State-selective photodissociation dynamics of formaldehyde: Near threshold studies of the H+HCO product channel

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The laser-induced photodissociation of formaldehyde in the wavelength range 309 < \lambda < 330 nm has been investigated using H (Rydberg) atom photofragment translational spectroscopy. Photolysis wavelengths corresponding to specific rovibronic transitions in the $\tilde{A}^1A_2 \rightarrow \tilde{X}^1A_1$ 2$^{14}2$, 2$^{24}2$, 2$^{24}2$, 2$^{24}2$, 2$^{24}2$, 2$^{24}2$, and 2$^{24}2$ bands of H$_2$CO were studied. The total kinetic energy release spectra so derived can be used to determine partial rotational state population distributions of the HCO cofragment. HCO product state distributions have been derived following the population of various different $N_K$ levels in the $\tilde{A}^1A_2$, 2$^{24}2$, and 2$^{24}2$ states. Two distinct spectral signatures are identified, suggesting competition between dissociation pathways involving the $\tilde{X}^1A_1$ and the $\tilde{a}^3A_2$ potential energy surfaces. Most rovibrational states of H$_2$CO($\tilde{A}^1A_2$) investigated in this work produce H+HCO($\tilde{X}^2A'$) photofragments with a broad kinetic energy distribution and significant population in high energy rotational states of HCO. Photodissociation via the $\tilde{A}^1A_2$ 2$^{24}2$ 1$_{1,1}$ (and 1$_{1,0}$) rovibrionic states yields predominantly HCO fragments with low internal energy, a signature that these rovibronic levels are perturbed by the $\tilde{a}^3A_2$ state. The results also suggest the need for further careful measurements of the H+HCO quantum yield from H$_2$CO photolysis at energies approaching, and above, the barrier to C–H bond fission on the $\tilde{a}^3A_2$ potential energy surface.


INTRODUCTION

Despite several decades of intense study, formaldehyde and its derivatives continue to be the focus of much scientific research.\textsuperscript{1–5} The basis of this interest lies in the many and diverse scientific subdisciplines to which formaldehyde chemistry applies. Spectral signatures of H$_2$CO have been observed in chemical environments ranging from combustion processes\textsuperscript{6} to the interstellar medium\textsuperscript{7} and have provided a means of monitoring atmospheric concentrations of the molecule.\textsuperscript{8–13} Moreover, the photophysics of the perturbed excited rovibronic states of formaldehyde continues to elude a complete quantum chemical explanation. It is therefore not surprising that to spectroscopists the study of formaldehyde is particularly appealing.

A number of published computational studies\textsuperscript{7,14–17} serve to complement the experimental investigations. The small size and discrete energy level structure of formaldehyde has permitted mapping of its potential energy surfaces (PESs) with the most accurate quantum chemistry methods and has facilitated studies of molecular processes such as nonradiative electronic transitions and photofragmentation.\textsuperscript{18} It is hoped that the information garnered by following the progress of formaldehyde from its initial optically prepared state through to dissociation products via both experimental and \textit{ab initio} methods will help to elucidate which parts of the molecular Hamiltonian control H$_2$CO photochemistry.

Photoinitiated unimolecular decomposition of formaldehyde by UV excitation yields two distinct product channels:

$$\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO} \quad (1)$$

$$\rightarrow \text{H} + \text{HCO}. \quad (2)$$

The threshold energies for product channels (1) and (2) are \(\sim 27,720\) and \(30,328.5\) cm$^{-1}$, respectively.\textsuperscript{19–21} Both of these processes are thought to occur via radiationless decay from the $\tilde{A}^1A_2$ state of formaldehyde, and both processes have been studied previously.\textsuperscript{3,19,22–26} Here, we focus on the radical product channel.

A 1983 review by Clouthier and Ramsay discusses much of the historical spectroscopic information regarding formaldehyde,\textsuperscript{27} though several articles have since refined this information.\textsuperscript{1,28–31} Key to our discussion of the photochemical processes that generate the formyl radical are the $\tilde{X}^1A_1$, $\tilde{A}^1A_2$, and $\tilde{a}^3A_2$ electronic states of formaldehyde (also referred to as the $S_0$, $S_1$, and $T_1$ states, respectively, illustrated in Fig. 1) and the interactions between them. Although electronically forbidden, the $S_1 \rightarrow S_0$ transition shows...
energy increases, however, the competition between dissociation mechanisms is influenced by several factors.

For this reason, the formyl radical product pathway should evolve from an $S_0$ dominated dissociation mechanism at energies far below the $T_1$ barrier to a $T_1$ dominated mechanism at energies above this barrier.

In terms of product state distributions, the $S_0$ and $T_1$ dissociation pathways may be expected to yield very different photofragment internal energies. Internal conversion on the $S_0$ pathway leads to randomization of parent internal energies prior to dissociation, thereby favoring "statistical" quantum state population distributions in the photofragment products. That said, Suits and co-workers have recently demonstrated that the CO fragments are formed with a bimodal rotational state population distribution, with a high $J$ component attributable to a "roaming" H atom channel—essentially an intramolecular hydrogen abstraction following an (energetically frustrated) attempt at C–H bond fission on the $S_0$ PES. In contrast, H+HCO products formed as a result of coupling to the quasibound $T_1$ PES are expected to have high kinetic energies and only low levels of vibrational and rotational excitation. Measurement of, and observations of variations in, product state distributions ought thus to offer insights into photodissociation mechanisms in the region of the $T_1$ barrier. In this study, we examine HCO product state distributions arising as a result of C–H bond fission following the population of specific rovibrational levels in the $^1A_2$ state of formaldehyde.

![Schematic potential energy surfaces for HCHO as a function of H–CHO bond distance. Both the $S_0$ and $T_1$ states correlate to the H+HCO radical products. Excitation to $S_1$ levels above the dissociation threshold can result in H+HCO formation either via internal conversion to high vibrational levels of $S_0$ or by intersystem crossing to the $T_1$ state. The dashed line at $\approx 27720$ cm$^{-1}$ indicates the onset energy for the formation of molecular products. Adapted from Ref. 21.](image)

S$\text{1} \rightarrow$ S$\text{0}$ IC can yield both the H$_2$+CO and H+HCO products, provided minimum threshold energy requirements are met. S$\text{1} \rightarrow$ T$\text{1}$ ISC, on the other hand, produces H+HCO exclusively. As a consequence, competition between the IC and ISC HCO formation mechanisms results, wherein dissociation occurs predominantly on the $S_0$ PES at threshold energies, whereas at energies near (and above) the $T_1$ barrier dissociation could occur on $S_0$ and/or $T_1$. This competition between dissociation mechanisms is influenced by several factors, which include (but are not limited to) (1) $S_1$-$S_0$ and $S_1$-$T_1$ coupling matrix elements, (2) $T_1$ barrier height, (3) proximities, densities, and widths of near-resonant $T_1$ energy levels and, below the $T_1$ barrier, (4) $T_1$ tunneling probabilities.

The spectral region between 31 000 and 33 000 cm$^{-1}$ is of particular interest since the minimum energy pathway over the $T_1$ barrier is predicted at $\approx 32 350$ cm$^{-1}$.

In this region, photodissociation channels can be accessed via the $S_1$-$S_2$ $^3\Delta_g (\tilde{v}=31 531.5$ cm$^{-1})$, $^2\Pi_g (\tilde{v}=31 803.2$ cm$^{-1})$, and $^2\Sigma^+_g (\tilde{v}=32 334.6$ cm$^{-1})$ vibronic bands. To the low wave number end of this region, $S_1$-$T_1$ coupling is expected to be small due to the low density ($\approx 0.3$ $T_1$ states/cm$^{-1}$) and relatively narrow widths of near-resonant $T_1$ states. With increasing energy, however, $T_1$ quantum state widths are expected to increase due to lifetime broadening as a result of quantum tunneling until, at energies above the $T_1$ barrier, $S_1$-$T_1$ coupling occurs via the $T_1$ dissociation continuum. In comparison, Stark level-crossing experiments have shown that $S_0$ quantum state widths are broad in this spectral region and that the density of $S_0$ states is expected to be significantly higher. Nevertheless, $S_1$-$S_0$ coupling matrix elements are expected to be much smaller than those describing $S_1$-$T_1$ coupling. For this reason, the formyl radical product pathway should evolve from an $S_0$ dominated dissociation mechanism at energies far below the $T_1$ barrier to a $T_1$ dominated mechanism at energies above this barrier.

**EXPERIMENT**

The H atom (Rydberg) atom photofragment translational spectroscopy (PTS) studies were performed using a modified version of the experimental apparatus that has been described previously.

The experiments required that three laser beams, which have been detailed previously, be spatially overlapped in the center of the interaction volume, where they intercept a skimmed, pulsed, molecular beam of formalddehyde, seeded in argon. Nascent H atoms produced by the photolysis laser pulse are excited in a two-photon, double resonant excitation scheme to a Rydberg state with a high principal quantum number ($n \approx 80$). H atoms are first excited with Lyman-$\alpha$ radiation (121.6 nm generated by frequency tripling 364.7 nm radiation in phase matched Kr and Ar) from their $n=1$, 1s state to the $n=2$, 2p level. A second photon (365 nm) then further excites the electron to a high-$n$ Rydberg state. "Rydberg tagged" H atoms with recoil velocities along the TOF axis travel under collision-free conditions to the detector (Johnston multiplier, type MM1-SG), where they are field ionized and their time of arrival recorded. Unwanted H$^+$ ions formed by 121.6 nm plus 364.7 nm absorption are extracted by applying a potential difference (50 V cm$^{-1}$) between a pair of annular electrodes positioned normal to the time of flight (TOF) axis above and below the
interaction volume. The H (Rydberg) TOF resolution was improved in this study by placing a 30×5 mm$^2$ slit shaped mask over the detector aligned with its long axis perpendicular to the molecular beam propagation axis. To detail the benefits of this mask, the resolution limits of the experiment are discussed in the Appendix.

Paraformaldehyde (prilled) was obtained commercially (Aldrich, 95%) and packed into a 7 µm stainless steel inline filter (Swagelok). Dried MgSO$_4$ was placed in a second filter further downstream, and both chemicals were kept in place with glass wool plugs. The filters were arranged behind the pulsed nozzle (in the order H$_2$CO, MgSO$_4$, and nozzle), and this entire arrangement was heated resistively to ~70 °C. The temperature was monitored with two thermocouples, positioned on the source oven and at the front of the nozzle. The paraformaldehyde liberates monomeric formaldehyde and water on heating. The MgSO$_4$ acts as a desiccant to absorb this water and stop the nozzle from clogging.

Ar ($\sim$2 bars) was passed through the filters and the pulsed valve to form a pulsed supersonic expansion of H$_2$CO. The composition of the molecular beam was investigated by introducing a small TOF mass spectrometer within the apparatus, so that the interaction volume is positioned centrally within the first acceleration region, and using the 121.6 nm radiation as a photoionization source (for any species with ionization potential $E_i \leq 10.2$ eV). In order to confirm the presence of H$_2$CO in the beam and to probe the beam temperature, action spectra for forming H$^+$ ions via the fragmentation channel yielding H+HCO radicals were recorded. In the absence of the photolysis laser beam there was negligible signal. When the photolysis laser was introduced to the experiment, the H atoms formed by the photolysis of H$_2$CO were ionized by 121.6 nm radiation and, by necessity, its 364.7 nm precursor also.

The dissociation energy for the hydrogen atom and formaldehyde radical product channel, $D_d$(H–CHO), $=30.328.5 \pm 0.5$ cm$^{-1}$, and the most accurate $ab$ initio calculations to date place the maximum of the $S_0$ state in the 31 000 and 33 000 cm$^{-1}$ region [Ref. 22] facilitates an effective coupling between the $S_1$ and $S_0$ PESs. In comparison, $\tilde{A}^1A_2$ and $\tilde{a}^3A_2$ coupling matrix elements are much larger (0.01–0.1 cm$^{-1}$), but their state mixing probability is offset by the relatively low density of $T_1$ states in the region [Ref. 22]. Moreover, because the $T_1$ PES is quasibound in the H+HCO near-threshold region, $T_1$ resonances are relatively sharp, leading to very localized regions of $S_1$-$T_1$ overlap. Coupling between the $S_1$ and $T_1$ PES is expected to increase with energy since $T_1$ resonances are increasingly broadened by quantum tunneling effects, and the transition state $S_0$ PESs in the $T_1$ dissociative continuum. Probing the dissociation characteristics in the near- and above-barrier regions should therefore provide a means of examining the dynamic signature for dissociation on the $T_1$ PES.

Both the $T_1$ and $S_0$ states correlate to radical products at infinite C–H bond distances. The $S_1$ PES couples to high vibrational levels of the electronic ground state (also referred to as $S_0$ levels) via vibronic perturbations provided by the nuclear kinetic energy operator $\hat{T}_N$. The magnitudes of the $S_1$-$S_0$ matrix elements are expected to be less than $10^{-4}$ cm$^{-1}$.

The dissociation energy for the hydrogen atom and formaldehyde radical product channel, $D_d$(H–CHO), $=30.328.5 \pm 0.5$ cm$^{-1}$, and the most accurate $ab$ initio calculations to date place the maximum of the $T_1$ barrier (transition state) to dissociation between 1710 and 2130 cm$^{-1}$ above the radical product asymptote. The PESs in this region are shown in Fig. 1, and the H$_2$CO($\tilde{A} \rightarrow \tilde{X}$) bands in this region are highlighted in the room temperature absorption spectrum shown in Fig. 2. The strongest features in the near threshold region for the H+HCO formation are the $\tilde{A}^1A_2 \rightarrow \tilde{X}^1A_2$, $2^3\Sigma^0_0^+$, $2^3\Sigma^0_0^-$, $2^1\Pi_1^0$, and $2^1\Sigma^1_0^+$ vibronic bands, while the $2^1\Sigma^1_0^+$ (overlapped with $1^3\Pi^0_0^+$) vibronic band spans the predicted energy of the exit channel barrier on the $T_1$ PES. Of particular interest in our attempt to probe the competition between the IC and ISC mechanisms of HCO formation are the $2^1\Sigma^1_0^+$, $2^1\Pi_0^+$, and $2^3\Pi_0^+$ band systems, as these transitions represent excitation to energy levels at or slightly below the $T_1$ barrier.

**RESULTS AND DISCUSSION**

The dissociation energy for the hydrogen atom and formaldehyde radical product channel, $D_d$(H–CHO), $=30.328.5 \pm 0.5$ cm$^{-1}$, and the most accurate $ab$ initio calculations to date place the maximum of the $T_1$ barrier (transition state) to dissociation between 1710 and 2130 cm$^{-1}$ above the radical product asymptote. The PESs in this region are shown in Fig. 1, and the H$_2$CO($\tilde{A} \rightarrow \tilde{X}$) bands in this region are highlighted in the room temperature absorption spectrum shown in Fig. 2. The strongest features in the near threshold region for the H+HCO formation are the $\tilde{A}^1A_2 \rightarrow \tilde{X}^1A_2$, $2^3\Sigma^0_0^+$, $2^3\Sigma^0_0^-$, $2^1\Pi_1^0$, and $2^1\Sigma^1_0^+$ vibronic bands, while the $2^1\Sigma^1_0^+$ (overlapped with $1^3\Pi^0_0^+$) vibronic band spans the predicted energy of the exit channel barrier on the $T_1$ PES. Of particular interest in our attempt to probe the competition between the IC and ISC mechanisms of HCO formation are the $2^1\Sigma^1_0^+$, $2^1\Pi_0^+$, and $2^3\Pi_0^+$ band systems, as these transitions represent excitation to energy levels at or slightly below the $T_1$ barrier.

**FIG. 2.** Room temperature absorption spectrum of the relevant part of the HCHO ($\tilde{A}^1A_2 \rightarrow \tilde{X}^1A_2$) band system. The most intense vibronic band features are labeled, as are the threshold energy for the onset of the radical product channel and the $ab$ initio estimate for the $T_1$ transition state region. See Ref. 31 for details.
shown in Fig. 3 along with the corresponding H⁺ action spectra acquired during the excitation of the $\tilde{A}^1A_2 \rightarrow \tilde{X}^1A_1$ 20 and 40 bands. Immediately apparent is the H⁺ signal at wave numbers $/H_11021$ cm⁻¹, which might appear to contradict the accepted value for $D_0$/H20849$ H–CHO$/H20850$.$ These are, in fact, P-type excitations ($\Delta J=-1$) that terminate on energy levels above the lower limit for H-atom formation.

The spectral simulations shown in Fig. 3 allow determination of a rotational temperature $T_{\text{rot}}$ of 10 K for the parent formaldehyde molecules though it should be pointed out that there are differences between the experimental and predicted line intensities that still elude definitive explanation. Possible reasons for these intensity discrepancies include (i) photodissociation of the primary HCO products and (ii) resonance enhanced two-photon excitation of H₂CO followed by dissociation, both of which will enhance the experimental H⁺ signal at a given photolysis wavelength, and (iii) variations in $S_1$-level coupling efficiencies to $S_0$ and $T_1$ levels. Simulations of other vibronic bands produced $T_{\text{rot}}$ values of up to 15 K, so we deduced that the actual rotational temperature of the formaldehyde parent molecules was $\sim 10$–15 K. Setting the photolysis laser to wavelengths corresponding to specific rovibronic transitions in formaldehyde enabled photodissociation from specific, known $J_{K_a,K_c}$ levels in the $\tilde{A}^1A_2$ state. It is worth commenting here that, under these conditions, we were unable to detect any H atom signal at several wavelengths investigated in the earlier studies from Wittig’s group. Only by reducing the argon backing pressure were we able to observe H atom signal at $\tilde{\nu}=31$ 768 cm⁻¹, for example, which is one of the photolysis wave numbers for which data is reported in Ref. 19. PGOPHER simulations indicate that $T_{\text{rot}}$ must be $>50$ K in order that the ground state level involved in this transition has an appreciable population.

H atom TOF spectra recorded after the dissociation of the C–H bond were analyzed in terms of the total kinetic energy release (TKER) for the system. The TKER can be defined in terms of the TOF, $t_H$, of the H atom,

$$TKER = 1/2 m_H \left( 1 + m_H/m_R \right) \left( d/t_H \right)^2,$$

where $d$ is the distance between the laser interaction region and the detector, $m_H$ and $m_R$ are the masses of the H atom (1.0078 amu) and the HCO partner fragment (29.018 amu), respectively. The internal energy of the HCO fragment can then be established using conservation of energy arguments,

$$E_{\text{phot}} = D_0(H – CHO) + E_{\text{int}} + TKER,$$

where $E_{\text{phot}}$ is the photon energy and $E_{\text{int}}$ is the internal energy of the HCO fragment. The maximum kinetic energy release (minimum flight time) for the hydrogen atoms is available from
TKER_{\text{max}} = E_{\text{phot}} - D_0 (H - \text{CHO}), \quad (5)

(i.e., E_{\text{int}}=0). For photodissociation to H+HCO from the \( \tilde{A}^1A_2 \) \( 2^2A^3 \) vibronic level at 31 555 cm\(^{-1}\), the predicted TKER_{\text{max}} is 1226.5 cm\(^{-1}\) (corresponding to \( t_H = 70 \) \( \mu \)s). This prediction is in very good agreement with the TOF spectra shown in Fig. 4. Worth noting further, however, are the yet faster hydrogen atom signals in the 14–60 \( \mu \)s range. Though inconsistent with one-photon dissociation to H+HCO products, a two-photon dissociation involving the same dissociative channel (i.e., giving an available energy \( E_{\text{avl}} = 32 780 \) cm\(^{-1}\)) would produce hydrogen atoms with minimum \( t_H \sim 14 \) \( \mu \)s, in very good accord with the experimental observation. Further support for this interpretation stems from the fact that the near H+HCO threshold bands of H\(_2\)CO show fluorescent lifetimes of 6–10 ns,\(^{37}\) thereby indicating that the associated one-photon excited energy levels are potentially metastable resonant intermediates.

A closer inspection of the TKER spectral region corresponding to one-photon dissociation reveals a great deal of structure. This arises because the quantized nature of the formyl radical cofragment internal energies constrains the correlated hydrogen atom kinetic energies to values reflecting the HCO rovibrational structure throughout the available energy space. H atom TOF spectra may be replotted in terms of formyl radical internal energies according to Eq. (4). Using the HCO molecular parameters determined in the pure rotational microwave study by Blake et al.,\(^{38}\) a term energy stick spectrum was generated, which facilitated the assignment of the HCO internal energy spectrum. The stick spectrum was then given a \( \sim 2 \) cm\(^{-1}\) linewidth (Gaussian, full width at half maximum) and was converted to a TKER spectrum for direct comparison with H atom TOFs. Line intensities were then adjusted to match approximately those of the

![FIG. 4. TOF spectra of H atom photofragments resulting from the photolysis of jet-cooled formaldehyde molecules at (a) 31 555 cm\(^{-1}\), (b) 31 542 cm\(^{-1}\), (c) 31 540.5 cm\(^{-1}\), and (d) 31 523 cm\(^{-1}\). In each case the electric vector of the laser was aligned at 90° to the TOF axis.](image)

![FIG. 5. Formyl radical internal energy spectra for H\(_2\)CO photolysis at (a) 31 522.1 cm\(^{-1}\) and (b) 31 540.5 cm\(^{-1}\). The black traces are experimental spectra extracted from the H atom TOF data, while the gray traces are the fitted spectra used to extract product state distributions. Assignment combs are given to show HCO rotational energy levels with longer teeth marking \( N \) levels that are multiples of five.](image)
experimental spectrum using a Gaussian distribution for the
K stacks, and a second Gaussian distribution for the N-level
intensities within each K stack. To fit the simulated spectrum
to the experimental data a gradient descent method was used
to minimize least squares errors as a function of mean K
standard deviation in K, mean N, standard deviation in N,
spectral linewidth, and a small term to account for spectral
term energy offset. The integrated spectral intensity was then
normalized such that product state distributions could be ex-
tracted for each rotational level. Since there was no physical
reason to assume that the spectral line intensity distributions
were, however, notable exceptions to
this that seem to be directly related to dissociation from spe-
cific rovibronic levels in the A1A2 state. Figure 5(b), which
shows the internal energy spectrum of HCO following the
photolysis of H2CO at 31 540.5 cm−1, is one example. This
excitation wave number corresponds to an S1 − S0 R-type
transition to the A1A2 2243 1,1 rovibronic level. As Fig. 6
shows, this dissociation yields HCO products with an inte-
grated K state population distribution that is markedly differ-
ent from the “more typical” distributions observed following
excitation to other A1A2 2243 rovibronic levels (such as the
20,2 level [Fig. 5(a)]. The concentration of population in low
internal energy states following dissociation from the A1A2
2243 1,1 level is consistent with the mechanism for dissociation
on the T1 surface proposed by Wittig and
co-workers,19,22 suggesting that the A1A2 2243 1,1 level is
directly perturbed by the a3A2 state. This situation may also
be described by estimating the fraction of Eavl partitioned
into the product internal energy (Eint). An analysis of TKER
spectra obtained following excitation within the A→ X 2241/2
band at wave numbers other than 31 540.5 cm−1 gives an
average value of Eint/Eavl=0.29(7)±0.03(1), whereas disso-
ciation via the 2241 1,1 level gives Eint/Eavl=0.19(4). The
errors given in brackets for the Eint/Eavl ratios are one stan-
dard deviation as determined by our fitting routine. Such
analyses necessarily underestimate the Eint/Eavl ratio since
the present experimental setup precludes detection of H at-
oms with near zero recoil velocities. Similar cold rotational
distributions were found when dissociating via the A1A2
2241 1,1 and 1,0 levels. Unfortunately, further confirmation
of the dissociation signatures from these levels could not be
made via other transitions due to lack of transition intensities
or blending with other spectral lines.

In general, only levels characterized by the same quan-
tum number J and the same overall symmetry species can
perturb one another.40 Given that there is no direct spin-orbit
interaction between the A1A2 and a3A2 states, Stevens and
Brand have discussed two mechanisms by which perturba-
tions can occur. The selection rules for such perturbations can be summarized in terms of vibronic symmetries and rotational quantum numbers:

(i) vibronic spin-orbit mechanism

(a) \( \Gamma_c^u \times 3 \Gamma_c^v \supset \Gamma_c^u \): \( \Delta J=0, \Delta N=0, \pm 1, \Delta K_a=0, \Delta K_c=\pm 1 \),

(b) \( \Gamma_c^u \times \Gamma_c^v \supset \Gamma_c^u \): \( \Delta J=0, \Delta N=0, \pm 1, \Delta K_a=\pm 1, \Delta K_c=\pm 1, \pm 3 \)

(c) \( \Gamma_c^u \times \Gamma_c^v \supset \Gamma_c^u \): \( \Delta J=0, \Delta N=0, \pm 1, \Delta K_a=\pm 1, \Delta K_c=0, \pm 2 \)

(ii) spin-orbit-orbital-rotation mechanism

(a) \( \Gamma_c^u=\Gamma_c^v, \Gamma_c^v=3 \Gamma_c^u \): \( \Delta J=0, \Delta N=0, \pm 1, \Delta K_a=0, \Delta K_c=\pm 2 \).

Since the \( \nu_2 \) and \( \nu_4 \) normal modes of the \( \tilde{A} 1A_2 \) state have \( a_1 \) and \( b_1 \) symmetries, the overall vibronic symmetry species for the \( 2^3 \) and \( 2^1 \) levels is \( B_2 \) in both cases. In the absence of rotation, the three components of the triplet state have \( A_1, B_1, \) and \( B_2 \) spin-orbital symmetries. The rotational symmetries about the \( a, b, \) and \( c \) axes are \( a_2, b_1, \) and \( b_2 \), respectively. For the \( \tilde{A} 1A_2 \) state to perturb the \( \tilde{A} 1A_2 \) \( 2^3 \) and \( 2^1 \) levels, triplet state vibronic species of \( B_1, A_2, \) or \( A_1 \) symmetry must undergo \( a-, b-, \) or \( c\)-type Coriolis interactions. The \( A_1 \) spin component must therefore have \( b_1, a_2, \) or \( a_1 \) vibrational symmetry, the \( B_1 \) spin component must have \( a_1, b_2, \) or \( b_1 \) vibrational symmetry, and the \( B_2 \) spin component must have \( a_2, b_1, \) or \( b_2 \) vibrational symmetry to facilitate interaction with the \( \tilde{A} 1A_2 \) state via the above-mentioned Coriolis mechanisms. This implies that \( \tilde{A} 3A_2 \) vibronic levels of any symmetry can potentially perturb the \( \tilde{A} 1A_2 \) \( 2^3 \) and \( 2^1 \) levels. To perturb the \( \tilde{A} 1A_2 \) \( 2^3 \) level the triplet state would require \(-3650 \text{ cm}^{-1}\) of vibronic excitation, while \(-6620 \text{ cm}^{-1}\) of vibronic excitation is needed to achieve close resonance with the \( \tilde{A} 1A_2 \) \( 2^1 \) vibronic level. Several \( T_1 \) vibrational levels fall in this energy region, but until there is a better knowledge of the fundamental vibronic frequencies and anharmonicities for the \( \tilde{A} 3A_2 \) state the perturbing \( T_1 \) vibrational levels cannot be assigned unambiguously. What is clear, however, is that observation of such localized variations in the \( N, K \) level population distributions in the HCO products must imply rather stringent resonance requirements on these \( S_1-T_1 \) perturbations, i.e., that the \( T_1 \) resonance widths at these energies (below the top of the \( T_1 \) barrier) are narrow.

Several singlet-triplet perturbations in the \( 2^3 \) and \( 2^1 \) levels of formaldehyde have been previously observed by Ramsay and Till using magnetic rotation spectroscopy. However, their spectra were taken in a room temperature cell with a 10 Torr pressure of formaldehyde, and none of the excitations observed in our study were reported. Similar studies of the \( 4^3 \) and \( 4^1 \) bands by Kerr et al. also identified singlet-triplet perturbations in the \( \tilde{A} 1A_2 \) \( 4^1 \) and \( \tilde{A} 1A_2 \) \( 4^3 \) levels. A series of magnetically active lines involving \( J' =16-19 \) in several \( K_a \) levels of the \( 4^3 \) band suggests a singlet-triplet perturbation with selection rules \( \Delta J=0, \Delta N=0, \Delta K_a=0, \) and \( \Delta K_c=0 \) since near-resonant interactions governed by these selection rules could involve several successive values of \( K_a \), whereas a \( \Delta K_a=\pm 1 \) perturbation would likely affect only one or two \( K_a \) values. These perturbations were attributed to the \( F_2 \) spin component \( (J=N) \) of the \( \tilde{a} 3A_2 \) \( 4^1 \) \( 1^1 \) vibronic level. Given that the observed \( F_2 \) perturbations occurred at relatively high \( J \) values in the \( 4^1 \) level, it would stand to reason that the \( F_2 \) spin component \( (J=N-1) \) should cross the singlet manifold at low \( J \) levels and perturb those near-resonant rovibronic states following a \( \Delta K_a=\pm 1 \) selection rule. Since the \( \nu_2 \) harmonic vibrational frequencies for the \( \tilde{A} 1A_2 \) and the \( \tilde{A} 3A_2 \) states are similar, it is tempting to attribute the unique product state distributions arising from the dissociation of the \( \tilde{A} 1A_2 \) \( 2^3 \) \( 1^1,1,0 \) state to a perturbation involving the \( 2^3 1^1 0 \) \( J(J,K) \) level of the \( \tilde{A} 1A_2 \) \( F_3 \) spin component. Similar arguments can be made in an attempt to assign the triplet state that perturbs the \( \tilde{A} 1A_2 \) \( 2^1 \) \( 1^1,0,0 \) level. However, the large number of magnetically active lines observed in the \( 2^3 1^1 \) and \( 2^1 1^1 \) bands belies the presence of at least two (likely more) perturbing triplet levels.

When the \( \text{H}+\text{HCO} \) dissociation channel is accessed from the \( \tilde{A} 1A_2 \) \( 2^3 \) state, \( E_{\text{rot}} \) is sufficient that the first excited vibrational level \((v_1=1)\) of HCO can be observed in the TKER spectra. Wittig and co-workers suggested that the \( v_3 =1: v=0 \) population ratio provides another measure of the relative importance of dissociation via coupling to the \( S_0 \) and/or \( T_1 \) PESs, and a careful analysis of the present, better resolved TKER spectra lends some support to this proposal. As Table I shows, the vibrational state population ratio \( N_{v=1}/N_{v=0} \) [crudely estimated from the relative amounts of the signal with \( E_{\text{int}} \) respectively, above and below 1087 \text{ cm}^{-1} \) (the \( v_3=1 \) term value, after background correction) is consistently low (in the range 0.10–0.29) but is lowest when exciting via the \( 2^3 1^1,1,0 \) level, which, by virtue of the deduced rotational state population distribution, we deem to be heavily perturbed by the \( T_1 \) state. We recognize three systematic errors in these estimations of vibrational population ratios. Firstly, as noted previously, the present experimental setup precludes measurement of products with zero TKER. The measured TOF data were truncated at an upper limit of 159 \mu s, thereby excluding photofragmentation processes yielding products with TKER <238 \text{ cm}^{-1}. Secondly, the inverse square relationship between the measured H atom TOF and the product TKER can introduce an error in as much as any stray counts (that tend to appear randomly in

### Table I. \( N_{v=1}/N_{v=0} \), vibrational state population ratios in the HCO fragments formed following dissociation from various rotational levels of the \( \tilde{A} 1A_2 \) \( 2^1 \) vibronic state of HCO.

<table>
<thead>
<tr>
<th>Photolysis wave number (cm(^{-1}))</th>
<th>HCO ( \tilde{A} 1A_2 ) ( 2^1 ) rotational state(s)</th>
<th>( N_{v=1}/N_{v=0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>31 829.0</td>
<td>2(<em>{2,0}) and 2(</em>{2,1})</td>
<td>0.29</td>
</tr>
<tr>
<td>31 814.5</td>
<td>2(_{1,2})</td>
<td>0.29</td>
</tr>
<tr>
<td>31 812.8</td>
<td>1(_{1,1})</td>
<td>0.20</td>
</tr>
<tr>
<td>31 810.5</td>
<td>1(_{1,0})</td>
<td>0.10</td>
</tr>
<tr>
<td>31 798.0</td>
<td>3(_{2,3})</td>
<td>0.17</td>
</tr>
<tr>
<td>31 794.4</td>
<td>1(_{0,1})</td>
<td>0.21</td>
</tr>
<tr>
<td>31 793.5</td>
<td>2(_{0,2})</td>
<td>0.22</td>
</tr>
</tbody>
</table>
time) make a disproportionate contribution to the low TKER signal. To compensate for such effects, a linear background was subtracted as and when necessary from the measured TOF profiles prior to transformation to TKER. Obviously, any population ratios derived as above are sensitive to the extent of any such subtraction. Finally, HCO($v=0$) products formed in rotational states with high $N, K$ quantum numbers have comparable energies to those of HCO($v_j=1$), low $N$ products, and thus appear at comparable TKERs. As Fig. 6 shows, dissociation via the $S_0$ PES results in a broader rotational state population distribution. Our attribution of all signal with $E_{	ext{kin}}>1089$ cm$^{-1}$ to HCO($v_j=1$) products is thus likely to result in an overestimation of the $N_j/N_0=0$ ratio in such cases and may explain, at least partly, the trends in this ratio displayed in Table I.

The observed vibrational excitation in the HCO products qualitatively supports the conclusions reached in an earlier study by Yin et al.$^3$—specifically that HCO products formed from $A^1A_2$ state levels that are perturbed by the $\tilde{a}^1A_2$ state carry population in the $3^1$ level, even when formed following excitation at energies above the $T_1$ transition state. In their study, Yin et al. employed laser-induced fluorescence (LIF), on the $B^3\Sigma^+ \leftrightarrow \tilde{X}^3\Sigma^+$ transition, to probe the HCO fragments in their ground and $3^1$ levels. Of necessity, these were probed via different vibronic transitions (the $0_0^0$ and $3_0^0$ bands). Although experimental considerations such as dye laser power curves were taken into account when relating the relative intensities of these bands, Yin et al.$^3$ had no rigorous means of accounting for differences in the Franck-Condon factors for the two transitions in their analysis. Bruna et al.$^{45}$ and Sappey and Crosley$^{46}$ both suggested that the Franck-Condon factors for the two probe transitions should be significantly different, with those for the $3_0^0$ band as much as two to three times larger than that for the $0_0^0$ band. We therefore provide complementary insight into vibrational branching ratios since, as discussed above, the intensity intensities of the H vibrational bands in the HCO TOF signals are largely unbiased against the vibrational state of the HCO cofragment.

As Fig. 7 shows, dissociation from the $A^1A_2$ $2^1S_1$ state of formaldehyde yields HCO radical fragments with both rotational and vibrational energy distributions more similar to those observed following dissociation via the $A^1A_2$ $2^1S_1$ $1_{1,1}$ and $A^1A_2$ $2^1S_1$ $1_{1,0}$ states. Such internal energy distributions are consistent with a dissociation mechanism directly accessing the $T_1$ surface. Given the energies of the rotational levels in question, $S_1\rightarrow T_1$ coupling likely occurs via the $T_1$ dissociative continuum. A quantitative analysis to extract product state distributions could not be undertaken for this series of data, however, due to a much poorer signal to noise ratio, the origin of which is twofold. First, as is apparent in Fig. 2, the absorption cross section for the $A^1A_2 \leftrightarrow \tilde{X}^1A_1$ $2^1S_1\rightarrow 0^1S_0$ transition is less than that of the $2^3\Sigma^+_j$ or $2^3\Pi^+_j$ vibronic bands, resulting in less excited state population and thus a reduced H atom PTS signal. Second, the increased fragment kinetic energies mean that the TOF spectra of interest now overlap with the tails of the two-photon dissociation signal. Nevertheless, qualitatively, it is clear that there is again some population (10%–30%) in the HCO $3^1$ vibrational level when exciting via the $2^1S_1$ transition. Thus, we concur with another conclusion reached by Yin et al.$^3$ i.e. that the extent of the HCO product rotation provides the most robust signature of the fragmentation pathway. Dissociation via the $S_0$ PES results in the population of high $N, K$ states of HCO, whereas $S_1\rightarrow T_1$ coupling leads to HCO products with low internal excitation.

Finally, it is worth considering the possible significance of the present findings with regard to the quantum yield, $\Phi_R$, of the radical (i.e., H$\rightarrow$HCO) channel following UV photolysis of formaldehyde and its dependence on wavelength $\lambda$. Both of these photofragments contribute to HO$_2$ production in the upper troposphere.$^{47}$ The current NASA recommendation$^{48}$ shows $\Phi_R$ (298 K) $> 0$ once $\lambda < 341$ nm, rising to a value of $\sim 0.75$ by $\lambda \sim 315$ nm and thereafter remaining flat down to $\lambda \sim 300$ nm. The maximum value of $\Phi_R$ ($\sim 0.75$) stems from early end-product analysis measurements by Horowitz and Calvert;$^{49}$ subsequent determinations of $\Phi_R$ (Refs. 50–54) have generally involved relative measurements, which have been put on an absolute scale by normalizing to the early results. The current consensus$^{48,52}$ is that ISC is the dominant nonradiative decay process from $S_j$ levels lying at energies above the exit channel barrier on the $T_1$ PES and that its rate (relative to $S_1 \rightarrow S_0$ IC) should increase with increasing energy. Such is consistent with the present observation that the HCO products resulting from dissociation via the $2^1S_1$ level are internally cold and with the findings of an early PTS study (at 283.9 nm) which failed...
to detect any CO attributable to the molecular (H₂+CO) product channel: signal to noise and resolution issues led to the (conservative) conclusion that (1−Φₚ) < 0.1 at this wavelength.²⁵ We do note, however, that excitation at a narrow range of energies just above the T₁ barrier region (32 700−32 900 cm⁻¹) has been shown to yield H+HCO products with an E_int distribution more characteristic of a dissociation mechanism involving S₁→S₀ IC.²² Since neither the S₁ nor T₁ states of H₂CO correlate directly with molecular products, IC from S₁ is the only straightforward route to forming H₂+CO. It is thus not easy to reconcile the consensus view that the fraction of S₁ molecules decaying via the IC route falls with increasing excitation energy (as the rate of S₁→T₁ ISC grows), with the recommendation that Φₚ is wavelength independent, yet nonlimiting, in the wavelength range 310 > λ > 290 nm.⁴⁸ There remains a need for further careful studies of the branching into radical and molecular products [channels (1) and (2)] and their wavelength dependence.

CONCLUSIONS

The benefits of using a strategically masked detector in photofragment translational spectroscopic studies of H₂CO are demonstrated. The H atom TOF spectra display resolved structure, attributable to the population of rotational states of the formyl partner fragment. A spectral analysis has allowed extraction of HCO rotational state population distributions following H₂CO dissociation via selected rotational levels of the H₂CO(S₁) molecules to radical products involves radiationless transfer to the T₁ and/or S₀ PESs. Consistent with early H (Rydberg) PTS studies,¹⁹,²² we find that HCO products arising via the S₁→S₀ IC route are characterized by broad rotational state population distributions, whereas those formed via dissociation on the T₁ PES (following S₁→T₁ ISC) are concentrated in low N, K states. These different product energy disposals have allowed the identification of specific parent S₁ levels, within both the 2²⁴S and 2²⁴P vibronic states, that appear to be perturbed by the T₁ state. Both fragmentation pathways lead to 10%−30% vibrational excitation of the HCO product, qualitatively supporting conclusions reached in a recent LIF study of the HCO products resulting from H₂CO photolysis in the same UV wavelength region.⁵³

Recent studies by Tulej et al.⁵⁶ serve to emphasize the fact that we must be resigned to some variation in product state distributions derived in different H₂CO photodissociation studies. The parent absorption spectrum consists of many predissociation broadened lines; thus, the relative populations projected to the S₁ state in any photoexcitation process will depend not just on the precise excitation laser wavelength and bandwidth, but also on the parent rotational temperature since the latter will affect the relative weightings of the various components contributing to any blended absorption lines. Given that each (υ′,J′,K′ₐ) level of the S₁ parent yields its own specific H+HCO product state distribution (PSD), the observed PSD following any given photolysis event has to be viewed as a superposition of the PSDs characteristic to each of the dissociating levels, weighted by the respective Boltzmann populations, line strength factors, etc.

ACKNOWLEDGMENTS

After completion of this work we were alerted to further work from Yin et al. (Ref. 57). The authors would like to thank Professor Scott Kable, Professor Andrew Orr-Ewing, Dr. Pablo Bruna, Dr. Colin Western, Chris Clouthier, Nick Treffik, and Maryam Moradi for helpful discussions and aid in data processing. Two of the authors (W.S.H. and H.-P.L.) would like to acknowledge funding from the Natural Sciences and Engineering Research Council of Canada (NSERC), and H.-P.L. acknowledges financial support through the Gordon and Jean Southam Fellowship of the Association of Commonwealth Universities. The Bristol authors are grateful to EPSRC for the award of the LASER portfolio grant.

APPENDIX: IMPROVEMENT OF THE TOF RESOLUTION

The H (Rydberg) TOF resolution was improved in this study by placing a 30×5 mm² slit shaped mask over the detector. The slit was aligned with its long axis (30 mm) perpendicular to the molecular beam propagation axis. To appreciate the benefits of this mask, the resolution limits of the experiment must be discussed. Some of these topics have been dealt with previously in theses from the Bristol research group.⁵⁸−⁶⁰

Experimentally recorded H atom TOF spectra are analyzed in terms of TKER for the system in question as outlined in Eq. (1). A small correction must be made to the derived TKER to account for the difference between the laboratory (lab) and center of mass (c.m.) frames of reference due to the velocity component of the molecular beam orthogonal to the TOF axis. For an expansion in Ar (vbeam ~ 557 m s⁻¹) the c.m. to lab correction factor is ~13 cm⁻¹ and varies as shown in Fig. 8.
The TOF to TKER or velocity transformation assumes that all H atoms striking the detector travel a distance \(d\) from the interaction region. In reality, a detector of finite area is required to achieve sufficient signal to record TOF spectra with an acceptable signal to noise ratio. H atoms striking opposite edges of the detector have different flight distances. This implies that H atoms with slightly different kinetic energies can reach the detector at the same time. The distance traveled by an H atom that hits the edge of the detector, \(d_e\), is greater than that for a particle that strikes the center, \(d\), thereby introducing an uncertainty to the TKER distribution and limiting the experimental resolution.

For the circular detector the flight distance from the interaction point to the detector edge is given in terms of the detector radius \(r\) by

\[
d_e = \sqrt{d^2 + r^2}.
\] (A1)

The uncertainty in the TKER for a given flight time then becomes

\[
\Delta \text{TKER} = \frac{1}{2} \left[ \frac{m_H}{m_R} \left( 1 + \frac{m_H}{m_R} \right) \frac{d^2}{r^2} \left( \frac{r^2}{d^2} \right) \right] = \text{TKER} \left( \frac{r^2}{d^2} \right).
\] (A2)

For a 15 mm radius detector and a flight length of 371 mm the uncertainty in the TKER resolution limit is 1.6 cm\(^{-1}\) for a TKER of 1000 cm\(^{-1}\). In the case of HCHO, the peak widths of the internal energy states of HCO are ~2–3 cm\(^{-1}\). One must also account for the relative orientation of the detector to the expanding Newton sphere. In the lab frame the face of the detector lies perpendicularly to the TOF axis, but in the c.m. frame the contribution of the velocity of the molecular beam causes the H atoms to approach the detector obliquely. This is particularly significant for slow H atoms and results in an increased uncertainty in the flight distance. The uncertainty is largest for H atoms traveling with velocities comparable to the molecular beam speed but can be the limiting factor in resolution even with relatively fast H atoms. Note that this effect is only relevant in the molecular beam propagation axis as the beam has a negligible velocity component in all other coordinates.

The angle \(\alpha\) between the molecular beam axis and the TOF axis in the c.m. frame is

\[
\alpha = \tan^{-1} \left( \frac{v_{\text{lab}}}{v_{\text{beam}}} \right).
\] (A3)

The offset \(x\) of the c.m. along the molecular beam axis is defined in terms of the flight distance to the center of the detector as

\[
x = \frac{d}{\tan \alpha} = \frac{d v_{\text{beam}}}{v_{\text{lab}}}.
\] (A4)

The effective flight lengths to the center (\(d_{c,m.}\)) and the edges of the detector [\(d_{c,m.}^N\) (far), \(d_{c,m.}^N\) (near)] in the c.m. frame depend on this offset, which in turn depends on the relative H atom lab frame and molecular beam velocities (see Fig. 9).
with the mask. The technique is, therefore, not appropriate for systems with absorption cross sections much smaller than that of formaldehyde nor is it necessary for systems where rotational resolution is not achievable due to a higher density of states. Regardless of the shape of the detector, slow H atoms are underdetected in this system. Simple correction factors, based on geometry, can be applied to the data to alleviate this minor complication.


See EPAPS Document No. E-JCPSA6-127-008727 for HCO fragment rotational lines between 31 518 and 31 815 cm⁻¹. This document can be reached via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).

