Near-UV photodissociation dynamics of formic acid

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H (Rydberg) atom photofragment translational spectroscopy has been used to study the photodissociation dynamics of jet-cooled formic acid molecules following excitation to their first excited singlet (S1) state at numerous wavelengths in the range 216–241 nm. Analysis of the resulting H-atom time-of-flight spectra indicates contributions from three H-atom formation channels, which we identify as the primary C—H and O—H bond fission processes and the secondary photolysis of HCOO(X) fragments resulting from primary C—O bond fission. It also allows determination of the bond dissociation energies: \( D_H^0 (H—CO_2H) \approx 30,000 \text{ cm}^{-1} \) and \( D_H (\text{HCOO—H}) = 39,080 \pm 100 \text{ cm}^{-1} \). The former bond fission is deduced to occur after intersystem crossing to the neighbouring \( \Delta^3 \text{A}^\ast \) state, and to involve passage over (or tunnelling through) a barrier in the C—H dissociation coordinate on the triplet potential-energy surface. O—H bond fission, in contrast, is shown to occur predominantly on the \( S_1 \) surface but it, too, must overcome an activation barrier, the magnitude of which we can estimate at ca. 5400 cm\(^{-1}\) measured relative to the asymptotic products \( H + HCOO(X) \) and/or \( \Delta \). The latter assignment affords a refined value for the 0 K heat of formation of the formyloxyl radical: \( \Delta H_0^0 (\text{HCOO}) = -119.5 \pm 3 \text{ kJ mol}^{-1} \).

Recent laser studies of the UV spectroscopy and photochemistry of formyl fluoride, HFCO, have led to major advances in our understanding of the fragmentation dynamics of this molecule following excitation to its first excited \((\Delta^3 \text{A}^\ast)\) singlet state. Specifically, a combination of jet-cooled parent spectroscopy (both parent-laser-induced fluorescence\(^1\)–\(^3\) and, at shorter wavelengths, measurements of the ‘action’ spectrum for forming H-atom photoproducts) and of the Doppler linewidths\(^4\)–\(^5\) and the times-of-flight\(^6\),\(^5\) of these nascent H atoms, have shown the C—H bond fission process to occur via intersystem crossing (ISC) and subsequent dissociation on the lowest triplet potential-energy surface. Both the C—H and C—F bond-fission channels show activation barriers. The C—H bond-fission process in HFCO has been characterised at a number of excitation wavelengths in the range 218–248 nm, and the detailed energy partitioning into product rotation, vibration and translation, rationalised in terms of a hybrid model which allows both dynamical (associated with the forces acting as the dissociating molecule traverses the transition-state region associated with the barrier maximum) and statistical contributions to the overall energy disposal.\(^6\)

Formic acid, HCOO\(H\), is isoelectronic with HFCO. The present work describes the results of a high-resolution photofragment translational spectroscopy (PTS) study of the various H-atom formation processes following near-UV excitation of HCOO\(H\), with a view to identifying similarities and differences between the photochemistry of these two molecules. The longest wavelength part of the electronic spectrum of HCOO\(H\) shows resolved rovibrionic structure;\(^6\)–\(^9\) the analysis of which confirms the \( \Delta^3 \text{A}^\ast(S_1) \rightarrow \Delta^1 \text{A}(S_0) \) transition symmetry and allows identification of the electronic origin at 37,431 cm\(^{-1}\) (267.2 nm).\(^7\) Both the strength and the diffuseness of the absorption increase with decreasing wavelength. The cross-section appears to peak near 210 nm, whilst the structure merges to an apparent continuum at \( \lambda \approx 200 \) nm. The observed vibrational structure has been assigned in terms of progressions involving \( \nu_3 \) (C—O stretch), \( \nu_5 \) (C—H bend), and the out-of-plane motions \( \nu_6 \) and \( \nu_7 \).\(^6\) Such vibrational activity is fully consistent with the assignment of this UV absorption system in terms of a \( \pi_{\text{e—o}} \rightarrow n_0 \) electronic promotion connecting the (planar) \( \Delta^1 \text{A}^\ast(S_0) \) ground state and an excited singlet state with a pyramidal equilibrium geometry in which both H atoms are twisted out of the plane defined by the O—C=O backbone, in an anti-configuration. Note that, although the excited state is non-planar, it is assumed to invert sufficiently easily that the \( \text{A}^\ast \) symmetry label is still applicable since the permutation group is isomorphous with \( C_2 \).\(^6\)

The experimentally observed fluorescence lifetime of the \( S_1 \) origin level is ca. 50 ns.\(^10\) Some two orders of magnitude shorter than the radiative lifetime of comparable carbonyl molecules like \( \text{H}_2\text{CO} \) or HFCO. Possible competing non-radiative decay processes include internal conversion (IC) to high levels of the \( S_0 \) state, ISC to the neighbouring \( T_1 \) state arising from the same \( \pi^\ast \rightarrow n \) excitation, and predissociation. Fragmentation routes that are energetically possible following excitation within the \( \Delta—X \) absorption system\(^11\) include the molecular eliminations:

\[
\text{HCO}_2\text{H} + h\nu \rightarrow \text{H}_2\text{O} + \text{CO}; \quad \Delta H_0 \approx 35 \text{ kJ mol}^{-1} \quad (1)
\]

\[
\rightarrow \text{H}_2 + \text{CO}_2; \quad \Delta H_0 \approx -6 \text{ kJ mol}^{-1} \quad (2)
\]

process (3) leading to OH radical formation:

\[
\text{HCO}_2\text{H} + h\nu \rightarrow \text{HCO}() + \text{OH}(\Delta X) \quad \Delta H_0 \approx 452 \text{ kJ mol}^{-1} \quad (3)
\]

and the two bond-fission channels leading to H-atom formation:

\[
\text{HCO}_2\text{H} + h\nu \rightarrow \text{H} + \text{CO}_2\text{H}(\Delta X) \quad (4)
\]

\[
\rightarrow \text{H} + \text{HCO}_2() \quad (5)
\]

The dynamics and the energetics of these two processes are major concerns of this paper, and are discussed in some detail later.

Brouard et al.\(^8\),\(^10\) have reported spectra showing the variation in \( \text{OH}(\Delta X) \) and \( \text{OH}(\Delta \text{A}) \) yield as a function of parent excitation wavelength. The electronically excited products are attributed to parent dissociation following two-photon absorption, resonance enhanced at the one-photon energy by
the predissociating $\tilde{A}$ state. More relevant to the present work, the spectrum for forming ground-state OH products shows a long wavelength threshold at $\lambda \approx 252$ nm (some 2400 cm$^{-1}$ above the S$_1$–S$_0$ origin) and gains in intensity with decreasing excitation wavelength. The quantum yield for channel (3) following excitation of HCO$_2$H at 222 nm has been estimated at $\Phi_3 \approx 0.8$.$^{11,12}$ Laser-induced fluorescence (LIF) and resonance-enhanced multiphoton ionisation (REMPI) probing of the OH(X) and HCO(X) products, respectively, reveal both to be formed with little internal energy, with the bulk of any excess energy provided by the photolysis event appearing in the form of product recoil.$^{8,13-15}$ Intriguingly, the measured fluorescence lifetimes of HCO-H$_3$ exhibit a clear decrease at slightly longer excitation wavelengths ($\lambda < 259$ nm, ca. 1200 cm$^{-1}$ above the S$_1$–S$_0$ origin),$^{16}$ suggesting that at least one other dissociation channel is operating at energies below the appearance threshold of channel (3). A similar conclusion was reached by Abe and Hayashi,$^9$ in their wavelength-dependent study of HCO$_2$H(Å–Å) fluorescence quenching induced by an external magnetic field. This work clearly implicated ISC as one ‘escape route’ for Å state HCO$_2$H molecules but, to date, details of the dissociation mechanism (or mechanisms) has remained elusive. Finally, we note that previous end-product and radical scavenging experiments employing broad band external magnetic field. This work clearly implicated ISC as one ‘escape route’ for Å state HCO$_2$H molecules but, to date, details of the dissociation mechanism (or mechanisms) has remained elusive. Finally, we note that previous end-product and radical scavenging experiments employing broad band light-fiel...
Fig. 1 TOF spectra of H atoms resulting from photolysis of jet-cooled HCOH molecules at 216.0 nm (46 282 cm\(^{-1}\)) [(a) and (b)] and 240.86 nm (41 505 cm\(^{-1}\)) [(c) and (d)]. The polarisation vector \(\mathbf{e}_{\text{phot}}\) was aligned, respectively, perpendicular [(a) and (c)] and parallel [(b) and (d)] to the TOF axis. Clearly, at both wavelengths, the ‘fast’ and ‘slow’ H-atom peaks display different angular anisotropies, suggesting that (at least) two processes contribute to these spectra.

Fig. 2 TKER spectra derived from the TOF spectra shown in Fig. 1, calculated assuming that the fragments partnering the observed H atoms have a mass of 45.018 u (i.e. have the chemical formula HCO\(_2\)H). The vertical arrows indicate the maximum TKERs for fragments associated with the O—H [(a) and (b)] and C—H [(c) and (d)] bond-fission channels, if we assume the bond dissociation energies given in the text.

This magnitude and some tunnelling contribution to the H + HCO\(_2\) yield.\(^3\) H atoms attributable to C—H bond fission are clearly identified at longer photolysis wavelengths (Fig. 3). Since the implied \(D_0(\text{H—CO}_2\text{H})\) is smaller than \(D_0(\text{HCOO—H})\) it seems reasonable to assume that C—H bond fission also occurs at the shorter excitation wavelengths, but that its contribution to the TKER spectrum is obscured by the overlapping, sharper and more intense peak we attribute to O—H bond fission. The fact that the ‘slow’ H atom peak associated with C—H bond fission also peaks well

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The good agreement between this value and the lower-energy dissociation threshold deduced in the present work validates our assignment of this threshold and serves to verify the internal consistency of the listed enthalpies. Kim et al. have reported $\Delta H_0^0(\text{HCO}_2) = 126 \pm 13 \text{ kJ mol}^{-1}$, from which we can predict $D_0(\text{HCOO} - \text{H}) = 461 \pm 13 \text{ kJ mol}^{-1}$ (38.540 \pm 1100 \text{ cm}^{-1}). As shown below, the accuracy with which we are able to define the threshold energy for O–H bond fission allows some refinement of $\Delta H_0^0(\text{HCO}_2)$.

Fig. 4 shows plots of the angular distributions of the ‘fast’ (15 < $t_{\text{dp}}/\mu s < 19$), intermediate (25 < $t_{\text{dp}}/\mu s < 28$) and ‘slow’ (38 < $t_{\text{dp}}/\mu s < 42$) H-atom photofragments resulting from photolysis of a jet-cooled sample of HCO$_2$H molecules at 216.0 nm (46 282 cm$^{-1}$). Following convention we attempt to fit these data in terms of the function:

$$I(\nu, \Theta) = (1/4\pi) f(\nu)[1 + \beta(l^2 \cos^2 \Theta - \frac{1}{2})]$$

where $f(\nu)$ is the speed distribution of the fragment, $\Theta$ is the angle between the $\nu$ vector of the photodissociation laser radiation and the velocity vector, $\nu$, of the recoiling fragment, and $\beta$ is the spatial anisotropy parameter. In the case of a prompt dissociation, $\beta$ takes limiting values of +2, following excitation via a transition whose dipole moment $\mu$ lies in the plane of the molecule, and −1 when $\mu$ is perpendicular to the molecular plane. As Fig. 4 shows, the ‘fast’ and ‘slow’ H-atom yields both show angular distributions peaking at 0°, but exhibit different $\beta$ parameters (0.9 ± 0.2 and 0.53 ± 0.15, respectively) which both fall far short of the limiting value +2, whilst the recoil velocity distribution for the ‘intermediate’ H atoms appears almost isotropic.

We now focus attention on the fast H-atom signal. One can envisage two possible explanations for these H atoms, the fastest of which appear with TKERs approaching that of the photolysis photon energy. One is two-photon dissociation of the parent molecule, such as has been invoked to account for the observed yield of electronically excited OH(A) fragments following excitation of HCO$_2$H at similar near-UV wavelengths. The alternative is secondary photolysis of HCO($\tilde{X}$) fragments formed in the primary step (3). Fig. 5 shows two depictions of the fast parts of three different TKER spectra, plotted on energy scales appropriate to H atoms recoiling from partner fragments with masses of 45.018 u (HCO$_2$) and 28.01 u (CO), respectively. The onsets in the former, the left hand column in Fig. 5, show no obvious correlation with the above zero TKER suggests the presence of a (somewhat larger) activation barrier in this exit channel also.

The endothermicity of reaction (3) is established from the well defined enthalpies of formation: $\Delta H_0^0(\text{OH}) = 38.9 \text{ kJ mol}^{-1}$, $\Delta H_0^0(\text{HCO}) = 41.4 \text{ kJ mol}^{-1}$ and $\Delta H_0^0(\text{HCO}_2\text{H}) = -371 \text{ kJ mol}^{-1}$. These values, together with $\Delta H_0^0(\text{H}) = 216.0 \text{ kJ mol}^{-1}$ and $\Delta H_0^0(\text{CO}_2\text{H}) = -220 \pm 3 \text{ kJ mol}^{-1}$ imply a value of $367 \pm 3 \text{ kJ mol}^{-1}$ (30 700 ± 250 cm$^{-1}$) for the endoergicity of fragmentation (4).
HCO absorption in the wavelength range 216–240 nm is associated with the parallel $B^2A' \rightarrow X^2A'$ transition\(^{31,32}\) and that the dissociation occurs rather promptly, whilst the broad spread of H atom TKERs suggests that the partner CO fragments are formed with a wide spread of internal energies. Franck–Condon considerations suggest that much of this excitation is likely to be in the form of CO vibration.

**Discussion**

The foregoing description suggests that both C–H and O–H bond-fission processes contribute to the primary photophysics of HCO\(_2\)H molecules following excitation within their \(S_1\)–\(S_0\) absorption system, and allows estimation of the respective dissociation energies. An additional yield of ‘fast’ H atoms is shown to arise from secondary photolysis of HCO(X) fragments formed via the C–O bond-fission channel (3). We now attempt to rationalise these observations, and complementary findings from previous studies of the near-UV photochemistry of HCO\(_2\)H, in terms of relevant portions of the potential-energy surfaces for the ground and low-lying excited electronic states of this molecule. Our knowledge of these excited states is limited. Iwata and Morokuma\(^{24}\) reported vertical excitation energies for the ground state and for the singlet and triplet excited states arising as a result of both \(\pi^* \rightarrow n\) and \(\pi^* \rightarrow \pi\) electron promotions. These suggest that the \(A^1\) state arising from the latter promotion might be the lowest-lying excited state, but that the corresponding \(1^3\AA\) state lies so far above the \(3^1\AA\) and \(1^1\AA\) states arising from the \(\pi^* \rightarrow n\) excitation to be of little relevance to the present study. However, they also emphasise the difficulty (at that time) of such triplet-state calculations and state that ‘no definite conclusion on the relative order of the triplet states’ can be drawn from these calculations. In what follows we begin by discussing the observed product yields, and their wavelength dependence, within a similar framework to that used when accounting for the UV photochemistry of HFCO\(_2\)H\(^{2,5}\) i.e. simply in terms of the two excited states arising from the \(\pi^* \rightarrow n\) excitation.

Symmetry arguments, analogous to those advanced in our recent considerations of the near-UV photochemistry of HFCO\(_2\)H\(^{4,5}\) suggest that ground-state HCO\(_2\)H molecules correlate with the ground-state products H + CO\(_2\)H(X\(^1\AA\)) whilst the photoexcited HCOOH(A\(^2\AA\)) molecules must correlate adiabatically with the lowest-energy excited set of products with overall symmetry A\(^1\). These correlations are shown schematically in Fig. 6. Lacking detailed \textit{ab initio} or spectroscopic information on excited states of the CO\(_2\)H (HOCO) fragment, we presume, as in FCO\(_2\)H, that they lie too high in energy to be relevant, given the excitation wavelengths used in the present studies and, consistent with existing thermochemical data, interpret the ca. 30 000 cm\(^{-1}\) dissociation energy as the threshold for forming ground-state H + CO\(_2\)H products.

We can envisage two routes by which the initially prepared HCO\(_2\)H(X) molecules might dissociate to these ground-state products: IC to the parent ground state or ISC to the T\(^1\) state. The lowest rovibrational levels of the S\(^1\) state fluoresce, but with a lifetime (ca. 50 ns) some one to two orders of magnitude shorter than the expected radiative lifetime.\(^{10}\) This indicates that HCO\(_2\)H molecules, even in the zero-point level of the S\(^1\) state, undergo some non-radiative decay process. The S\(^1\) → S\(^0\) fluorescence intensity is observed to reduce in the presence of an external magnetic field.\(^{9}\) This observation, and analogy with HFCO\(_2\)H\(^{2,5}\) suggests that the predominant non-radiative decay route for HCO\(_2\)H molecules in the lowest rovibrational levels of the S\(^1\) state is ISC to the T\(^1\) state. C–H bond fission in HFCO involves passage over (or tunneling through) an exit channel barrier on the T\(^1\) potential-energy surface. This barrier has been rationalised in terms of a
The association pathway remains a matter of some debate. Scalar and vi-roiding an estimate of the height of the energy barrier (again mates of the reaction enthalpy by 
This threshold energy exceeds the best thermochemical esti-
fragment at all wavelengths investigated in the present work.
range 250
3
energy. A barrier of this magnitude could also imply some role of
symmetry appropriate for non-planar conÐgurations.
Solid tie-lines show the parent Ðnitive correlations appropriate for
symmetries, whilst the dashed lines indicate the avoided crossings relevant to the present discussion that apply under the reduced (C
symmetry appropriate for non-planar conÐgurations.

tendency for alignment of the angular momentum vector of the OH(X) fragments and (iv) the distribution of OH(X) fragment 
recoll velocity vectors is isotropic. These conclusions appear to be largely independent of the choice of photolysis 
wavelength or, therefore, of the precise vibronic composition of the initially prepared HCO
molecules.

All these observations would be consistent with a fragmentation process that occurs over a timescale that is long com-
pared with the parent excited state vibrational (and rotational) period and, for this reason, Ebata et al.13,15 favoured S
IC and subsequent dissociation on the ground-state surface as the likely fragmentation route. As in HFCO, however, there is 
no obvious reason why the ground-state potential-energy surface should exhibit a barrier in this bond-Ðssion channel. For 
this reason, and because there is clear evidence that S
IS occurs at slightly lower excitation energies, it is worth considering whether this dissociation channel actually proceeds via the triplet surface. Indeed, given that S
IS occurs and the fact that the T
surface should 
correlate with the ground-state OH + HCO products, the only reason why dissociation on the T
surface should not contribute to the observed OH(X) yield would be if the exit channel barrier is too high. However, the S
surface should also correlate with the ground-state OH + HCO products and Brouard et al.8 have argued (by analogy with 
HNO
) that most (if not all) of the observed products actually arise via C—O bond fission on the S
surface and that the fragmentation timescale, the parent vibrational energy redistribution and the eventual energy disposal in the products are all manifestations of the detailed topology of this S
potential-energy surface. Such a view is supported by the quantum yield measurements,11,12 which indicate channel (3) to 
be the dominant fragmentation route following photolysis at 222 nm. Careful study of parent absorption linewdiths under jet-cooled conditions, and the way in which they vary with excitation energy, might provide evidence for the stepped 
reduction in excited-state lifetime that would be likely given the onset of such an adiabatic fragmentation route.

Finally, we consider the other observed primary X—H bond-Ðssion channel, for which we propose an appearance 
threshold of ca. 224.85 nm, ca. 5400 cm
above the deduced bond dissociation energy. At this point we should mention the possibility that this substantial yield of slow H atoms is associated with C—H bond fission, leading to formation of electronically excited CO
fragments. Short of being able to conÐrm, or reject, the presence of an excited electronic state of the CO
fragment lying ca. 9000 cm
above the ground state, it is difficult to comment further on this possibility, but analogy with FCO suggests that such an explanation is unlikely.

Our favoured explanation involves the primary O—H bond-Ðssion process (5). Ab initio theory28 and experimental 
measurements of the photoelectron spectrum of HCO
2
dCO
negative ions28 reveal the near degeneracy of (and vibronic coupling between) the ground (2A
1
) and first excited (2B
2
) states of the formyloxyl radical, both of which have planar C
equilibrium geometries and both of which will transform as 2A
in the distorted (C
) point group. The second excited state, of 2A
symmetry (2A
in C
symmetry) lies only ca. 4300 cm
above the ground state.28 The correlation diag-
ram (Fig. 6) illustrates one way in which the experimental observations might be satisÐed. The ground state of HCO
should correlate with the ground-state products H + HCO2B1A
(2A
), whilst the photoexcited HCO
1A
(2A
) molecules should correlate diabatically with the second excited asymptote H + HCO
B2A
(2A
). This latter correlation must be crossed by another tie-line linking the H + HCO
B2A
(2A
) products with a higher energy 1A
state of HCO
(ceivably the 1A
state arising from the
π+π excitation). This crossing will manifest itself as a

![Fig. 6 Schematic correlation diagram for the fragmentation of HCOOh](https://example.com/image.png)
conical intersection (with respect to the out-of-plane bend) between these two excited singlet potential-energy surfaces as shown in Fig. 6.

Thus, we propose that HCO\(_2\)H(\(A\)) molecules dissociate on the lower energy of these two excited-singlet adiabatic potential-energy surfaces, to yield H + HCO\(_2\) products in their \(\tilde{X}\) and/or \(\tilde{A}\) states. Such a picture provides an explanation for: (i) the yield of these products relative to those attributable to the C–H bond-fission channel. No argument based on available phase space or product state densities, such as might apply if both fragmentations occurred on the \(T_1\) surface, could accommodate such a large showing from this higher-energy product channel. (ii) The observed barrier in this exit channel, the actual magnitude of which will be influenced by the extent of configuration mixing as the molecule evolves along the O–H dissociation co-ordinate.

The comparative narrowness of this feature in the TKER spectrum suggests that most of the energy associated with the barrier to the \(H + HCO_2\) back-reaction is released as product translation. The finding that these products exhibit a recoil velocity distribution characterised by a small positive \(\beta\) value is, at first sight, surprising, given the perpendicular nature of the \(S_1\)–\(S_0\) transition. The likely explanation for this observation rests on the fact that the parent transition involves a pyramidal–planar geometry change, the resulting \(S_0\) molecules are therefore created with substantial out-of-plane bending motion (which may well be amplified by the conical intersection), which carries through into out-of-plane recoil of the H atoms.

Such a conclusion suggests that the value of \(\Phi\) measured at 222 nm,\(^{11,12}\) just above the appearance threshold for channel (5), might well be close to its maximum and that future measurements at shorter excitation wavelengths might well show a decline as the alternative pathway (5) becomes increasingly competitive. It also allows determination of a refined value for the enthalpy of formation of the formyloxyl radical: \(\Delta H^\circ_{(HCO_2)} = -119.5 \pm 3\) kJ mol\(^{-1}\), where the quoted error bounds allow for uncertainties both in the experimentally determined dissociation energy (\(\leq 1\) kJ mol\(^{-1}\)), and in the exact value of \(\Delta H^\circ_{(HCO)}\).

**Conclusions**

This work is concerned with fragmentation pathways leading to the formation of H atoms following photoexcitation of jet-cooled HCOH molecules in the wavelength range 216–241 nm. It complements previous studies of the OH(\(X\)) and, to a lesser extent, the HCO(\(\tilde{X}\)) fragments arising via the competing dissociation pathways (3).\(^8,10,12,15\) We observe features attributable to primary O–H and C–H bond fission [channels (5) and (4), respectively] and to H atoms resulting from secondary photolysis of HCO(\(X\)) fragments arising via channel (3), and deduce dissociation energies for both of the primary bond fissions: \(D_h(H\rightarrow CO2H) \approx 30,000\) cm\(^{-1}\) and \(D_h(HCOO\rightarrow H) = 39,080 \pm 100\) cm\(^{-1}\). Consideration of all the available data, and comparison with recent photochemical investigations involving the isoelectronic molecule HFCO, suggests that HCOH molecules in their S\(_1\) excited state decay via a number of competing decay pathways. C–H bond fission is an exoergic process for all levels of the S\(_1\) state. As in HFCO, however, this process is deduced to occur on the triplet surface (accessed by ISC), and to involve passage over (or tunnelling through) an exit channel barrier. Two further fragmentation channels, (3) and then (5), open as we ascend in energy. Both are deduced to involve passage over exit channel barriers. Correlation arguments do not preclude either, or both, of these processes occurring on the triplet surface after ISC, but the observed dynamics and the deduced efficiencies of both fragmentation pathways encourage the assumption that both occur predominantly on the S\(_1\) surface. Further insight into the photochemistry of formic acid, and the competition between the various possible non-radiative and dissociative decay channels available to HCO\(_2\)H(\(S_1\)) molecules, should be provided by further PTS experiments involving the partially deuteriated species HCO\(_2\)D and DCO\(_2\)H, by \textit{ab initio} calculations of relevant portions of the various excited-state potential-energy surfaces, by further high-resolution measurements of the jet-cooled \(S_1 \leftrightarrow S_0\) excitation spectrum of HCOH (concentrating particularly on the variation of transition linewidth with excitation frequency) and by measurements of the wavelength dependence of the various product quantum yields.

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