

TABLE I. Resonance frequencies (MHz) and homogeneous triplet spin dephasing rates (μs^{-1}) of the zero-field transitions of $[\text{Rh}(\text{bpy})_3]\text{Cl}_3$ in the lowest triplet state.

	ω_{ij}	T_M^{-1}	$(k'_i - k'_j)^2, \text{rel}^a$
$2 E (T_y \leftrightarrow T_z)$	1049	0.25 ± 0.08	1
$ D - E (T_z \leftrightarrow T_x)$	2161	0.33 ± 0.15	1
$ D + E (T_y \leftrightarrow T_x)$	3215	~ 1.3	4

^aRelative radiative decay constants according to Refs. 1 and 6: $k'_x = 1.0$, $k'_y = 0.2$, $k'_z = 0.59$.

conclusions emerge. First, the experiments for $\text{Rh}(\text{bpy})_3^{3+}$ in the $^3\pi\pi^*$ excited state show that the magnetic resonance spectrum can be studied to an accuracy of approximately 10^2 kHz, i.e., an improvement of the spectral resolution by at least three orders of magnitude with respect to its normal ODMR in zero field. Second, upon comparison of the T_M values with the lifetimes of the triplet sublevels (which were determined from microwave recovery experiments to be in the millisecond range⁶), it is concluded that homogeneous broadening of the metal–chelate zero-field ODMR transitions is not determined by population relaxation, but involves a pure dephasing process. Third, the $2|E|$ and $|D| - |E|$ transitions have comparable dephasing rates, whereas the phase relaxation for the $|D| + |E|$ transition is faster by a factor of 4. This result is compatible with a dephasing model, proposed by Zewail,¹⁰ which assumes pure spin dephasing to arise from elastic phonon scattering at the triplet state spin sublevels; the scattering cross section is determined by the admixture of singlet character into the triplet substate by selective spin–orbit couplings. According to this model, one anticipates⁶ that T_M^{-1} is proportional to the square of the difference in the radiative decay rate constants of the sublevels involved in the spin transition. In Table I we present the values of the radiative decay constants as determined from optically detected adiabatic rapid passage

experiments⁶; these result are in agreement with those given in Ref. 1. It is seen that, as in a number of other cases,^{11,12} the phase relaxation of the $\text{Rh}(\text{bpy})_3^{3+}$ complex ion in the $^3\pi\pi^*$ state is in agreement with the spin–orbit induced dephasing model. In addition, one might consider the influence of nuclear spin flippings, through second-order hyperfine couplings,¹³ on the triplet spin dephasing of the transition metal complexes. Such effects could be small, however, due to an effective quenching in zero field of the triplet spin magnetic moment of the transition–metal complexes in the T_1 state.^{13,14} Coherence experiments which investigate the influence of an external magnetic field on the triplet spin dephasing in the transition metal complex crystals and the pure pyridine and phenanthroline molecular crystals are currently in progress.

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Real-time femtosecond probing of “transition states” in chemical reactions^{a)}

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Transition state(s) (TS) of chemical reactions are fundamental in defining the region(s) of internuclear separation (R^*) on the potential energy surface (PES) at which the reagent molecule is “passing on” to products.¹ In contrast to the many successes in applying spectroscopies to the characterization of *stable* reagents and *stable* products, TS spectroscopy has been very limited, because of the TS ultra-short lifetime (few vibrational periods) and the very low

density of TS molecules that can be probed at R^* . Recently, elegant ideas of time-integrated emission,² absorption,³ and scattering⁴ spectroscopy have been developed to infer the dynamics of the TS. Here, we offer a real-time technique that, because of its time resolution (~ 40 fs), promises to provide direct information concerning the TS and the spectroscopy of reaction intermediates in the process of falling apart (dissociation) or forming a chemical bond (associ-

ation).

In this Communication, we describe the technique of femtosecond transition-state spectroscopy (FTS), and its first application to the reaction



where the TS in this case refers to the range of R (from 2.7 Å to many Å) for the unbound molecule on the excited surface. FTS relies on the following idea: If a femtosecond pulse is used to excite bound ICN molecules to an upper repulsive (C-I) surface $V_1(R)$, then a packet is formed at time zero on the PES. A second femtosecond pulse probes the birth of the CN fragment as a function of *time* and *wavelength* at different R 's (Fig. 1). A key point here is that the PES corresponding to fragment separation in the ground or excited electronic state be different with R ; changes in $V(R)$ have been shown to account for the red wing spectra in experiments involving dissociation and collision, and are expected to be general.⁵ With this "two-dimensional" arrangement (t, λ) of the pump-probe femtosecond photofragment method⁶ it is therefore possible to probe the dynamics of TS on the PES. To obtain details of the PES, the reader is referred to the important theoretical work of Heller,⁷ Kinsey,⁸ Shapiro,⁹ and the review by Polanyi.⁵

The femtosecond pulses were generated from a home-built CPM laser,¹⁰ which can provide pulses of ~ 40 fs duration following the design of Shank and colleagues. The pulse was then amplified in a four-stage dye-amplifier, built in our laboratory. After amplification, a prism pair was used to compensate for dispersion. The pump pulse (100–150 fs and

$\sim 0.15 \mu J$) was the doubled output of the red beam (612.8–616.8 nm, 2 nm width) and the probe pulse (~ 50 nJ) was generated by mixing the red light with the 1.06 μ radiation. Care was taken to measure the coherence time and duration of the amplified pulse prior to experimental measurements.

The linearly polarized pump and probe femtosecond pulses were then delayed in a Michelson interferometer and collinearly recombined to overlap in an ICN (0.2–0.05 Torr) slow flow gas system. The LIF of the CN ($B^2\Sigma^+ \leftarrow X^2\Sigma^+$)¹¹ transition was detected at right angles. We also detected fluorescence probing to the red (388.9–390.5 nm) of the free CN transition bandhead at 388.5 nm.

Figure 1 displays the transients obtained at different wavelengths. At the blue edge ($\lambda = 388.9$ nm), we observed a rise of the CN fluorescence.⁶ To the red of this wavelength ($\lambda = 389.5$ nm), we observe a rise and decay, in contrast to the previous case. The dramatic change in the shape of the transients for different probing wavelengths prompted the following check-type experiments: (i) power dependence of pump and probe, (ii) polarization dependence, (iii) absolute intensity of the transient signal, (iv) coherence interaction between pump and probe (different λ) pulses,¹² (v) gating of the CN fluorescence (emission vs scattering), and (vi) dependence of transients on pulse frequency and time characteristics. These experiments will be detailed elsewhere,¹³ but the important points here are that the appearance of the buildup/decay is wavelength dependent and the signal is (essentially) linear in pump or probe power.

The PES of the reaction has been discussed by a number of authors.¹⁴ For the bimolecular approach of CN and I, the repulsion at shorter R is expected to be less if the CN is electronically excited. Accordingly, the difference between $V_1(R)$ and $V_2(R)$ will decrease as R decreases. (In other cases it may increase.) Thus, for red wavelength probing we interrogate molecules at short R 's and for blue wavelength probing we interrogate (essentially) free CN molecules at large R 's. The transition gives the R^* region at which the fragments become free from each other. In a simple kinetic scheme, the TS is created with τ_1 and decays with τ_2 and from our transients this takes place on ≤ 200 fs. The terminal velocity in the center of mass is $\sim 2 \times 10^5$ cm/s. This means that $\{R^*\}$ is no more than ~ 4 Å; the I to CN center-of-mass distance is 2.75 Å at equilibrium. The TS, therefore, lives for about four times the vibrational period of the I–CN bond. On this time scale the parent ICN rotates (classically, $\langle J \rangle = 32$) only 7° —almost stationary.

The available energy E_{av} for the reaction in our experiment at $\lambda = 306$ (308) nm is $= 7122$ (6910) cm^{-1} . The kinematics of this reaction for the two channels (I and I^*) have been studied by many groups, and are referenced in recent papers.^{15–18} At the wavelengths of interest here we energetically favor the I channel because of the E_{av} .^{11(c)} The possibility of "trapping" at the vdW well and conical intersections^{14(f),15} do exist, and we hope that by careful λ and t dependence studies we will be able to obtain these differences. There are also the problems of distribution in R 's and the coherence effects which we ignored. The TS mentioned here represent series of configurations in $V(R)$ vs R space, and extension of the technique to the detection of TS as de-

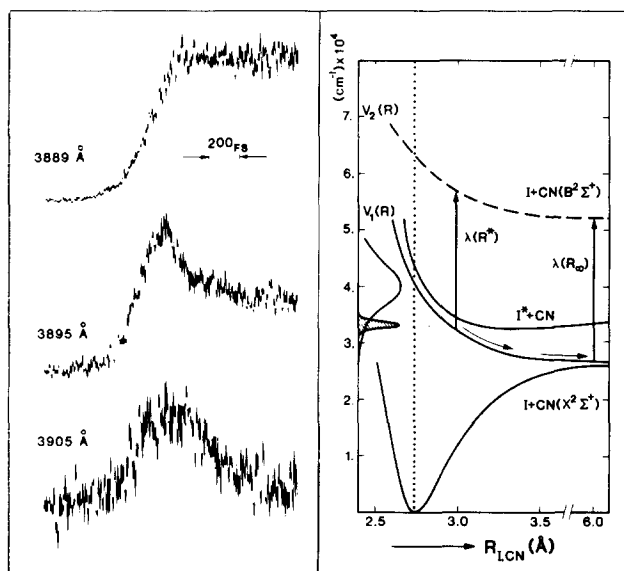


FIG. 1. (Right) Schematic for femtosecond probing of the transition state using a pump-probe (t, λ tuning) method. The PES are drawn to indicate the different probe wavelengths at "free" and "perturbed" CN transitions. The band on the vertical axis is the absorption spectrum (Ref. 18), and the profile of our pulse (shaded). The difference in $\lambda(R^*)$ and $\lambda(R_\infty)$ is not to scale, and the vdW wells are not shown. Note $\lambda(R^*)$ spans the different ranges of R (see the text). (Left) Femtosecond transients at the different probe wavelengths indicated. The time scale is also displayed. More detailed analysis (see Ref. 19) will be given later (Ref. 13). The experimental conditions are given in text, and these transients (each displayed on a different scale) were obtained under identical conditions except for tuning of the wavelength. The coherence time and autocorrelation traces were obtained after each scan.

fined in rate theory will also be a challenge.

In summary, these FTS experiments promise to provide real-time dynamics of TS and intermediates in unimolecular¹⁹ and special bimolecular²⁰ reactions.

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FT-ICR probes of silicon cluster chemistry: The special behavior of Si₃₉⁺

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The physical structure and reactivity of semiconductor surfaces is a subject of intense scientific and technological interest.¹ Particularly for network bonding substances such as silicon and germanium, it is known that extensive reconstruction of the near surface layers occurs in order to minimize the number of surface dangling bonds.² This restructuring, in turn, has a direct effect upon the surface chemistry. In order to develop a predictive model of semiconductor surface structure and chemistry, it will be essential to have a good understanding not only of the bulk bonding behavior and band structure of crystalline and amorphous phases, but also fundamental, predictive understanding of small clusters of the semiconductor where low coordination surface bonding dominates.³ This Communication describes an advance toward this question of cluster

structure and chemistry, involving a new FT-ICR cluster apparatus and chemical probes of the surfaces of large silicon cluster ions.

Fourier transform ion cyclotron resonance (FT-ICR) probes of silicon cluster ion chemistry are not new. Silicon is one of the few elements for which clusters can be made in a vacuum by laser vaporization. Over the past year, groups both at AT&T Bell Labs⁴ and the Naval Research Laboratory⁵ have produced small silicon cluster ions by laser vaporization of a silicon target directly inside the analysis cell of a commercial FT-ICR spectrometer, and explored a variety of interesting ion-molecule reactions as a function of cluster size. The central result from both groups is that in the range from Si₁⁺ through Si₈⁺ the reactivity towards most reactants (such as CH₃SiH₃, NO₂, H₂O, NH₃, O₂, etc.) decreases