© *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *53*, *1530—1536 (1980)* [Vol. 53, No. 6

Vibrational Distribution of HF Produced by Mercury Photosensitized Decomposition of Fluoroethylenes

Hajime Watanabe, Hiroyuki Horiguchi, and Soji Tsuchiya*
Department of Pure and Applied Sciences, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

(Received December 15, 1979)

Distributions of vibrationally excited HF produced by Hg-photosensitized reactions of fluoroethylenes are determined by means of the IR emission measurement of HF fundamentals. The distributions are almost of Boltzmann type with temperatures of 11400, 13700, 7200, 5700, 5700, and 2200 K for respective parent molecules of CH_2=CHF, CH_3CF=CH_2, CH_2=CF_2, *cis*-, *trans*-CHF=CHF, and CHF=CF_2. The fractions of vibrational energy of HF† among the energies available for distribution in various degrees-of-freedom of product molecules are 19, 23, 11, 7.6, 7.6, and 1.7% for the above molecules, respectively. The statistical calculation results in much less energy disposal in HF vibration in the decompositions of CH_2=CHF, CH_3CF=CH_2, and CH_2=CF_2, while the distributions of HF† in CHF=CHF and CHF=CF_2 are closer to those predicted by the statistical calculation. The deactivation rate of HF† in CH_2=CHF is about three times larger than that in CH_2=CF_2, and the latter values resemble those in HF.

Experimental observations on energy partitioning among internal and external degrees-of-freedom of product molecules in chemical reactions have given deep insight into the mechanism and dynamics of the relevant molecular processes. In this paper, we discuss the energy partitioning in the Hg-photosensitized reaction of HF elimination from fluoroethylene (hereafter F-ethylene). The first experiment which demonstrated production of vibrationally excited HF (hereafter HF†) in photolysis of F-ethylenes was made by Berry and Pimentel,1) who confirmed lasing actions of HF†. Almost at the same time, Clough, Polanyi, and Taguchi2) determined the vibrational distribution of HF† produced by the reaction of Hg*+CH_2=CF_2. The distribution shows relatively larger populations in higher levels than those predicted by the statistical calculation. The non-statistical vibrational energy disposal in the HCl produced by the UV photolyses of Cl-ethylenes was also reported by Berry,3) who postulated a simple Golden Rule model to simulate the vibrational distribution of HCl. It was also reported that vibrationally excited HF was produced in reactions of H and O atoms with fluoroethylenes, and that the vibrational distribution of HF was predicted well by the model proposed by Berry.4,5)

As for the mechanism of the present Hg-photosensitized reaction, Trobridge and Jennings6) observed the quantum yield of CH≡CH from CH_2=CHF to be almost unity indicating the HF elimination as a dominant reaction channel. They also suggested two kinds of excited species as reaction intermediates. Discussion of the same line was given on the basis of the calculation of energy levels by Strausz *et al.*,7) who postulated the mechanism: $\text{F-ethylene}\xrightarrow{\text{Hg}^*}(\text{F-ethylene})^*_{\text{triplet}}\longrightarrow(\text{F-ethylidene})^*_{\text{triplet}}\longrightarrow(\text{F-ethylidene})^*_{\text{singlet}}\longrightarrow\text{decomposition}$. Experimental studies to test this postulate were carried out by measuring yields of isomerization in *cis*- or *trans*-CHF=CHF7) and of CH≡CH from CH_2=CHF.8)

We report here observations of the vibrational distributions of HF formed by the Hg-photosensitized decompositions of CH_2=CHF, CH_2=CF_2, *cis*- and *trans*-CHF=CHF, CH_3CF=CH_2, and CHF=CF_2. The method is based on the IR emission measurement of HF† by the use of a modulation technique to separate the vibrational relaxation effect from the initial vibrational excitation. The results will be compared with the statistical partitioning of the excess energy among all degrees-of-freedom concerned.

Experimental

The apparatus is similar to that employed in the previous study.9) A gas mixture of Ar and F-ethylene was made to flow through a quartz reaction cell (24 cm long and 3 cm dia.) *via* a liquid N_2 trap to a rotary vacuum pump (900 dm^3 min^{-1}). A pressure increase due to addition of F-ethylene to the main flow of Ar was monitored differentially by a capacitance manometer (M. K. S. Baratron, 210H). A trace of Hg vapor which was less than 1×10^{-3} Torr** was mixed to the flow. The reaction cell was surrounded by six low pressure Hg lamps (Toshiba, 10 W germicidal lamp) whose power was supplied through ballast resistor from an ac source (Elgar, 251) with variable frequencies in the range of 50 Hz—10 kHz in order to modulate the 253.7 nm intensity at twice the frequency of the ac source. One end of the reaction cell was sealed by a CaF_2 window from which the ac component of the IR emission spectrum of HF† was observed by a monochromator (Spex, 1700 III with a grating of 300 l mm^{-1}, blazed at 3 μm) equipped with a photovoltaic InAs detector (Santa Barbara Research Center). The output of the detector was treated by a preamplifier (P. A. R., 181) and a lock-in amplifier (Ithaco, 393) whose reference signal was taken from the modulated 253.7 nm radiation. Thus, both the intensity and the phase-delay angle of the emission were determined, and this made it possible to obtain information on both the production of HF† and its relaxation. Since an average residence time in the reaction cell was about 50 ms and the 253.7 nm radiation intensity was on the order of 10^{15} photon $cm^{-3}s^{-1}$, a fraction of decomposed F-ethylene did not exceed 10% when its partial pressure was less than 10^{-2} Torr. Vinyl fluoride, 1,1-difluoroethylene (Matheson, 99.9% and 99.0%, respectively), *cis*- and *trans*-1,2-difluoroethylene, 2-fluoropropene, and 1,1,2-trifluoroethylene (P.C.R.) were treated by repeated solidification at liquid N_2 temperature. Gas chromatographic analyses of the latter four compounds were made to confirm less than 1% of impurities included.

** 1 Torr ≈ 133.322 Pa.

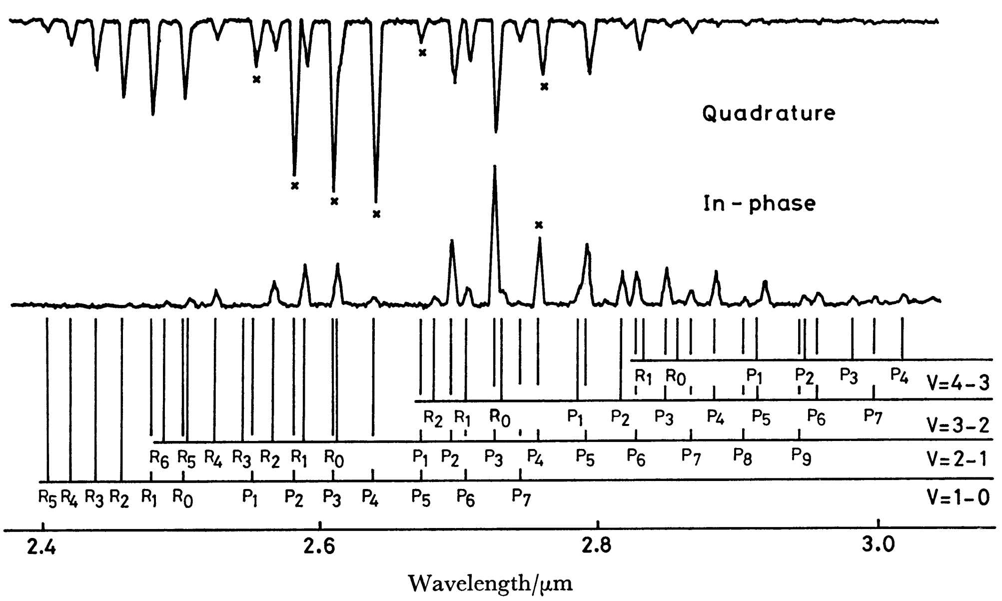


Fig. 1. AC components of emission spectrum of HF fundamentals observed in the mixture of 0.008 Torr CH_2=CHF+5 Torr Ar at 1.2 kHz modulation.
Lines marked by x are subjected to absorption of atmospheric water vapor.

Results

Analysis of Data. Figure 1 shows an example of the observed IR emission spectrum of HF†. Based on the molecular constants of HF given by Webb and Rao,[10)] each emission line may be assigned to respective vibration-rotation transition as noted in Fig. 1. In order to determine a relative population in each vibration-rotation level from the spectrum, the spectroscopic data summarized by Meredith and Smith[11)] and Herbelin and Emanuel[12)] were employed. The emission intensity of the $v'J'$—$v''J''$ transition is formulated as

$$I_{v'J',v''J''} = [hc(\omega_{v'J',v''J''})^4/(2J'+1)(\omega_{v',v''})^3] \times S_{J',J''}F_{v'J',v''J''}A_{v',v''}N_{v'J'}, \qquad (1)$$

where $\omega_{v'J',v''J''}$ and $\omega_{v',v''}$ are the wavenumbers of the relevant transition and the band center, respectively, and $S_{J',J''}$ represents the contribution of rotation to the dipole matrix element, and $A_{v',v''}$ is the spontaneous emission rate of the vibrational transition, and $N_{v',J'}$ is the population of the $v'J'$ state. In Fig. 2, plots of log $[I_{v'J',v''J''}/(\omega_{v'J',v''J''})^4 S_{J',J''}F_{v'J',v''J''}]$ are shown as a function of $J'(J'+1)$. The rotational equilibrium at room temperature is established in levels of $v'=1$—3 in the reaction system with the Ar pressure of more than 1 Torr. Thus, the rotational distribution in the level v' is described by

$$N_{v'J'} = N_{v'0}\exp[-B_{v'}J'(J'+1)/kT_{\mathrm{rot}}]. \qquad (2)$$

$N_{v'0}$ is determined by extrapolation of linear lines in Fig. 2, and is denoted hereafter as N_v. The population in the $v=4$ level is estimated from the line intensity of P(3 or 4) line of $v=4\rightarrow3$ transition assuming $T_{\mathrm{rot}}=300$ K. As is seen from Fig. 2(b), a rotational non-equilibrium distribution is found in a low pressure reaction system. The observed distribution is almost in accord with that reported by Clough *et al.*,[2)] and is partially relaxed due to collisional transitions in the gas phase as well as on the wall of the cell. Since it is difficult to estimate the selection rule for rotational transitions in collisions with the cell wall, the initial distribution may not be determined from the data obtained in the present flow apparatus.

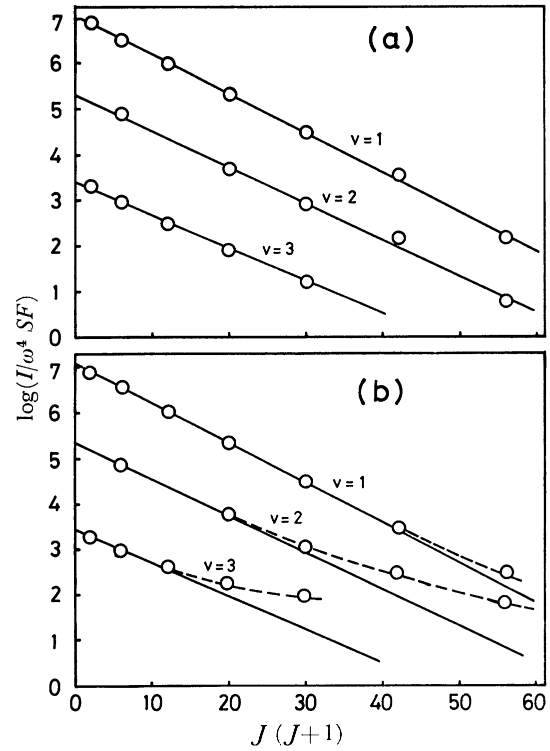


Fig. 2. Plots of log$(I/\omega^4 SF)$ *vs.* $J(J+1)$.
The emission spectrum is observed at 1.2 kHz modulation in the mixtures of (a) 0.006 Torr CH_2=CF_2+3 Torr Ar and (b) 0.001 Torr CH_2=CF_2+0.2 Torr Ar. The slopes of the solid lines result in the rotational temperature of *ca.* 300 K.

Corresponding to the modulated 253.7 nm radiation intensity, the population in the level v is described as

$$N_v = \bar{N}_v + \tilde{N}_v \exp(\mathrm{i}\omega t), \tag{3}$$

where the first term represents the DC component of N_v and the second the AC, and $\tilde{N}_v$ is a complex number to describe the quantity with a phase-delay angle. The kinetic equation for the population in the level v is formulated as follows.

$$\mathrm{d}N_v/\mathrm{d}t = K_v - R_{v,v-1}N_v + R_{v+1,v}N_{v+1}, \tag{4}$$

where K_v is the production rate of HF† in the level v, and $R_{v,v-1}$ the collisional plus radiative transition rate of $v \rightarrow v-1$. Here, it is assumed that a single quantum transition for the deactivation of HF†. An error caused by this assumption would not be very large, because the initial vibrational populations in higher levels are much smaller than those in lower levels as described later, and thus the contribution of multiple quantum transitions to the population in the relevant level v must be negligible. Equation 4 may be rewritten by the use of Eq. 3 as

$$\mathrm{i}\omega\tilde{N}_v = \tilde{K}_v - R_{v,v-1}\tilde{N}_v + R_{v+1,v}\tilde{N}_{v+1}. \tag{5}$$

The imaginary part of this equation results in the equation

$$R_{v,v-1} = \omega(\cot\phi_v) + R_{v+1,v}(\tilde{N}^{\mathrm{I}}_{v+1}/\tilde{N}^{\mathrm{I}}_v), \tag{6}$$

where $\tilde{K}^{\mathrm{I}}_v = 0$ and $\cot\phi_v = \tilde{N}^{\mathrm{R}}_v/(-\tilde{N}^{\mathrm{I}}_v)$ in which subscripts R and I denote the real and imaginary parts, respectively. The real part of Eq. 5 gives the formula

$$\tilde{K}^{\mathrm{R}}_v = \omega(-\tilde{N}^{\mathrm{I}}_v) + (R_{v,v-1}\tilde{N}^{\mathrm{R}}_v - R_{v+1,v}\tilde{N}^{\mathrm{R}}_{v+1}). \tag{7}$$

Thus, if the population in each level is obtained as a function of ω, the relaxation rate $R_{v,v-1}$ and the formation rate $\tilde{K}^{\mathrm{R}}_v$ of HF† in respective vibrational level may be determined.

Vibrational Relaxation of HF†. In Fig. 3, tangent of the phase-delay angle of the R(1) line of the $v=1 \rightarrow 0$ transition is plotted against the modulation frequency. According to Eq. 6, tan ϕ_{vJ} is almost proportional to ω if the contribution of cascading supply to the population in the vJ level is not large. From Fig. 3, it is found that tan ϕ_{vJ} is not dependent on the Ar pressure if it exceeds 1 Torr, while tan ϕ_{vJ} is reduced at lower pressures of Ar. This means that Ar may not contribute to the deactivation of HF† and that the decrease of tan ϕ_{vJ} at a lower pressure may be attributed to deactivation of HF† by collisions on the wall of the cell. Thus, the later experiments were carried out in the mixture of Ar+F-ethylene at the total pressure of more than 1 Torr which is high enough to avoid the wall-collision effect.

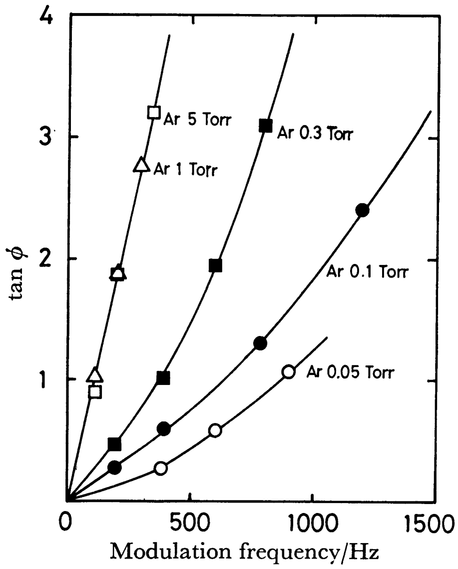


Fig. 3. Tangent of the phase -delay angle of R (1) line of $v=1 \rightarrow 0$ transition as a function of Ar pressure with the CH_2=CF_2 partial pressure of 0.006 Torr.

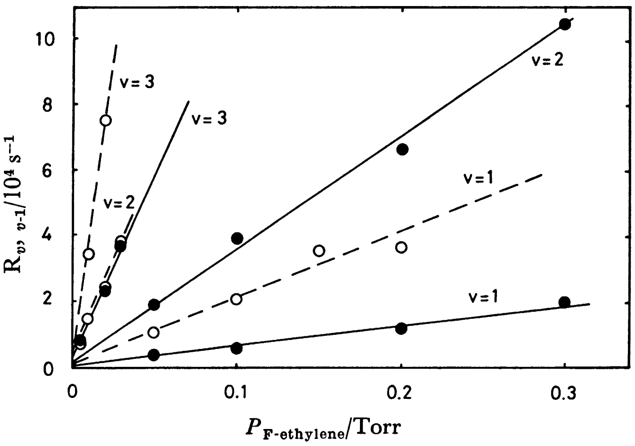


Fig. 4. The observed deactivation rate $R_{v,v-1}$ of HF† in the mixture of 5 Torr Ar +F-ethylene as a function of the partial pressure of F-ethylene.
Solid line: CH_2=CF_2, broken line: CH_2=CHF.

TABLE 1. DEACTIVATION RATE CONSTANT/$10^5\ \mathrm{s}^{-1}\ \mathrm{Torr}^{-1}$ OF HF† AT ROOM TEMPERATURE

v	Collision partner			
	CH_2=CHF	CH_2=CF_2	*cis-* and *trans-* CHF=CHF	HF
1	2.2±0.2	0.60±0.04	0.8±0.2	0.84[a)]
2	11±2	3.5±0.3	4±1	4.2[b)]
3	34±5	11±2	10±2	6.2[b)]
4	40	30	—	10[b)]

a) Ref. 13. b) Ref. 14.

In the analysis of the data by the use of Eq. 6, multiple quantum transitions are disregarded. However, the magnitude of the second term in the r.h.s. of Eq. 6 does not exceed 10% of the first term and thus, the error due to the above approximation must be much less than 10% and the obtained rate of $R_{v,v-1}$ may be interpreted as $\sum_{\delta \geq 1} R_{v,v-\delta}$. The determined rates are plotted as a function of the partial pressure of F-ethylene in Fig. 4. The linear relation indicates that the dominant deactivation process occurs by collisions of HF† with F-ethylene. The slopes of these lines give the deactivation rate constants of HF† as summarized in Table 1. The deactivation of HF† in CH_2=CHF is about three times more efficient than in CH_2=CF_2, and the rate constants of HF(v=1,2) are of the magnitude similar to those in HF.[13,14)] While, larger rate constants of

HF(v=3,4) in F-ethylene than in HF indicate that the resonance effect is improved in higher levels of HF† for the V-V energy transfer from HF† to the CH stretching modes of F-ethylene.

Vibrational Distribution of HF. The observed sets of $|\tilde{N}_v|$ and ϕ_v of HF† produced from six kinds of F-ethylenes are given in Fig. 5. Values of ϕ_v's increase at higher modulation frequencies approaching to 90°, though they are relatively small for higher vibrational levels. The latter fact would be due to larger deactivation rates in higher levels. Contrary to this result, $|\tilde{N}_v|$ of $v=1$ or 2 is reduced very much as the modulation frequency increases. This means that the vibrational relaxation from upper vibrational levels contributes in large part to populations in lower levels. Thus, in order to determine the initial vibrational distribution, it is necessary to take into proper account the vibrational relaxation effect according to Eq. 7. First, $R_{v,v-1}$ is determined utilizing Eq. 6 and assuming no initial population in levels of $v \geqslant 5$. The data employed to estimate $R_{v,v-1}$ are obtained with a modulation frequency which results in ϕ_v's in the range of 30°—50°. This range is selected to obtain good accuracy of the determined $R_{v,v-1}$'s. Then, the relative magnitude of K_v may be determined by extrapolating the data of Fig. 5 to the case of infinitely fast modulation, where

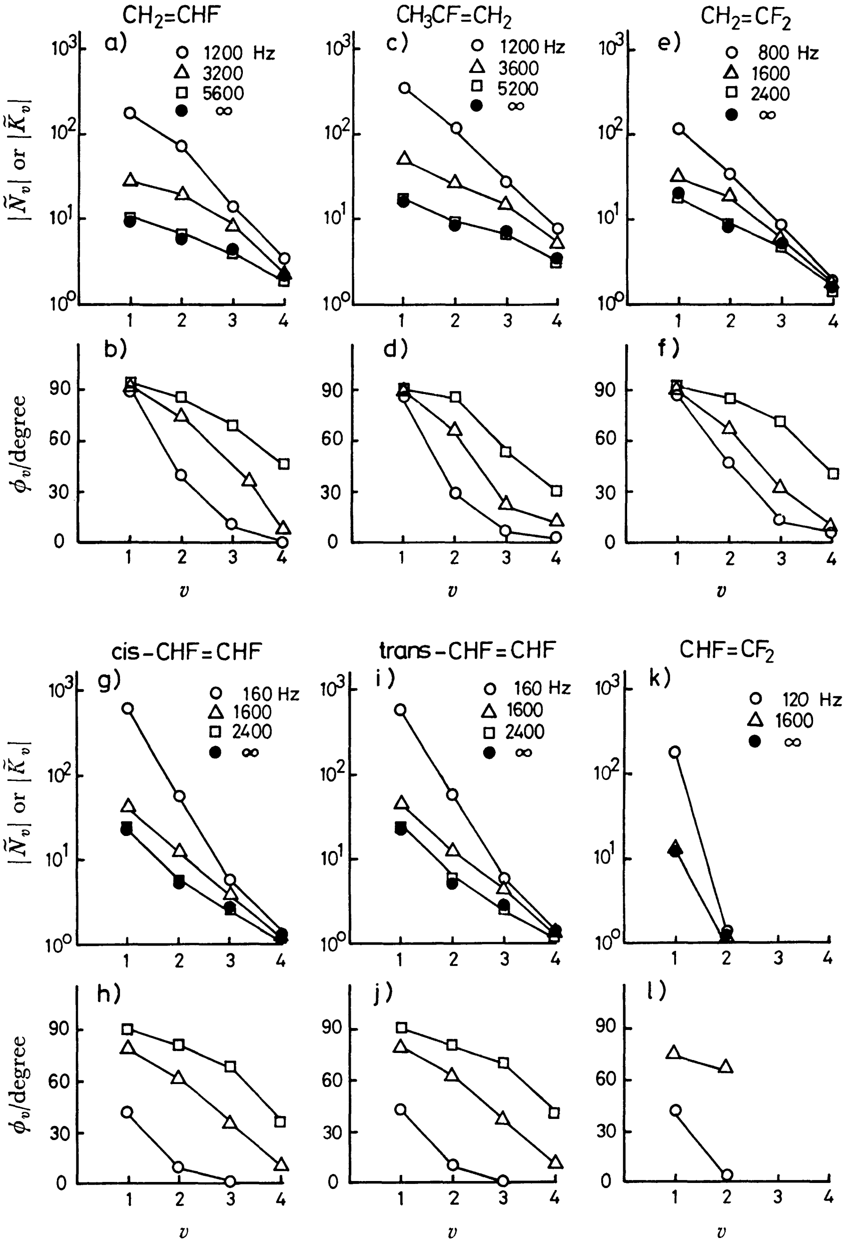


Fig. 5. Observed sets of $|\tilde{N}_v|$ and ϕ_v of HF† in the vibrational level v as a function of the modulation frequency. (a, b): CH_2=CHF 7 mTorr in Ar 5 Torr, (c, d): CH_3CF=CH_2 5 mTorr in Ar 5 Torr, (e, f): CH_2=CF_2 6 mTorr in Ar 3 Torr, (g, h): *trans*-CHF=CHF 7 mTorr in Ar 5 Torr, (i, j): *cis*-CHF=CHF 7 mTorr in Ar 5 Torr, (k, *l*): CHF=CF_2 5 mTorr in Ar 5 Torr.

TABLE 2. INITIAL VIBRATIONAL DISTRIBUTION OF HF† PRODUCED IN THE Hg-PHOTOSENSITIZED REACTION OF F-ETHYLENE

Parent molecule	CH_2=CHF	CH_3CF=CH_2	CH_2=CF_2	*cis*- and *trans*- CHF=CHF	CHF=CF_2
$v=1$	1.00	1.00	1.00	1.00	1.00
$v=2$	0.56 ± 0.02	0.53 ± 0.02	0.41 ± 0.01	0.21 ± 0.01	0.08 ± 0.01
$v=3$	0.42 ± 0.03	0.44 ± 0.03	0.29 ± 0.02	0.11 ± 0.01	—
$v=4$	0.24 ± 0.06	0.30 ± 0.10	0.10 ± 0.04	0.06 ± 0.03	—
T_{vib}/K	11400	13700	7200	5700	2200
ΔH/kJ mol^{-1} [a]	88	71	105	105	247
E_{avail}/kJ mol^{-1} [b]	379	397	364	364	222
f_{vib}/% [c]	19	23	11	7.6	1.7
f_{vib}^{calcd}/% [d]	5.7	1.8	4.7	4.7	1.7

a) Heat of reaction at 298 K. b) Energy available for partitioning in product molecules. c) Observed fraction of energy converted to HF vibration from E_{avail}. d) Statistically calculated value of f_{vib}.

$\phi_v=90°$. The initial distributions of HF† are plotted also in Fig. 5 and their numerical values are given in Table 2. The values are close to the uncorrected ones of $|\bar{N}_v|$ obtained at a modulation frequency of *ca.* 5 kHz. This fact rationalizes the procedure to uncover the initial vibrational distribution from the observed relaxed distribution. The initial distribution is almost of the Boltzmann type with 11400, 13700, 7200, 5700, 2200 K for respective parent molecules of CH_2=CHF, CH_3CF=CH_2, CH_2=CF_2, *trans*- and *cis*-CHF=CHF, and CHF=CF_2. The result for CH_2=CF_2 is in good agreement with that reported by Clough *et al.*[2)]

Discussion

A schematic diagram explaining the energy levels of initial, intermediate, and final states in the reactions of CH_2=CHF and CH_2=CF_2 is given in Fig. 6. As pointed out already,[7)] the triplet state of F-ethylene may be realized in the initial stage of the reaction. The lowest level of the triplet state is estimated by Coggiola *et al.*[15)] to be around 420 kJ mol^{-1} from the ground state. Unfortunately, no information is obtained from the present experiment to judge whether the reaction proceeds *via* a second excited intermediate of F-ethylidene or it does through a vibrationally high state of the ground state F-ethylene.[17)] Energetically, E_{avail} calculated from ΔH_f's listed in Table 3 must be shared among internal and external degrees-of-freedom of product molecules HF and CH≡CH or CH≡CF. E_{avail} for the reaction of CH_3CF=CH_2 is estimated assuming the products of HF + CH_3C≡CH though no experimental evidence is available. If HF and CH_2=C=CH_2 are produced, E_{avail} is reduced to 389 kJ mol^{-1}. Assuming the Boltzmann distribution of HF† with T_{vib} in Table 2, the amount of the HF† vibrational energy disposed may be calculated, although this procedure might overestimate populations in levels of $v\geqslant5$. As noted in Table 2, 23—1.7% of E_{avail} is converted to the vibrational energy of HF†. It may be noticed that if a parent molecule involves more hydrogen atoms, a larger fraction of E_{avail} is disposed into the HF† vibration. Shock-tube experiments of thermal decomposition of F-ethylene were carried out to determine the activation energies listed in Table 3. It is only a speculation, however, that the activated state in the thermal decomposition is similar to the critical transition state in the Hg-photosensitized reaction. Two isomers of *cis*- and *trans*-CHF=CHF result in quite the same distribution of HF†. This leads to the conclusion that the critical state just before the decomposition is common to both isomers, and accords with the fact that the quantum yields for the *cis*↔*trans* isomerization are identical for both of the forward and backward directions.[7)]

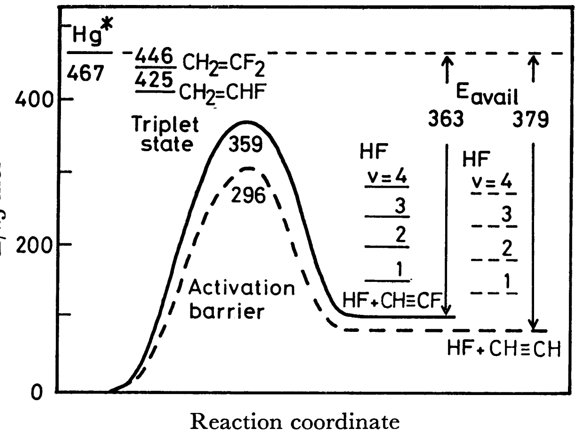
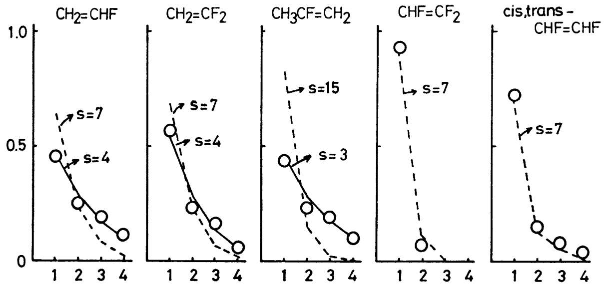


Fig. 6. Schematic potential energy diagram of HF elimination from CH_2=CHF and CH_2=CF_2.
The data source is given in Table 3.

A statistical calculation on the partitioning of E_{avail} in various degrees-of-freedom of product molecules is carried out for the Hg-photosensitized decompositions of F-ethylenes. In the calculation, the following assumptions are postulated. (1) A loose complex of HF and CH≡CH, CH≡CF, or CH_3C≡CH is assumed in the transition state for the decomposition. (2) The complex is formed on the top of the barrier which is realized in the effective potential composed of a long-range attractive potential due to a multipole interaction and the centrifugal force originating from the orbital angular momentum between HF and CH≡CH, CH≡CF, or CH_3C≡CH. (3) The angular momentum of the complex is in thermal equilibrium at the translational temperature of the reaction system. The vibrational state



Vibrational level of HF

Fig. 7. The observed vibrational distribution (○) of $HF^\dagger$ and the statistically calculated one.
Broken lines are the results calculated assuming total number of vibrational modes in a loose complex as active modes and solid lines are those assuming limited number of modes as active modes.

density is calculated by the Whitten-Rabinovitch equation[24] and the ones in another degrees-of-freedom are given in a book of Forst.[25] The calculation is based on the RRKM theory modified by Safron *et al.*[26] The vibrational frequencies of CH≡CH, CH≡CF, and $CH_3C≡CH$ are taken from Tables of Shimanouchi,[27] and CF≡CF from Ref. 20. The calculated results are shown in Fig. 7 together with the experimental data. The statistical calculation for CH_2=CHF, $CH_3CF=CH_2$, and $CH_2=CF_2$ gives much less populations in higher vibrational levels, while the calculation for *cis*- and *trans*-CHF=CHF and $CHF=CF_2$ results in the values close to the experimental ones.

The fact that the distributions of HF from *cis*-, *trans*-CHF=CHF and $CHF=CF_2$ are close to the statistical expectation may lead to the conclusion that the reaction scheme is different from that in other species. Strausz *et al.*[7] gave a speculation that CHF=CHF and $CHF=CF_2$ did not decompose *via* an intermediate of ethylidene type and resulted in primary products: C=CHF and HF in which HF was produced by the αα-elimination directly from excited F-ethylene. If this is the case, E_{avail} must be reduced very much causing less energy disposal to the HF vibration than that observed in the present experiment. According to Strausz *et al.*'s discussion, in the other molecules than CHF=CHF and $CHF=CF_2$, the decomposition occurs from the corresponding ethylidenes. However, more direct experimental information must be accumulated in order to discuss their speculation. As far as the present experiment is concerned, no positive evidence for their postulate was obtained.

The excess populations of $HF^\dagger$ in comparison with the statistical expectation might be attributed to a non-random distribution of E_{avail} among the internal degrees-of-freedom of the CH≡CH·HF and CH≡CF·HF complexes. If the number of oscillating modes *s* is limited to three or four, the disagreement between the calculation and the experiment disappears as shown in Fig. 7. This may support the conclusion that E_{avail} is locally distributed among particular degrees-of-freedom in the complex. However, the disagreement may be caused by another mechanism. As described in Fig. 6, a potential barrier exists in the course of the decomposition. Hence, a strong force is possible to act upon the separating HF and CH≡CH or CH≡CF while sliding down the barrier. This possibility was suggested by Berry[3] as a cause for the vibrational excitation of HF in his bootstrap model. The similar type of discussion on energy partitioning has been made in F-substitution reactions of Cl- or Br-ethylenes. McDonald and coworkers[28] have made IR emission measurements of various modes of F-ethylenes produced, and found statistical distributions if a potential barrier does not exist on the passage to the reaction exit and non-statistical distributions if a barrier exists.

TABLE 3. HEATS OF FORMATION ΔH_f, ACTIVATION ENERGIES FOR THERMAL DECOMPOSITION E_a, TRIPLET ENERGY LEVEL E_t OF F-ETHYLENES AND RELATED SPECIES

Species	ΔH_f, 298 *K*/ kJ mol^{-1}	E_a/kJ mol^{-1}	E_t[h]/kJ mol^{-1}
CH_2=CHF	−135.2[a]	297[g]	426
$CH_2=CF_2$	−334.4[b]	359[e]	447
cis-CHF=CHF	−330[c]	288[e]	414
trans-CHF=CHF	−330[c]	276[e]	405
$CHF=CF_2$	−49[b]	—	426
$CH_3CF=CH_2$	−159[c]	—	—
CH≡CH	226.51[d]		
CH≡CF	42[e]		
CF≡CF	21[d]		
$CH_3C≡CH$	185.1[f]		
HF	−272.3[d]		

a) Ref. 17. b) Ref. 18. c) Estimated by a method described in Ref. 19. d) Ref. 20. e) Ref. 21. f) Ref. 22. g) Ref. 23. h) Ref. 15.

In Table 3, it is seen that the heat of the HF elimination reaction of $CHF=CF_2$ is much larger than those of CH_2=CHF and $CH_3CF=CH_2$, so that the barrier height for the backward reaction, $E_a-\Delta H$, is reduced to *ca.* 80 kJ mol^{-1} in the reaction of $CHF=CF_2$. Since no experimental data of ΔH_f is available for *trans*- and *cis*-CHF=CHF, an approximate method,[19] in which a mean contribution of each bond in F-ethylene molecules to ΔH_f is empirically estimated, is adopted to result in a common value of ΔH_f for three compounds of *trans*- and *cis*-CHF=CHF and $CH_2=CF_2$. However, $-\Delta H_f$ of CHF=CHF is probably between those of $CH_2=CF_2$ and $CHF=CF_2$, so that $E_a-\Delta H$ of CHF=CHF may not be of a smaller magnitude than that of $CH_2=CF_2$. Thus, it would be reasonable that the observed vibrational distributions of HF formed from *trans*- and *cis*-CHF=CHF and $CHF=CF_2$ are close to those calculated statistically, while the other F-ethylenes produce $HF^\dagger$ with non-statistical vibrational distributions due to energy release through high exit barriers.

The above findings are supported by the crossed molecular beam reactions studied by Farrar and Lee.[29] Recently, they report a result slightly different from the IR chemiluminescence measurement of McDonald and coworkers. Non-statistical velocity distributions of products are found for both of CH_2=CHBr+F and +Cl reactions,[30] of which the product vibrational distribution is statistical in the former reaction and nonstatistical in the latter on the basis of the IR emission measurement. If a molecule activated by a collision with a reactive or excited atom has a significant amount of energy exceeding a barrier height, the resulting short lifetime of the activated molecule may result in a non-statistical velocity distribution of product molecules. While, an intramolecular vibrational relaxation changes a non-statistical distribution to a statistical one before product molecules emit IR photons. This is an explanation for the discrepancy between the two experiments. However, since HF has discrete vibration-rotation levels in the present energy region and an intramolecular relaxation is impossible, the distribution observed in this experiment must be interpreted as the ones at the reaction exit. Thus, the observed vibrational distribution of HF is caused mainly by a dynamical force which acts on HF separating from CH≡CH or CH≡CF while sliding down from the barrier top.

This work was supported partly by a Grant-in-Aid for Scientific Research from the Ministry of Education (No. 211606).

References

1) M. J. Berry and G. C. Pimentel, *J. Chem. Phys.*, **51**, 2274 (1968); *IEEE J. Quantum Electron.*, **QE-6**, 176 (1970).

2) P. N. Clough, J. C. Polanyi, and R. T. Taguchi, *Can. J. Chem.*, **48**, 2919 (1970).

3) M. J. Berry, *J. Chem. Phys.*, **61**, 3114 (1974).

4) W. E. Jones, G. Matinopoulos, J. S. Wasson, and M. T. H. Liu, *J. Chem. Soc., Faraday Trans. 2*, **74**, 831 (1978).

5) W. E. Jones, G. Matinopoulos, and J. S. Wasson, *J. Chem. Soc., Faraday Trans. 2*, **74**, 2128 (1978).

6) A. R. Trobridge and K. R. Jennings, *Trans. Faraday Soc.*, **61**, 2168 (1965).

7) O. P. Strausz, R. J. Norstrom, D. Salahub, R. K. Gosavi, H. E. Gunning, and I. G. Csizmadia, *J. Am. Chem. Soc.*, **92**, 6395 (1970).

8) S. Tsunashima, H. E. Gunning, and O. P. Strausz, *J. Am. Chem. Soc.*, **98**, 1690 (1976).

9) H. Horiguchi and S. Tsuchiya, *J. Chem. Phys.*, **70**, 762 (1979).

10) D. U. Webb and K. N. Rao, *J. Mol. Spectrosc.*, **28**, 121 (1968).

11) R. E. Meredith and F. G. Smith, *J. Quant. Spectrosc. Rad. Transfer*, **13**, 89 (1973).

12) J. M. Herbelin and G. Emanuel, *J. Chem. Phys.*, **60**, 689 (1974).

13) R. A. Lucht and T. A. Cool, *J. Chem. Phys.*, **60**, 1026 (1974).

14) P. R. Pool and I. W. M. Smith, *J. Chem. Soc., Faraday Trans. 2*, **73**, 1434 (1977).

15) M. J. Coggiola, O. A. Mosher, W. M. Flicker, and A. Kuppermann, *Chem. Phys. Lett.*, **27**, 14 (1974).

16) According to the recent theoretical calculation of *ab initio* surface of CH_2=CHF by Kato and Morokuma, the triplet surface has a high barrier for reaction, so that non-adiabatic transition to the singlet surface must occur before decomposition. Kato and Morokuma, 14th Symposium on High Speed Reactions, Tokyo (1979).

17) V. P. Kolesov and T. S. Papina, *Zh. Fiz. Khim.*, **44**, 1101 (1970).

18) J. R. Lacher and H. A. Skinner, *J. Chem. Soc., A*, **1968**, 1034.

19) G. J. Janz, "Thermodynamic Properties of Organic Compounds," Academic Press, New York (1967).

20) "JANAF Thermochemical Tables," Nat. Stad. Ref. Data Ser., Nat. Bur. Stand., 37, U. S. Government Printing Office, Washington, D. C. (1972).

21) J. M. Simmie and E. Tschuikow-Roux, *J. Phys. Chem.*, **74**, 4075 (1970).

22) J. Collins and F. P. Lossing, *J. Am. Chem. Soc.*, **80**, 1568 (1958).

23) J. M. Simmie, W. J. Quiring, and E. T. Tschuikow-Roux, *J. Phys. Chem.*, **74**, 992 (1970).

24) G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 2466 (1963).

25) W. Forst, "Theory of Unimolecular Reactions," Academic Press, New York (1973).

26) S. A. Sarfron, N. W. Weinstein, D. R. Herschbach, and J. C. Tully, *Chem. Phys. Lett.*, **12**, 564 (1972).

27) T. Shimanouchi, "Tables of Vibrational Frequencies," Consolidated Volume, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. 39, U. S. Government Printing Office, Washington, D. C. (1972).

28) J. G. Moehlmann and J. D. McDonald, *J. Chem. Phys.*, **62**, 3052 (1975); J. F. Durana and J. C. McDonald, *J. Chem. Phys.*, **64**, 2518 (1976).

29) J. M. Farrar and Y. T. Lee, *J. Chem. Phys.*, **65**, 1414 (1976).

30) R. J. Buss, M. J. Coggiola, and Y. T. Lee, *Faraday Discuss. Chem. Soc.*, **67**, 162 (1979).