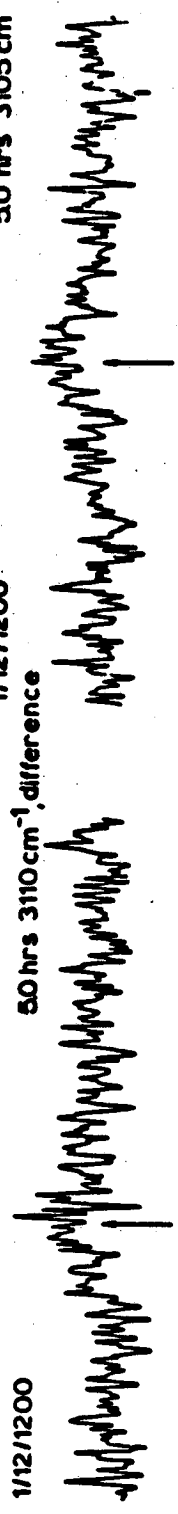
.104  
0



1/12/1200

50 hrs 3105 cm⁻¹, diff.

50 hrs 3110 cm⁻¹, difference



.6/1600

50 hrs 3110 cm⁻¹, diff.

1/12/1200



1/1/100

50 hrs 3110 cm⁻¹, diff.

42 hrs 3105 cm⁻¹, diff.

1/1/100



3130 cm⁻¹

3115

3100

3085

3130 cm⁻¹

3115

3100

3085

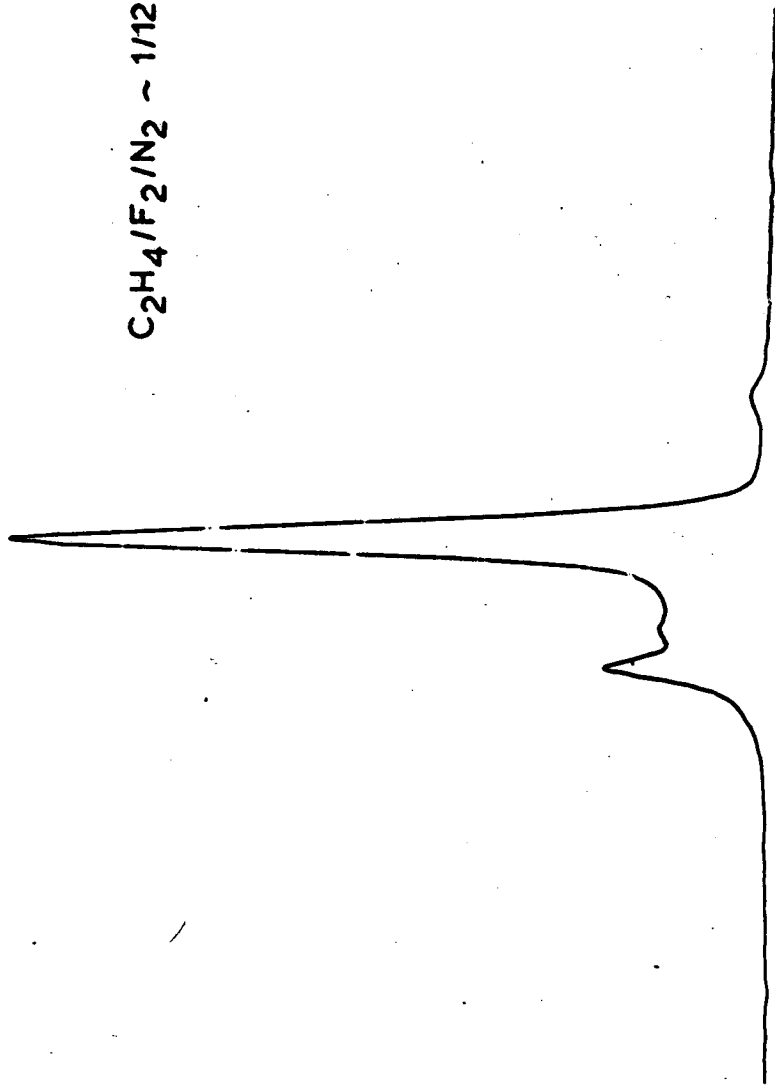
$\nu_{12}$ , C<sub>2</sub>H<sub>4</sub>

C<sub>2</sub>H<sub>4</sub>/F<sub>2</sub>/N<sub>2</sub> ~ 1/12/1200

Absorbance

.122

0



.0072

0



1450 cm<sup>-1</sup>

1444

1438

1432

1426

Fig. 2



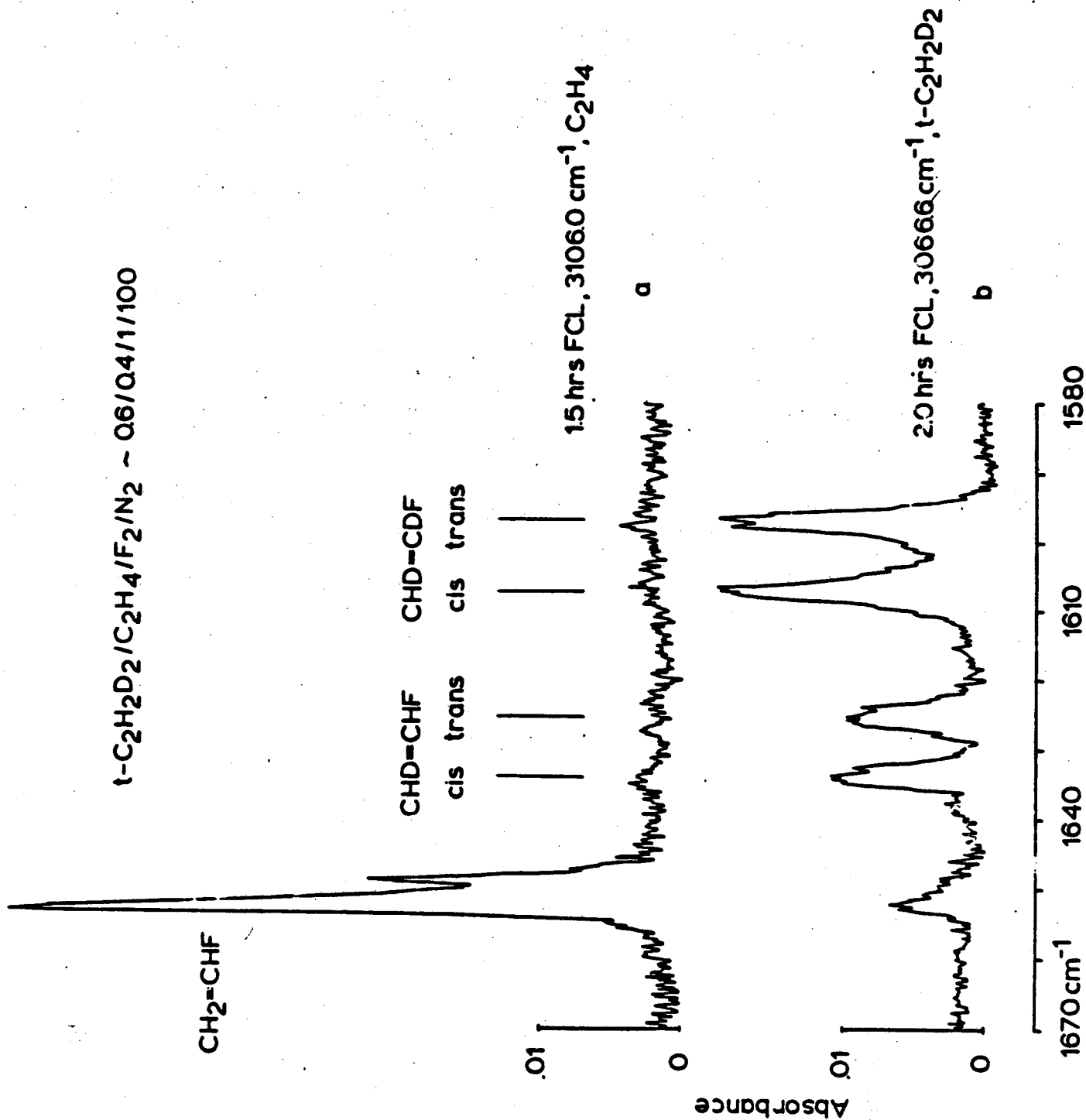


Fig. 3

$t\text{-C}_2\text{H}_2\text{D}_2/\text{C}_2\text{H}_4/\text{F}_2/\text{N}_2 \sim 0.6/0.4/1/100$

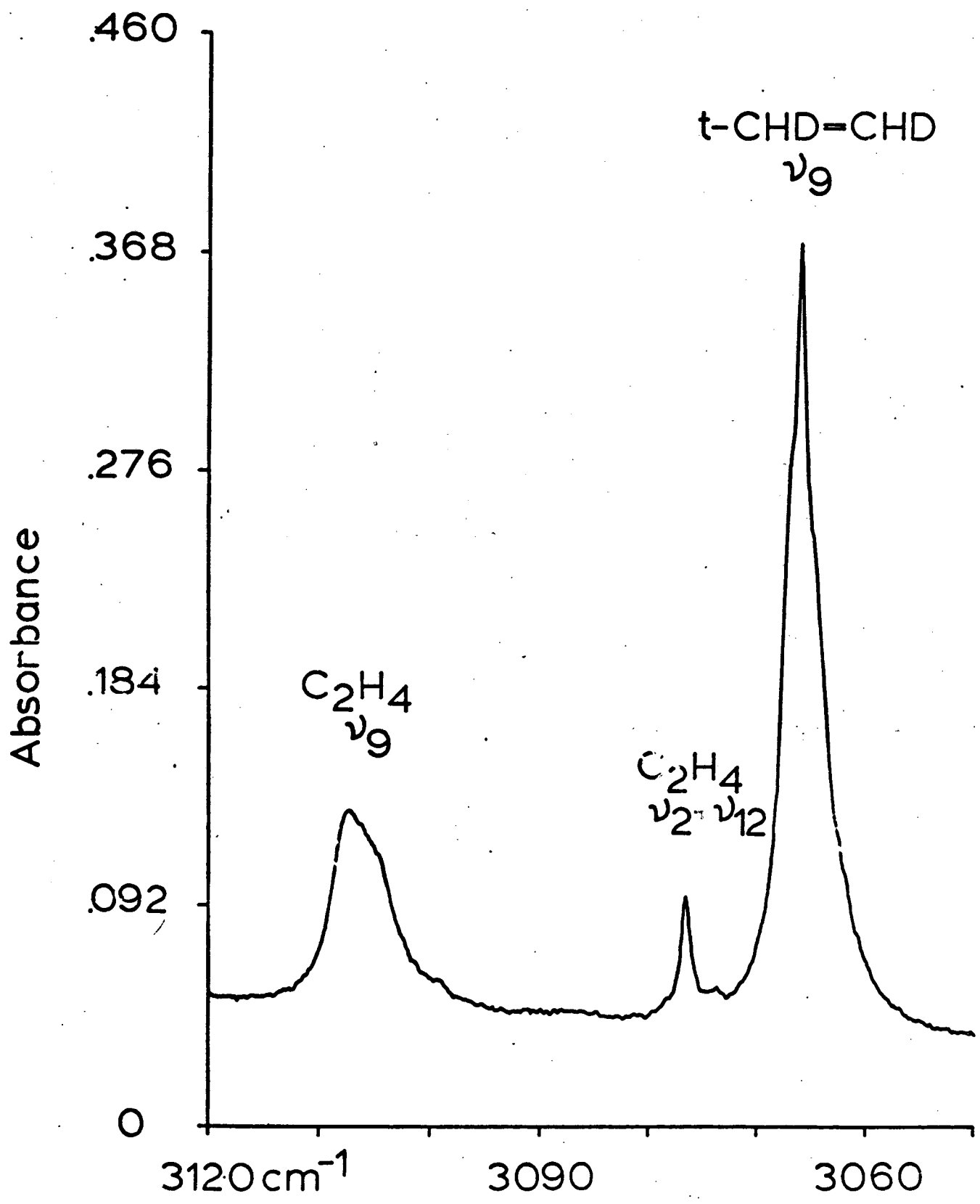


Fig. 4

$C_2H_4/F_2/N_2 \sim 1/1/100$   
selective excitation of  $\nu_9$

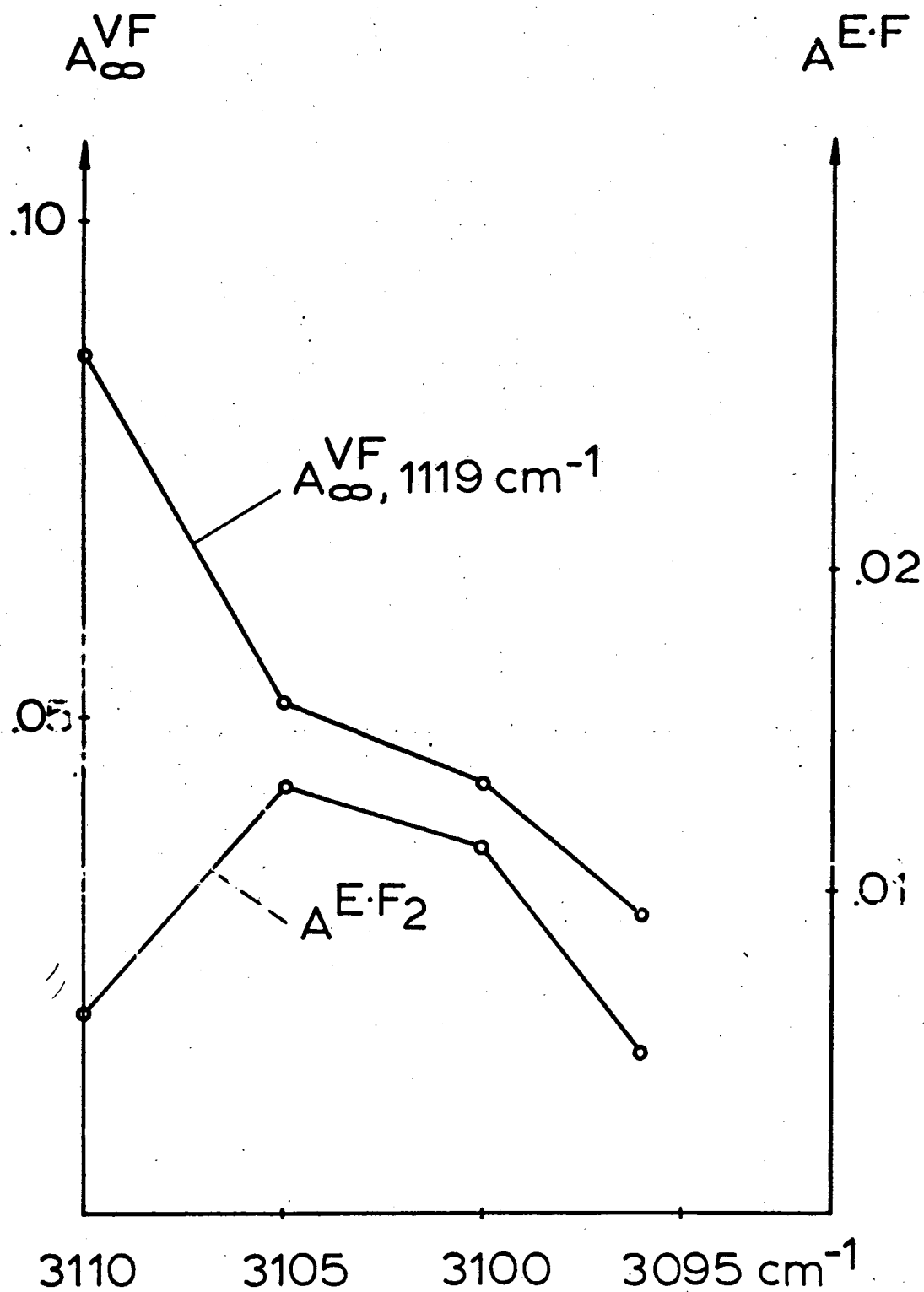


Fig. 5

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