MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.61 Physical Chemistry I
Fall, 2017

Professor Robert W. Field

Supplement to Lecture 32: Zewail Wavepacket Experiment

Suggested reading: Field pp 91-97.

Ahmed Zewail was awarded the 1999 Nobel Prize in Chemistry for “Femtosecond Transition State (FTS) Spectroscopy.” These experiments were described as the first time that the mechanisms of real intramolecular dynamics were ”clocked” in real time. In a pump/probe scheme, a femtosecond pump pulse creates a wavepacket on a repulsive or predissociated electronically excited V_1 potential energy surface at $t = 0$ by excitation from the $v = 0$ level of the electronic ground state, V_0 (ability to tune center energy of wavepacket by a small amount). After each excitation pulse, the time-evolving wavepacket is probed by a femtosecond pulse with a chosen center wavelength at a time-delay $t = \tau$. This delay time is scanned, pulse-by-pulse, to determine the time at which the center of the wavepacket crosses through the “Optically Coupled Region (OCR).” The probe pulse excites a portion of the wavepacket from the V_1 potential surface to a higher energy repulsive potential surface, V_2. The V_2 potential surface is repulsive, dissociating to an electronically excited fragment. The detected signal is the time-integrated $\sim$ 10 nanosecond lifetime fluorescence from this excited fragment. The dynamically relevant information is encoded in the intensity vs. τ of this time-integrated fluorescence, which samples the femtosecond passage of the wavepacket through the OCR that is selected by the center wavelength of the probe pulse.

The ICN photodissociation experiment shows the effect of the presence of the I atom on the frequency of the CN $\mathrm{B}^2\Sigma^+ - X^2\Sigma^+$ electronic transition. As the I atom moves away from the CN molecule, the energy of the CN electronic excitation increases from its value in the ICN molecule to that of the free CN molecule. Did we know this before doing the experiment? As the ICN bond stretches, the electronic structure of the CN moiety changes. This is mechanism!

The photodissociation of NaI is mediated by a covalent-to-ionic curve crossing. The diabatic (crossing) potential energy curves (solid lines) are the ones for which the electronic character does not change rapidly as the molecule traverses the internuclear distance of the curve crossing. The adiabatic curves (dashed lines), which are what "clamped nuclei" quantum chemical calculations generate, exhibit a rapid change of electronic character at the internuclear distance of the avoided crossing. As the molecule moves through the curve-crossing region, it must decide whether it is going to follow the diabatic or the adiabatic potential. Landau-Zener theory tells us the velocity-dependence of the probability of jumping across the energy gap between the ionic and the covalent adiabatic curves. If you drive too fast, you will be unable to stay on the road on a sharp curve. The sharpness of the curve is determined by the magnitude of the interaction matrix element between the diabatic potential curves. A very gentle curvature is the signature of a very large interaction matrix element. In the Zewail experiments, the velocity in the curve-crossing region can be systematically slightly adjusted by the choice of the center wavelength of the pump pulse. At an NaI energy far above that of the curve-crossing, the velocity in the crossing region is very large and the molecule stays on one of the diabatic potentials, in effect jumping the gap between adiabatic curves. At an energy near that of the curve crossing, the molecule would go through the crossing region slowly and stay on one of the adiabatic curves, with the result that the wave packet that is born covalent, is nearly 100% converted to ionic at the internuclear distance of the crossing. Zewail's NaI experiments provide a direct experimental determination of the internuclear distance of the curve crossing and an explicit illustration of Landau-Zener theory.

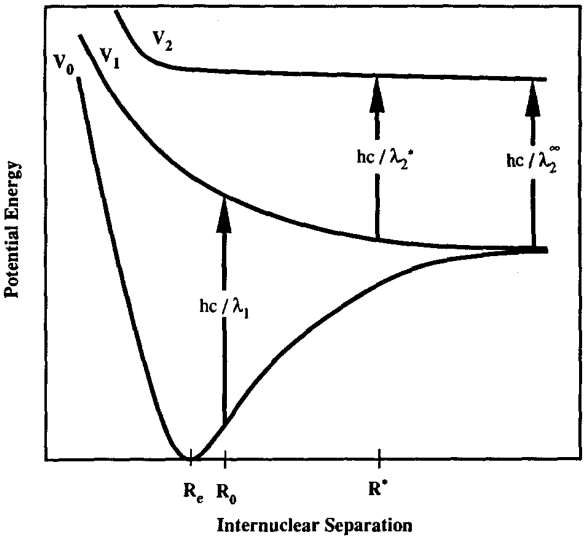

Figure 1: **Pump/Probe Scheme for Photodissociation of ICN** (Figure 1 of Ref. 24). This is a reduced dimension representation of three singlet potential energy surfaces of ICN: the bound ground electronic state, V_0 with minimum at R_e, an excited unbound state, V_1, which dissociates to $\mathrm{CN}(\mathrm{X}^2\Sigma^+)$ and $\mathrm{I}(^2\mathrm{P}_{3/2})$, and a higher energy unbound state, which dissociates to $\mathrm{CN}(\mathrm{B}^2\Sigma^+)$ and $\mathrm{I}(^2\mathrm{P}_{3/2})$. A $t = 0$ pulse from the pump laser, with center wavelength λ_1, excites a vertical turning-point-to-turning-point ($\mathrm{P}_0 = 0$, $\mathrm{P}_1 = 0$) transition at $R = R_0 > R_e$ to the V_1 potential surface. The wavepacket on the V_1 potential surface experiences a force in the increasing $\mathrm{R}_{\text{I-CN}}$ direction, which causes the $\mathrm{P}_{\text{I-CN}}$ momentum to increase monotonically with time. At $t = \tau$, a pulse from the probe laser, with center wavelength $\lambda_2^\star$ or λ_2^∞ probes for the arrival of the wavepacket at $\mathrm{R}_{\text{I-CN}} = R^\star$ or R^∞. The energy of the vertical (ΔR=0) and momentum-conserving (ΔP=0) transition also increases monotonically with time as the wavepacket travels outward on V_1. This $\mathrm{V}_2-\mathrm{V}_1$ transition is essentially an excitation of the CN B$-$X electronic transition in the presence of the departing I atom. The R= $\mathrm{R}_{\text{I-CN}} = R^\star$ Optically Coupled Region (OCR) is interrogated by a probe pulse with center wavelength $\lambda_2^\star > \lambda_2^\infty$, where λ_2^∞ is the wavelength of the free CN B$-$X $v' = 0 - v'' = 0$ band. The detected signal is CN B-X spontaneous fluorescence. Reproduced with permission from Figure 1 in M. J. Rosker, M. Dantus, and A. H. Zewail, "Femtosecond real-time probing of reactions. I. The technique," *J. Chem. Phys.* **89**, 6113–6127 (1988). Copyright 1988, AIP Publishing LLC.

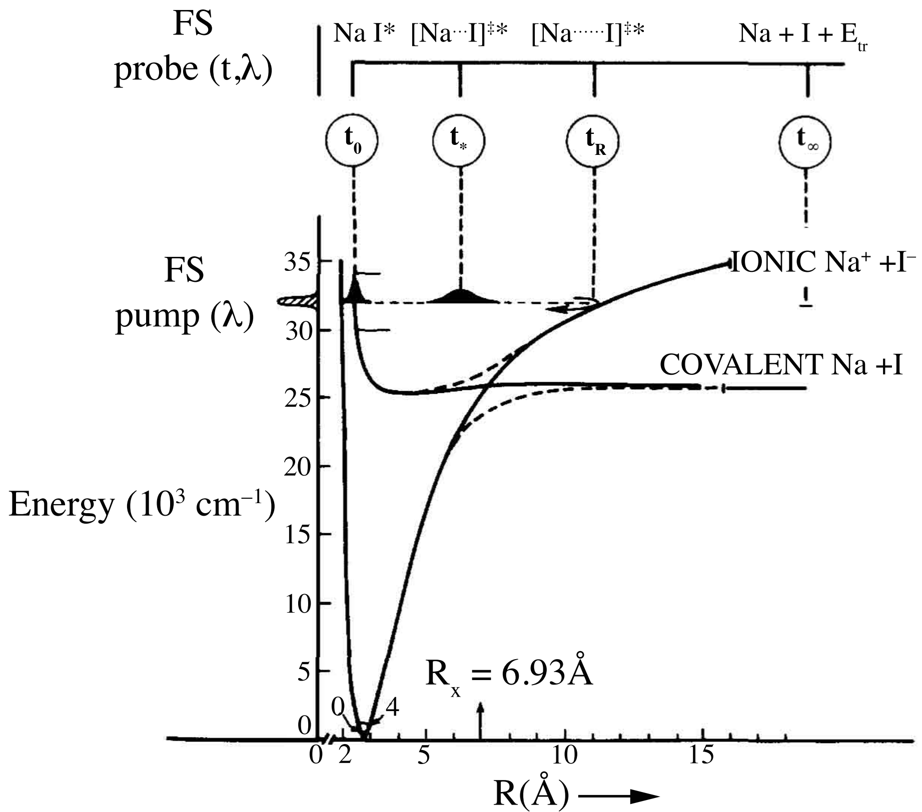

Figure 2: **Wavepacket Transit through an Ionic∼Covalent Potential Energy Curve Crossing in NaI** (Figure 1 of Ref. 26). The diabatic (solid lines) $\mathrm{Na}^+,\mathrm{I}^-$ and Na,I potential energy curves cross at $\mathrm{R}_x = 6.93$Å. The avoided crossing between the adiabatic potential curves is shown as dashed lines. At $t = t_0$ the 310 nm pump pulse creates a wavepacket at the inner turning point of the covalent (Na $^2\mathrm{S}$, $\mathrm{I}^2\mathrm{P}_{3/2}$) potential curve at $\mathrm{R}\approx\mathrm{R}_e(\mathrm{X}^1\Sigma^+)$ and P= 0. By adjusting the center wavelength of the pump pulse, the center total-energy (electronic plus vibrational) of the wavepacket can be adjusted between 30,000 and 34,000 cm^{-1}. The excitation energy of the ionic∼covalent curve crossing is $\sim 26,000\ \mathrm{cm}^{-1}$. The wavepacket is accelerated outward, passes through the curve-crossing region at $t_\star$, and bifurcates, one part traveling on the bound ionic potential and the other part traveling irreversibly outward on the unbound covalent potential. The ionic part is reflected at t_R at the outer turning point of the ionic potential, passes with P< 0 through the R= 6.93 Å curve crossing region where it bifurcates again, and the resultant ionic and covalent parts are reflected outward at the inner turning points of the ionic and covalent potential curves, respectively. Each outward passage of a wavepacket through the curve crossing region results in a wavepacket traveling irreversibly outward on the unbound covalent potential, eventually forming free $\mathrm{Na}(^2\mathrm{S})$ and $\mathrm{I}(^2\mathrm{P}_{3/2})$ atoms. The probe pulse (not shown) interrogates the dynamics by exciting $\mathrm{Na}(^2\mathrm{S}),\mathrm{I}(^2\mathrm{P}_{3/2})$ weakly-bound molecules to a higher energy repulsive electronic state that dissociates to $\mathrm{Na}(^2\mathrm{P}) + \mathrm{I}(^2\mathrm{P}_{3/2})$ atoms. Excitation at center-wavelength longer than 589 nm samples NaI molecules en route to full dissociation. Excitation centered at 589 nm provides what is essentially a time-integrated sample of the accumulation of the free $\mathrm{Na}(^2\mathrm{S})$ atoms. Reproduced with permission from Figure 1 in T. S. Rose, M. J. Rosker, and A. H. Zewail, "Femtosecond real-time observations of wave packet oscillations (resonance) in dissociation reactions," *J. Chem. Phys.* **88**, 6672–6673 (1988). Copyright 1988, AIP Publishing LLC.

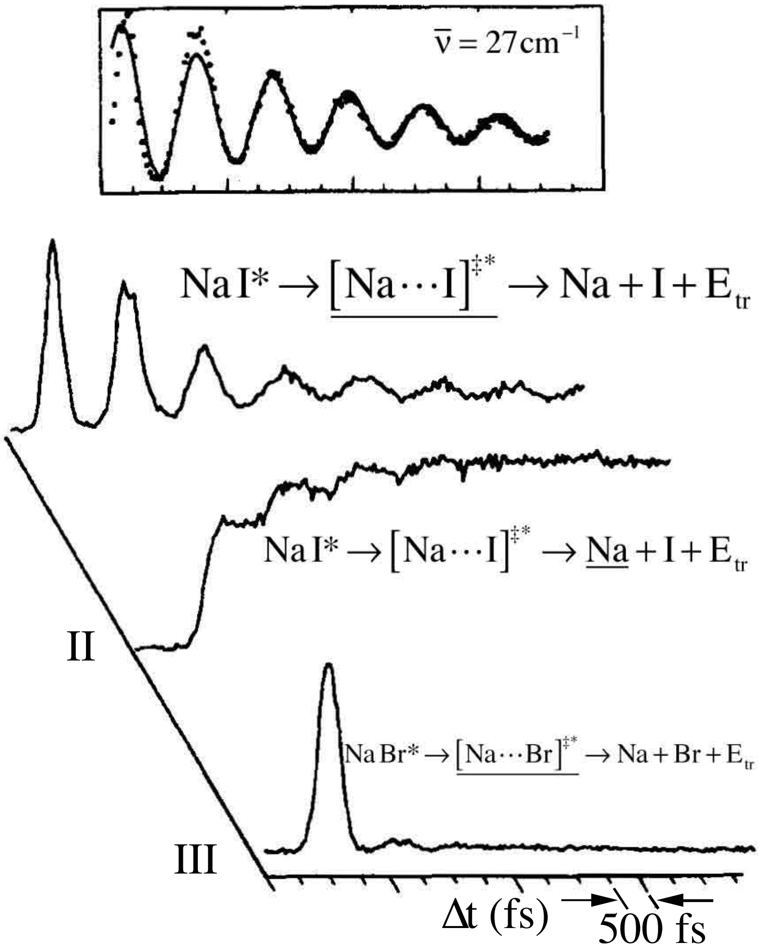

Figure 3: **Clocking of the Photodissociation of NaI (and NaBr) as the Nuclear Wavepacket Repeatedly Traverses the Ionic/Covalent Curve Crossing** (Figure 2 of Ref. 26). The wavepacket, illustrated in Fig. 6.5, is created at $t = t_0$ at the inner turning point on the covalent excited electronic state. At each outward-bound traversal of the curve-crossing region, part of the wavepacket follows the covalent adiabatic curve irreversibly outward to separated Na(^{2}S)+I(^{2}P$_{3/2}$) atoms. If the probe laser center-wavelength is tuned slightly to the red of the 589 nm free Na atom $^2\mathrm{P}\leftarrow{}^2\mathrm{S}$ transition, each time a wavepacket of incompletely separated Na,I molecules passes through the Optically Coupled Region, some not quite free Na atoms are excited to the ^{2}P state, from which spontaneous fluorescence is detected. The series of Na atom fluorescence pulses shown in Spectrum I samples each outward passage of a wavepacket through the curve-crossing region. The temporal spacing of the pulses corresponds to a 36 cm^{-1} vibrational frequency. When the center-wavelength of the probe laser is tuned to 589 nm, the arrivals of free Na atom wavepackets are displayed in Spectrum II as a periodic series of upward steps. Spectrum III shows that the (upper) adiabatic potential curve for NaBr is shallower and "leakier" than that for NaI. Reproduced with permission from Figure 2 in T. S. Rose, M. J. Rosker, and A. H. Zewail, "Femtosecond real-time observations of wave packet oscillations (resonance) in dissociation reactions," *J. Chem. Phys.* **88**, 6672–6673 (1988). Copyright 1988, AIP Publishing LLC.

Landau-Zener References

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H. Lefebvre-Brion and R. W. Field, *Spectra and Dynamics of Diatomic Molecules*, pp. 510-514 and 536 (Landau-Zener) and pp. 163-177 (Diabatic vs. Adiabatic).

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