

Lecture-8

CSO202: Atoms, Photons & Molecules

Debabrata Goswami

The Royal Swedish Academy of Sciences has awarded the 1999
Nobel Prize in Chemistry to

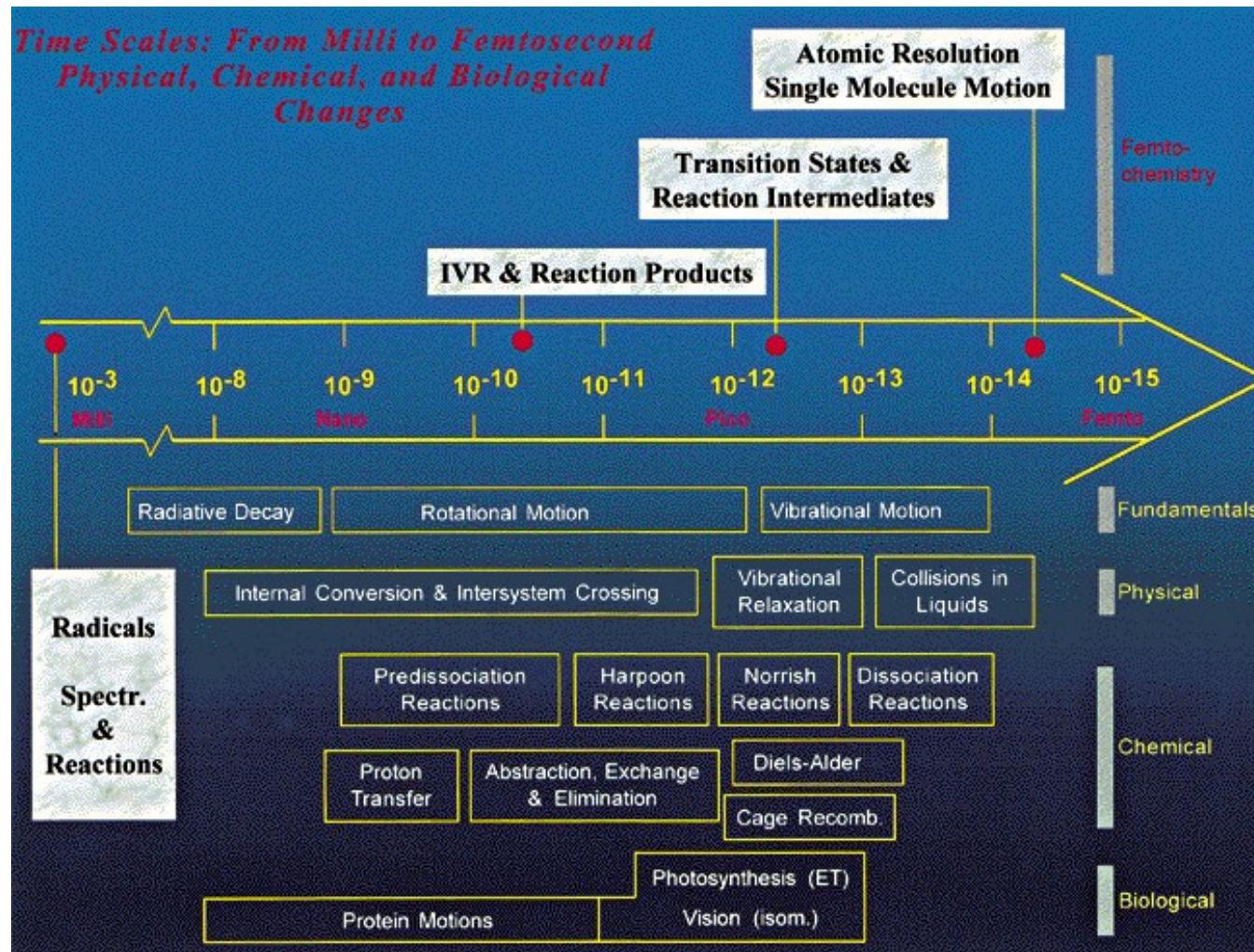
**Professor Ahmed H. Zewail, California Institute of Technology,
Pasadena, USA**



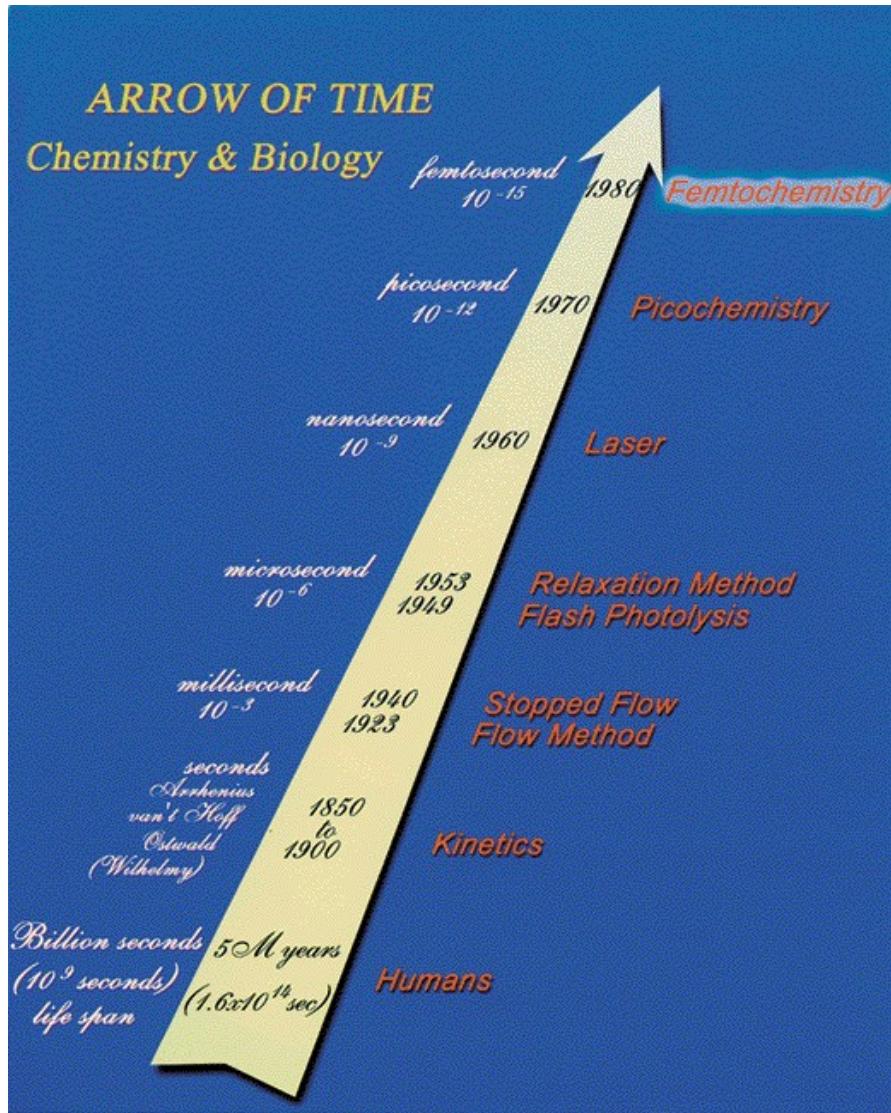
**for showing that it is possible with rapid laser technique to see
how atoms in a molecule move during a chemical reaction.**

The Academy's citation:

***For his studies of the transition states of chemical reactions
using femtosecond spectroscopy.***

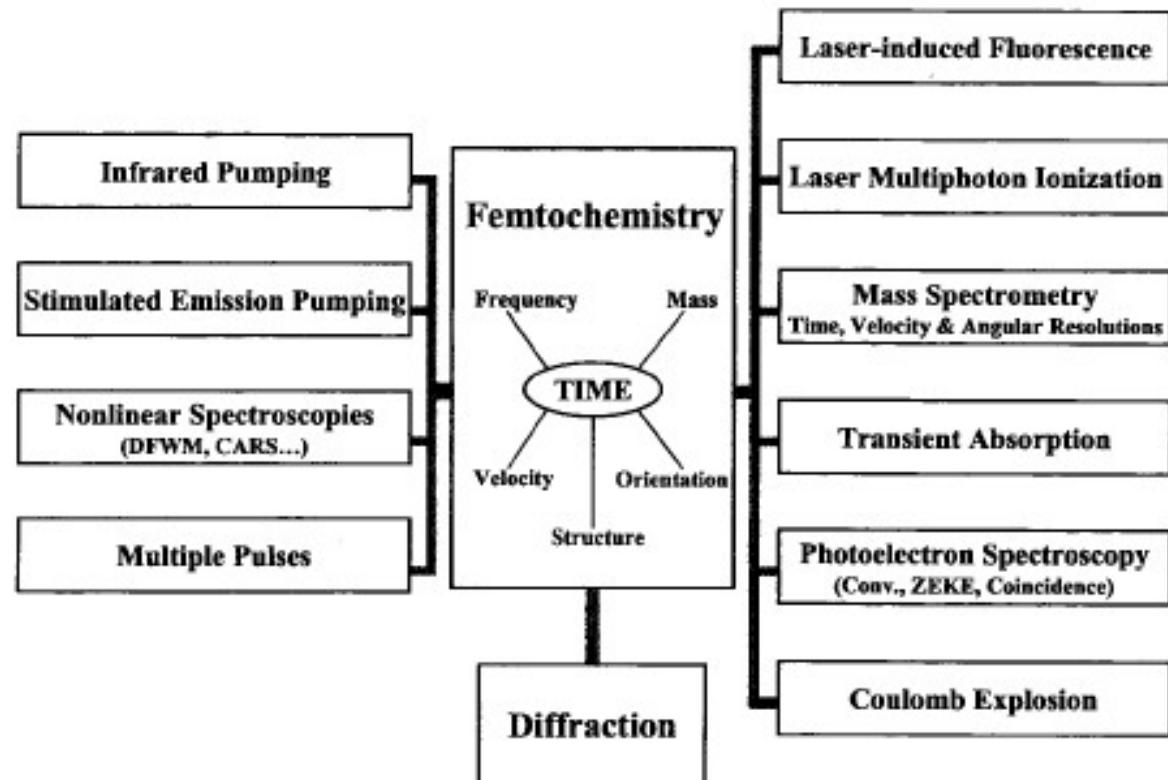


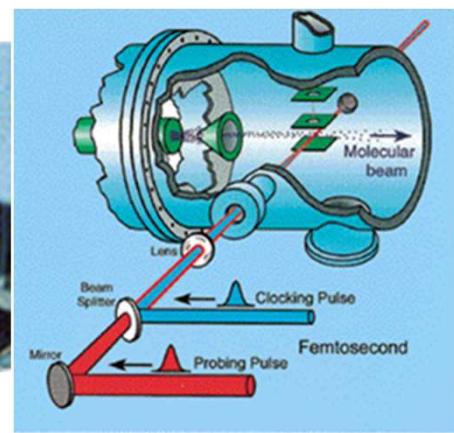
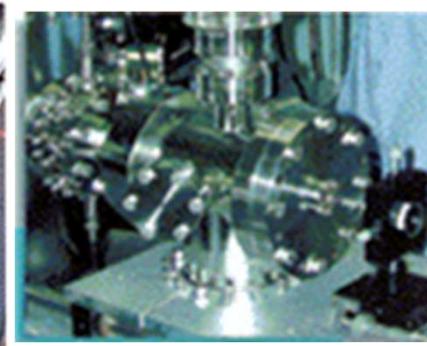
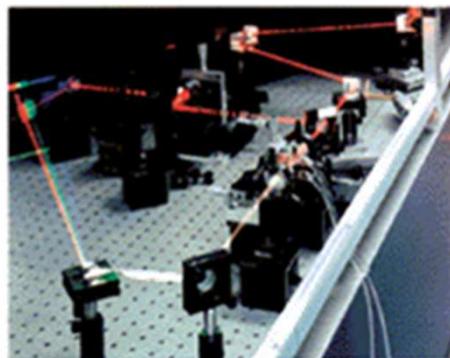
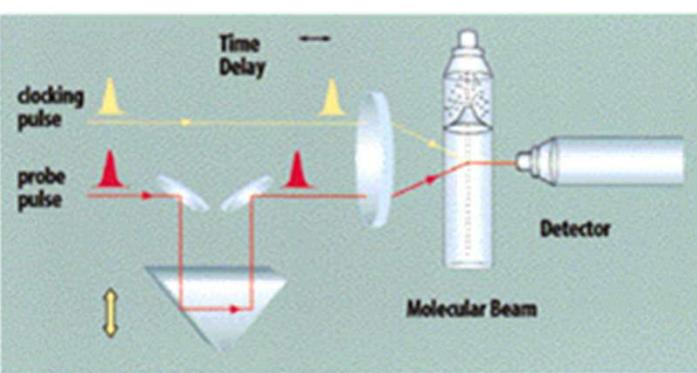
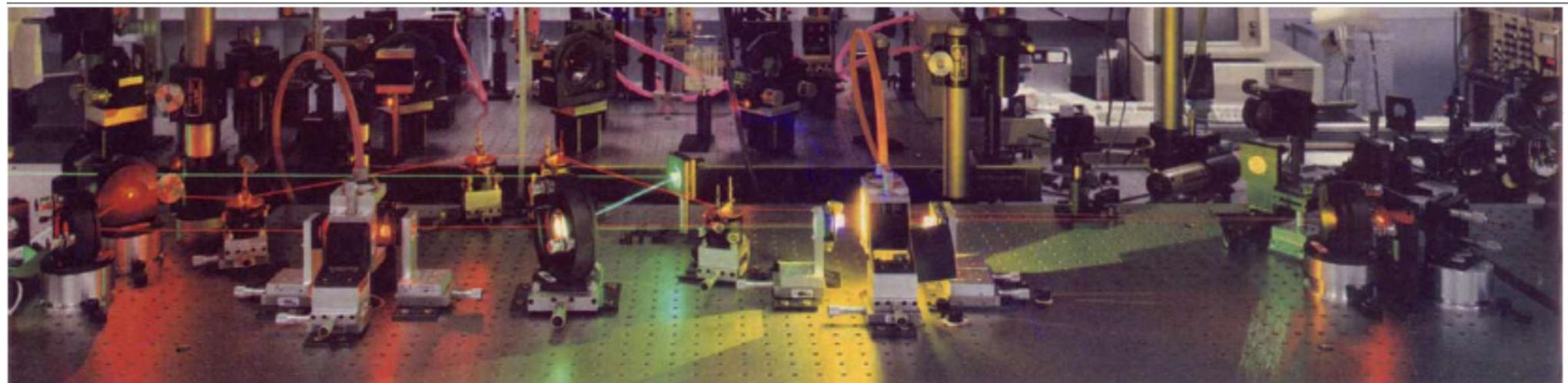
Time scales. The relevance to physical, chemical, and biological changes. The fundamental limit of the vibrational motion defines the regime for femtochemistry. Examples are given for each change and scale.



Arrow of time in chemistry and biology, some steps over a century of development.

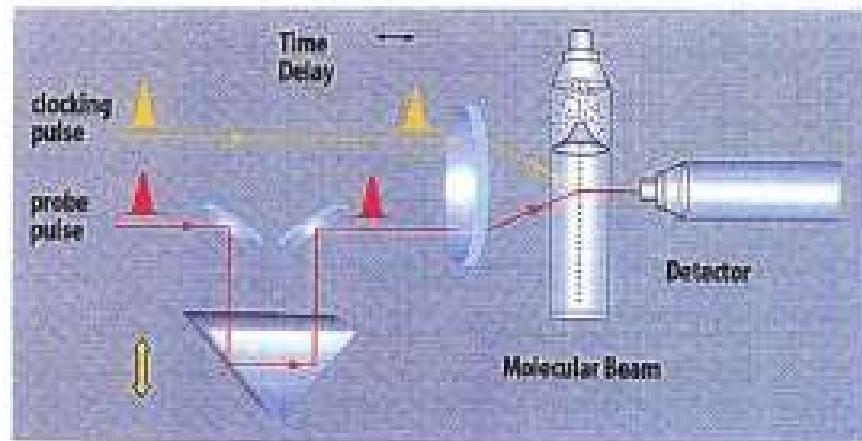
Techniques for probing femtochemistry



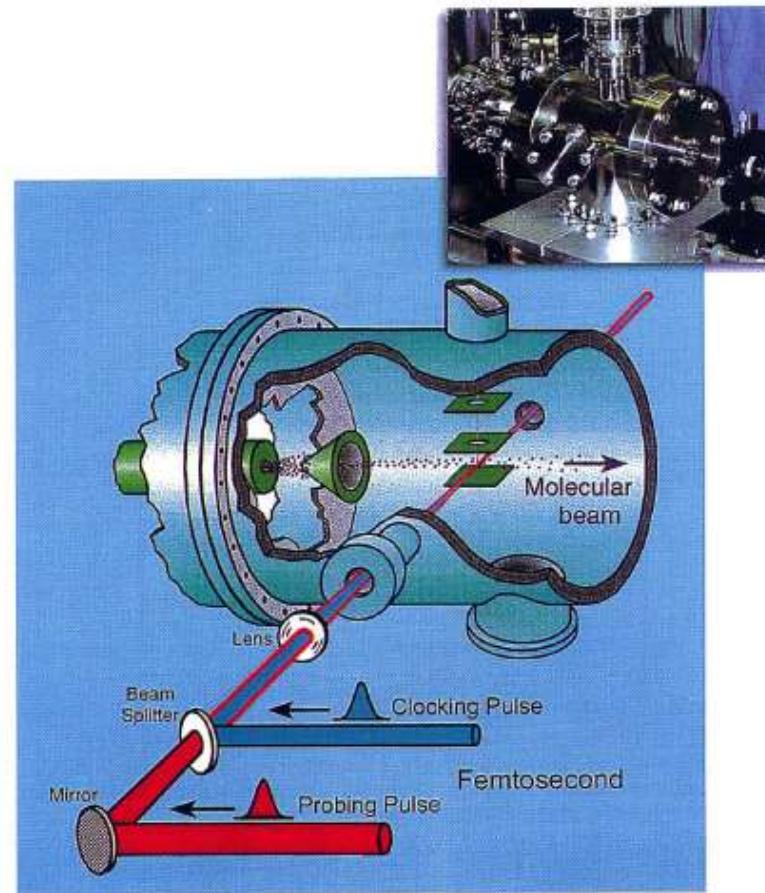


Femtochemistry apparatus, typical of early Femtolands. Laser system: (top) the first CPM oscillator used in Femtoland I; (bottom) the continuum generation to the right and the experimental layout for clocking, to the left. Molecular beam apparatus of Femtoland III, together with a view of the beam/laser arrangement.

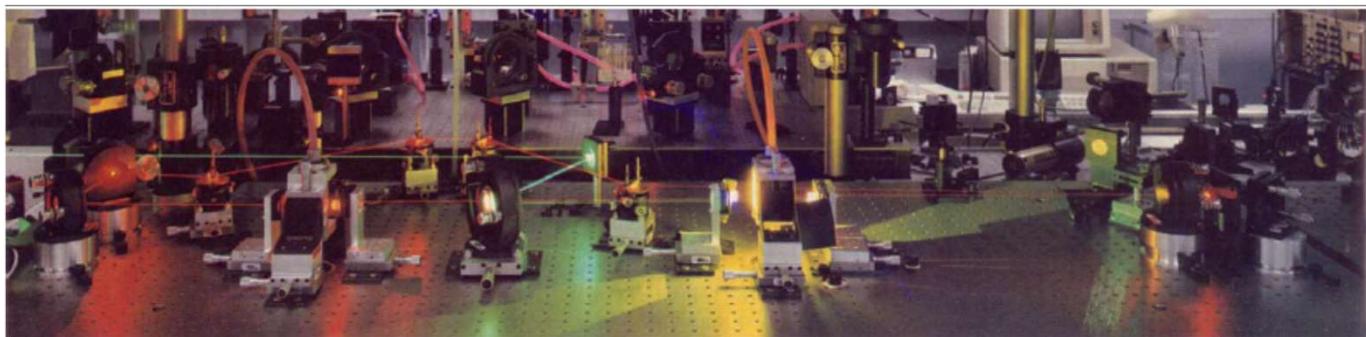
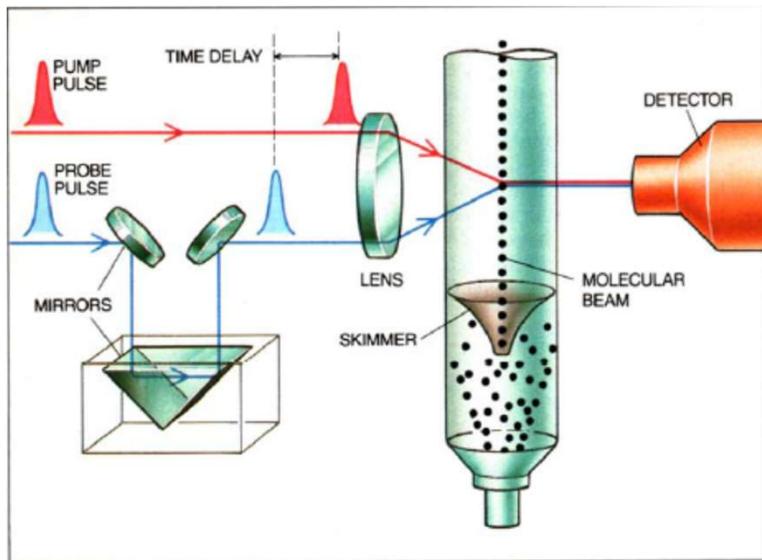
Zewail's Femtochemistry apparatus



Femtochemistry set up



CSO 202 : Atoms Molecules and Photons



J. Chem. Phys., 1987, 87(4), 2395

The Nobel Prize in Chemistry 1986

"for their contributions concerning the dynamics of chemical elementary processes"



Dudley R. Herschbach

Harvard University
Cambridge, MA, USA



Yuan T. Lee

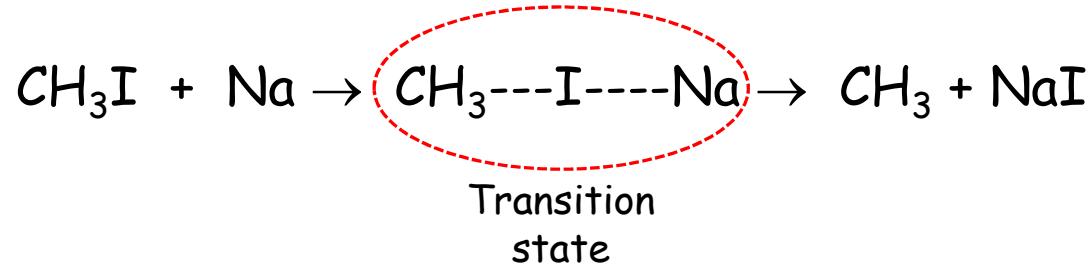
University of California
Berkeley, CA, USA



John C. Polanyi

University of Toronto
Toronto, Canada

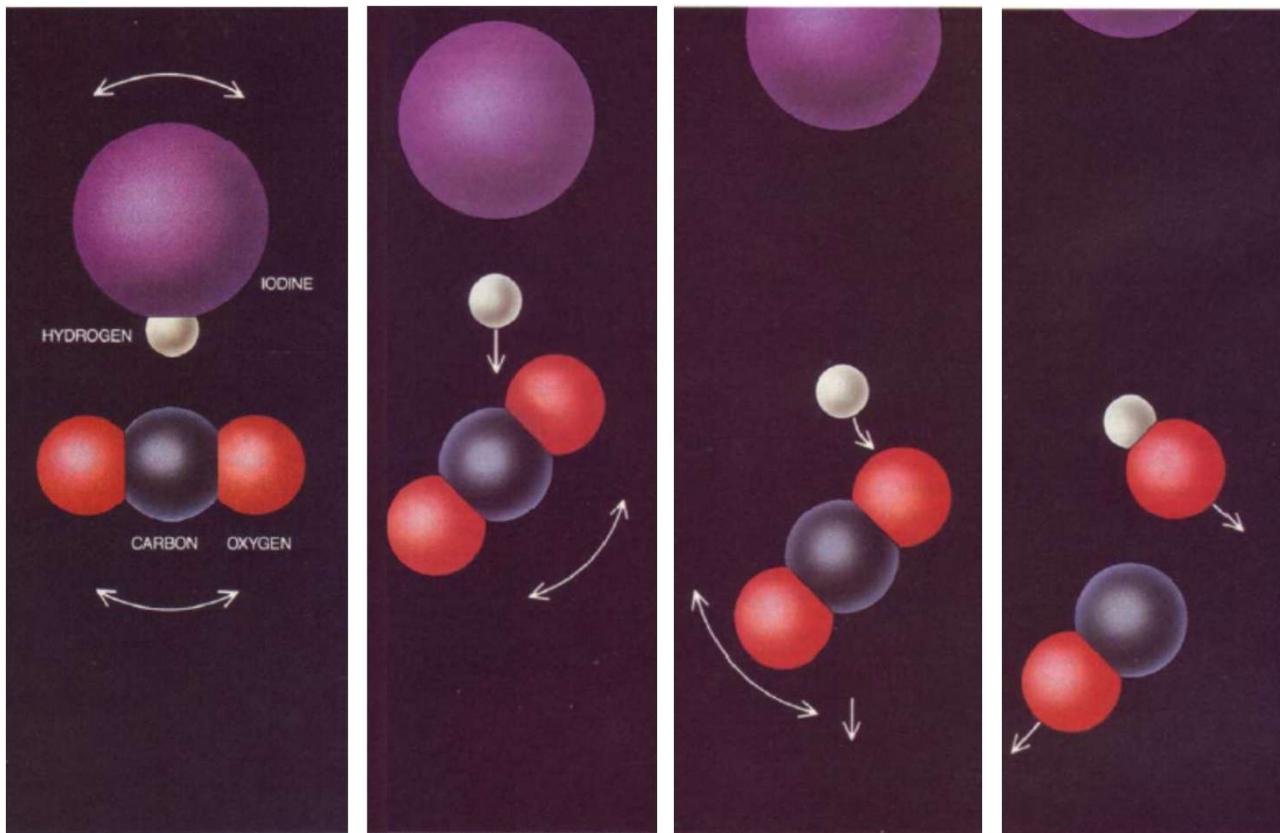
Consider a chemical transformation



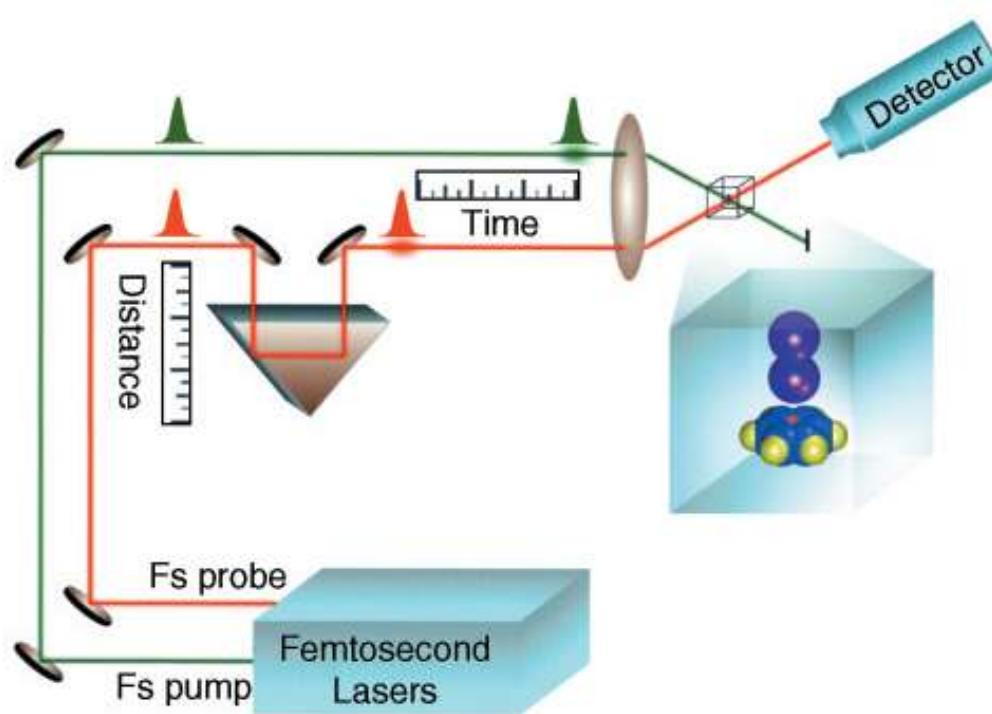
In any chemical reaction the motions of the electrons and nuclei of atoms determine how the molecules interact, and those interactions in turn create the forces that govern the reaction's dynamics.

If one can determine how molecular motions change during the critical transition phase, we can understand how new chemical bonds form and old ones disappear.

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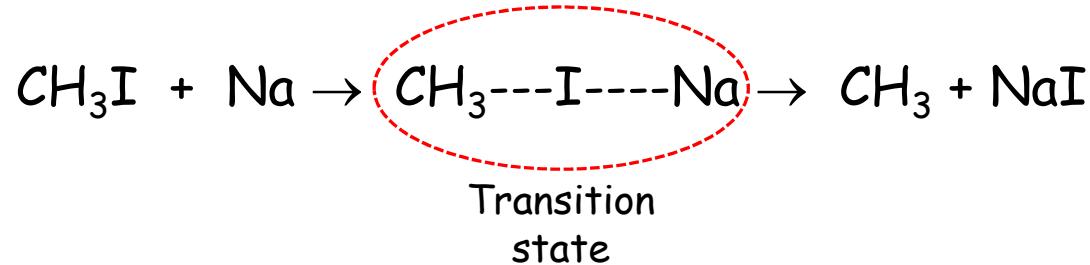


Molecular structures for a reaction in progress involving two molecules (bimolecular).



The concept of femtosecond (pump-probe) experiments. After the probe pulse has been delayed by diversion through a variable length optical path, femtosecond pump and probe pulses are focused into a volume containing the molecules to be studied. The detector responds to the probe pulse by any of a variety of schemes

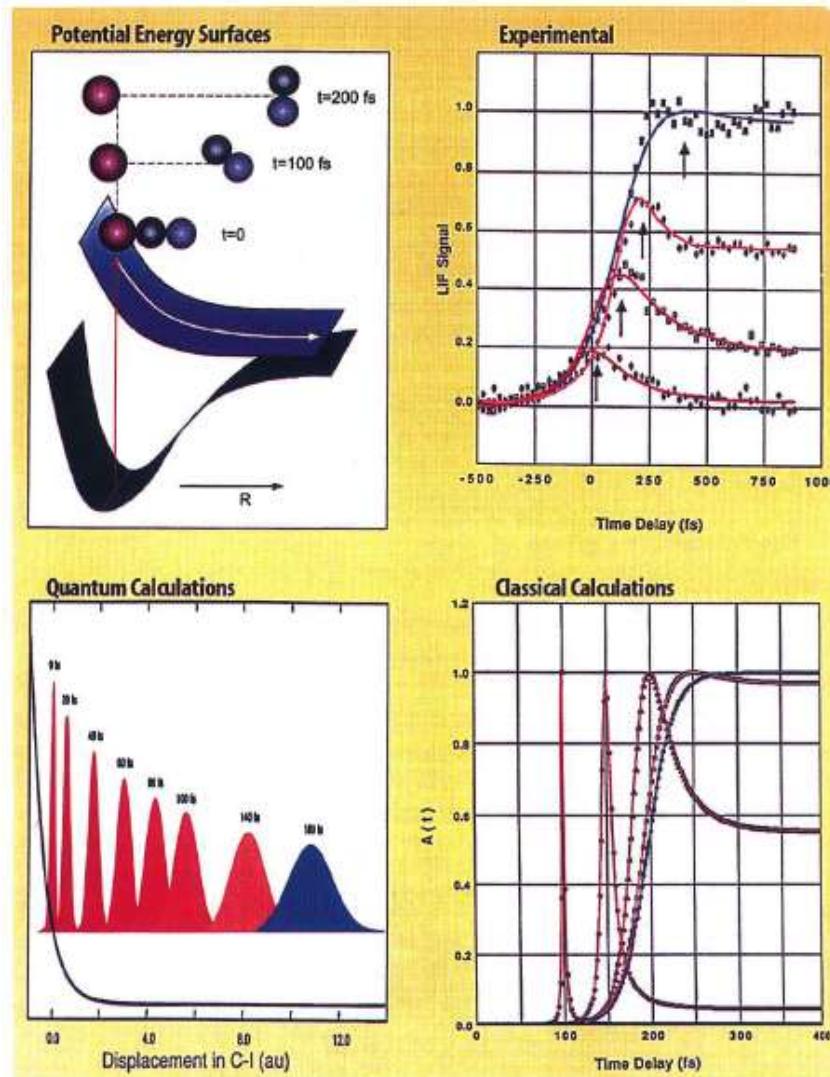
Consider a chemical transformation

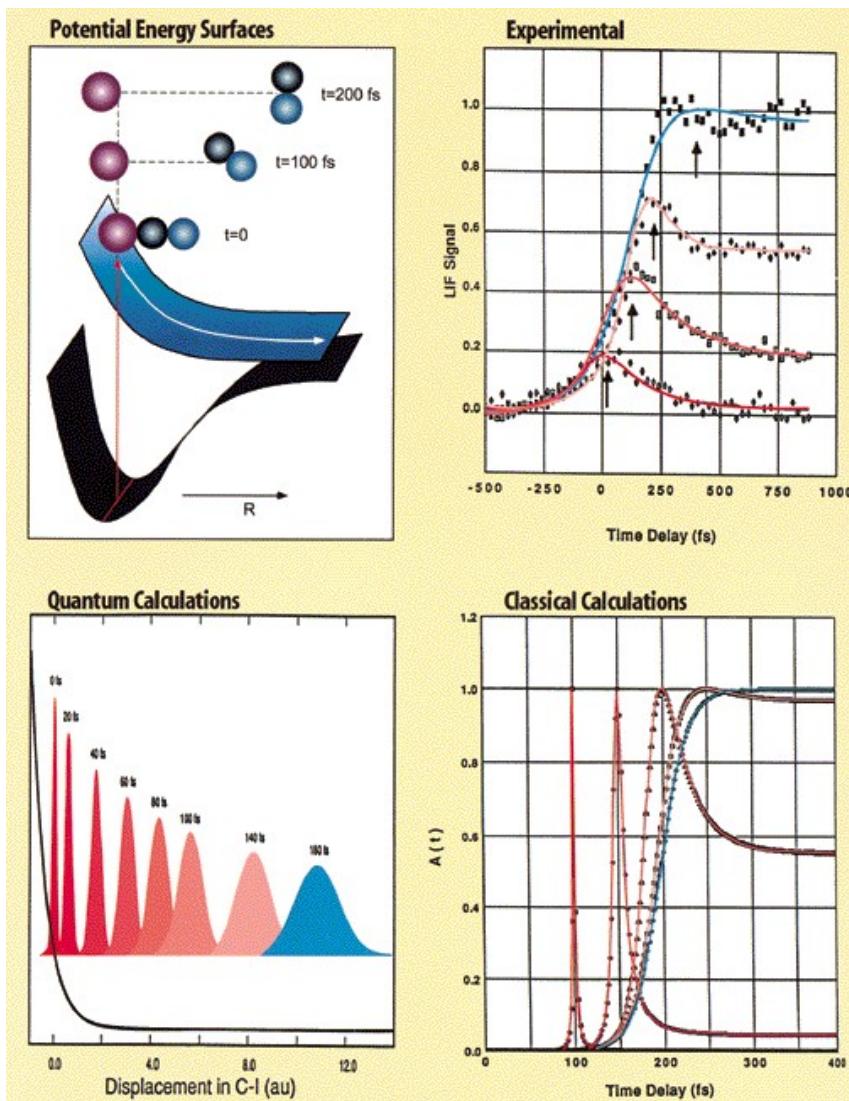


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If one can determine how molecular motions change during the critical transition phase, we can understand how new chemical bonds form and old ones disappear.

The classical femtosecond ICN discovery





Femtochemistry of the ICN reaction is the first to be studied. The experimental results show the probing of the reaction in the transition-state region (rise and decay) and the final CN fragment (rise and leveling) with a precise clocking of the process; the total time is 200 fs. The I fragment was also detected to elucidate the translational energy change with time. Classical and quantum calculations are shown.

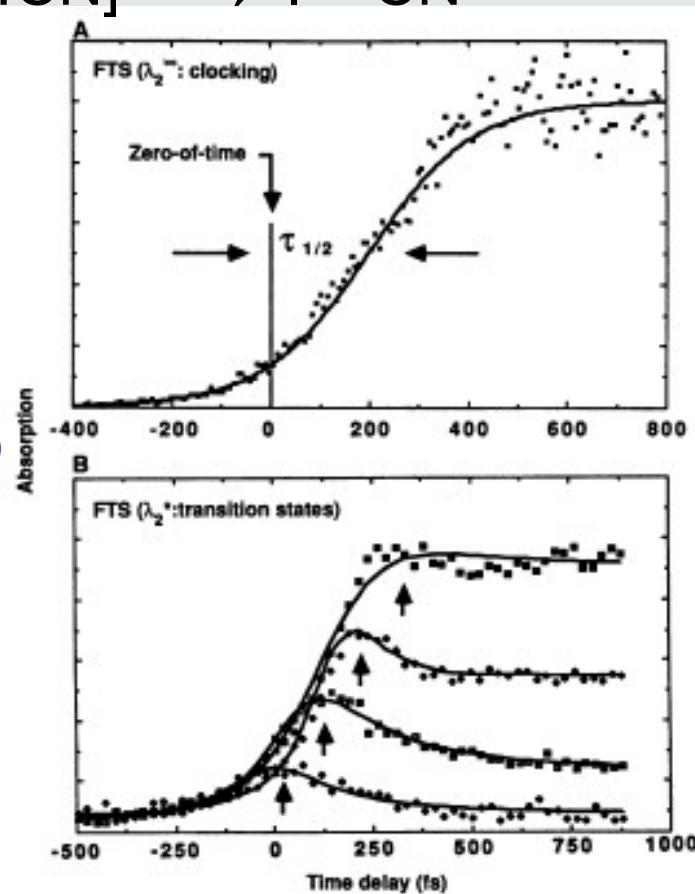
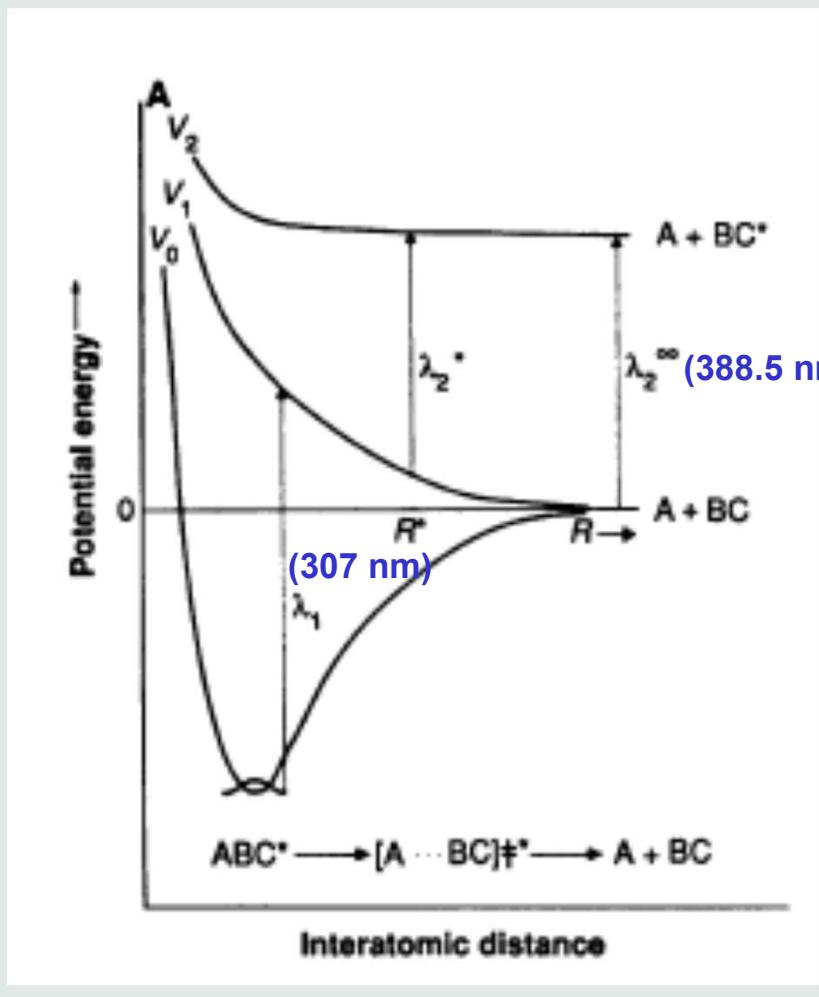


Fig. 4. FTS results for the reaction $\text{ICN}^* \rightarrow [\text{I} \cdots \text{CN}]^{\#*} \rightarrow \text{I} + \text{CN}$. (A) The delayed appearance of free CN fragments (by 205 ± 30 fs) was probed at λ_2^{∞} (388.5 nm). In these experiments the zero-of-time was established to determine the bond-breaking time $\tau_{1/2}$. (B) Transients taken for different λ_2^* probings to the red wavelengths (389.7, 389.8, 390.4, and 391.4 nm) of absorption by free fragments. Note that as tuning is increased more to the red, the absorption maximum shifts to earlier times, as expected (see text).

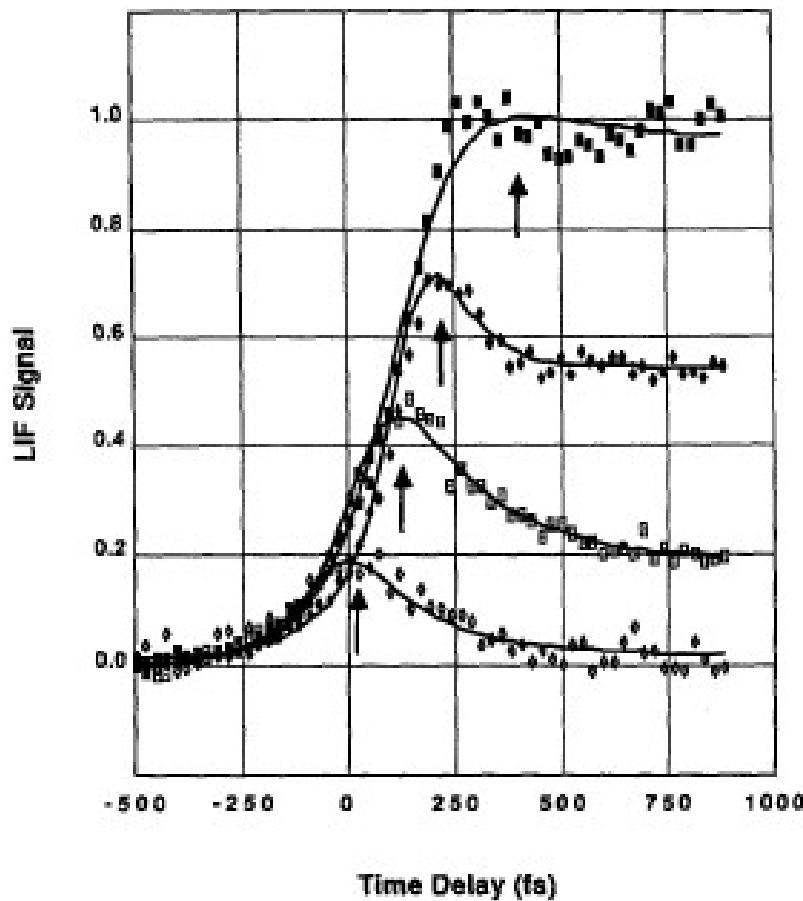
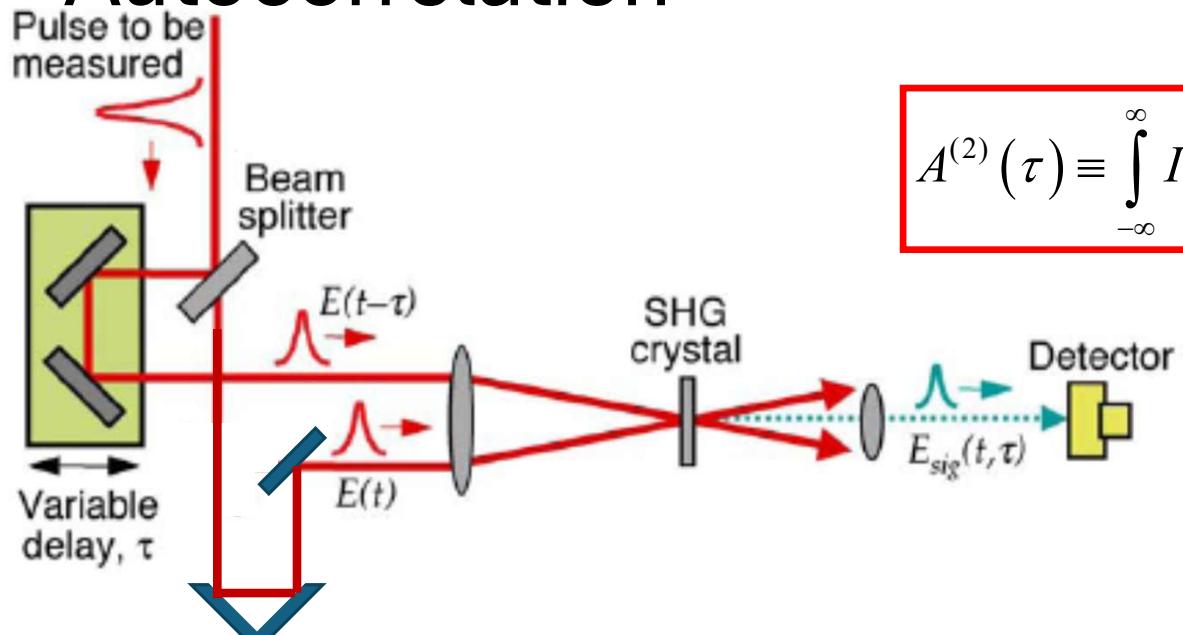
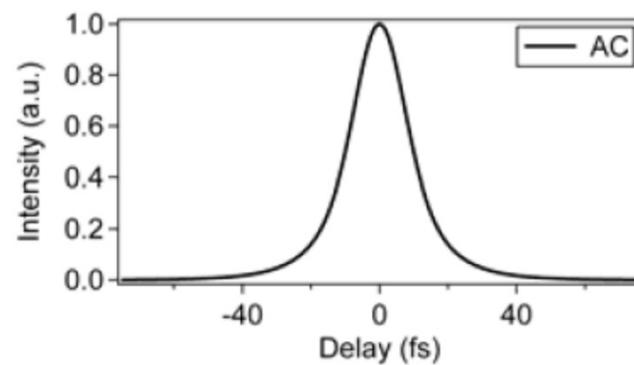
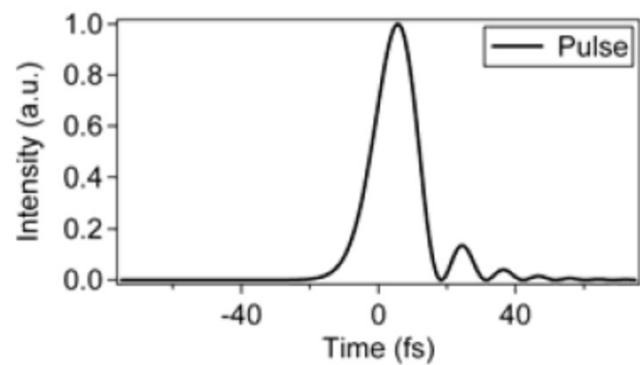


FIG. 7. Typical off-resonant FTS results for the ICN reaction. Key: solid squares: $\lambda_2 = 389.7$ nm; solid diamonds: $\lambda_2 = 389.8$ nm; open squares $\lambda_2 = 390.4$ nm; open diamonds: $\lambda_2 = 391.4$ nm. The zero-of-time is determined separately for each data set using the DEA-MPI technique. The solid lines and arrows are guides to the eye, showing the approximate peak positions for each data set. (Comparison with theory is discussed in more detail in paper II.)

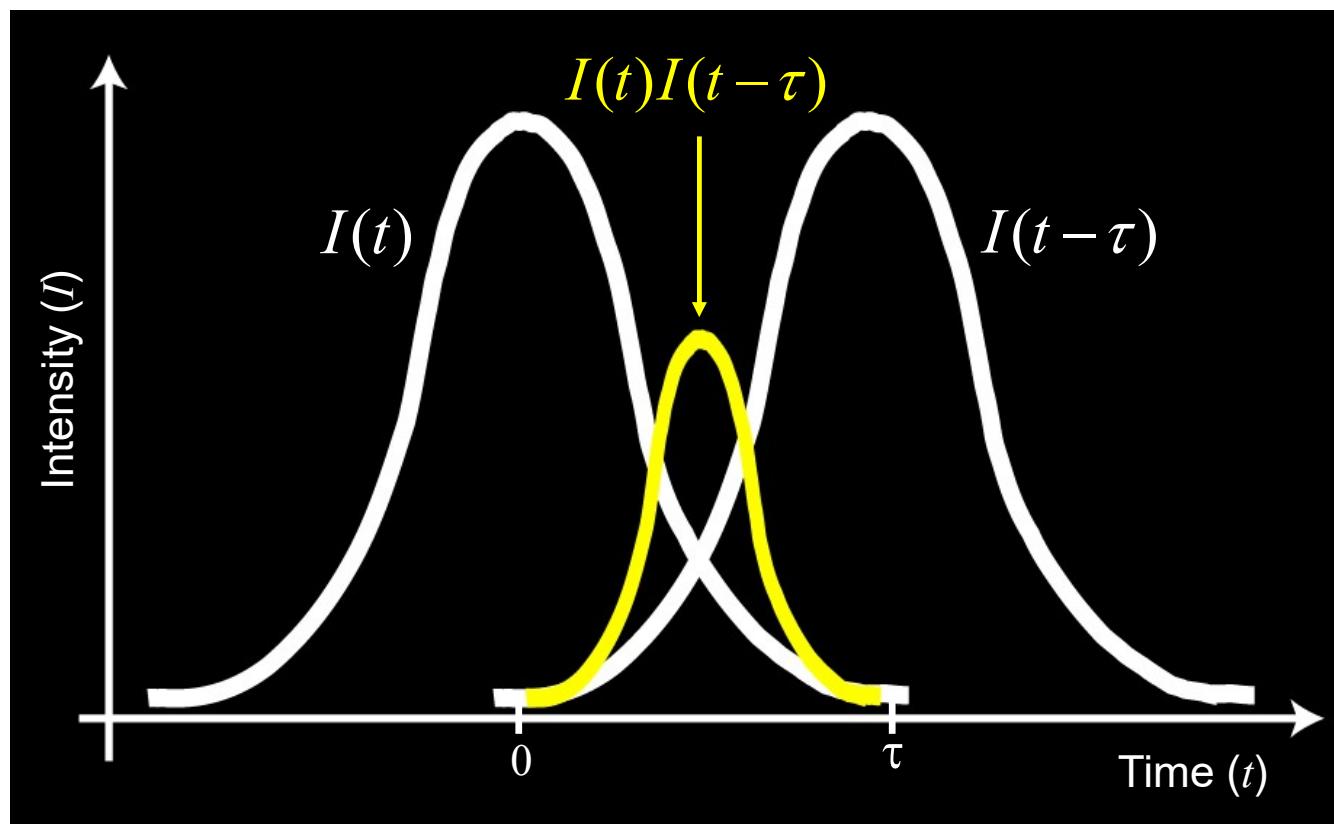
Autocorrelation



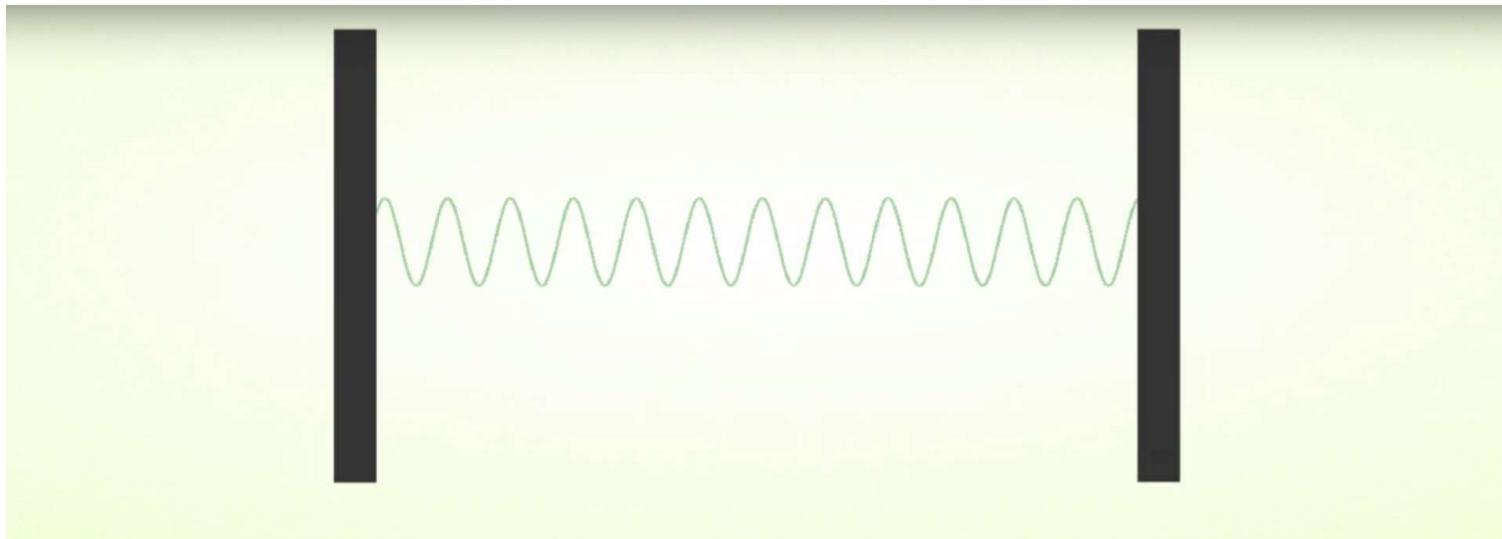
$$A^{(2)}(\tau) \equiv \int_{-\infty}^{\infty} I(t)I(t - \tau) dt$$



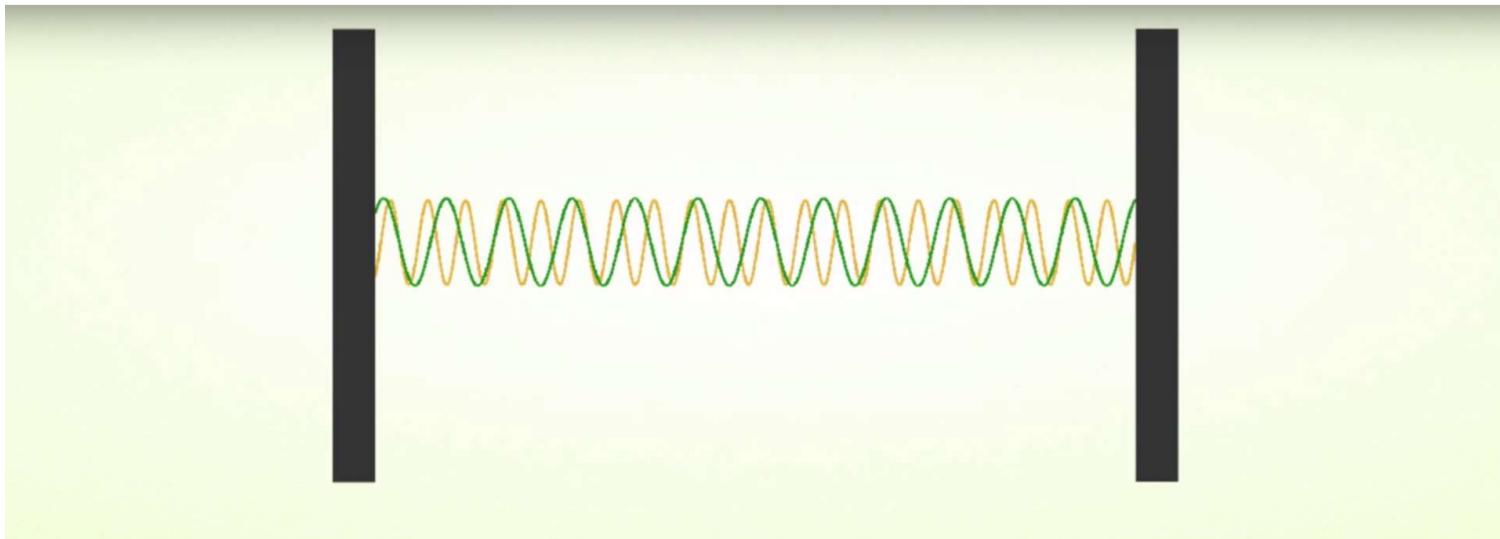
Autocorrelation



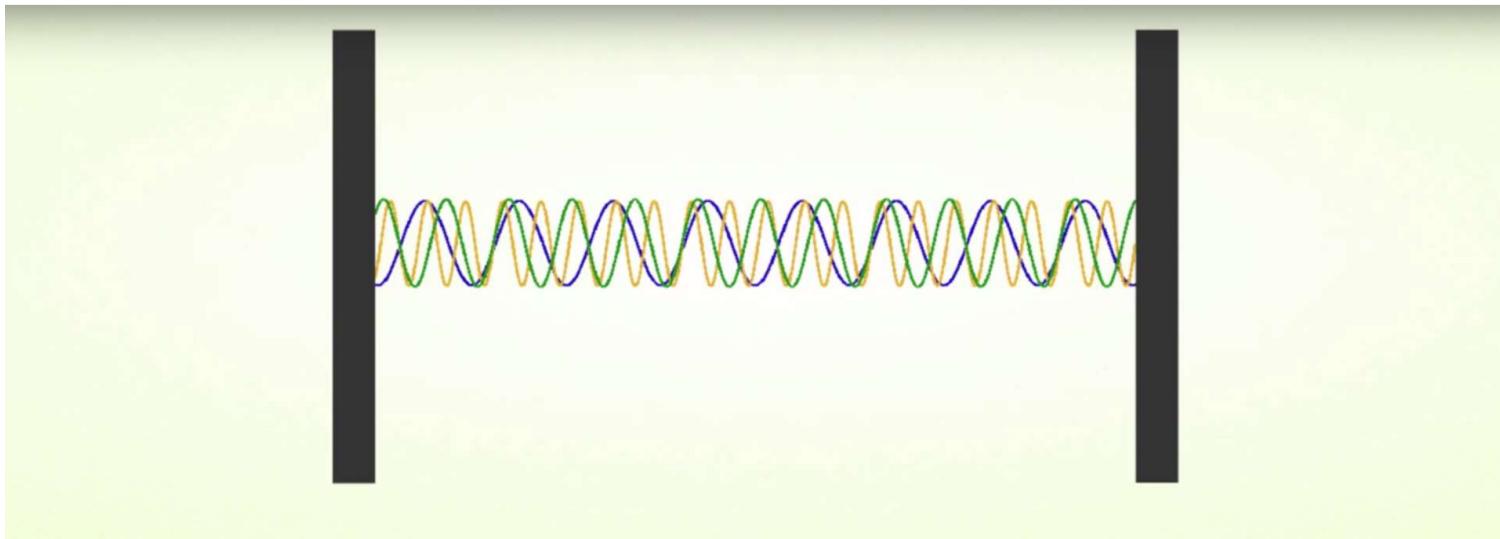
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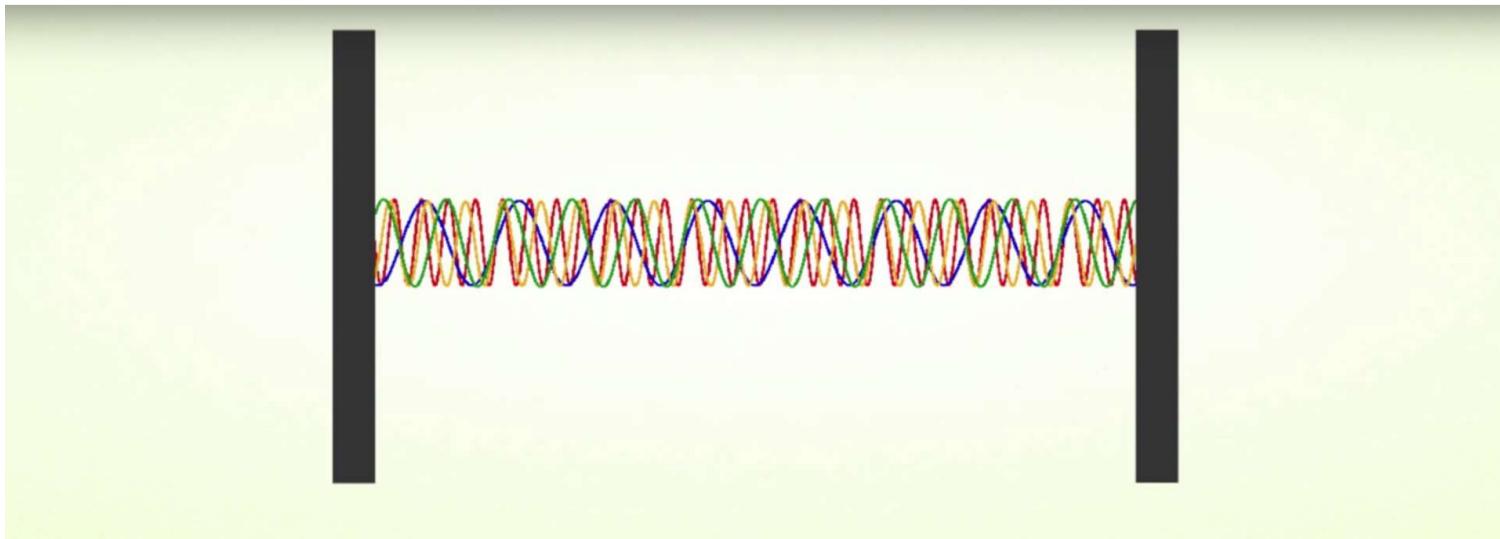
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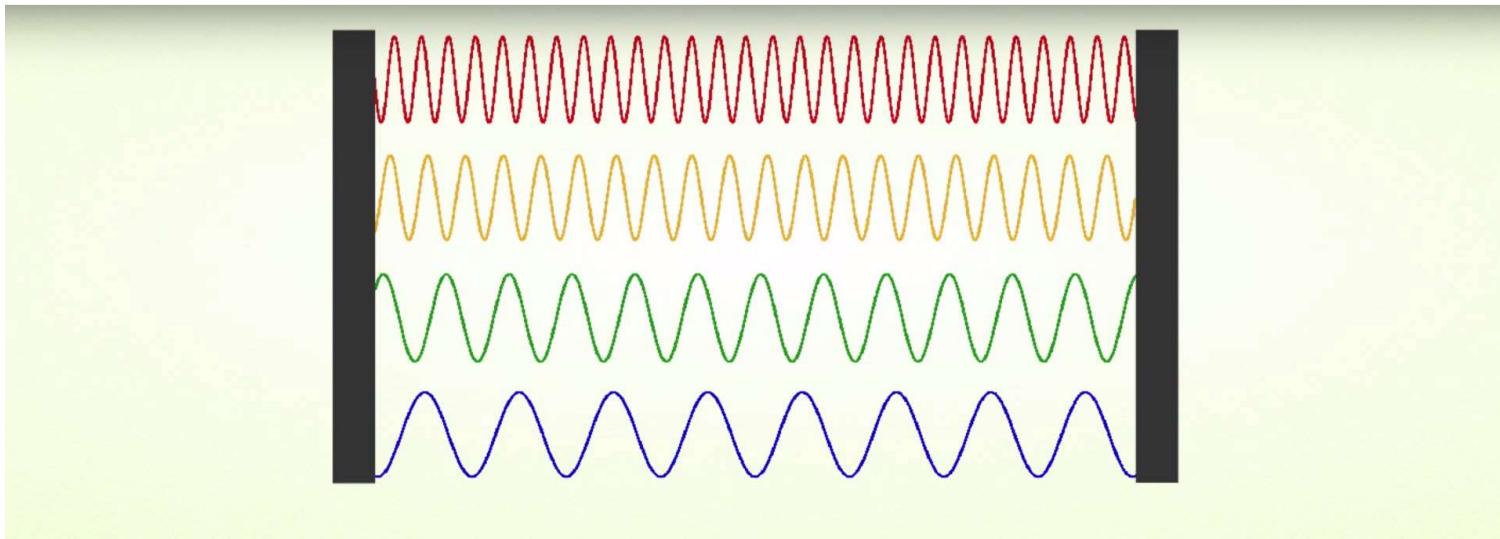
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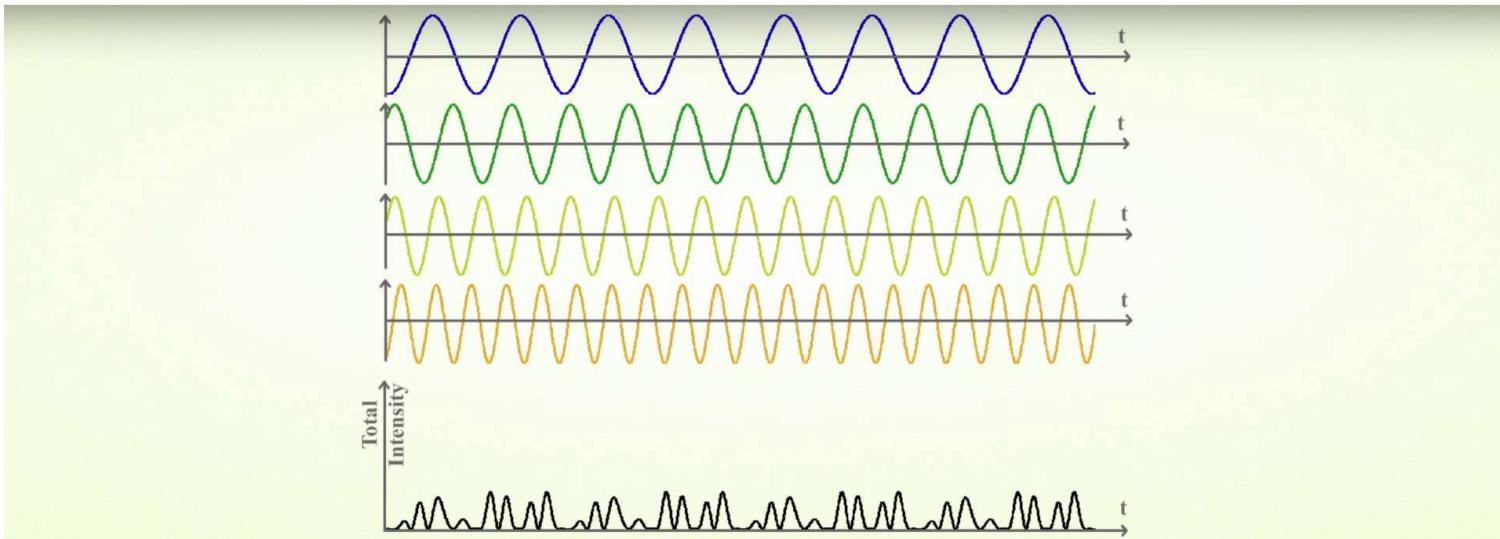
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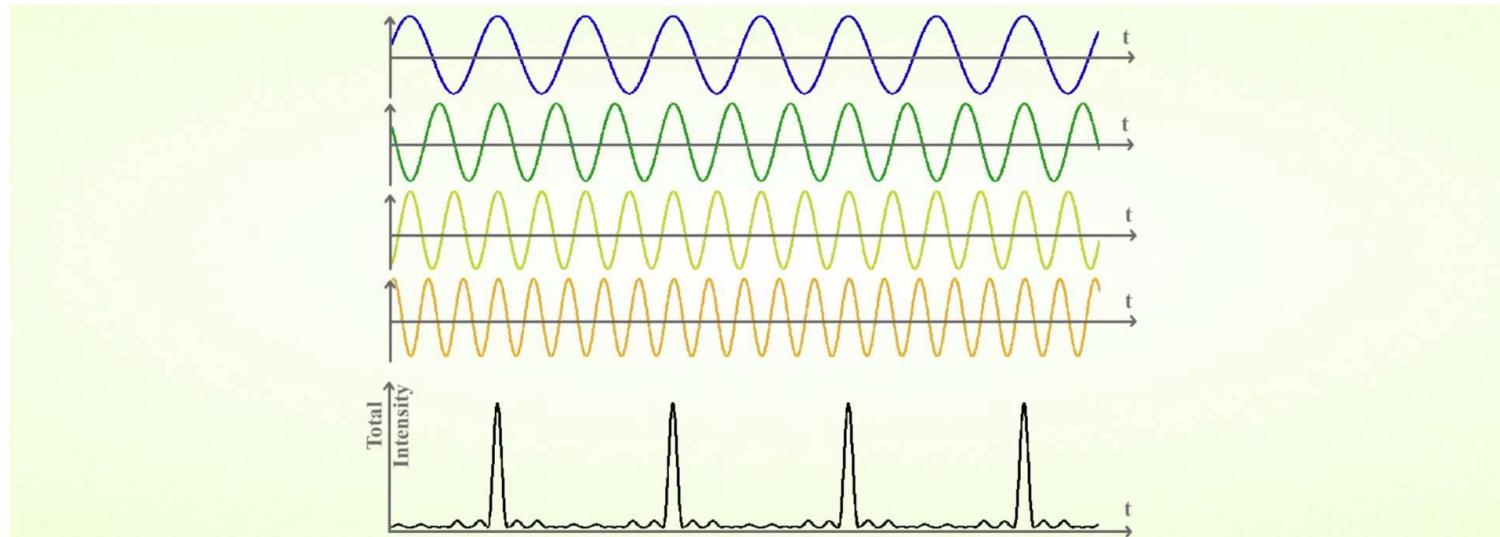
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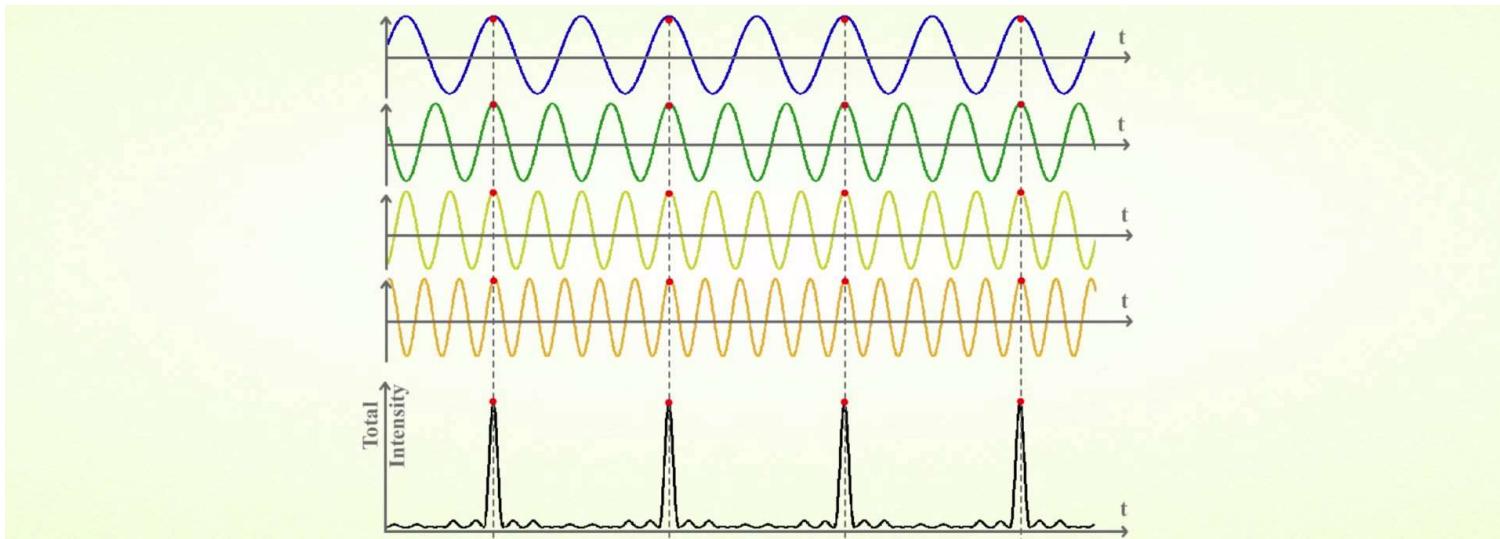
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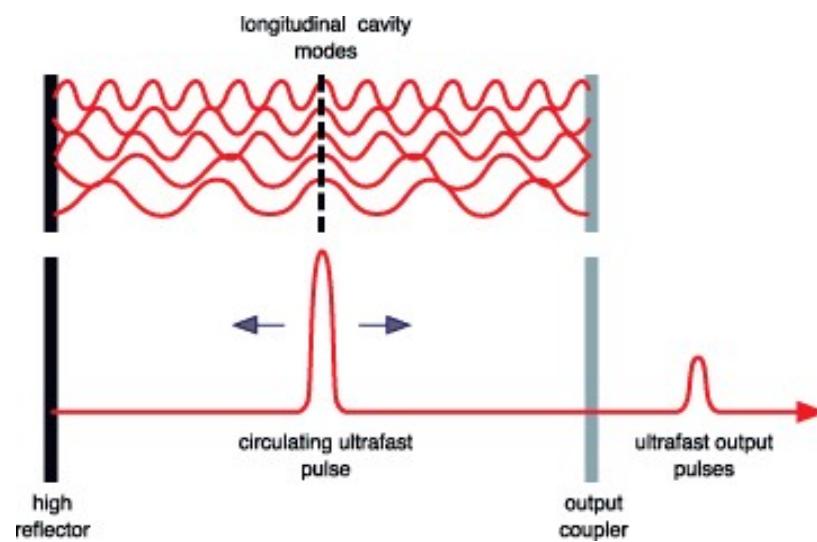
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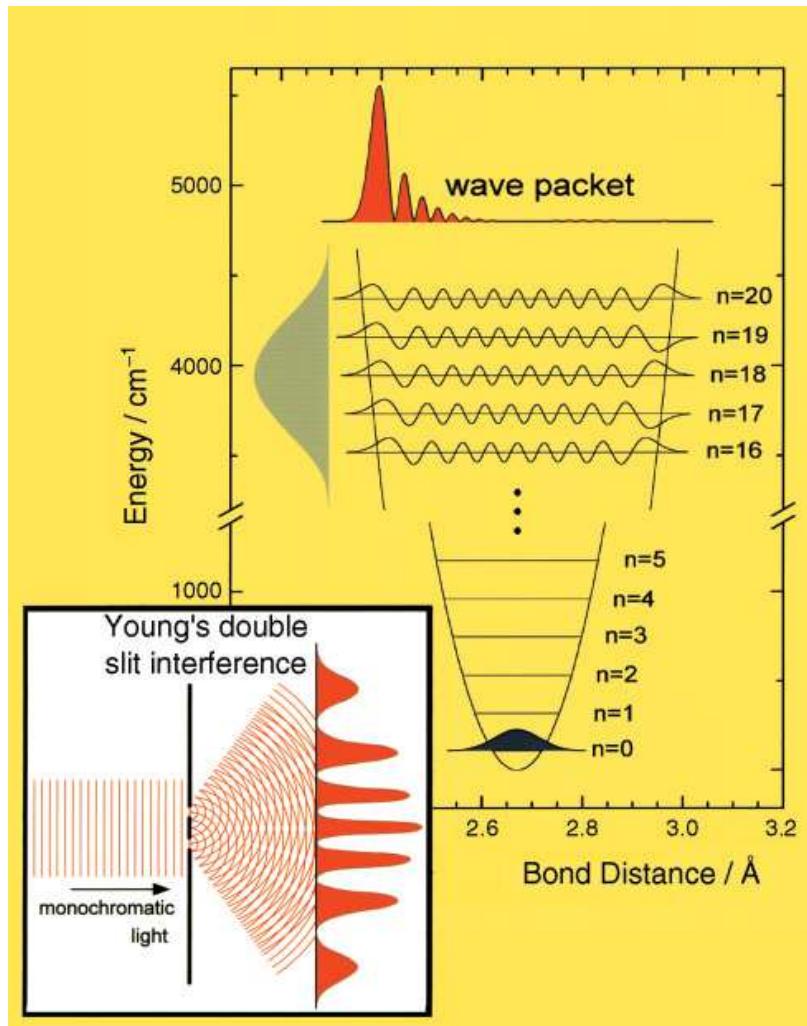


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Diatomc molecule in a harmonic oscillator potential: stationary wave functions and formation of a localized wave packet.
Inset: Thomas Young's experiment (1801) on the interference of light.

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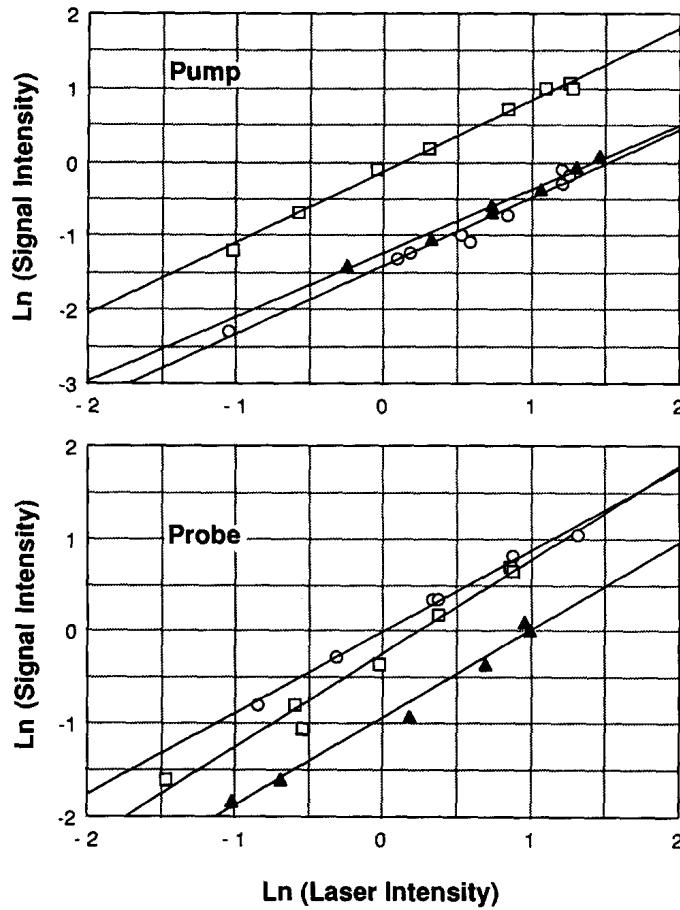


FIG. 3. Power dependence of the LIF signal. The observed LIF is plotted as a function of the pump or probe intensity on a log-log scale. Key: open squares: on-resonance transients; solid triangles and open circles: off-resonance transients for different time delays. The lines shown are best fits to the data. Note that, in all cases, the slopes of the lines are near unity.

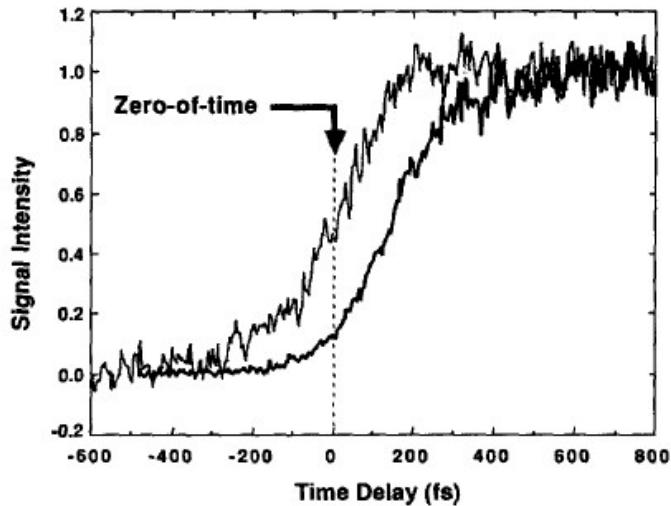
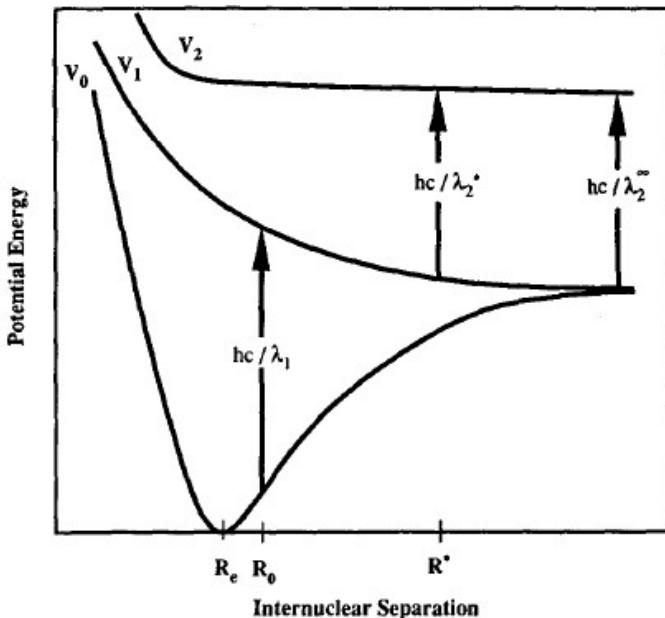


FIG. 6. Typical on-resonant FTS results for the ICN reaction. Top: The thin line is the MPI signal of DEA, which gives the detection-response function and the zero-of-time, as indicated (see text and paper II). The darker line is the FTS data for ICN, taken with $\lambda_2 = \lambda_2^*$. Note the time delay between these traces, $\tau_{1/2}$.



The PES's of an idealized molecule. V_0 , is the PES of the ground state, which has its minimum at $R = R_e$. At time $t = 0$, a pump photon of wavelength λ_1 is absorbed, as indicated by the vertical transition to V_1 . The internuclear separation increases as the system evolves on this repulsive potential. At time $t = \tau$, a pulse of wavelength λ^* (or λ^∞) probes the vertical transition from V_1 to a higher PES, V_2 .

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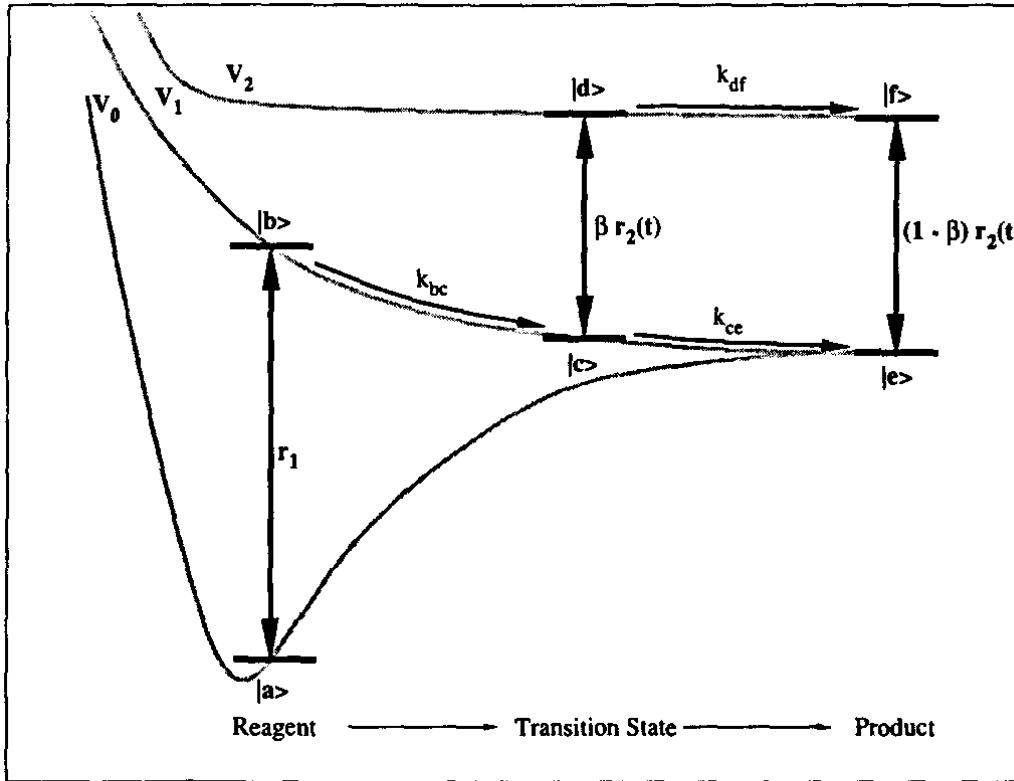


FIG. 9. Schematic of the simple kinetic (six-level) model. The continuum of transition states is described as a single pair ($|c\rangle$, $|d\rangle$) of states. The pumping and probing rates are $r_1(t)$ and $r_2(t)$, respectively. The k_{ij} give the spontaneous transition rates from $|i\rangle$ to $|j\rangle$, as shown. β is defined in the text. Stimulated emission by the pump and probe is indicated by the double headed arrows.

We get the following coupled rate equation

$$\begin{bmatrix} \dot{n}_a \\ \dot{n}_b \\ \dot{n}_c \\ \dot{n}_d \\ \dot{n}_e \\ \dot{n}_f \end{bmatrix} = \begin{bmatrix} -r_1(t) & r_1(t) & 0 & 0 & 0 & 0 \\ r_1(t) & -k_{bc} - r_1(t) & 0 & 0 & 0 & 0 \\ 0 & k_{bc} & -k_{ce} - \beta r_2(t) & \beta r_2(t) & 0 & 0 \\ 0 & 0 & \beta r_2(t) & -k_{df} - \beta r_2(t) & 0 & 0 \\ 0 & 0 & k_{ce} & 0 & -(1-\beta)r_2(t) & (1-\beta)r_2(t) \\ 0 & 0 & 0 & k_{df} & (1-\beta)r_2(t) & -(1-\beta)r_2(t) \end{bmatrix} \begin{bmatrix} n_a \\ n_b \\ n_c \\ n_d \\ n_e \\ n_f \end{bmatrix}$$

where we make the following definitions:

$n_i(t)$ ≡ the instantaneous population of state $|i\rangle$,

k_{ij} ≡ the rate of spontaneous decay of molecules from state $|i\rangle$ to state $|j\rangle$,

$r_1(t)$ ≡ the instantaneous rate at which the pump pulse excites from state $|a\rangle$ to state $|b\rangle$,
and

$r_2(t)$ ≡ the instantaneous rate at which the probe pulse excites from state $|c\rangle$ to state $|d\rangle$ and from $|e\rangle$ to $|f\rangle$.

Further, β is defined as a dimensionless parameter describing the relative ratio of the two probe absorptions.

Thus, by definition, $\beta = 1$ if the probe is tuned perfectly to the transition-state absorption ($|c\rangle \rightarrow |d\rangle$), whereas $\beta = 0$ if the probe is tuned completely to the final state transition ($|e\rangle \rightarrow |f\rangle$). The rate at which the pump excites the system (from $|a\rangle$ to $|b\rangle$) is given by

$$r_1(t) = I_1(t)\sigma_{ab}\lambda_1/hc,$$

and, similarly for the probe,

$$r_2(t) = I_2(t)\sigma_{ef}\lambda_2/hc.$$

Boundary conditions

$$n_a(-\infty) = N,$$

$$n_b(-\infty) = \dots = n_f(-\infty) = 0,$$

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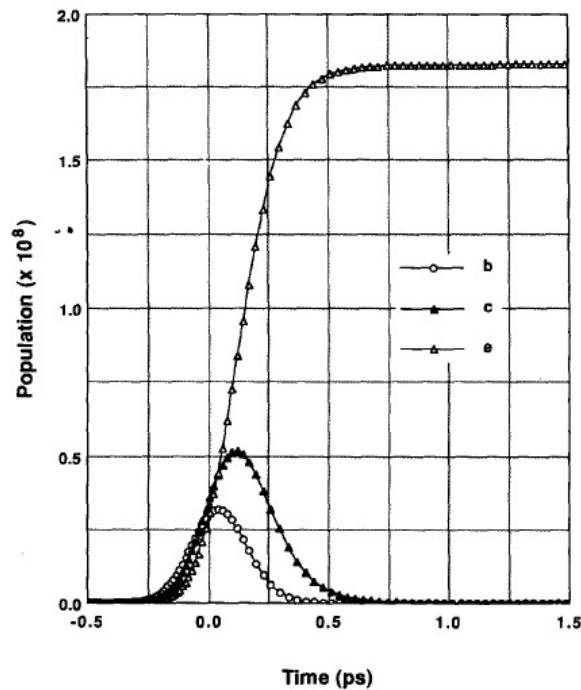


FIG. 10. Population evolution of the simple kinetic model. The instantaneous population of three of the six states are shown as a function of time. Key: open circles = $n_b(t)$, solid triangles = $n_c(t)$, open triangles = $n_e(t)$. Assumed parameters (see the text for definitions): $k_{ba} = 2 \times 10^{13} \text{ s}^{-1}$, $k_{ce} = k_{df} = 10^{13} \text{ s}^{-1}$, τ (delay time) = 500 fs, $N = 10^{12}$ molecules, $\sigma_{ab} = 4 \times 10^{-20} \text{ cm}^2$, $\sigma_{cd} = 5 \times 10^{-17} \text{ cm}^2$, and $\beta = 0.95$. In addition, the energies of the pump and probe beams were taken to be 150 and 50 nJ, respectively, with a common width of 150 fs and beam radius of 40 μm . Note that for ~ 250 fs, the population of the transition state (n_c) is a significant fraction of that of the final state (n_e).

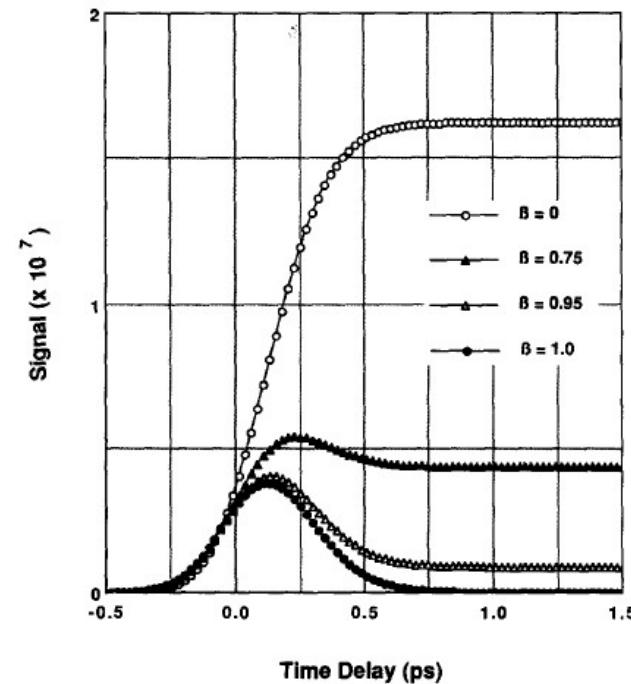


FIG. 11. Predicted FTS results from the simple kinetic model. The signal was calculated using the same parameters as for Fig. 10, as a function of the tuning parameter β . Key: open circles: $\beta = 0$; solid triangles: $\beta = 0.75$; open triangles: $\beta = 0.95$; and solid circles: $\beta = 1.0$. Here, the signal is the population in level $|f\rangle$ (sampled at long times; see Fig. 10) as a function of pump-probe delay time.

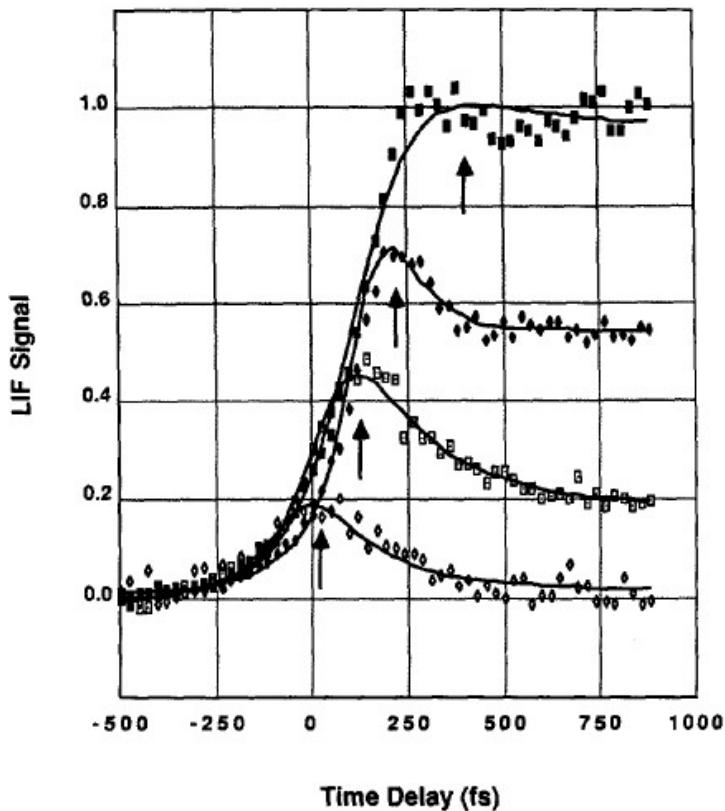
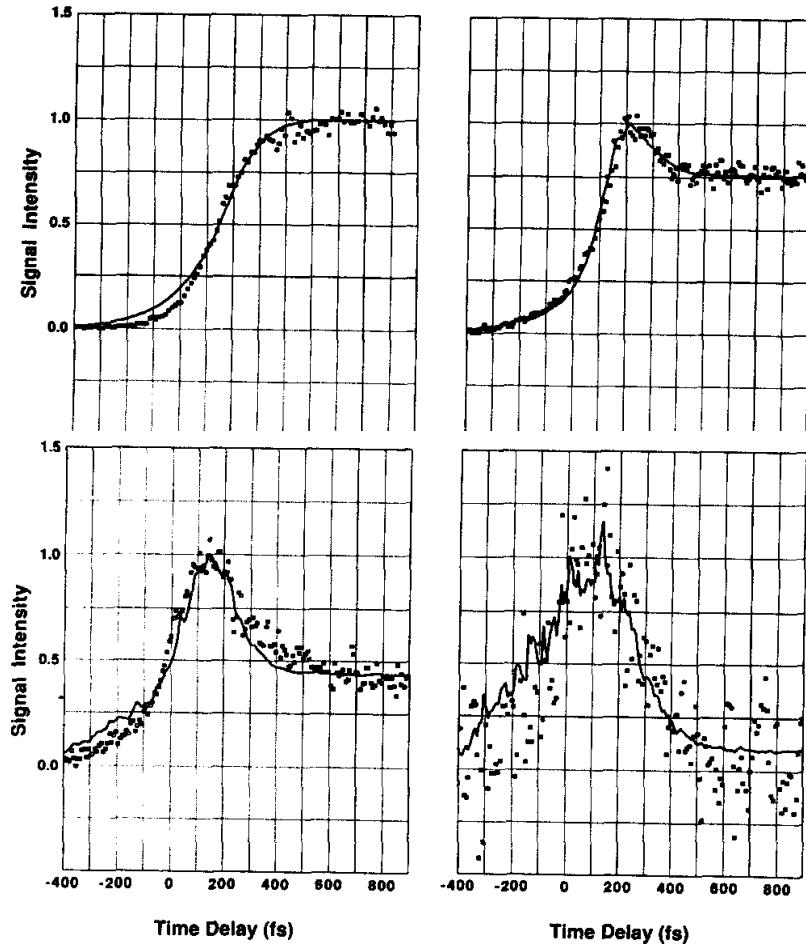
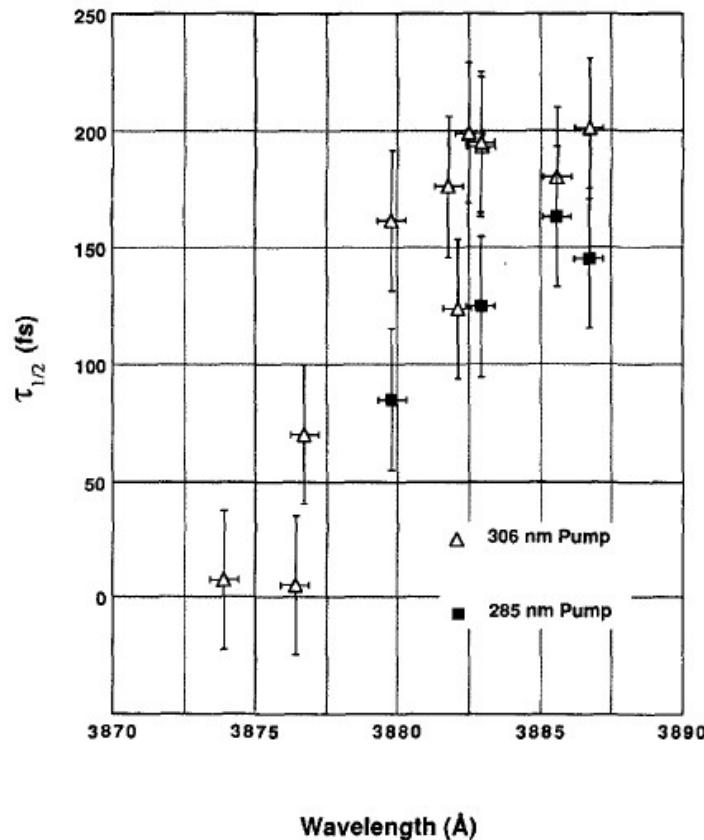


FIG. 7. Typical off-resonant FTS results for the ICN reaction. Key: solid squares: $\lambda_2 = 389.7$ nm; solid diamonds: $\lambda_2 = 389.8$ nm; open squares $\lambda_2 = 390.4$ nm; open diamonds: $\lambda_2 = 391.4$ nm. The zero-of-time is determined separately for each data set using the DEA-MPI technique. The solid lines and arrows are guides to the eye, showing the approximate peak positions for each data set.



Tuning to the Red

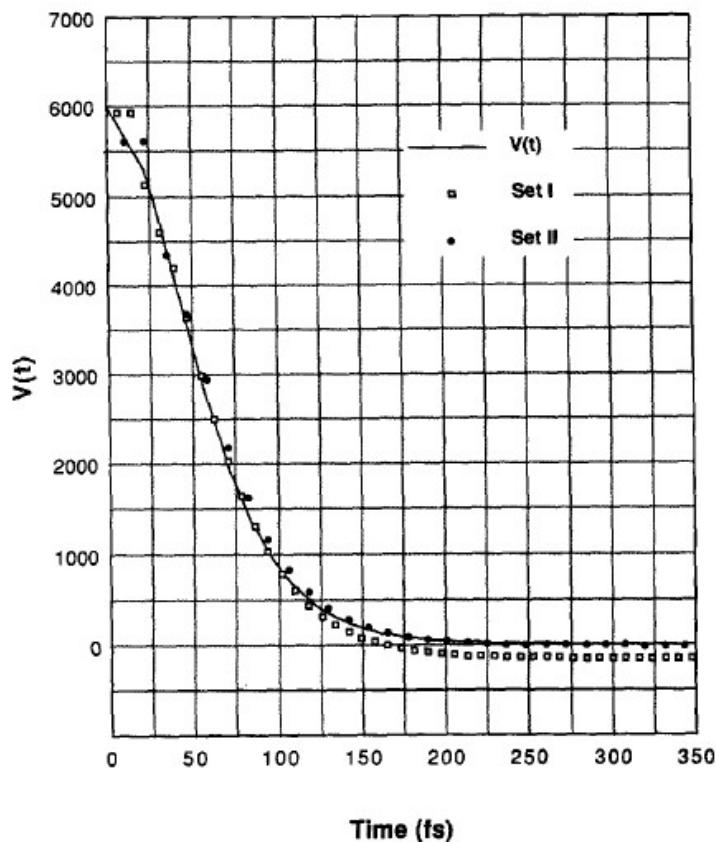
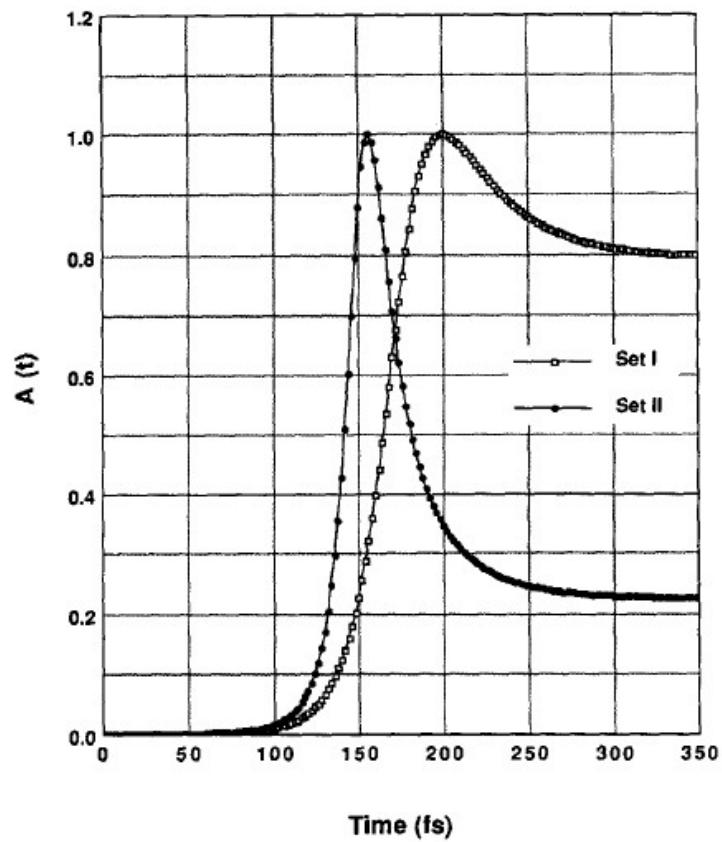
FIG. 5. Typical ICN transients as a function of probe wavelength. The probe wavelengths were (a) $\lambda_2^* = 388.9$ nm, (b) $\lambda_2^* = 389.8$ nm, (c) $\lambda_2^* = 390.4$ nm, and (d) $\lambda_2^* = 391.4$ nm. The solid lines were generated by fitting the classical model of Eq. (5) convolved with the measured experimental response for each transient.



Tuning to the Blue

FIG. 8. Delay time as a function of probe wavelength. The values of $\tau_{1/2}$ obtained are shown for an approximate pump wavelength of 306 nm (open triangles) and 285 nm (solid squares). The FWHM of the probe was $\sim 60 \text{ cm}^{-1}$ in each case.

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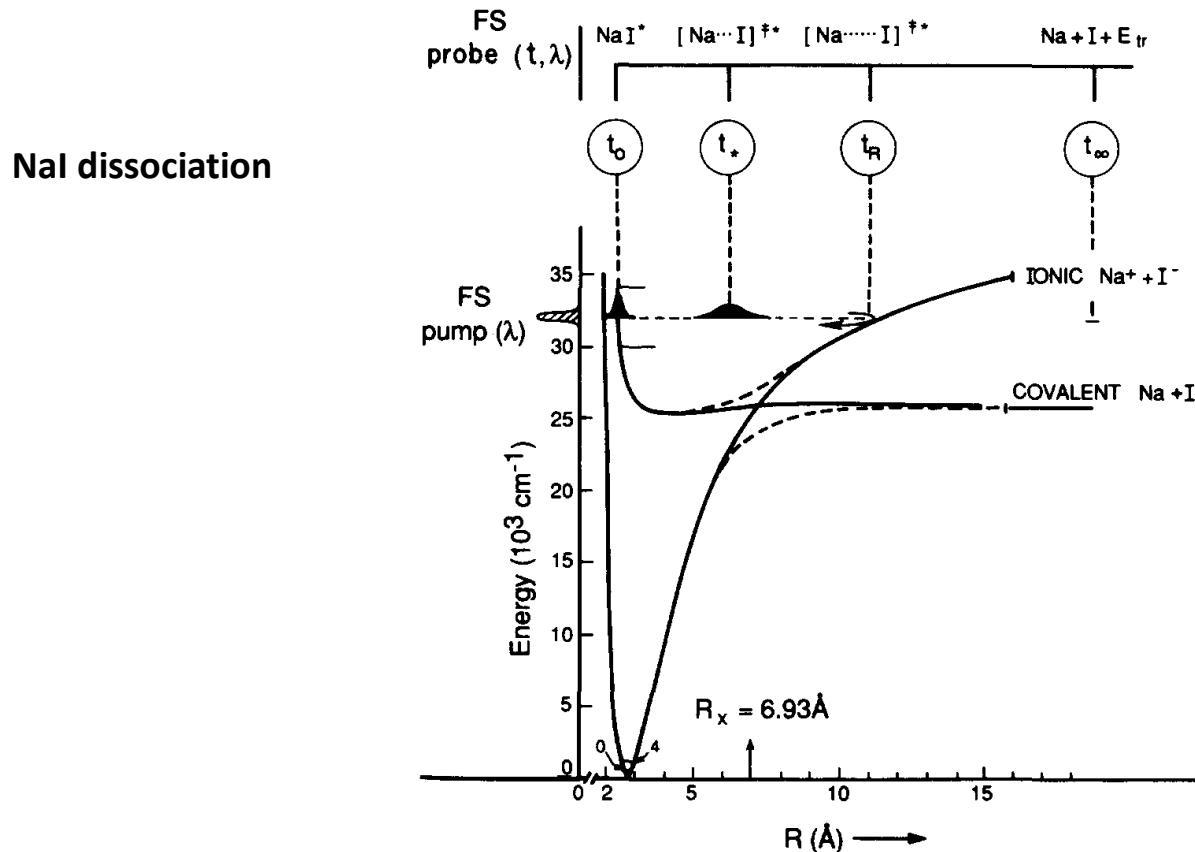


FIG. 1. A display of the potential energy surfaces involved, and the method of FTS. The times t_0 , t_* , t_R , and t_∞ refer to the time of evolution of packet as it moves along the coordinate R and spreads. At the top of the figure, the different transition configurations are given. The fs pump pulse was at 310 nm, and the probe was generated from a continuum ($\lambda = 560$ nm to $\lambda = 630$ nm). The $\text{Na} + \text{I}$ 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.

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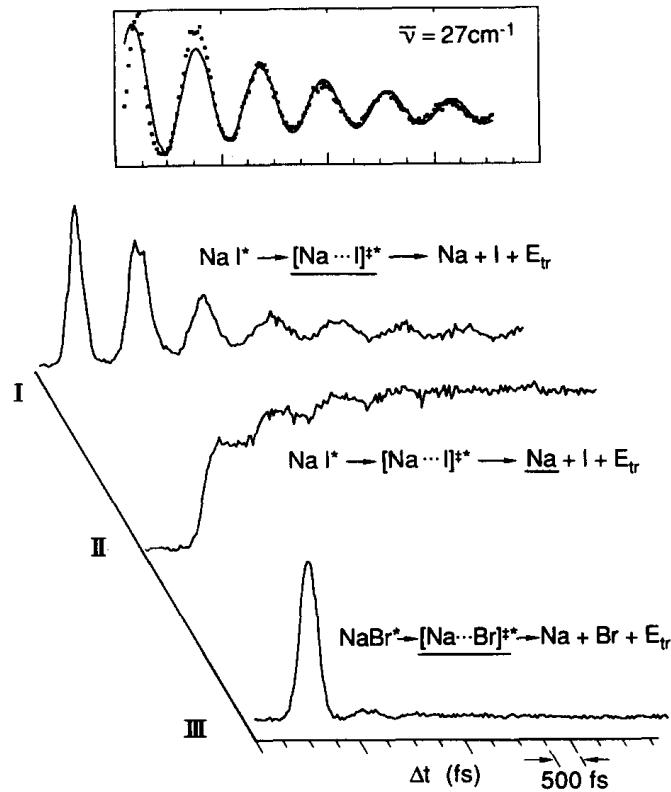


FIG. 2. Experimental results for the two reactions of NaI and NaBr. For the NaI reaction, we provide both the on-resonance and off-resonance Na atom detection (LIF), indicated by the underlining of the relevant species. Results, not shown, were also obtained at a number of other wavelengths, and will 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.

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