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The Photodissociation Dynamics of Hexafluoropropene Examined at 193 nm

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Abstract

The photodissociation of hexafluoropropene at 193 nm was studied using photofragment translational spectroscopy. One primary channel results in loss of a fluorine atom; from the maximum translational energy release, a value of 121 kcal/mol was found for the C-F bond dissociation energy. In addition, elimination of CF_2 and CF_3 competes with C-F bond cleavage. A branching fraction, CF_2:F:CF_3, of 0.47:0.36:0.17 was found among these three primary channels. A comparison of UV photolysis and infrared multiphoton dissociation experiments suggests that excitation and dissociation on an excited state surface competes with internal conversion and dissociation from the ground state.

1. Introduction

In a flash photolysis experiment on hexafluoropropene using UV light, the major product, C_2F_4, was attributed to the recombination of CF_2 radicals produced in reaction (1).[1]

$$C_3F_6 \rightarrow CFCF_3 + CF_2 \tag{1}$$

From a mercury-sensitized photolysis experiment, hv > 220 nm, researchers suggested the formation of C_2F_4 occurs via a stepwise reaction mechanism where reaction (1) is followed by isomerization (2).[2]

$$CFCF_3 \rightarrow C_2F_4 \tag{2}$$

More recently, the UV absorption spectrum of hexafluoropropene was measured in the wavelength range from 185 - 210 nm.[3] Over this range, CF_2 was monitored by UV absorption spectroscopy and its quantum yield was found to be 1.0. In addition, from the structureless absorption spectrum of C_3F_6, excitation to a repulsive electronic state and dissociation within 100 femtoseconds was predicted via reaction (1). A recent kinetics experiment has identified C_2F_3 as a 193 nm photolysis product of C_3F_6, indicating that carbon-carbon single bond rupture takes place.[4]

$$C_3F_6 \rightarrow CF_3 + C_2F_3 \tag{3}$$

Also, at 193 nm the formation of F atoms (4) in the photolysis of hexafluoropropene has been suggested.[5]

$$C_3F_6 \rightarrow F + C_3F_5 \tag{4}$$

However, the relative contributions of either of these reactions have not been measured.

The infrared multiphoton dissociation (IRMPD) of hexafluoropropene has been previously studied using photofragment translational spectroscopy.[6] Simple bond rupture of the carbon-

carbon single bond (3) was observed with an activation energy estimated at 100-105 kcal/mol. CF_2 was also found to be a primary dissociation product; however, the identity of its dissociation partner was unclear. The formation of either trifluoromethylfluorocarbene (1) or tetrafluoroethylene (5) with CF_2 is thermodynamically feasible.

$$C_3F_6 \rightarrow C_2F_4 + CF_2 \tag{5}$$

Reaction (1) results from direct cleavage of a carbon-carbon double bond while reaction (5) requires a fluorine migration or isomerization before the final products are formed. Breaking a carbon-carbon double bond has been previously observed in the photolysis of tetrafluoroethylene.[7] In that experiment $^1CF_2$ and $^3CF_2$ were the only products observed by photofragment translational spectroscopy. A careful investigation of the photodissociation of hexafluoropropene at 193 nm should reveal the relative importance of C-F bond rupture as compared to cleavage of the carbon-carbon double or single bond. Furthermore, comparing the UV and IRMPD dissociation pathways will give information about whether the dissociation is from an excited state or proceeds after internal conversion to the ground state.

2. Experimental Section

These experiments were performed on a rotating source molecular beam machine that has been previously described.[8] Conditions similar to those in the IRMPD experiment were used,[6] except that a Lambda Physik EMG 101 Excimer laser operating on the ArF transition (193 nm) crossed the molecular beam at the interaction region instead of a CO_2 laser. The laser was unpolarized in the measurements of the velocity distributions of the products. A linear power dependence of the signal was observed up to a laser power of 25 mJ/pulse, indicating the

dissociation signal results from single-photon excitation. To obtain the anisotropy parameter (β) of the product angular distribution with respect to the polarization of the laser, a stacked pile of 8 fused-silica plates at Brewster's angle was used to produce 85% polarized light.[9] The polarization angle of the laser was determined using a half-wave retarder. Typical polarization measurements were carried out at a given detector angle by measuring the signal intensity at two polarization angles that were parallel and perpendicular to the velocity vector of the product in the center-of-mass coordinate system.[10]

3. Results and Analysis

3.1. $C_3F_6 \rightarrow C_3F_5 + F$. Unambiguous evidence for the fluorine atom elimination channel is found in the time-of-flight spectrum for $C_3F_5^+$ (*m/e* = 131) shown in Fig. 1a. The time-of-flight spectrum in Fig. 1b from $C_3F_4^+$ (*m/e* = 112), which is similar to that of $C_3F_5^+$, results entirely from dissociative ionization of C_3F_5 in the electron impact ionizer. The difference in the slow edge of these two features results from the high molecular beam background at C_3F_5, which makes subtraction of the background problematic. The translational energy distribution, shown in Fig. 2, is peaked well away from zero, and the average energy is 17.7 kcal/mol.

The time-of-flight spectra at each laser polarization were divided into four sections, and a maximum anisotropy parameter, β, of -0.68 ± 0.08 was calculated. The value of β in the well-known electric dipole expression (6) can range from -1 to 2 for a direct dissociation with a completely perpendicular or parallel transition, respectively.[11]

$$I(\theta) = (1/4\pi)[1 + \beta P_2(\cos\theta)] \qquad (6)$$

In equation 6, θ is the angle between the electric field vector of the laser and the center-of-mass velocity vector of the products, and $P_2(\cos\theta)$ is the second degree Legendre polynomial. When the use of only 85% polarized light is taken into account, the β parameter is adjusted to be -0.90 $\pm$ 0.08.[12] The β parameter value is an average of multiple measurements with an uncertainty of one standard deviation.

3.2. $C_3F_6 \rightarrow CFCF_3/C_2F_4 + CF_2$ The time-of-flight spectrum of *m/e* = 100 ($CFCF_3^+/C_2F_4^+$) in Fig. 1c, which is significantly faster than that of $C_3F_5^+$, cannot be attributed to the fragmentation of slower C_3F_5. This is strong evidence for the formation of the $CFCF_3/C_2F_4$ + CF_2 channel. The translational energy distribution for this channel (Fig. 2) is peaked near 7 kcal/mol, with an average of 9.6 kcal/mol. The contribution of C_3F_5 at this mass is found to be negligible. A polarization dependence for this reaction is also observed with a maximum anisotropy parameter, β, of 0.20 $\pm$ 0.08. This value is corrected to 0.29 $\pm$ 0.08, as above, for 85% polarized light.

3.3. $C_3F_6 \rightarrow CF_3 + C_2F_3$. The time-of-flight spectra for *m/e* = 81 ($C_2F_3^+$), *m/e* = 69 (CF_3^+), and *m/e* = 50 (CF_2^+) are shown in Fig. 3. The $C_2F_3^+$ (Fig. 3a) signal consists of fragmentation from *m/e* = 100 and *m/e* = 131 as well as a contribution from a third primary channel. The evidence for the presence of a third primary channel was based on the time-of-flight spectrum of *m/e* = 69 (CF_3^+) that is shown in Fig. 3b. The slow products observed in the time-of-flight distribution could not be completely explained by contributions from dissociative ionization of $C_3F_5^+$ and $CF_3CF^+/C_2F_4^+$, but including the third channel gives a good total fit. The translational energy distribution resulting from this third channel, a simple C-C bond rupture, is peaked near

zero with an average of 2.2 kcal/mol. As illustrated in Fig. 3c, the signal at m/e = 50 can be completely explained using these three primary channels.

3.4 Branching Fraction. A summary of possible channels in hexafluoropropene dissociation at 193 nm is shown in Fig. 4.[13] The branching fraction[14], CF_2:F:CF_3, is 0.47:0.36:0.17 at 25 mJ/pulse. The relative contribution from each primary fragment, at each *m/e* ratio was determined and corrected for the ionization cross sections. The uncertainty in this ratio is approximately ± 0.1 for each channel. This uncertainty arises from the poor signal-to-noise ratio at this laser power and the difficulty in exact assignment of parent ion fragmentation. The major channel is CF_2 loss (~ 47 %), which is similar to the IRMPD experiment[6] where CF_2 loss is also the predominant channel, accounting for approximately 80 % of the dissociation products.

4. Discussion

4.1. Bond Dissociation Energies. From the conservation of energy, an estimate of the bond dissociation energy for a reaction channel can be obtained from photofragment translational spectroscopy experiments by using Equation (7).

$$E_{int}(\text{reactant}) + E_{h\nu} = D_o + E_T + E_{int}(\text{products}) \tag{7}$$

If the internal energy of the reactant is assumed to be minimal and the maximum translational energy corresponds to products with no internal energy, a simple calculation (8) gives the bond dissociation energy.

$$D_o = E_{h\nu} - E_T(\text{max}) \tag{8}$$

For reaction (3), Equation (8) gives a C-F bond dissociation energy of 121 kcal/mol for hexafluoropropene. This value is an upper limit to the true bond dissociation energy and an

uncertainty of at least ± 2 kcal/mol is present, resulting primarily from the uncertainty in the E_T(max) measurement. The assumption that some of the products are in their ground state is reasonable for a simple bond rupture eliminating an atom. The translational energy distribution peaking at ~ 19 kcal/mol indicates that most of the excess energy is stored in the repulsive interaction between the products. Repulsive dissociations are efficient in converting excess energy into translation.[15] For the other channels, CF_2 and CF_3 loss, that form two polyatomic species, the use of Equation (8) to find the bond dissociation energy is not reliable, since both fragments can contain significant amounts of internal energy and the formation of ground state products may be negligible.

4.2. Comparison with the IRMPD experiment. In both the IRMPD[6] and these UV experiments, CF_2 loss and CF_3 loss were observed. The translational energy distribution for CF_3 peaks at zero (Fig. 2), indicating that there is no exit potential energy barrier and the internal energy in the excited molecule is distributed extensively among all the vibrational modes. This implies internal conversion to the ground state occurs before the C-C single bond breaks. Using RRKM theory and the parameters from reference 6, the estimated dissociation lifetime for ground state hexafluoropropene with 148 kcal/mol internal energy is ~8 nsec. Although thermal heating and deposition of a large number of IR photons into a molecule create slightly different vibrational population distributions[16], this approximation give a reasonable estimate of the lifetime. The predicted lifetime of 8 nsec after internal conversion would average out all anisotropy effects.

The non-negligible anisotropy parameter that is observed for CF_2 loss (β = 0.29) indicates that a portion of the dissociation process proceeds on an excited surface, which is in contrast to

the IRMPD experiments. A range of distributions was determined for the CF_2 elimination channel in the IRMPD experiments. The translational energy derived from the UV experiments lies within this range. It is likely the translational energy distribution for CF_2 loss in UV photodissociation is a combination of the ground state and excited state processes. The anisotropy parameter indicates the involvement of the excited state, however, the presence of reaction (3) suggests that internal conversion also occurs. Competition between CF_3 loss and CF_2 loss is expected on the ground state potential energy surface as shown by the IRMPD experiments. The branching ratio, CF_2:CF_3, of 4.0:1.0 for the IRMPD experiments differs from that for the UV experiment (2.9:1.0). The significant fraction of reaction (3) produced in the UV experiment might indicate that a larger amount of energy is deposited in hexafluoropropene with UV excitation as compared with IRMPD, and the larger A factor for the simple bond rupture reaction allows this channel to become more prevalent at higher internal energies.

4.3. Reaction Anisotropies and Mechanisms. The presence of the F-atom elimination channel, not observed in any IRMPD or thermal experiments, indicates that this dissociation process takes place on an excited potential energy surface. The strong polarization effect (β = -0.90) suggests a transition perpendicular to the C-F bond; based on the observed anisotropy we believe this is a $\pi \rightarrow \sigma^*$ transition. Since the electronic excitation involves the double bond the observed F atom elimination is likely from a C-F bond adjacent to the double bond. The β parameter for CF_2 loss (β = 0.29) is less than that expected for a predominantly parallel transition (2.0). Competition between ground state CF_2 loss and excited state CF_2 loss could substantially reduce the polarization effect. In addition, because of the asymmetry of hexafluoropropene the

transition dipole for the $\pi \rightarrow \pi^*$ transition may not lie directly along the carbon-carbon double bond axis, which would further reduce the effect.[.17]

Although Zewail and co-workers have observed hydrogen migrations taking as little as 60 femtoseconds in methyl salicylate after near UV excitation (280-330 nm),[18] migration of the much heavier fluorine atom would not be expected to occur on such a short time scale. However, it may be possible for a fluorine migration to take place on the same time scale as internal conversion followed by dissociation. Dissociation of hexafluoropropene to the products trifluoromethylfluorocarbene (1) or tetrafluoroethylene and $^1CF_2$ (5) are both consistent with our experimental observations. The translational energy distribution is peaked at 7 kcal/mol, which suggests an exit barrier in the reaction channel. Since this distribution is a summation of two processes, the barrier may be on both the ground state and the excited state. This exit barrier could result from the electron pairing energy gained to form two singlet species (CF_2 and $CFCF_3$) [19] or from the formation of the closed shell species tetrafluoroethylene.

There are still three other reactions that are energetically accessible at 193 nm (see Fig. 4). The formation of $^3CF_2$ with trifluoromethylfluorocarbene or tetrafluoroethylene is possible. There is no distinct evidence for either of these channels, and another electronic excited state would have to be involved to explain the coupling to a triplet state. However, to confirm the minor roles of these channels, phosphorescence from the photolysis products of hexafluoropropene should be measured. Similar experiments have been performed on tetrafluoroethylene.[7] Production of three $^1CF_2$ fragments is thermodynamically possible, but the time-of-flight spectrum for CF_2 can be explained without invoking this channel. Moreover,

this process, which involves a fluorine migration, is likely to have a barrier on the order of 20 kcal/mol and be inaccessible at 193 nm.[20]

In summary, we have observed three primary channels in the UV photolysis of hexafluoropropene. F atom elimination (4) is unique to photolysis and the dependence of the angular distribution of the products on the polarization of the laser indicates this reaction takes place on an excited potential energy surface. CF_2 loss takes place both from an excited state and from the ground state. After internal conversion, the vibrationally excited hexafluoropropene dissociates by either eliminating CF_2 or CF_3 as was observed in the previous IRMPD investigation.

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Gov. Printing Office: Washington, DC,1971). A value for C_3F_5 of -167 ± 4 kcal/mol can be estimated from our C-F bond dissociation energy of 121 kcal/mol.

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Figure Captions

Fig. 1. Time-of-flight spectra for the heavy fragments from the UV photolysis of hexafluoropropene at 20°. (a) The circles are the data points and the line is the fit to $C_3F_5^+$. (b) Time-of-flight spectrum for $C_3F_4^+$. (c) Time-of-flight spectrum for m/e = 100. The dashed line represents a second primary channel.

Fig. 2. Center-of-mass translational energy distributions derived from the time-of-flight data in Figs. 1 and 3. The squares represent the CF_2 loss channel while the circles indicate the translational energy distribution from the fluorine atom elimination channel. The simple bond rupture channel results in the distribution shown by the triangles.

Fig. 3. Time-of-flight spectra for the lower molecular weight products at 20°. (a) The time-of-flight spectrum for $C_2F_3^+$ has a contribution from m/e = 131 (solid line), m/e = 100 (dashed line), and a third contribution (dotted line) from reaction (4), which produces C_2F_3 directly. (b) The contributions at CF_3^+ include fragmentation of m/e = 131 (solid line), m/e = 100 (dashed line) and the momentum matched partner to C_2F_3 (dotted line). (c) The predominant contributions at CF_2^+ are from the fragmentation of m/e = 100 (dashed line) and its partner, CF_2, (dash-dot-dash line). Possible contributions from both products of reaction (4) are shown by dotted lines.

Fig. 4. Energy level diagram for hexafluoropropene. Possible dissociation channels and the maximum amount of energy available for translation are shown. The amount of energy available for reaction (3) is found in this experiment (see text) while the estimate for reaction (4) is from reference 5.

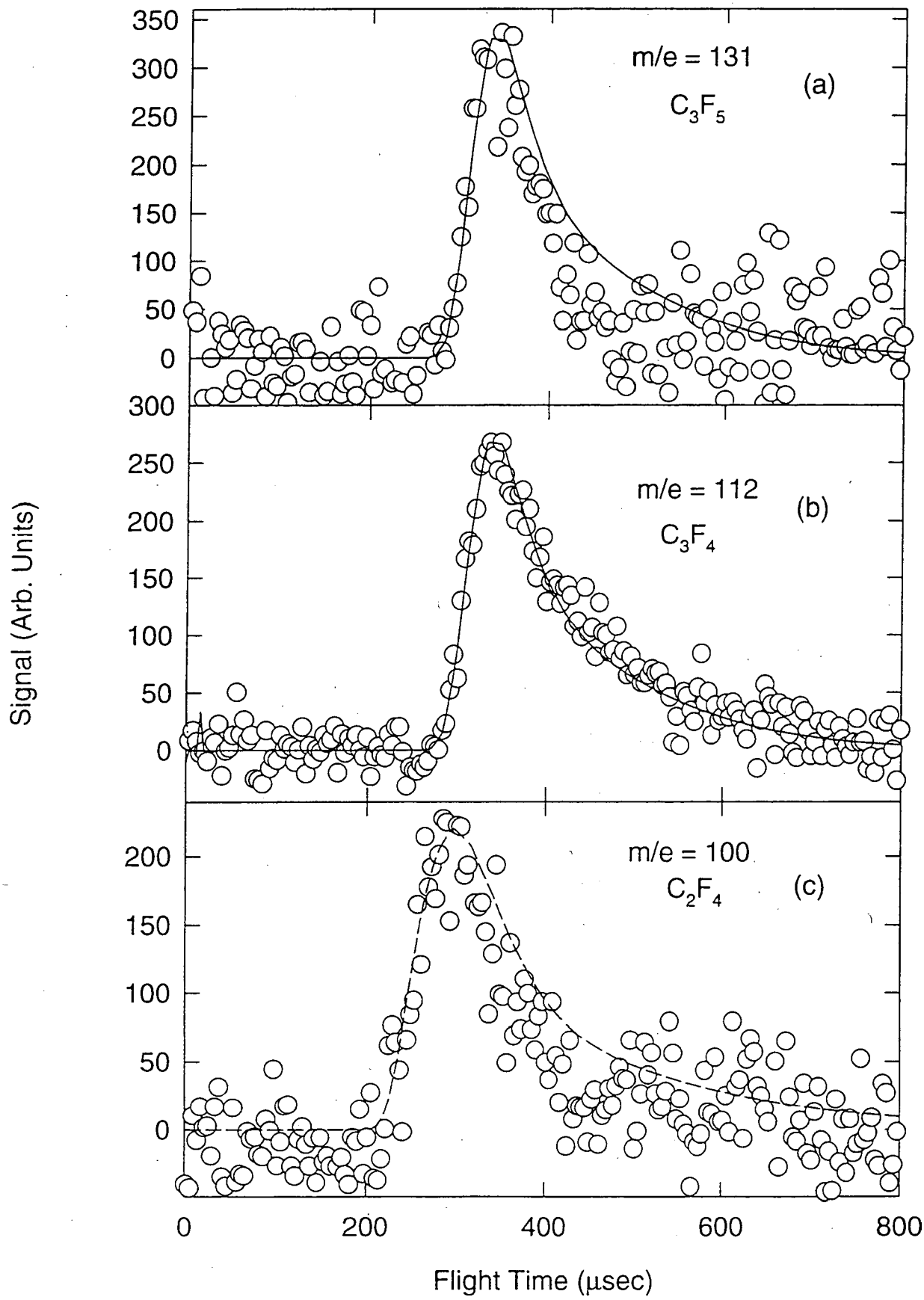
m/e = 131
C_3F_5
(a)
m/e = 112
C_3F_4
(b)
m/e = 100
C_2F_4
(c)
Signal (Arb. Units)
Flight Time (μsec)
0
200
400
600
800

Figure 1

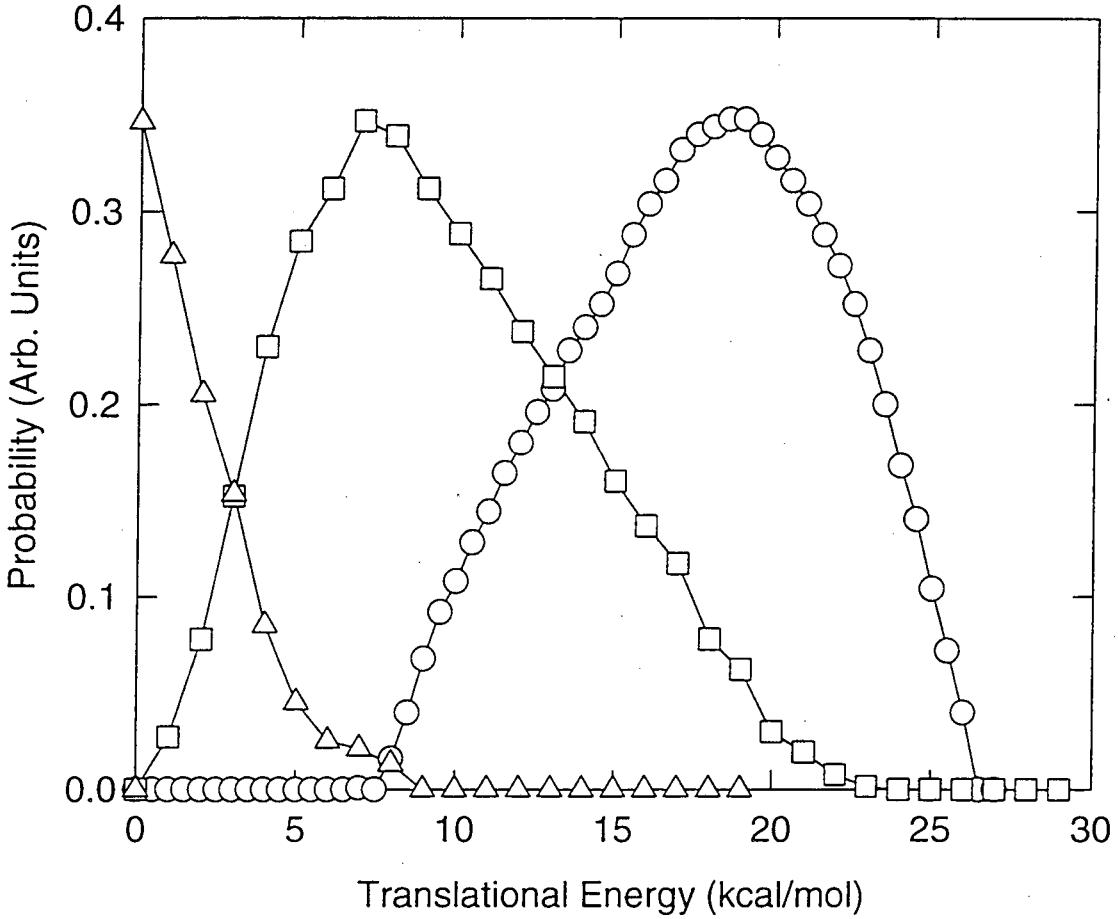
0.4
0.3
0.2
0.1
0.0
Probability (Arb. Units)
0
5
10
15
20
25
30
Translational Energy (kcal/mol)

Figure 2

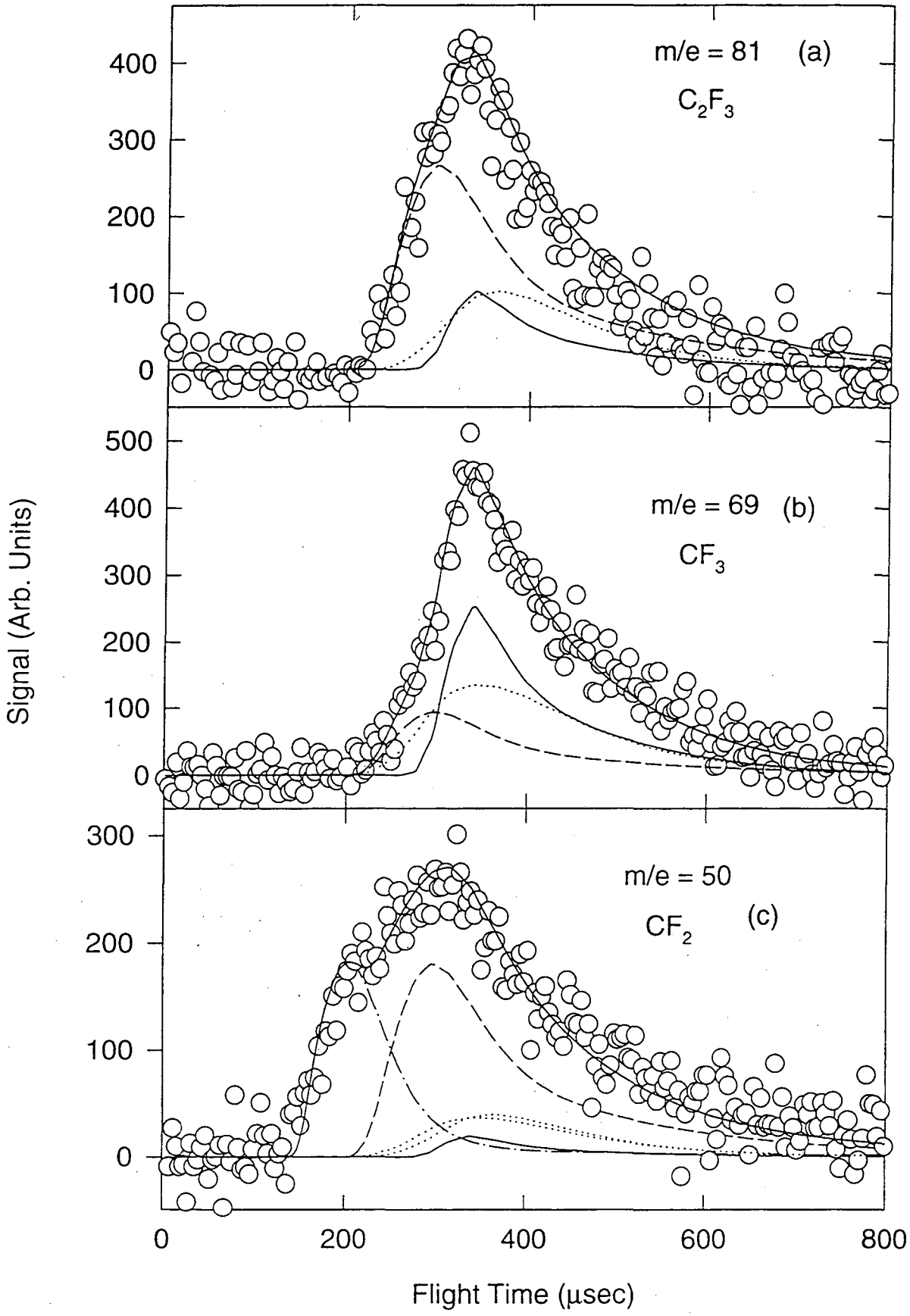
m/e = 81 (a)
C_2F_3
m/e = 69 (b)
CF_3
m/e = 50
CF_2 (c)
Signal (Arb. Units)
Flight Time (µsec)
0
100
200
300
400
500
600
800

Figure 3

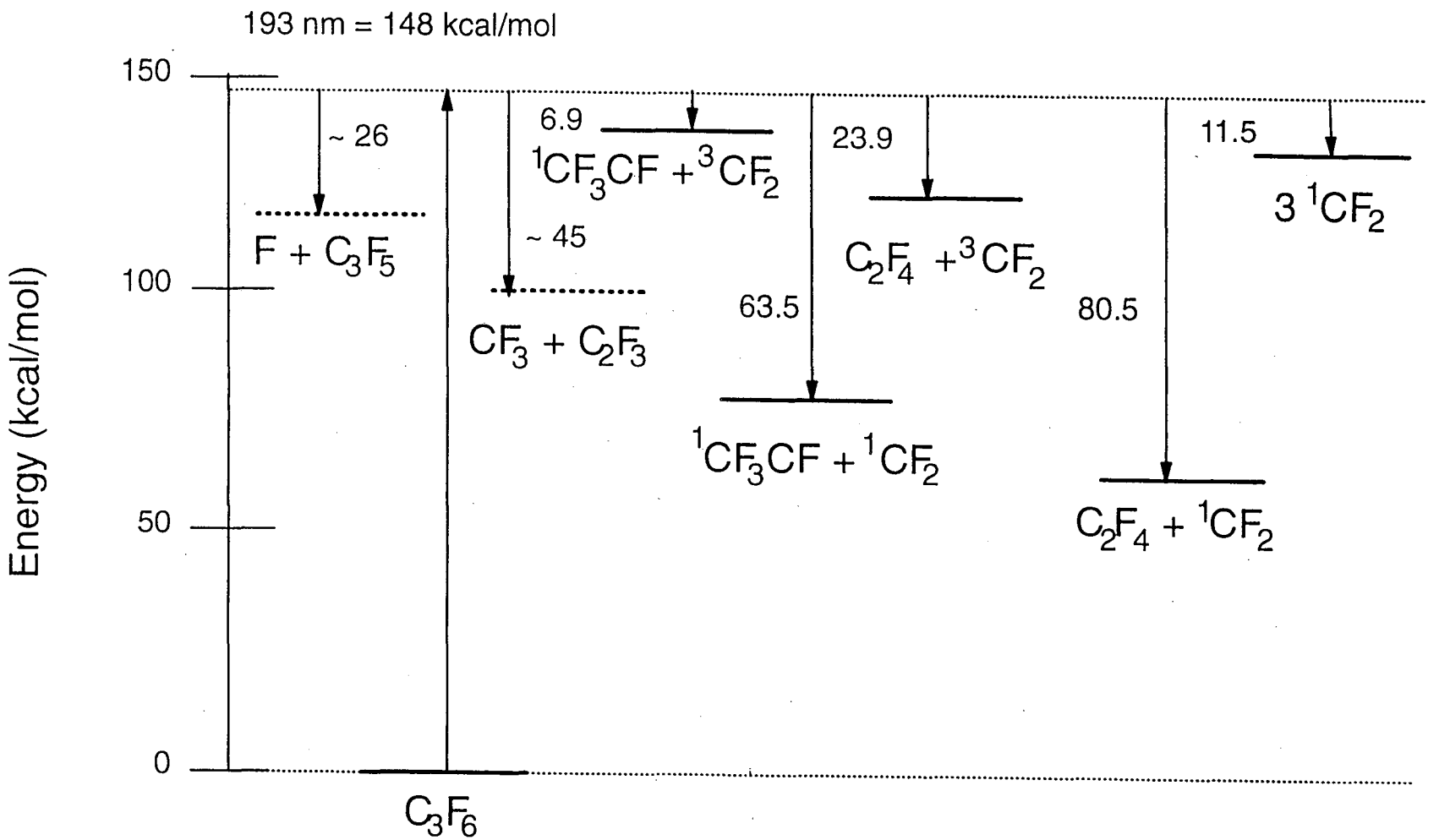
193 nm = 148 kcal/mol
Energy (kcal/mol)
150
100
50
0
~ 26
F + C3F5
~ 45
CF3 + C2F3
6.9
1CF3CF + 3CF2
63.5
1CF3CF + 1CF2
23.9
C2F4 + 3CF2
80.5
C2F4 + 1CF2
11.5
3 1CF2
C3F6

Figure 4

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