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## COMMUNICATIONS

## Picosecond mass spectrometry of a collisionless photodissociation reaction

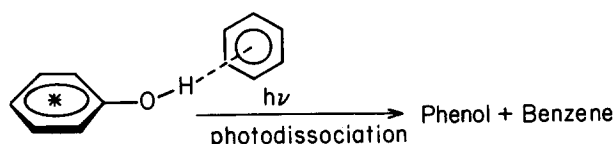
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(Received 11 February 1985; accepted 8 March 1985)

We wish to report on the direct observation (in real time) of a photodissociation reaction under collisionless conditions. This is achieved by the technique of picosecond mass spectrometry in skimmed molecular beams. In these experiments, three beams are overlapped: the two color picosecond pulses overlap with the molecular beam spatially and temporally and with each other spatially. One of the picosecond pulses (pump) excites the molecule to a vibrational state in  $S_1$  while the second one (probe) ionizes it. The fragments are analyzed with (TOF) mass spectrometry, similar to the detection schemes of Bernstein *et al.*<sup>1</sup> and Schlag *et al.*<sup>2</sup> This pump-probe configuration allows one to gate on the mass of interest while varying the time delay between the pump and probe using a Michelson interferometer; our time resolution is  $\sim 2$  ps, which allows for direct time measurements of the reaction rates and for studying the early-time fragmentation of the molecules.

The system here is the van der Waals phenol-benzene molecule:



where the binding energy between phenol and benzene is  $\sim 4$  kcal/mol.<sup>3</sup> This is a particularly attractive system for several reasons: (a) the phenol modes are very well assigned in  $S_1$ ;<sup>4</sup> (b) only phenol modes (OH or ring) can be excited, i.e., benzene is not part of the initial excitation; (c) similar to other hydrogen-bonded systems<sup>5</sup> the excitation spectrum of the phenol-benzene complex is displaced sufficiently from the monomer phenol.<sup>6</sup> Throughout the paper we will report results of the picosecond transients obtained by mass gating on the phenol-benzene (1:1) complex or phenol monomer.<sup>7</sup>

The laser system consists of a (R560) dye laser, synchronously pumped by a mode-locked  $\text{Ar}^+$  laser and amplified in three stages (R6G) by the second harmonic of a

$\text{Nd}^{+3}$ :YAG laser (20 Hz). Using a three plate birefringent tuning element, pulses are obtained with a 5 ps duration and  $\sim 1$  Å bandwidth. The amplified pulse energy is typically 1 mJ.

From a single dye laser pulse both the pump and probe wavelengths must be generated with the restrictions that the probe should not give a large ionization signal alone, and also that fragmentation of the complex upon ionization should be limited.<sup>7</sup> This was accomplished by anti-Stokes shifting the dye laser in methane ( $\Delta = 2914$   $\text{cm}^{-1}$ ). The pump is then generated by mixing the anti-Stokes beam with the dye laser in a KDP crystal. The probe is just the frequency doubled dye laser. The probe beam is separated from the pump and directed to a variable delay line, after which the two beams are recombined collinearly and focused into the supersonic beam. When the pump and probe are overlapped in space and time, an enhancement by a factor of 10 for the monomer signal (3–4 for the complex) could be obtained.

Our pulsed molecular beam is skimmed before the interaction region, a total of 10 cm downstream. For the monomer results, a backing pressure of 20 psi He is used and the sample is heated to 60 °C. To form the complex the carrier gas is flowed over benzene held at  $-15$  °C ( $\sim 8$  Torr). Under these conditions we could easily observe the complex bands which are shifted 147  $\text{cm}^{-1}$  to the red of the monomer, as reported by Ito and co-workers.<sup>6</sup>

Four bands are measured in both phenol and phenol- $d_1$  for which complex dissociation is evident, covering the range of 2050–2500  $\text{cm}^{-1}$  excess vibrational energy in  $S_1$  (see Fig. 1). At lower excess energies both the monomer and the complex display ns decays, which approach the electronic lifetime of phenol systems.<sup>8</sup> The monomer decay had little measurable change over the range of excess energy studied here.

The results reported here point to two important findings. First, the photodissociation rates (Fig. 1) over the range 0–2500  $\text{cm}^{-1}$  depend on the excess energy in the vibrational (benzene-type) modes of the phenol moiety, with an apparent

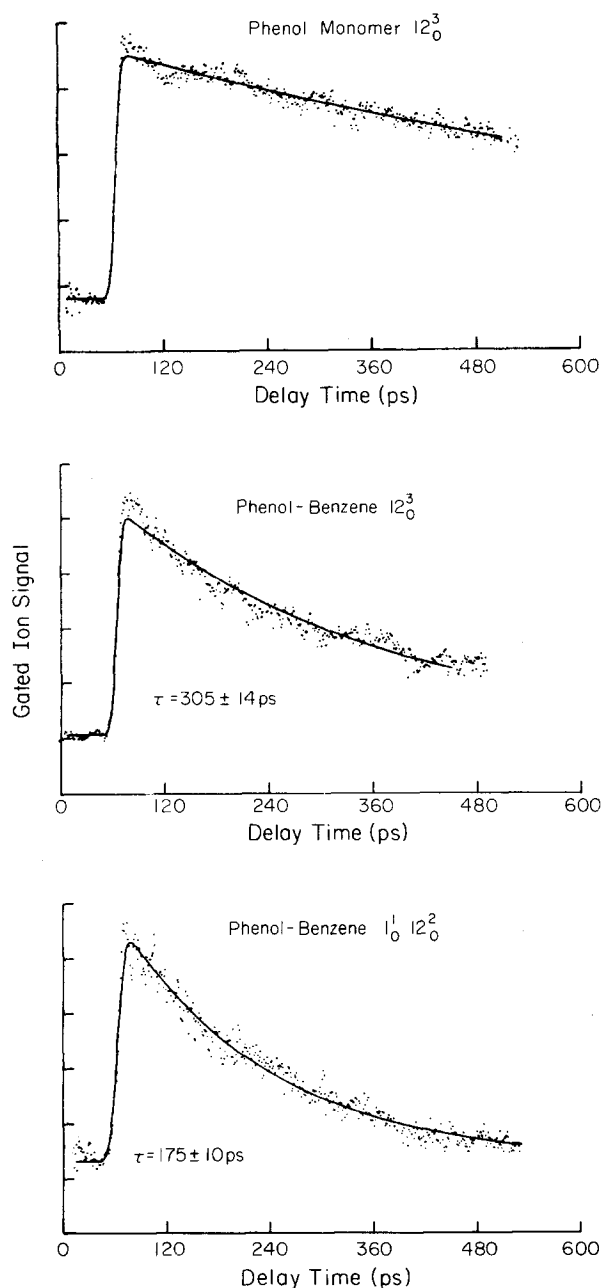


FIG. 1. Mass-gated ion signal as a function of pump-probe delay time. In the top figure the phenol  $12_0^3$  resonance ( $2345\text{ cm}^{-1}$  excess energy) is pumped and signal collected by gating at the monomer mass ( $m/e = 94$ ). The lower two figures were obtained by pumping the phenol-benzene complex ( $2345$  and  $2500\text{ cm}^{-1}$ ) and collecting signal at the complex mass ( $m/e = 172$ ). Our mass resolution is typically  $\pm 2$ . No signal was observed from ions of higher mass. Similar transients were obtained for different excess energies ( $E_x$ ) and the rates are:  $E_x(\text{cm}^{-1}) = 1564 (0.9\text{ ns}^{-1})$ ,  $2056 (2.1\text{ ns}^{-1})$ ,  $2207 (3.4\text{ ns}^{-1})$ ,  $2345 (3.3\text{ ns}^{-1})$  and  $2500 (5.7\text{ ns}^{-1})$ . At lower excess energies ( $0$ ,  $783$ , and  $1273$ ) there is essentially no decay on our time scale, i.e., rates are  $< 0.5\text{ ns}^{-1}$ .

threshold at  $\sim 4\text{--}5\text{ kcal/mol}$ . This is consistent with a ground state bond enthalpy of  $4.1\text{ kcal/mol}$ .<sup>3</sup> Second, when exciting the ring mode ( $\nu_{12}$ ) at an excess energy of  $\sim 7\text{ kcal/}$

mol we observe rapid dissociation (rate  $\sim 0.5 \times 10^{10}\text{ s}^{-1}$ ) of the complex. This observation indicates that photodissociation is preceded by an efficient redistribution of energy from the phenol ring mode to the reaction coordinate.<sup>9</sup> These rates translate to a linewidth of  $0.9\text{ GHz}$ . Previous work on the dissociation of van der Waals molecules have utilized linewidth measurements to obtain the rates which, depending on the system studied, varied from  $\text{ns}^{-1}$  to subpicosecond<sup>-1</sup>.<sup>10,11</sup> It will be extremely important to measure the linewidth of our system under very high resolution and compare with the results we report here.

In conclusion, these molecular beam picosecond mass-spectrometry experiments offer new opportunities for examining the real time behavior of reactions with a resolution of  $\sim 2\text{ ps}$ . We are currently examining the question of mode specificity of the reaction and exploring other systems, including larger complexes. This first report confirms our optimism about the sensitivity of the method which, unlike fluorescence studies,<sup>5,12</sup> provides excellent time resolution and assigns the mass of the species under examination.

This work was supported by the National Science Foundation under Grant No. DMR-8105034.

<sup>a)</sup> Camille & Henry Dreyfus Foundation Teacher Scholar.

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<sup>7</sup>Some of the bound complexes are fragmented in the ionization process. However, this is a function of the probe laser alone and as such is independent of the delay time.

<sup>8</sup>In cyclohexane the phenol  $S_1$  lifetime is  $2.1\text{ ns}$  [I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules* (Academic, New York, 1971).] Our phenol monomer lifetimes at low excess vibrational energies ( $< 1600\text{ cm}^{-1}$ ) are comparable to the solution value, and the complex decays are even longer. No attempt is made here to provide accurate values for these ns decays as our time window of interest here is on the ps time scale.

<sup>9</sup>Direct excitation of the phenol OH stretch, which is along the reaction coordinate axis, would be extremely interesting but unfortunately is beyond the blue edge of our laser tuning range at present.

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