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Real-time picosecond clocking of the collision complex in a bimolecular reaction: The birth of OH from H+CO₂

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Picosecond (and femtosecond) photofragment spectroscopy¹⁻⁵ has recently provided time-resolved, state-to-state dynamics of molecular photofragmentation.⁶⁻⁸ The focus of these experiments was on unimolecular reactions, where two main issues are fundamental to the dynamics: the nature of the "half-collision" and the degree to which statistical theories account for the time evolution of product state distributions (PSDs).

In contrast to unimolecular fragmentation, bimolecular reactions involve a full collision, and the dynamics⁹ of the collision complex is crucial to the fate of product(s). Traditionally, these reactions have been studied by the crossed molecular beam scattering technique.^{10,11} From the anisotropy of the products' angular distribution (PAD) in the center-of-mass coordinate system it is possible to infer whether the reaction proceeds by the "direct-mode" (subpicosecond interaction time) or via a "long-lived" (few rotational periods) collision complex.^{12,13} In this regard, quasiclassical trajectory calculations on semiempirical potential surfaces¹⁴ and statistical theories¹⁵⁻²⁴ of formation and decay of collision complexes have been instructive. More recently, spectroscopic methods have been utilized,²⁵⁻²⁷ but the main body of experimental information²⁸⁻³⁰ has come from *post-collision* observables, i.e., PSDs (via chemiluminescence³¹ and LIF³²), PADs,³³ and products' polarization.³⁴

In this Communication, we report the first direct (real-time) measurement of product formation from a bimolecular reaction: the birth of OH from the hot atom reaction H + OCO.³⁵⁻³⁷ The reaction steps are: H + CO₂ → HOCO → HO + CO. In our pump-probe experiments, a picosecond laser pulse initiates the reaction via photodissociation of the van der Waals (vdW) molecule IH...OCO, prepared in a seeded supersonic beam expansion. The "clocking" of the reaction is accomplished by the use of a picosecond probe pulse (for OH LIF monitoring), delayed in time with re-

spect to the initiation pulse (Fig. 1). UV photolysis of such a vdW precursor molecule ensures that the initial H velocity (~20 km s⁻¹) is preferentially directed along the hydrogen bond to the OCO, limiting the range of impact parameters³⁸⁻⁴⁰ and "orienting" the reactants.³⁸⁻⁴² The essential element in our experiment is that the UV photolysis picosecond (pump) pulse acts as a precise trigger setting off the H atom "projectile," thus establishing the *zero of time* for the bimolecular collision.

The experimental apparatus is similar to that employed in Refs. 6-8. The seeded molecular beam was obtained by expanding mixtures of 5% HI and 8% CO₂ in He (*P* ≈ 1800 Torr). The beam was characterized by electron impact (15-30 eV) TOF mass spectrometry. The mass spectra displayed peaks for HI, CO₂, HI·CO₂, (CO₂)_n and very little of HI·(CO₂)₂. Care was taken to trap I₂ (at -15 °C) before nozzle expansion. The complex HI·CO₂ concentration was typically 3%-5% relative to HI.

The picosecond pump pulse (239 nm) was generated by mixing the second harmonic of the 616 nm light with the 1.06 μ of a YAG laser. The probe was the second harmonic of the 616 nm pulse. The cross correlation between 616 and 308 nm was obtained using a LiIO₃ crystal. The probe was tuned to the Q₁(1) transition of OH using a cell of H₂O₂.⁷ On-resonance enhancement for OH LIF was evident from probe wavelength tuning experiments. Typically, for the molecular beam *X/D* ~ 40. The OH signal level was <0.2 photons/pulse. Following Wittig *et al.*,^{38,39} care was taken to optimize the 1:1 vdW complex in the expansion. Signal processing and treatment of the data followed Refs. 6-8.

The experimental results are displayed in Fig. 2. The rise time of the OH signal after deconvolution is found to be ~5-15 ps. This first direct observation of the time evolution of the nascent product of a bimolecular reaction represents the transient decay time of the collision complex, formed with

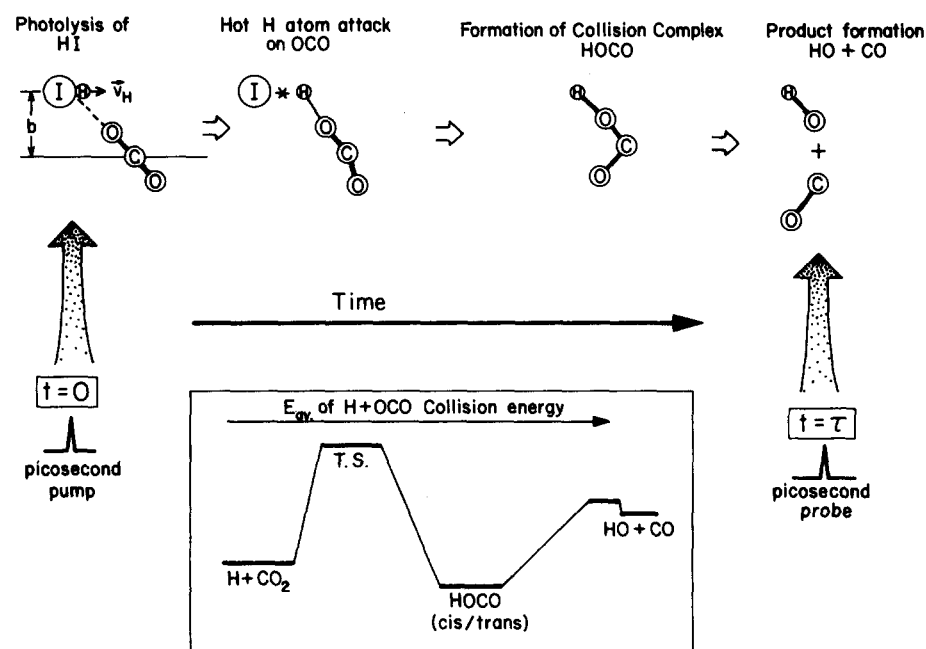


FIG. 1. Scheme of the experiment and potential energy surface (PES) of the bimolecular reaction $\text{H} + \text{CO}_2$. The picosecond photolysis pulse initiates the hot-atom reaction forming the HOCO collision complex. This dissociates to yield the OH product which is detected by the probe picosecond laser pulse delayed by a time τ with respect to the pump. The insert is a simplified picture of the PES taken from theoretical and experimental work (see the text).

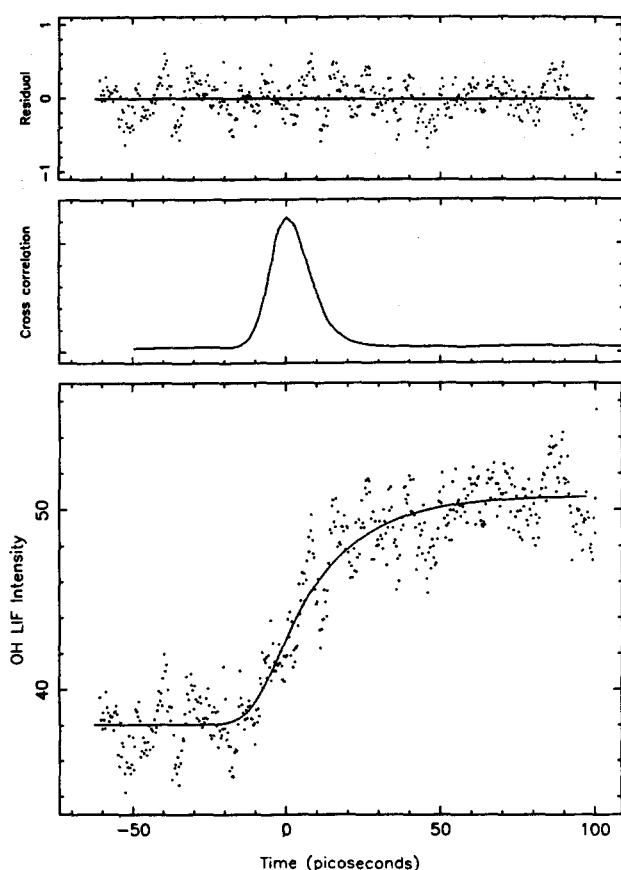


FIG. 2. Experimental results. Typical "transient" showing the OH LIF signal vs delay time τ . The experimental data points have been fitted (solid curve) assuming an exponential risetime (15 ps) and convoluting with the measured cross-correlation function (shown in the insert). The weighted residuals are also plotted (above) vs τ . From a number of experiments, the rise time range is 5–15 ps. More recent results (Ref. 47) deconvoluted with the proper system response function for pump and probe pulses, and obtained with improved S/N, give $\tau_r = 5 \pm 2$ ps.

the given available energy. For the photolysis wavelength used, the initial relative translational energy, E_{tr} ($\approx E_{av}$) of the $\text{H} + \text{OCO}$ reagents is calculated to be 200 kJ mol^{-1} assuming collinear incidence. The slower H atoms from the I^* branch, in contrast, yields $E_{tr} = 112 \text{ kJ mol}^{-1}$, only slightly above threshold.³⁵

For the subject reaction there is considerable knowledge of the potential surface based on theory⁴³ and experiment.^{35–40,44,45} The minimum energy path has an entrance barrier corresponding to a threshold energy of $\sim 105 \text{ kJ mol}^{-1}$,^{35,38} followed by a potential well supporting a complex, HOCO (itself studied by matrix isolation spectroscopy),⁴⁶ followed by a small exit barrier⁴⁴ to $\text{OH} + \text{CO}$. The initial H atom velocity is $\sim 200 \text{ \AA/ps}$ and the available energy of collision with CO_2 is above the transition state barrier.³⁹ Thus, the initial step is assumed to be complete within our pulse, but the rapid H-atom attack slows down depending on the vibrational motion in HOCO, which leads to a slower rate for the formation of $\text{OH} + \text{CO}$. The measured OH rise time can now be used to model the PSD and possible deviations from statistical behavior. Experiments at different photolysis wavelengths will yield the energy dependence of the formation and decay of the complex.

Planned experiments also include direct detection of the appearance of the HOCO and extension of the technique to the femtosecond time domain.^{5,48} This will make it possible to clock not only complex-mode bimolecular reactions, but also subpicosecond, direct-mode hot atom bimolecular reactions.

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NOTES

Ab initio calculation of the equilibrium geometry of NH_4^+ and NH_3 and the symmetric stretching potential of NH_4^+

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Although the NH_4^+ ion has been the subject of intensive investigation by high-resolution infrared spectroscopy over the last four years,¹⁻⁵ it has so far not been possible to derive an accurate value for the equilibrium bond length solely from experimental data. Estimates of r_e on the basis of experimental data and some assumptions have been made by Crofton and Oka,⁷ who reported a value of 1.026(5) Å and Nakanaga and Amano,⁴ who arrived at 1.021 ± 0.003 Å. Probably the most reliable *ab initio* values have been published by Yamaguchi and Schaefer.⁶ Their largest basis set, consisting of (10s,6p,2d) for nitrogen and (6s,1p) for hydrogen and contracted to [6,4,2/4,1], yielded $r_e = 1.0185$ Å at

the CI-SD level and 1.0217 Å when Davidson's correction was employed to approximately account for the effects of higher substitutions.

In this note, the results of more extended *ab initio* calculations at the CEPA⁷ level of approximation (coupled electron pair approximation) are reported for the equilibrium geometries of NH_4^+ and NH_3 . Two different basis sets were employed. The smaller one, which is already larger than the extended basis set of Yamaguchi and Schaefer⁶ and which consists of 73 contracted Gaussian-type orbitals, (11s,7p,2d/6s,2p) in contraction [8,5,2/4,2], was previously employed in CEPA-1 calculations for HN_2^+ ⁸ and pro-