

Near ultraviolet photolysis of HFCO: The H+FCO channel

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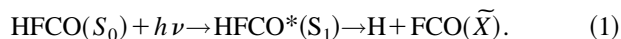
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The technique of H (Rydberg) atom photofragment translational spectroscopy has been used to study the process $\text{HFCO}(S_1) \rightarrow \text{H} + \text{FCO}(\tilde{X})$, near its appearance threshold, at excitation wavelengths ca. 247 nm. Analyses of the resulting total kinetic energy release spectra lead to an accurate determination of the C–H bond strength: $D_0(\text{H–FCO}) = 34950 \pm 20 \text{ cm}^{-1}$. The resulting FCO fragments are observed to be formed with little internal energy, distributed mainly in the form of *a*-axis rotation. Fragmentation is shown to involve S_1 – T_1 intersystem crossing, followed by rapid passage along the minimum energy path to the eventual H+FCO products. This minimum energy path involves passage over (or H atom tunnelling through) a saddle point, the height of which is $\geq 4740 \text{ cm}^{-1}$ above the dissociation asymptote. The observed propensity for *a*-axis rotation in the FCO product reflects changes in the parent geometry as it evolves along the C–H dissociation coordinate on the T_1 surface; past the saddle point, the barrier energy is released largely in the form of product recoil. © 1997 American Institute of Physics. [S0021-9606(97)02514-2]

INTRODUCTION

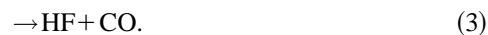
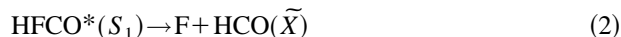
The near ultraviolet spectroscopy and photophysics of formyl fluoride, HFCO, have been the subject of a number of previous studies. The S_1 – S_0 band system arises as a result of an $\pi^* \leftarrow n$ electron promotion centered on the C=O moiety. It shows extensive rovibronic structure,^{1–3} the analysis of which identifies the band origin at 37491.7 cm^{-1} and confirms *ab initio* predictions⁴ that the S_1 state has a pyramidal equilibrium geometry with an extended C=O bond length and compressed $\angle\text{FCO}$ bond angle relative to that of the (planar) ground state. The barrier to inversion in the S_1 state is sufficiently small [ca. 2580 cm^{-1} (Ref. 3)], however, that the S_1 – S_0 transition is best viewed in the C_s point group as $\tilde{A}^1 A'' - \tilde{X}^1 A'$.

Recent companion studies in Bristol^{5,6} of the parent $S_1 \leftarrow S_0$ laser induced fluorescence (LIF) excitation spectrum and of the “action” spectrum for forming H atom photofragments have identified an appearance threshold of ca. 39690 cm^{-1} for H atom formation via the radical dissociation pathway:



Doppler line shape analysis shows these H atoms to carry significant recoil energy.⁵ This observation, and the deduced recoil anisotropy, has been explained by assuming that dissociation proceeds via intersystem crossing (ISC) to the $T_1(\tilde{a}^3 A'')$ triplet state which is calculated to have a similarly nonplanar equilibrium geometry and, more importantly from the present perspective, a potential energy barrier in the C–H dissociation coordinate.^{7,8} Other unimolecular decay processes available to these photoexcited HFCO molecules in-

clude $S_1 \rightarrow S_0$ radiative decay,^{6,9} internal conversion (IC) to the ground state, the alternative bond fission (2) and the molecular elimination channel (3):



Given recent estimates for the heat of formation of the FCO radical [$-153 \pm 12 \text{ kJ mol}^{-1}$ (Ref. 10)], together with $\Delta H_f^0(\text{H}) = 216.04 \text{ kJ mol}^{-1}$, $\Delta H_f^0(\text{F}) = 77.3 \text{ kJ mol}^{-1}$, and $\Delta H_f^0(\text{HCO}) = 43 \pm 8 \text{ kJ mol}^{-1}$ (Ref. 11) and the value for $D_0(\text{H–FCO})$ derived below, we deduce that process (2) should be exoergic at excitation energies above ca. 31500 cm^{-1} . However, theory⁷ indicates a substantial barrier in this exit channel and there do not appear to be any reported observations of products arising via this dissociation pathway.

In contrast, the latter process has received considerable attention. An early flash photolysis–chemical laser experiment¹² provided some measure of the vibrational energy disposal in the nascent HF fragments. However, the most important studies, at least from the photochemical viewpoint, are those of Choi and Moore^{9,13} who used stimulated emission pumping (SEP) from the S_1 state to populate (known) highly excited rovibrational levels of the ground S_0 state. These levels all lie below the energetic threshold for the bond fission channels (1) and (2), so detailed linewidth measurements and LIF probing of the nascent CO(X) fragments provide detailed, state-specific information on the decay process (3). As a result, the activation energy for ground state molecules dissociating via this molecular elimination pathway is now reasonably well defined at $\sim 176 \text{ kJ mol}^{-1}$ (14750 cm^{-1}) (Refs. 13 and 14).

In comparison, the H atom loss process following excitation to the S_1 state of HFCO has received scant attention until now, though a study of HFCO photolysis at two of the standard excimer laser wavelengths (248 and 193 nm) sug-

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gests that the radical channel (1) dominates at both wavelengths.¹⁵ Here we report the first application of the technique of H (Rydberg) atom photofragment translational spectroscopy (PTS)¹⁶ to studies of the energy disposal accompanying fragmentation pathway (1) at wavelengths ca. 247 nm, i.e., at photon energies just above the appearance threshold for forming H atom photoproducts.

EXPERIMENT

The experimental method has been detailed previously.¹⁷ HFCO was prepared by the reaction of cyanuric fluoride and formic acid¹⁸ and stored at 77 K when not in use. When required for experiments, however, ca. 1 atm. of N₂ was passed over the HFCO sample (now maintained as a liquid at dry ice temperature) and the seeded mixture then introduced into the reaction chamber in the form of a skimmed, pulsed molecular beam. The necessary photolysis wavelengths were provided by a Nd-YAG pumped dye laser (Spectra-Physics GCR-5 plus PDL-2) operating on the dye coumarin 500, with subsequent frequency doubling of the dye laser output. As usual, the experimental observable is a time-of-flight (TOF) spectrum of the nascent H atom photofragments. Accurate knowledge of the flight path, together with the requirement that linear momentum be conserved, allows us to transform this data into a total kinetic energy release (TKER) spectrum.

RESULTS AND DISCUSSION

Figure 1 shows TKER spectra of the H+FCO fragments resulting from linearly polarized photolysis (ϵ perpendicular to the TOF axis) of a jet-cooled sample of HFCO molecules at (a) 248.20 nm (40 279 cm⁻¹) and (b) 245.50 nm (40 721 cm⁻¹)—wavelengths that correspond to excitation within the parent $\tilde{A}-\tilde{X}4_0^16_0^{2+}$ and $4_0^15_0^16_0^{2+}$ absorption bands, respectively.^{3,6} Dixon and Hancock have demonstrated,⁵ via Doppler lineshape analysis, that the dissociation of quantum state selected HFCO (*S*₁) molecules results in an anisotropic distribution of H atom recoil velocities. In the present studies, however, the combination of our limited photolysis laser resolution (ca. 0.5 cm⁻¹) and the fact that we generally chose to excite the more intense *Q* branch absorption maxima precluded photoselection of a single parent rovibronic level and, as a result, both the magnitude and the detailed appearance of these and all other TKER spectra we have recorded for this molecule were observed to be largely insensitive to the alignment of ϵ .

The TKER spectra show fine structure, the analysis of which can provide insight into the internal energy disposal in the partner FCO radical. Accurate spectroscopic parameters for the ground state of this radical and for the $\nu_1(\text{C}=\text{O})$ and $\nu_2(\text{C}-\text{F})$ stretch fundamentals are available in the literature.¹⁹ The frequency of the ν_3 bending vibration in the ground state [626 cm⁻¹ (Ref. 20)] appears to have been determined in a matrix only. FCO is a near prolate symmetric top; thus its pattern of rotational energy levels exhibits coarse *K* structure (associated with *a*-axis rotation), each with a closely spaced manifold of *N* levels ($N \geq K_a$) stretch-

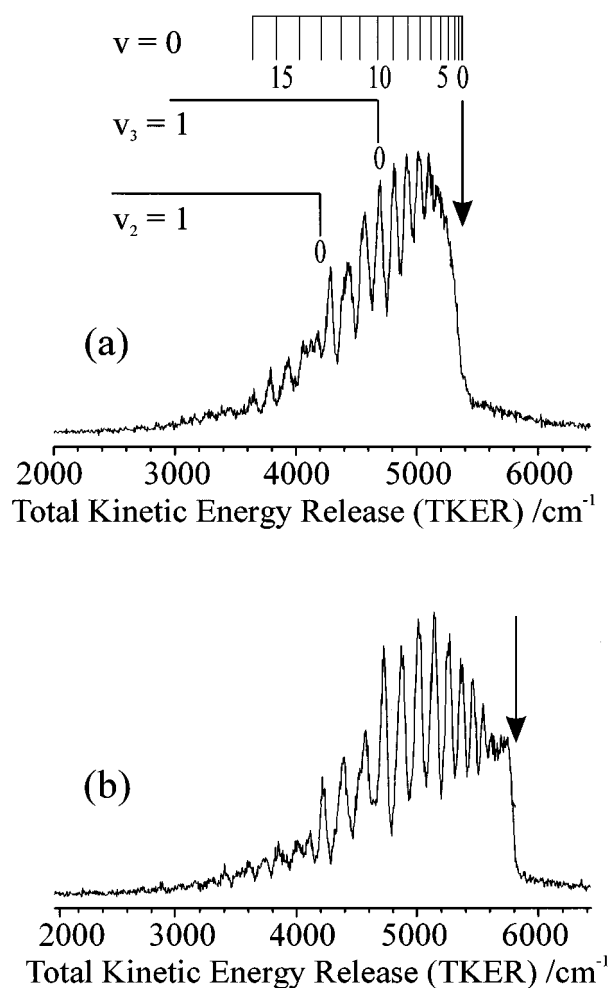


FIG. 1. TKER spectrum of the H+FCO fragments resulting from linearly polarized photolysis (ϵ perpendicular to the TOF axis) of a jet-cooled sample of HFCO molecules at (a) 248.20 nm (40279 cm⁻¹) and (b) 245.50 nm (40721 cm⁻¹). The vertical arrow in each spectrum indicated the deduced TKER(max), i.e., the TKER associated with formation of FCO fragments in their $v=N=0$ level, while the combs festooned above (a) indicate the relative energies of the $v=0$, $N=K_a$ levels and the energetic thresholds for the first two excited vibrational levels.

ing to higher internal energy. The onsets of the various K_a stacks associated with the $v=0$ state of FCO are indicated by the comb superimposed over the TKER spectrum in Fig. 1(a), as are the energetic thresholds for the first two excited vibrational levels. The observation of such clearly resolved structure enables accurate determination of the TKER associated with formation of H atoms together with FCO fragments in their $v=0$, $N=0$ state from which, by energy conservation, we can deduce an accurate value for the C-H bond strength in HFCO: $D_0(\text{H}-\text{FCO}) = 34950 \pm 20 \text{ cm}^{-1}$.

Having established this bond strength it is possible to recast TKER spectra such as those shown in Fig. 1 in terms of the FCO internal energy. The results are shown in Figs. 2(a) and 3(a). Clearly, in both cases, most of the FCO fragments are formed in their ground vibrational state. Further, the fact that the various resolved features associated with each K_a value appear both fairly narrow (ca. 90 cm⁻¹ FWHM) and symmetrical indicates a strong bias towards

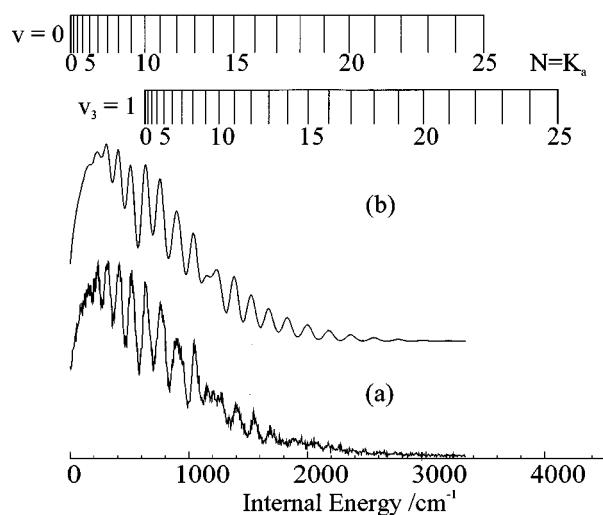


FIG. 2. (a) Internal energy spectrum of the FCO fragments resulting from the 248.20 nm photolysis of a jet-cooled sample of HFCO, together with (b) the best-fit simulation obtained assuming a $v=0:v_3=1$ population ratio of 4:1, a Gaussian population distribution over the $N=K_a$ states associated with both levels with $K_a(\text{max})=8$ and $\Delta K_a=9$, and a quantum state width of 90 cm^{-1} (FWHM, Gaussian).

forming fragments with a narrow range of N quantum numbers. The accompanying best-fit simulations [Figs. 2(b) and 3(b)] were obtained assuming a Gaussian population distribution over just the $N=K_a$ product states, floating the intensity and the quantum number of the most populated level, $K_a(\text{max})$, the width (FWHM) of the K_a distribution, ΔK_a , the relative populations of the $v=0$ and $v_3=1$ levels, and the energy width of each quantum state. This exercise leads to the conclusion that most of the internal energy in the FCO photofragments arising *via* dissociation channel (1), at least near its long wavelength appearance threshold, appears in the

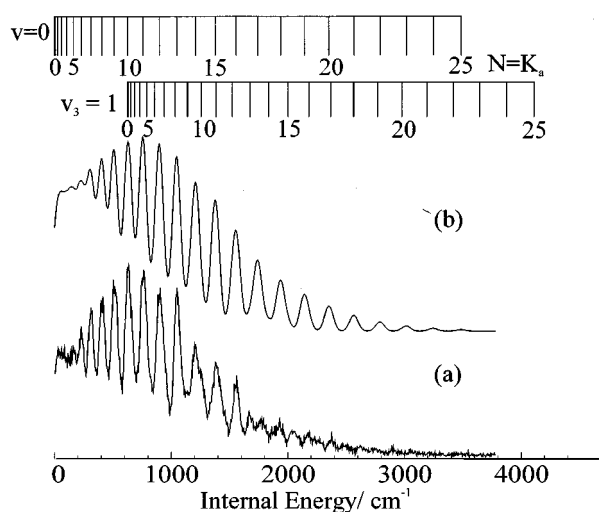


FIG. 3. (a) Internal energy spectrum of the FCO fragments resulting from the 245.50 nm photolysis of a jet-cooled sample of HFCO, together with (b) the best-fit simulation obtained assuming a $v=0:v_3=1$ population ratio of 9:1, a Gaussian population distribution over the $N=K_a$ states associated with both levels with $K_a(\text{max})=10$ and $\Delta K_a=11$, and a quantum state width of 85 cm^{-1} (FWHM, Gaussian).

form a -axis rotational motion. The ‘‘excess’’ energy [i.e., $h\nu - D_0(\text{H-FCO})$] available for partitioning into fragment translational and/or internal excitation in the case of 248.20 nm photoexcitation is $5330 \pm 20\text{ cm}^{-1}$. Analysis of the internal energy spectrum shown in Fig. 2 allows estimation of the mean energy appearing in product rovibrational excitation, $\langle E_{\text{int}} \rangle \sim 740\text{ cm}^{-1}$, from which we deduce that the bulk (86%) of the excess energy in this near threshold dissociation is channelled into product recoil.

The value for $D_0(\text{H-FCO})$ determined here lies some 4740 cm^{-1} below the long wavelength threshold in the action spectrum for forming H atoms following excitation to the S_1 state of HFCO.^{5,6} This difference provides a direct measure of the *minimum* height [measured relative to the $\text{H+FCO}(\bar{X})$ asymptote] of the potential barrier in the exit channel leading to C–H bond fission, in good agreement with a recent determination from H atom Doppler line shape analysis.^{5,6} Clearly, the observed onset is likely to involve H atom tunnelling through, rather than passing over, this exit channel barrier. Given that S_1 levels at this level of excitation have lifetimes on the order of 10^{-8} s ,⁶ H atom production via channel (1) could be expected to become competitive and observable as soon as the tunnelling rate exceeds ca. 10^8 s^{-1} , i.e., at energies some considerable way below the top of the barrier.

Correlation arguments⁵ indicate that the S_0 state of HFCO correlates with ground state H+FCO products, while the parent $S_1(\bar{A}^1A'')$ state correlates with the excited products $\text{H+FCO}(\bar{A})$. This latter asymptote is endoergic at all excitation wavelengths used in the present study. The corresponding $T_1(\bar{a}^3A'')$ triplet state of the parent also correlates with these excited products at planar geometries, but with the ground state products under the reduced symmetry appropriate for nonplanar configurations.⁵ Thus the two possible mechanisms whereby HFCO(S_1) molecules can fragment to H+FCO products at these excitation energies are both indirect, involving IC to the S_0 state continuum and/or ISC to the T_1 state. Crane *et al.*³ have provided clear evidence for IC following $S_1 \leftarrow S_0$ excitation at energies below the observed onset for fragmentation channel (1), but the current consensus indicates that the subsequent dissociation involves the molecular elimination channel (3).^{9,13} Neither simple correlation arguments,⁵ nor the best available *ab initio* calculations,^{4,8} indicate that the S_0 potential energy surface of HFCO should exhibit any significant barrier in the C–H dissociation coordinate.

Such is not the case for the T_1 surface, however. The C–H exit channel of this surface supports the bottom half of a conical intersection. The magnitude of the associated energy barrier decreases with increasing out-of-plane bending, but is calculated^{7,8} to still be very significant at the transition state to fragmentation *via* channel (1). Given the proclivity for H atom tunnelling, the theoretical barrier height derived in the more recent calculations [ca. 7700 cm^{-1} (Ref. 8)] is not wholly incompatible with the experimental observations and, as we now show, the predicted transition state geometry is broadly consistent with the measured energy disposal. The calculated⁸ transition state is pyramidal, with a much ex-

tended (1.53 Å) C–H bond directed at an angle of 75° out of the plane defined by the FCO partner (cf. ca. 1.10 Å and ca. 52° at the equilibrium geometry of the T_1 state). If the fragmentation simply involved further extension of the C–H bond along this axis, the impact parameter, b , associated with this trajectory (relative to the FCO center of mass) would be 0.43 Å. This should be compared with the value we derive by equating

$$K_a(\max)\hbar = \mu\nu b. \quad (4)$$

For the case of 248.8 nm photolysis of HFCO, $K_a(\max) = 8$ and the average recoil velocity $\nu = 11\,000\text{ m s}^{-1}$, resulting in an impact parameter $b = 0.47 \pm 0.06\text{ Å}$. An impact parameter of this magnitude could be accommodated by invoking a further reduction in the $\angle\text{FCO}$ bond angle (which would have the effect of moving the fragment center of mass further from the C atom) or, more probably, by assuming that the trajectory of the departing H atom actually moves further out of the plane defined by the FCO moiety.

Thus we reach a fairly detailed picture of the near threshold fragmentation of HFCO via dissociation channel (1). Franck–Condon considerations dictate that the photoexcited S_1 molecules will be created with substantial out-of-plane motion. The $S_1 \leftarrow S_0$ absorption spectrum is richly structured at the excitation energies relevant to this study, implying that the S_1 molecules survive for many rotational periods prior to prompt electronic rearrangement to the T_1 state and rapid passage along the minimum energy path to the eventual H+FCO products. The preference for, and the extent of, a -axis rotation in the FCO product is largely determined by the change in out-of-plane bond angle (and, to a lesser extent, the reduction in $\angle\text{FCO}$ bond angle) as the dissociating molecules evolve on the T_1 surface towards the transition state. The observed degree of product a -axis rotation is shown to be broadly consistent with the theoretically predicted geometry for the saddle point in the C–H exit channel on the T_1 surface. The recoiling H atom departs near perpendicular to the FCO plane and the energy release once

past the barrier appears primarily in the form of product recoil. A comprehensive report of analogous studies of this dissociation process at numerous wavelengths in the range 250–218 nm will be published elsewhere.

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