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IR multiple photon dissociation of fluorinated ethanes and ethylenes: HF vibrational energy distributions[a]

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The IR multiple photon dissociation of fluorinated ethanes and ethylenes produces vibrationally excited HF via collisionless molecular elimination. The $HF^\dagger$ fluorescence spectra have been measured and analyzed in order to determine the relative vibrational level populations produced by the dissociation processes. These results are compared to those obtained by others who used alternate methods of excitation. The measured vibrational level distributions cannot be adequately represented by single temperature Boltzmann distributions or by a statistical partitioning of the available energy. It is estimated that less than 30% of the *fixed* energy appears as vibrational excitation of the HF fragment.

I. INTRODUCTION

The infrared multiple photon dissociation (IRMPD) of halogenated ethanes and ethylenes has been shown to occur primarily by molecular elimination of a hydrogen halide molecule.[1-11] In previous studies of the infrared multiple photon absorption (IRMPA) of fluorinated ethanes and ethylenes, we[4,5,10] as well as others[6] have shown that the dissociation processes produce vibrationally excited HF molecules, hereafter referred to as $HF^\dagger$, in the absence of collisions. Spontaneous emission from $HF^\dagger$ is readily detected with an IR detector and provides a simple and convenient means by which the dissociation process can be monitored in a time resolved way. In this manner, we have studied the effects that collisions between the absorbing species and inert gas molecules have on the unimolecular dissociation yield,[5] and have been able to estimate the unimolecular decomposition rates associated with IRMPD of molecules of this type.[10] In this previous work, the IR detector monitored simultaneously the $HF^\dagger$ emission from all of the low lying vibrational levels which were populated via the dynamics of the dissociation processes. In order to determine the relative vibrational level populations and the extent of rotational excitation within the HF fragment, we have incorporated a monochromator into our detection system, thereby allowing us to measure the $HF^\dagger$ fluorescence spectra. Analyses of the observed fluorescence spectra yield the relative HF vibrational level populations and the effective rotational temperatures.

This paper presents the results of analyses of the $HF^\dagger$ fluorescence spectra observed via the IRMPD of vinyl fluoride, ethyl fluoride, 1,1-difluoroethane, and 1,1-difluoroethylene. The results are compared to those of other investigators who have examined the vibrational energy level distributions of $HF^\dagger$ formed by molecular elimination from similar molecules which have been excited by means other than IRMPA.

The dissociation of fluorinated ethanes and ethylenes via molecular elimination of HF is only slightly endothermic ($\Delta H^\circ_{298} \cong 8.7$, 17, 24, and 28 kcal mol^{-1} for CH_2CHF,[12] CH_3CH_2F,[13] CH_3CHF_2,[14] and CH_2CF_2,[15] respectively), but the molecules must absorb sufficient energy to overcome large activation energies ($E_a \cong 60$, 70, 62, and 86 kcal mol^{-1}, for CH_3CH_2F,[16] CH_2CHF,[13] CH_3CHF_2,[17] and CH_2CF_2,[15] respectively). Thus, even when molecules are prepared with negligible *excess* energy above the minimum required for dissociation, large amounts of energy are made available for excitation of the various degrees of freedom of the fragments. The lowest energy dissociation channels for these molecules correspond to α, β type molecular elimination.

II. EXPERIMENTAL

The experimental technique and arrangement are straightforward and have been described in detail elsewhere.[4,5,18] Briefly, the output from a CO_2 TEA laser (Lumonics, 1.5 J, multimode, line tunable) is focused into a large stainless steel sample chamber with a 30 cm f.l. Ge lens. The partially mode-locked laser pulse consists of an initial spike of approximately 100 ns (FWHM), followed by a tail that normally extends to ~0.8 μs. The beam focus is estimated to be ~2 mm^2 from burn patterns and circular aperture transmission measurements. Infrared spontaneous emission is detected perpendicular to the laser beam with an InSb photovoltaic detector.

In order to analyze the $HF^\dagger$ fluorescence signals, a 125 mm f.l. low resolution monochromator (Oriel 7240) was incorporated into the detection system. The laser focal volume was imaged onto the input slit of the monochromator with a pair of $f/1$ CaF_2 lenses (37.5 mm diam). The InSb detector was placed directly at the output slit. The position of the monochromator and/or laser focal volume were adjusted to provide maximum signal/noise ratio (S/N). The monochromator housing was continuously purged with dry N_2 to eliminate the absorption of $HF^\dagger$ fluorescence by atmospheric water vapor. Unfortunately, S/N considerations severely limited the resolution capability of the measurements. For most of the experiments, the slits were $\cong 1.5$ mm, which gives a resolution of 0.0.035–0.040 μm (FWHM) at 2.5 μm. With this resolution, the individual vibration–rotation (V, R) lines of HF are not completely resolved, and so the measurements were restricted to obtaining the contour or envelope of the emission spectrum. This contour was then compared to computer

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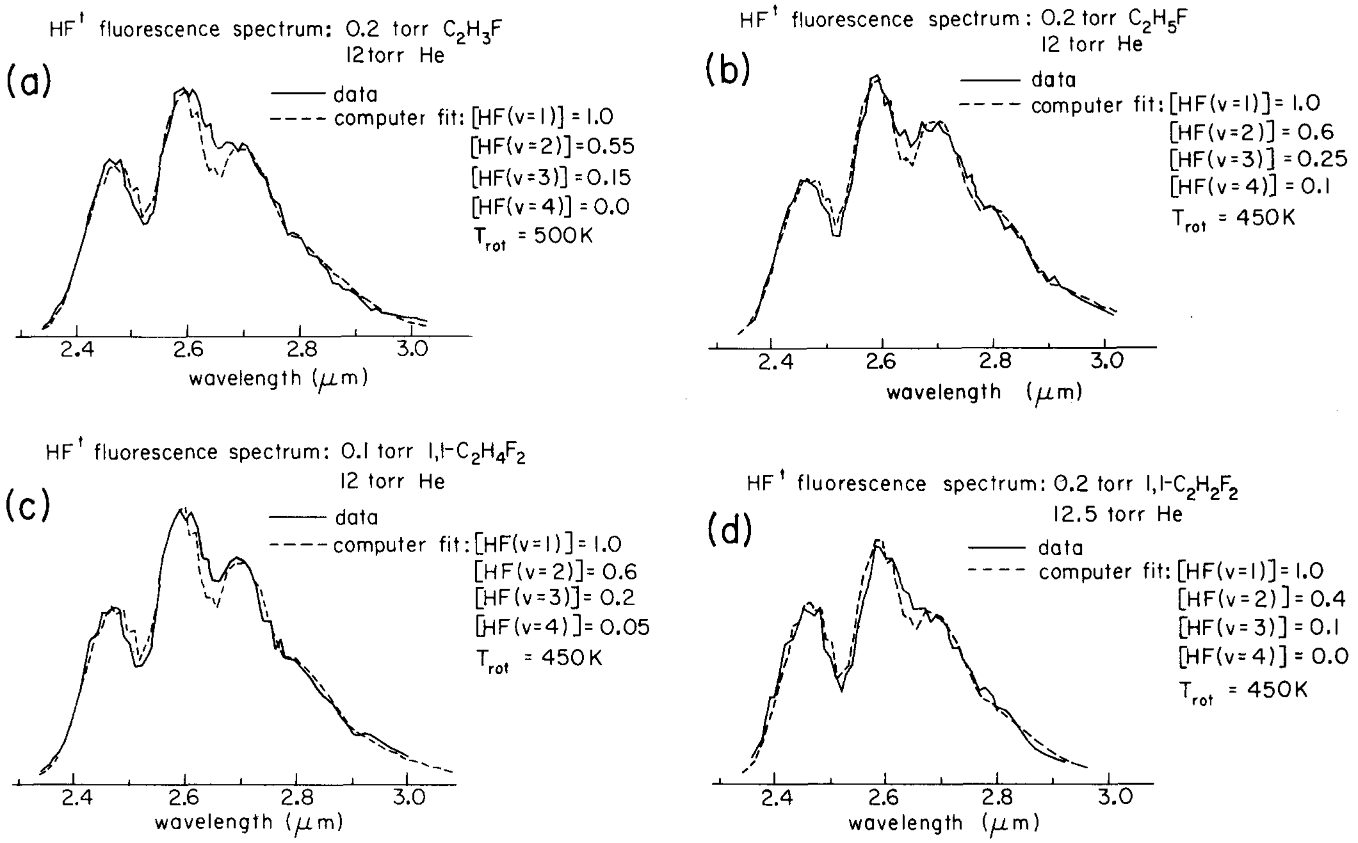

FIG. 1. HF† fluorescence spectra resulting from the IRMPD of (a) C_2H_3F, (b) C_2H_5F, (c) 1,1-$C_2H_4F_2$, and (d) 1,1-$C_2H_2F_2$, in the presence of 12 Torr He. The (001)–(100) P20 CO_2 laser transition was used for (a), (c), and (d), and the (001)–(020) P20 transition was used for (b). In all experiments the fluence was ~40 J cm^{-2}, and the data were corrected for the wavelength dependences of the detector and monochromator. The data were taken at 0.01 μm intervals (0.035 μm resolution) and are connected with a solid line. The computer fit assumes T_{rot} is the same in all vibrational levels.

generated contours, and the "best fit" was used to determine the relative vibrational level populations. Details of the computer generated contours and the curve fitting technique are described in the Appendix. Signals from the detector were filtered (100 kHz), amplified, and sent to a transient digitizer/signal averaging system (Nicolet, 100 ns gate). The peak of the fluorescence signal was then measured and recorded. The maximum laser pulse rate available (1 Hz) severely limited the application of signal averaging techniques. Typically, 16 or 32 (at 0.5 Hz) laser pulses were averaged per data point. Data points were typically obtained at 0.01 μm intervals (~4 points within the FWHM resolution), and corrected for the wavelength dependences of the detector and monochromator. The entire emission contour was obtained in several segments in order to minimize effects due to gas sample depletion and long term laser pulse energy variation. The data were adjusted for these slow variations whenever they were present. Because of low S/N, data collection was limited to high laser fluence conditions (~50 J cm^{-2}), and the effects of laser fluence on the vibrational level distribution could not be investigated. Inadequate grating efficiency prevented analysis of fluorescence signals produced by emission in the 3–5 μm region, where C–H stretch emission from the parent species and its fragments occurs.

Vinyl fluoride, 1,1-difluoroethylene, and 1,1-difluoroethane (Matheson 99.9%, 99.0%, and 98.0% purity respectively) were degassed at 77 K and used without further purification. Ethyl fluoride (Chemical Procurements Lab) was found to contain large amounts (~20%) of C_2H_4 but was used unpurified. Under typical experimental conditions, spontaneous emission from vibrationally excited C_2H_4 and any of its fragments is weak by comparison to the HF† signals and does not overlap appreciably with the observed HF† fluorescence spectra.

III. RESULTS AND DISCUSSION

The HF† fluorescence spectra observed in the IRMPD of CH_2CHF, CH_3CH_2F, CH_3CHF_2, and CH_2CF_2 are shown in Fig. 1. The solid lines represent the experimental data, taken at 0.01 μm intervals and joined together for simplicity. The dashed lines represent the best computer fits to the data (see the Appendix), using the indicated level populations. The computer fit is calculated at 0.01 μm intervals and joined together, thereby simulating the data acquisition method. The addition of buffer gas to the irradiated samples served a dual purpose. First, the buffer gas (He) enhances the unimolecular dissociation yield,[4,5] thereby increasing the S/N at a given pressure of parent species. Previously,[5] we have shown that this HF† signal enhancement is due to rota-

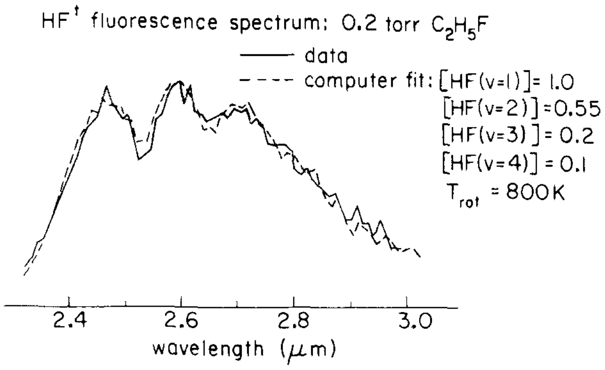

FIG. 2. HF† fluorescence spectrum resulting from the IRMPD of 0.2 Torr C_2H_5F *without* buffer gas. The (001)–(100) *P*20 CO_2 laser line was used at a fluence of ~40 J cm^{-2}. The data were taken at 0.01 μm intervals (0.035 μm resolution) and are corrected for the wavelength dependence of the detector and monochromator. The computer fit assumes T_{rot} is the same in all vibrational levels.

tional relaxation of the pumped species, rather than intermolecular or thermal processes. Second, it promotes rotational relaxation of the HF fragment, thereby sharpening the features of the fluorescence contour, and thus allows a more accurate computer fit to be obtained. The parent pressure was maintained as low as practicable, in order to minimize vibrational quenching processes which might alter nascent vibrational level distributions. Vibrational quenching of HF(v = 1, 2, 3, 4) by He (≲ 15 Torr) is not expected to occur on the same time scale as the rise of the fluorescence signal.[19] However, quenching by the parent species and by HF(v = 0) may have occurred to a certain extent,[21] especially for HF(v = 3, 4). Fluorescence decay times observed in the portion of the spectrum that corresponds to emission primarily from HF(v = 3, 4) ($\lambda \gtrsim 2.8$ μm, see Appendix) were ~10 μs (e^{-1} point), as compared to the detection system risetime (10%–90%) of about 3.7 μs. H_2 was added to all samples as a check for the presence of F atoms[4] via the well-known $F + H_2$ reaction.[18] The HF† signal showed no effect with H_2 addition, indicating that F atom production is negligible in our experiments.

The question as to whether or not the addition of buffer gas changes the nascent HF vibrational level populations was briefly investigated for two of the molecules. Figure 2 shows the HF† fluorescence spectrum obtained for the case of ethyl fluoride without buffer gas. Aside from a marked difference in the rotational temperature, there does not appear to be a marked change in the HF vibrational level populations. For the case of 1,1-difluoroethane, rotational temperatures > 1000 K were observed, and there appeared to be a slight increase in the level populations. Analysis of HF† fluorescence signals derived from 1,1-difluorethane are complicated by the fact that this molecule can undergo two consecutive molecular eliminations within a single laser pulse,[5] so that the observed spectrum is the composite result produced by HF molecular elimination from 1,1-difluoroethane itself, and from its primary dissociation product, vinyl fluoride.[24] In addition, α, α type elimination, which presumably produces a different HF† fluorescence spectrum, may be competing with the α, β elimination channel. Kim *et al.*[25] have estimated that for 1,1-difluoroethane excited by radical recombination of CH_3 and CHF_2 at 298 K, approximately 10% of the dissociation is due to α, α elimination. Data obtained without buffer gas are more difficult to analyze because of the higher apparent rotational temperature, which makes it more difficult to obtain an adequate computer fit to the data. The computer fit assumes that a single temperature Boltzmann distribution correctly describes the population of rotational states, and this need not be the case under these conditions. Insufficient *S*/*N* prevented investigation of the effect of buffer gas on the level distributions for vinyl fluoride and 1,1-difluorethylene.

A summary of the relative HF vibrational level populations is given in Table I. Level populations are normalized to the HF(v = 1) level population. It is clear that

TABLE I. Summary of the relative HF vibrational level populations observed in the IRMPD of CH_2CHF, CH_3CH_2F, CH_2CF_2, and CH_3CHF_2. Also shown are the level populations observed for similar molecules by other investigators who used alternate means of excitation. Values in parentheses are calculated according to Ref. 28.

Molecule	Excitation method	Relative HF (v) populations HF (v = 0)	HF (v = 1)	HF (v = 2)	HF (v = 3)	HF (v = 4)	Ref.
CH_2CHF	IRMPA	···	1.0	0.55 ± 0.1	0.15 ± 0.05	≲0.05	this work
CH_3CH_2F	IRMPA	··· (0.83)	1.0 (1.0)	0.60 ± 0.1 (0.60)	0.25 ± 0.05 (0.24)	≲0.15 (0.07)	this work
CH_2CF_2	IRMPA	···	1.0	0.40 ± 0.1	0.10 ± 0.05	≲0.05	this work
CH_3CHF_2	IRMPA	···	1.0	0.60 ± 0.1	0.20 ± 0.05	≲0.10	this work
CH_3CF_3	chemical[a]	··· (1.15)	1.0 (1.0)	0.43 ± 0.02 (0.437)	0.13 ± 0.007 (0.126)	0.033 ± 0.007 (0.028)	26
CH_2CF_2	triplet Hg sensitization	···	1.0	0.40 ± 0.02	0.21 ± 0.01	0.072 ± 0.011	26
CH_3CF_3	chemical[a]	1.25 ± 0.1	1.0	0.55 ± 0.08	···	···	27
	chemical[b]	1.43 ± 0.2	1.0	0.55 ± 0.08	···	···	27

[a] From $CH_3 + CF_3$.

[b] From $H + CH_2CF_3$.

the HF level populations produced by the IRMPD of the molecules investigated here are very similar to the level populations measured by other investigators for similar molecules, using alternate methods of excitation (also shown in Table I). Level populations decrease monotonically from HF(v =1), with HF(v =4) being the highest level which can be detected. Unfortunately, the experiment provides no direct information concerning the formation of HF(v =0). The vibrational level populations cannot be adequately characterized by a Boltzmann distribution at a single temperature.

The UV photolysis of fluorinated ethanes and ethylenes has been investigated by Berry *et al.*[27,30,31] who observed stimulated emission from $HF^\dagger$ produced by molecular elimination. They found $\{[HF(v+1)]/[HF(v)]\} < 1$ for all levels, both in the case of direct photoelimination[30] and in the case of elimination from recombined radicals[27,31] (see Table I). It is clear from the results shown in Table I that, under appropriate experimental conditions, the IRMPD process could also be used to obtain stimulated emission from $HF^\dagger$

It is interesting to compare the HF vibrational level populations obtained from CH_2CF_2 via triplet Hg sensitization[26] to those obtained via IRMPD. Triplet Hg sensitization provides 112 kcal mole^{-1} of internal energy, which is approximately 28 kcal mole^{-1} above the minimum energy required for molecular elimination of HF from the ground electronic state.[15] This amount of excess energy is, as the work of Lee *et al.*[9] and others[2,3,4] suggest, roughly what is expected in the IRMPD of molecules of this type at high laser fluence. Thus, excited molecules have been prepared by two different excitation methods, with approximately equal amounts of internal energy, and have been found to result in very similar level populations of the $HF^\dagger$ elimination fragment. This suggests that the dissociation dynamics for this and similar molecules are not appreciably influenced by the manner in which the energy for reaction is provided [i.e., the molecule has no memory of the excitation event (s)]. Further, this suggests that the dissociation occurs via the same excited state for both types of excitation. In the case of IRMPA, this state would most likely correspond to a vibrationally excited ground electronic state, and this implies that in the case of triplet Hg excitation, the excited triplet state initially produced[32] eventually crosses over to the singlet ground electronic state from which dissociation occurs. This conclusion disagrees with those of Tsunashima *et al.*[33] who have suggested that the dissociation produced by triplet Hg sensitization occurs via the isomeric triplet ethylidene structure, $CF_2H\ddot{C}H$.

Clough *et al.*[26] and Berry[34] have shown that a statistical treatment for the description of the HX (X = F, Cl) vibrational level populations in the four-center molecular elimination from several halogenated ethanes and ethylenes excited via chemical activation,[26] triplet Hg sensitization,[26] and UV photolysis,[34] is inadequate. The IRMPD results shown in Table I are in agreement with this characteristic of the elimination process. Clough *et al.*[26] have pointed out that the *excess* energy (= energy in excess of that required to reach dissociation threshold), which, on the basis of RRKM theory,[35] is statistically distributed within the transition state and might be expected to be statistically distributed among the dissociation products, cannot alone account for the observed vibrational excitation in HF. The amount of excess energy available is simply not enough to populate the high vibrational levels of HF which are observed. For the case of IRMPA activation of the molecules investigated here, excess energies in the range 20–35 kcal mol^{-1} are expected under the present experimental conditions, and the same argument applies. The relative level populations shown in Table I represent the composite result of partitioning of the *excess* energy according to some probability function, and partitioning of the *fixed* or *localized* energy associated with transition state[36] (= energy available to the products at dissociation threshold) according to some other probability function. *Assuming* that one can consider the partitioning of the *excess* and *fixed* energies as completely independent processes, then from the vibrational level populations and knowledge of one of the probability distribution functions the other can be deduced. If one further assumes that a statistical treatment for the disposition of the *excess* energy is adequate, then the nascent vibrational level populations that result from the partitioning of the *fixed* energy can be inferred. Lee *et al.*[9,37] have been successful in modeling measured translational energy distributions with statistical distributions for dissociation reactions in which there is no appreciable barrier which could contribute towards excitation of the fragments. For molecular elimination in the types of molecules investigated here, a statistical partitioning of 20–35 kcal mol^{-1} of excess energy would result in only a small perturbation[38] to the observed HF level populations, as the energy appears mainly in the larger dissociation fragment. Thus, the relative level populations which are characteristic of the threshold transition state should be only slightly lower[38] than the results shown in Table I, and the excitation within the HF fragment originates primarily from the fixed energy, as has been previously suggested.[26] It should be pointed out that under the proper experimental conditions, IRMPA offers a viable means of preparing a variety of molecules with little excess energy, so that the properties of the transition state that determine the vibrational level populations can be investigated.[40]

Assuming that the value of 0.8 obtained by Sirkin *et al.*[27] for $[HF(v=1)]/[HF(v=0)]$ for the case of CH_3CF_3 (see Table I) is representative of the cases investigated here, then the average HF vibrational energy can be estimated. The results thus obtained are shown in Table II, and they indicate that vibrational excitation of the HF fragment varies some with HF precursor, ranging from 16% to 31% of the fixed energy. The fluorinated ethanes channel a larger fraction of the fixed energy into HF vibration than the fluorinated ethenes. Recent experiments by Lee *et al.*[9] indicate that in the case of four-center elimination of HCl from CH_3CCl_3, CH_3CF_2Cl, and $CHClCF_2$, $\lesssim 20\%$ of the fixed energy appears as translational energy of the fragments. Previous studies[43] suggested that as much as 30% of the fixed energy should appear in translation. In any case, assuming that these translational energy measurements

TABLE II. Average vibrational energy partioned into the HF fragment produced by the IRMPD of CH_2CHF, CH_3CH_2F, CH_2CF_2, and CH_3CHF_2. The average energy calculation assumes $[HF(v=1)]/[HF(v=0)]=0.8$, based on the results of Sirkin *et al.*[27] The critical energy, E_0, has been estimated from the experimentally determined thermal activation energy, E_a: $E_0 \cong E_a + 2$ kcal mol^{-1}.

Molecule	Critical energy (E_0) (kcal mol^{-1})	Localized energy (kcal mol^{-1})	Average HF vibrational energy (kcal mol^{-1})
CH_2CHF	68	51	≤ 10
CH_3CH_2F	58	49	≤ 12
CH_2CF_2	84	56	≤ 9
CH_3CHF_2	60	36	≤ 11

are representative of the molecules investigated here,[44] this suggests that 40%–65% of the fixed energy is made available for excitation of the vibrational degrees of freedom of the polyatomic fragment as well as the rotational degrees of freedom of both fragments. For the case of vinyl fluoride, the conspicuous absence of emission from the C–H stretch of C_2H_2[45] (centered at 3.04 μm, see Fig. 1) suggests that most of the vibrational energy within C_2H_2 is to be found in the bending modes (730 and 612 cm^{-1}) and the C–C stretch (1974 cm^{-1}). A statistical partitioning of the energy *within* C_2H_2 would indeed favor the lower frequency modes. If it is the sudden structural distortion[34] which occurs as the molecule passes through the transition state configuration on the way to becoming fragments which determines the excitation of the various vibrational modes. this observation is also in accord. The C–H bond lengths are not expected to change more than a few percent (except for the one which becomes part of HF) in proceeding from the ground state configuration, through the transition state configuration, to the C_2H_2 fragment.

The high rotational temperatures observed in the IRMPD of ethyl fluoride (Fig. 2) and 1,1-difluoroethane indicate that considerable rotational excitation is taking place as the fragments separate, which is indicative of a noncentral repulsive force acting between the fragments. *Nascent* rotational excitation is higher than that shown in Fig. 2, as some rotational relaxation occurs at the pressures at which the data were obtained (0.2 Torr).

In principle, knowledge of the potential energy surface which governs this type of dissociation would allow one to predict the distribution of energy in the fragments. Such detailed knowledge is not presently available for the molecules investigated here. In connection with his work on the vibrational energy content of the HCl elimination product produced by UV photolysis of various chloroethylenes, Berry[34] has proposed an interesting model in which the vibronic populations of HCl are governed by the dynamics of a sudden structural distortion, accompanied by an intramolecular relaxation process. The HCl "molecule" within the chloroethylene is taken as a displaced and perturbed oscillator which is suddenly released, becoming a free HCl vibrator. Intramolecular vibrational energy transfer then occurs as the molecular fragments separate. In terms of a model such as this, the fact that CH_3CH_2F provides more energy for vibrational excitation of HF than CH_2CF_2, suggests that within the transition state, the HF bond length for the case of CH_3CH_2F is larger than in the case of CH_2CF_2 (i.e., a more highly displaced oscillator), implying a "looser" transition state for CH_3CH_2F relative to that for CH_2CF_2.

It is interesting to note that the vibrational level distributions shown in Table I are very similar to those which would be expected for an oscillator which is initially displaced from its equilibrium position and suddenly released. To illustrate this, we have carried out a straightforward calculation[28] of the level populations which would be observed if a simple harmonic oscillator, which is initially stretched, were suddenly released. Here, we vary the amount of initial displacement, and neglect any intramolecular energy transfer processes. The level populations thus obtained are shown in Table I (in parentheses), below the experimental values obtained for the cases of CH_3CF_3 and CH_3CH_2F. These calculated distributions correspond to initial displacements of 0.124 and 0.146 Å, respectively ($r_e = 0.9171$ Å for HF). Such small displacements imply that within the transition state configuration the HF bond must be already almost completely formed. This result is at odds with the conventional transition state models adopted in most RRKM calculations of the rate of decomposition.[25,43,47] Such models for α, β elimination usually consider the HF bond to be of low order, typically 0.1–0.2, whereas the small displacements obtained above would correspond to HF bond orders of 0.57–0.62.[48]

IV. CONCLUSIONS

Under the present experimental conditions, the IRMPD of the fluorinated ethanes and ethylenes which we have studied does not produce significantly different results than those obtained using other methods of activation, at least insofar as the partitioning of vibrational energy in the HF fragment is concerned. The nonstatistical partitioning of energy within HF does not imply that the energy within the HF precursor is not randomized among the vibrational degrees of freedom, since excitation in HF is due primarily to the fixed energy available at dissociation threshold. A straightforward calculation of the HF vibrational energy distribution due to a displaced HF oscillator, and invoking no energy transfer processes, indicates that our observations are in accord with a tight transition state in which the HF bond is 0.12–0.15 Å larger than the equilibrium value of 0.92 Å.

V. ACKNOWLEDGMENT

The authors gratefully acknowledge illuminating discussions with J. J. Tiee and R. E. Weston, and thank the reviewer for bringing to our attention the work of Cooks *et al.*[41]

VI. APPENDIX

The computer generated HF† fluorescence spectra were synthesized as follows, using a Tektronix 4051 calculator. First, the frequencies were determined for each V, R transition ($v \leq 4$) of the HF molecule, using

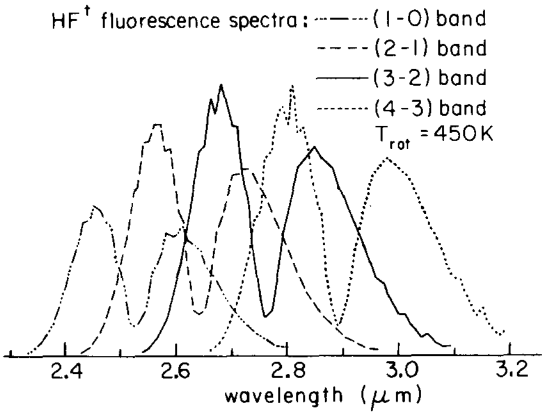

FIG. 3. Computer simulated HF† fluorescence spectra for the (1–0), (2–1), (3–2), and (4–3) bands at a rotational temperature of 450 K, and a resolution of 0.035 μm (FWHM).

spectroscopic data from Wilkins.[49] Individual line intensities were then calculated using the formula:[50]

$$I_{em} \propto \frac{C_{em}\nu^4}{Q_r} R S_J \exp\{-(BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3)/kT\} ,$$

where

$S_J = J+1$ for $\Delta J = +1$ (P branch)

$S_J = J$ for $\Delta J = -1$ (R branch)

$C_{em} \propto$ magnitude of (transition dipole moment)^2

ν = frequency of the transition

Q_r = rotational partition function evaluated at T

R = relative vibrational level population

B, D, H = rotational constants of upper state

J = rotational quantum number of upper state

T = rotational temperature, T_{rot}

k = Boltzmann constant

I_{em} = emission intensity.

Relative values of C_{em} were obtained from the work of Herbelin *et al.*,[51] which gives the Einstein coefficients for the various vibrational transitions of HF. An important assumption made here for the computation of the intensities, is that the rotational population distribution for all vibrational levels is accurately described by a Boltzmann distribution at a single, well defined, rotational temperature. With added buffer gas, sufficient rotational relaxation probably occurs within the rise time of the fluorescence signal [compare T_{rot} in Figs. 1(b) and 2] so that this assumption is justified.

The computer program then evaluated the HF† fluorescence intensity that would be observed at any particular wavelength, by adding the contributions from each line, weighted according to a simple triangle slit function (0.035 μm FWHM). This procedure was repeated at 0.01 μm intervals over the wavelength region of interest, simulating the data acquisition method. The fluorescence intensity values thus generated were plotted on the calculator display screen, and transferred onto paper with a hard copy unit.

Figure 3 shows the fluorescence spectra for each of the first four $\Delta v = 1$ emission bands of HF, assuming equal vibrational level populations at a rotational temperature of 450 K, and a resolution of 0.035 μm. These curves were generated in the manner described above. At this resolution, the envelopes of the P- and R-branch transitions for each individual emission band are well defined, but the emission from adjacent vibrational levels overlaps considerably. However, for low rotational temperatures (< 1000 K), examination of the R-branch region of the (1–0) band emission ($\lambda < 2.5$ μm) provides a quick estimate of the effective rotational temperature. To determine the relative vibrational level populations, Fig. 3 was used as a guideline to obtain initial values. These values were then varied, each time generating a contour, which was compared to the experimental data to determine the best fit. The uncertainties in the relative vibrational level populations obtained in this way are approximately ±0.1 for $v = 2$, and ±0.05 for $v = 3$. Only an upper limit on the population of $v = 4$ could be obtained from the data.

[1] F. M. Lussier and J. I. Steinfeld, Chem. Phys. Lett. 50, 175 (1977).

[2] A. J. Colussi, S. W. Benson, R. J. Hwang, and J. J. Tiee, Chem. Phys. Lett. 52, 349 (1977).

[3] T. H. Richardson and D. W. Setser, J. Phys. Chem. 81, 2309 (1977).

[4] C. R. Quick, Jr. and C. Wittig, Chem. Phys. 32, 75 (1978).

[5] C. R. Quick, Jr. and C. Wittig, J. Chem. Phys. 69, 4201 (1978).

[6] G. A. West, R. E. Weston, Jr., and G. W. Flynn, Chem. Phys. 35, 275 (1978).

[7] F. M. Lussier, J. I. Steinfeld, and T. F. Deutsch, Chem. Phys. Lett. 58, 277 (1978).

[8] Aa. S. Sudbo, P. A. Schulz, E. R. Grant, Y. R. Shen, and Y. T. Lee, J. Chem. Phys. 68, 1306 (1978).

[9] Aa. S. Sudbo, P. A. Schulz, Y. R. Shen, and Y. T. Lee, J. Chem. Phys. 69, 2312 (1978).

[10] C. R. Quick, Jr., J. J. Tiee, T. A. Fischer, and C. Wittig, Chem. Phys. Lett. 62, 435 (1979).

[11] C. Reiser, F. M. Lussier, C. C. Jensen, and J. I. Steinfeld, J. Am. Chem. Soc. 101, 350 (1979).

[12] Calculated from the thermochemical data found in S. W. Benson, *Thermochemical Kinetics*, 2nd ed. (Wiley, New York, 1976).

[13] J. M. Simmie, W. J. Quiring, and E. Tschuikow-Roux, J. Chem. Phys. 74, 992 (1970).

[14] V. P. Kolesov, S. N. Shtekher, A. M. Martynov, and S. M. Skuratov, Zh. Fiz. Khim. 42, 3033 (1968). These authors provide $\Delta H^\circ_{298}(CH_3CHF_2) = -117.3$ kcal mol^{-1}. ΔH°_{298} (products) were obtained from Refs. 12 and 13.

[15] J. M. Simmie and E. Tschuikow–Roux, J. Phys. Chem. 74, 4075 (1970).

[16] E. Tschuikow–Roux, W. J. Quiring, and J. M. Simmie, J. Phys. Chem. 74, 2449 (1970).

[17] P. Cadman, M. Day, and A. F. Trotman–Dickenson, J. Chem. Soc. A 2498 (1970).

[18] C. R. Quick, Jr. and C. Wittig, Chem. Phys. Lett. 48, 420 (1977).

[19] Green and Hancock[20] have measured the quenching rate coefficient of HF ($v = 1$) by He and found this to be ≲40 s^{-1} Torr^{-1}. Even allowing for larger rate coefficients for the higher vibrational levels of HF, with 15 Torr He quenching should not

occur on the time scale of the rise of the fluorescence signal.

[20] W. H. Green and J. K. Hancock, IEEE J. Quantum. Electron. **9**, 50 (1973).

[21] The quenching of $HF^\dagger$ by itself is very fast. Osgood *et al.*[22] have found the rate coefficients for the quenching of HF ($v = 2, 3, 4$) by HF ($v = 0$) to be 8×10^5, 1.6×10^6, and 1.4×10^6 s^{-1} $Torr^{-1}$, respectively. Assuming that 10% of the parent species (at 0.2 Torr) are dissociated in the focal region (high fluence conditions), then vibrational decay times for HF ($v = 3, 4$) could be as short as ~ 6 μs (neglecting diffusion and any excess translational energy in the HF photofragments) The quenching of $HF^\dagger$ by fluorinated ethanes and ethylenes has not been reported, and not much is known about the quenching of highly vibrationally excited polyatomic molecules. Anlauf *et al.*[23] have measured the quenching of HF ($v = 1, 2$) by room temperature, C_2H_2, C_2H_4, and C_2H_6, found the rate coefficients to be $\lesssim 3 \times 10^5$ s^{-1} $Torr^{-1}$. Quenching of HF ($v = 3, 4$) is expected (based on the measurements by Osgood *et al.*[22]) to be about a factor of 2 higher. Thus, under typical experimental conditions (0.2 Torr of parent) vibrational decay times ~ 10 μs are expected for HF ($v = 3, 4$). Experimentally, the $HF^\dagger$ fluorescence decay time is a weak function of the parent pressure. For example, the decay time decreases from 58 to 43 μs while varying the pressure of vinyl fluoride from 0.03 to 0.5 Torr. A stronger dependence than this is observed in the presence of He buffer gas, which suggests that the quenching of HF in these samples is complex. It is conceivable that HF up-pumping may even occur: if $\langle T_{vib} \rangle$ of the molecules with which HF collides is higher than $\langle T_{vib} \rangle$ of HF, then $\langle T_{vib} \rangle$ of HF may increase.

[22] R. M. Osgood, Jr., P. B. Sackett, and A. Javan, J. Chem. Phys. **60**, 1464 (1974).

[23] K. G. Anlauf, P. H. Davison, and J. A. Herman, J. Chem. Phys. **58**, 5354 (1972).

[24] The extent to which dissociation of vinyl fluoride occurs under our experimental conditions has not been directly measured, but is expected to be large. Gas chromatographic product analyses in related experiments indicated that equal amounts of vinyl fluoride and acetylene (the primary dissociation product of vinyl fluoride) could be easily produced at high laser fluences.

[25] K. C. Kim, D. W. Setser, and B. E. Holmes, J. Phys. Chem. **77**, 725 (1973).

[26] P. N. Clough, J. C. Polanyi, and R. T. Taguchi, Can. J. Chem. **48**, 2912 (1970).

[27] E. R. Sirkin and M. J. Berry, IEEE J. Quantum Electron. **QE-10**, 701 (1974).

[28] In the "sudden approximation," the probability of occupying any given vibrational energy level is proportional to the square of the overlap integral of the wave functions for the initial and the final states.[29] In this calculation, a simple harmonic oscillator has been assumed, and the wavefunction for the initial state was taken to be a free, unperturbed ground state oscillator wavefunction which is slightly displaced from the equilibrium position by a distance d. Under these conditions, the probability, P_n, of occupying the nth vibrational level is given by[29] $P_n \propto d^{2n}/2^n n!$.

[29] See, for example, L. I. Schiff, *Quantum Mechanics*, 3rd ed. (McGraw-Hill, New York, 1968), pp. 95 and 292.

[30] M. J. Berry and G. C. Pimentel, IEEE J. Quantum Electron. **QE-6**, 176 (1970).

[31] M. J. Berry and G. C. Pimentel, J. Chem. Phys. **49**, 5190 (1968).

[32] 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).

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

[34] M. J. Berry, J. Chem. Phys. **61**, 3114 (1974).

[35] See, for example, P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley, New York, 1972).

[36] The fixed or localized energy corresponds to the activation energy for the molecular addition reaction.

[37] Y. T. Lee, Y. R. Shen, M. J. Coggiola, and P. A. Schulz, Phys. Rev. Lett. **38**, 17 (1977).

[38] A calculation of the extent to which a statistical partitioning of 20–35 kcal mol^{-1} would change the nascent distribution produced by the fixed energy indicated that the level populations would change by no more than 10% in all cases. In the calculation, the probability of a particular HF vibrational level being populated was taken to be proportional to the vibrational energy level sum of the polyatomic fragment evaluated at an energy equal to the excess energy minus the energy of the HF vibrational level in question. The sums were evaluated using the method of Whitten and Rabinowitch.[39]

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

[40] Activated ionic species with little excess energies can also be produced by electron impact[41] and photoionization[42] processes which produce metastable molecular ions with sufficient internal energy to undergo unimolecular dissociation.

[41] R. G. Cooks, K. C. Kim, and J. H. Benyon, Int. J. Mass Spectrom. Ion Phys. **15**, 245 (1974).

[42] D. Reinke, R. Kraessig, and H. Baumgärtel, Z. Naturforsch. Teil A **28**, 1021 (1973).

[43] (a) B. E. Holmes and D. W. Setser, J. Phys. Chem. **79**, 1320 (1975); (b) K. C. Kim and D. W. Setser, *ibid.* **78**, 2166 (1974), and references cited therein.

[44] Cooks *et al.*[41] have examined the translational energy release accompanying the molecular elimination of HF from the ionic counterparts of the fluorinated ethanes and ethylenes investigated here. Their results for the fluoroethanes show that $\sim 20\%$ of the fixed energy appears as translational energy of the fragments while for the fluoroethenes, much larger fractions appear as translation ($\sim 65\%$ for C_2H_3F and $\sim 46\%$ for CH_2CF_2). It is not clear at this time how these results can be correlated with the results obtained for the neutral species.

[45] The spontaneous emission lifetime of the C–H stretch of C_2H_2 is only ~ 2.4 times longer[42] than that of the (1–0) band of HF. From the observed fluorescence spectrum we conclude that HF contains four or five times more energy than the C–H stretch of C_2H_2.

[46] L. A. Gribov and V. N. Smirnov, Sov. Phys. Uspekhi **4**, 919 (1962).

[47] J. C. Hassler and D. W. Setser, J. Chem. Phys. **45**, 3246 (1966).

[48] Obtained from the calculated initial displacements by applying Pauling's empirical correlation rule which relates bond length to bond order. See L. Pauling, J. Am. Chem. Soc. **69**, 542 (1947).

[49] R. L. Wilkins, The Aerospace Corporation, Report No. SAMSO-TR-77-198, September, 1977.

[50] G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed. (Van Nostrand, New York, 1950), p. 127.

[51] J. M. Herbelin and G. Emmanuel, J. Chem. Phys. **60**, 689 (1974).