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Citation: *The Journal of Chemical Physics* **88**, 6672 (1988); doi: 10.1063/1.454408

View online: <http://dx.doi.org/10.1063/1.454408>

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Femtosecond real-time observation of wave packet oscillations (resonance) in dissociation reactions

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(Received 22 February 1988; accepted 9 March 1988)

Femtosecond "transition state" spectra (FTS) of the elementary chemical reaction $\text{ICN}^* \rightarrow [\text{I} \cdots \text{CN}]^{\ddagger*} \rightarrow \text{I} + \text{CN}$ have previously been reported.¹ For these types of reactions on a repulsive surface the molecules are in the transition state (or more accurately in the states of the transition region) for only 100 fs or so. This has been evidenced by the rise and decay observed in the ICN experiments,^{1(a),1(b)} and deduced by simple theory.^{1(c)} If, however, in the process of falling apart, more than one degree of freedom is involved (vibrational or electronic), the system might exhibit a quasibound state (or resonance).² Manifestations of such a resonance in the real-time probing of fragment separation should be: (1) a delay in the appearance of free fragments, and possibly (2) the appearance of oscillations (reflecting the resonance frequency) of the wave packet of the dissociating molecules. An insightful wave packet approach to molecular photodissociation has been developed by Heller,³ and highlighted by the Kinsey experiments.⁴

With these ideas in mind, we attempted to obtain FTS of the reactions of alkali halides, where we expected such temporal features. The work by Berry and others⁵ has provided the foundation for the description of the surfaces. Because of the crossing between the *ionic* ground state and the *covalent* excited state, at fragment separation R_x , there are two channels for the reaction (Fig. 1). En route to products, the $[\text{M} \cdots \text{X}]^{\ddagger*}$ transition state molecules decide between these covalent and ionic channels. There are two limiting possibilities: either the packet is trapped on the *adiabatic* surface without crossing (resonance), or it crosses on the *diabatic* surface, as was the case for ICN. These two limits give rise to entirely different temporal behavior. If a resonance exists, the observed oscillation will give the detailed nature of the surface and coupling.

In this Communication, we report the real-time observation of strong wave packet oscillations (resonance) in a dissociation reaction. A strong resonance in the reaction of NaI, and a much weaker resonance in the reaction of NaBr, were seen. These observations were made by exciting the salt to the covalent state(s) along the M-X coordinate using a femtosecond pump pulse. A fs probe pulse was used at different delay times and wavelengths (t and λ spectra)¹ to detect the free product (on resonance with Na D lines at 589 nm) or perturbed Na (off-resonance) atoms. As discussed later, these results are, in general, consistent with the spectroscopy.

Figure 2 depicts the results for the two reactions using our femtosecond laser apparatus,¹ which utilized an amplified CPM laser⁶; continuum generation was used for the probe. For NaI, Fig. 2(I), the average oscillation period is 1.25 ps, which translates to 27 cm^{-1} . [Detecting on reso-

nance with the D lines, Fig. 2(II), the oscillations are integrated to a rise, just like the ICN experiment.] For NaBr, Fig. 2(III), this spacing is similar, but we observed severe damping. It is concluded that the packet for NaI is in an adiabatic well, and the crossing is inefficient. In contrast, for NaBr the crossing is much more effective and is less supportive of a bound state. The oscillations give a vibrational frequency of $0.8 \times 10^{12} \text{ s}^{-1}$. Since the oscillations for NaI are damped in $\sim 10 \text{ ps}$, the average probability of crossing on the outward phase per oscillation is 0.1.⁷ A more complete Landau-Zener calculation^{8,9} allows for the characterization of the quasibound vibrational/rotational states as was done by Schaefer *et al.*¹⁰ in their thorough application of Child's formalism¹¹ to NaI [crossing of $X^1\Sigma^+$ with $A(O^+)$]. Our results are consistent with the theory of Grice and Herschbach.¹²

The spectroscopy of NaI has been studied extensively⁵ in the Franck-Condon range (short R). Information at long R is obtained¹² from collision experiments like those done on

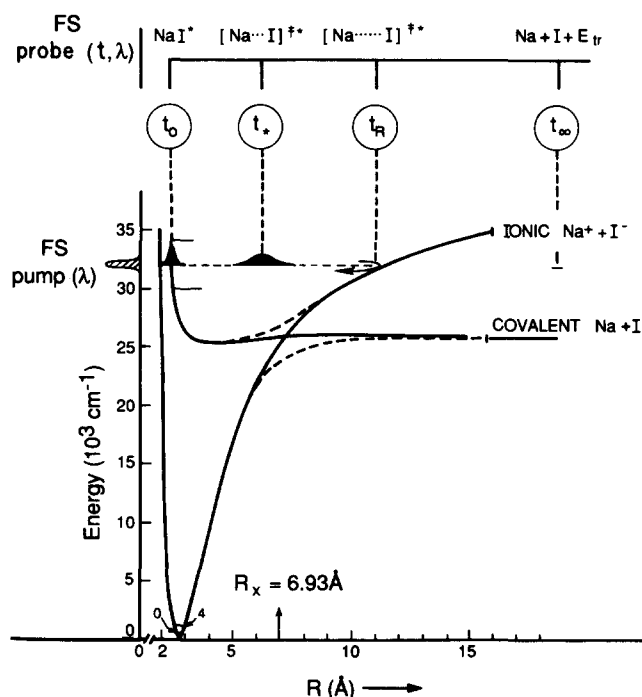


FIG. 1. A display of the potential energy surfaces involved, and the method of FTS. The times t_0 , t_* , t_R , and t_∞ refer to the time of evolution of packet as it moves along the coordinate R and spreads. At the top of the figure, the different transition configurations are given. The fs pump pulse was at 310 nm, and the probe was generated from a continuum ($\lambda = 560 \text{ nm}$ to $\lambda = 630 \text{ nm}$). The Na + I product states correlate with the states ($\Omega = 0^+$ and 1) of NaI and are depicted by the covalent surface in this figure. In our full report later we will discuss details of the dynamics on these surfaces.

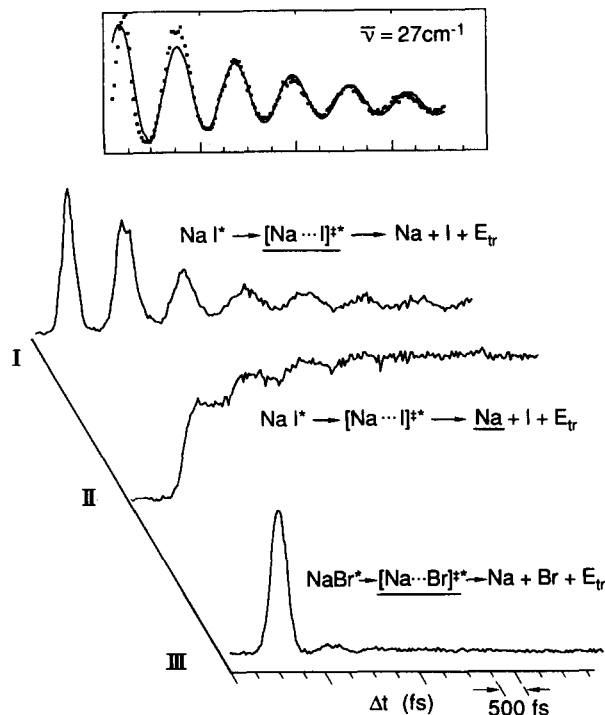


FIG. 2. Experimental results for the two reactions of NaI and NaBr. For the NaI reaction, we provide both the on-resonance and off-resonance Na atom detection (LIF), indicated by the underlining of the relevant species. Results, not shown, were also obtained at a number of other wavelengths, and will be detailed later. The modulation depth depends on the probe wavelength. The two salts (Aldrich, purity 99.9%) were degassed under vacuum for over 8 h (400 °C), and heated to ~ 600 °C. The experiments were also repeated at lower temperatures to check for dimerization. The signal is (essentially) linearly dependent on the probe and pump intensities.

(Na)K + I.¹³ A key feature in the broad spectrum of the excited state is the apparent interval of 36 cm^{-1} .^{5,14} The jet excitation spectrum,¹⁵ which shows rich progressions, has been used to deduce the shape of the well. Schaefer *et al.*¹⁰ have now provided a complete analysis of the spectrum of NaI in a bulb and also in a jet; they applied Child's predissociation formalism¹¹ and deduced the important molecular parameters. The spacings in their spectrum give $Y_{10} = 27.28 \text{ cm}^{-1}$ ¹⁰ and for states in the range of our excitation, the spacing is calculated to be 29 cm^{-1} , consistent with our results.

In our transients, there is damping and apparent increase in width of the oscillations with time, indicating some "dephasing" of the packet. Here, the lifetimes of the different levels depend on their involvement in the crossing (short-lived) or in the fluorescence (long-lived). An interesting question is how does the dephasing influence the observed dissociation rate. We are planning further work on modeling packet shape and dephasing, and the theoretical work by several authors will be of great help.¹⁶⁻²³ We also plan stimulated gain experiments from the upper surface to compare with Polanyi's wing emission experiments.²⁵

In conclusion, FTS¹ of systems with more than one degree of freedom promises to provide a real-time view of wave

packet decay and resonances in reactions. Since the recoil velocity is typically 1 km s^{-1} , our fs time window gives a view of these dynamics with $< 0.5 \text{ \AA}$ resolution for fragment separation.

This work was supported by the AFOSR (Grant No. 87-0071).

^{a1} John Simon Guggenheim Foundation Fellow.

^{b1} Contribution No. 7737.

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