時間分解光電子分光による非断熱遷移の実時間観測

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Motivation: Nonadiabatic Transitions

"Nonadiabatic transitions" – A theoretical concept

- invoked to explain many experimental observations
- not something that is seen "directly"
- but *it may be possible to do so now*

Basic building block of

- electron transfer
- wavepacket engineering
- reaction control
- "quantum chaos"

Our Tool: Pump-Probe Photoelectron Spectroscopy

- Femtosecond pump-probe spectroscopy:
  - Good tool for dynamics studies.
- Photoionization as a probe:
  - More information: photoelectron energy and angle distributions.
  - No dark states.
- Problems in theoretical description:
  - Photoionization amplitudes nontrivial to calculate (constant assumed).
  - Difficulty in including ion continuum in dynamics calculation (energy/internal coordinate dependence of ionization have been neglected).

Formulation(1): Wave Function/Hamiltonian

Equation of Motion

$$i\frac{\partial}{\partial t}\Psi(t) = [T_{\mathrm{N}} + H_{\mathrm{el}} + V(t)]\,\Psi(t) \tag{1}$$

Total Wavefunction

$$\Psi(\mathbf{r}, R, t) = \chi_{\mathrm{g}}(R, t)\Phi_{\mathrm{g}}(\mathbf{r}; R) + \chi_{\mathrm{e}}(R, t)\Phi_{\mathrm{e}}(\mathbf{r}; R) + \int d\mathbf{k}\chi_{\mathbf{k}}(R, t)\Phi_{\mathbf{k}}^{(-)}(\mathbf{r}; R) \tag{2}$$

Pump-Probe Interaction

$$V(t) = V_{\mathrm{pump}}(t) + V_{\mathrm{probe}}(t; \Delta T) = f_1(t)\sin(\omega_1 t)\boldsymbol{\varepsilon}_{\mathrm{pump}} \cdot \mathbf{d} + f_2(t)\sin(\omega_2 t)\boldsymbol{\varepsilon}_{\mathrm{probe}} \cdot \mathbf{d} \tag{3}$$

$\Phi_{\mathbf{k}}^{(-)}$: electronic wave function representing ionized state.

χ_{g}, χ_{e}, and $\chi_{\mathbf{k}}$: nuclear wave packets on the potential surfaces.

Formulation(2): Coupled Equations of Motion

$$
\begin{aligned}
i\frac{\partial}{\partial t}\chi_{\rm g}(R,t) &= [T_{\rm N}+V_{\rm g}]\,\chi_{\rm g}(R,t)+\langle\Phi_{\rm g}(R)|T_{\rm N}|\Phi_{\rm e}(R)\rangle\chi_{\rm e}(R,t) \\
&+\langle\Phi_{\rm g}(R)|V_{\rm pump}(t)|\Phi_{\rm e}(R)\rangle\chi_{\rm e}(R,t) \qquad (4a)\\
&+\int d\mathbf{k}\langle\Phi_{\rm g}(R)|V_{\rm probe}(t)|\Phi_{\mathbf{k}}^{(-)}(R)\rangle\chi_{\mathbf{k}}(R,t)
\end{aligned}
$$

$$
\begin{aligned}
i\frac{\partial}{\partial t}\chi_{\rm e}(R,t) &= [T_{\rm N}+V_{\rm e}]\,\chi_{\rm e}(R,t)+\langle\Phi_{\rm e}(R)|T_{\rm N}|\Phi_{\rm g}(R)\rangle\chi_{\rm g}(R,t) \\
&+\langle\Phi_{\rm e}(R)|V_{\rm pump}(t)|\Phi_{\rm g}(R)\rangle\chi_{\rm g}(R,t) \qquad (4b)\\
&+\int d\mathbf{k}\langle\Phi_{\rm e}(R)|V_{\rm probe}(t)|\Phi_{\mathbf{k}}^{(-)}(R)\rangle\chi_{\mathbf{k}}(R,t)
\end{aligned}
$$

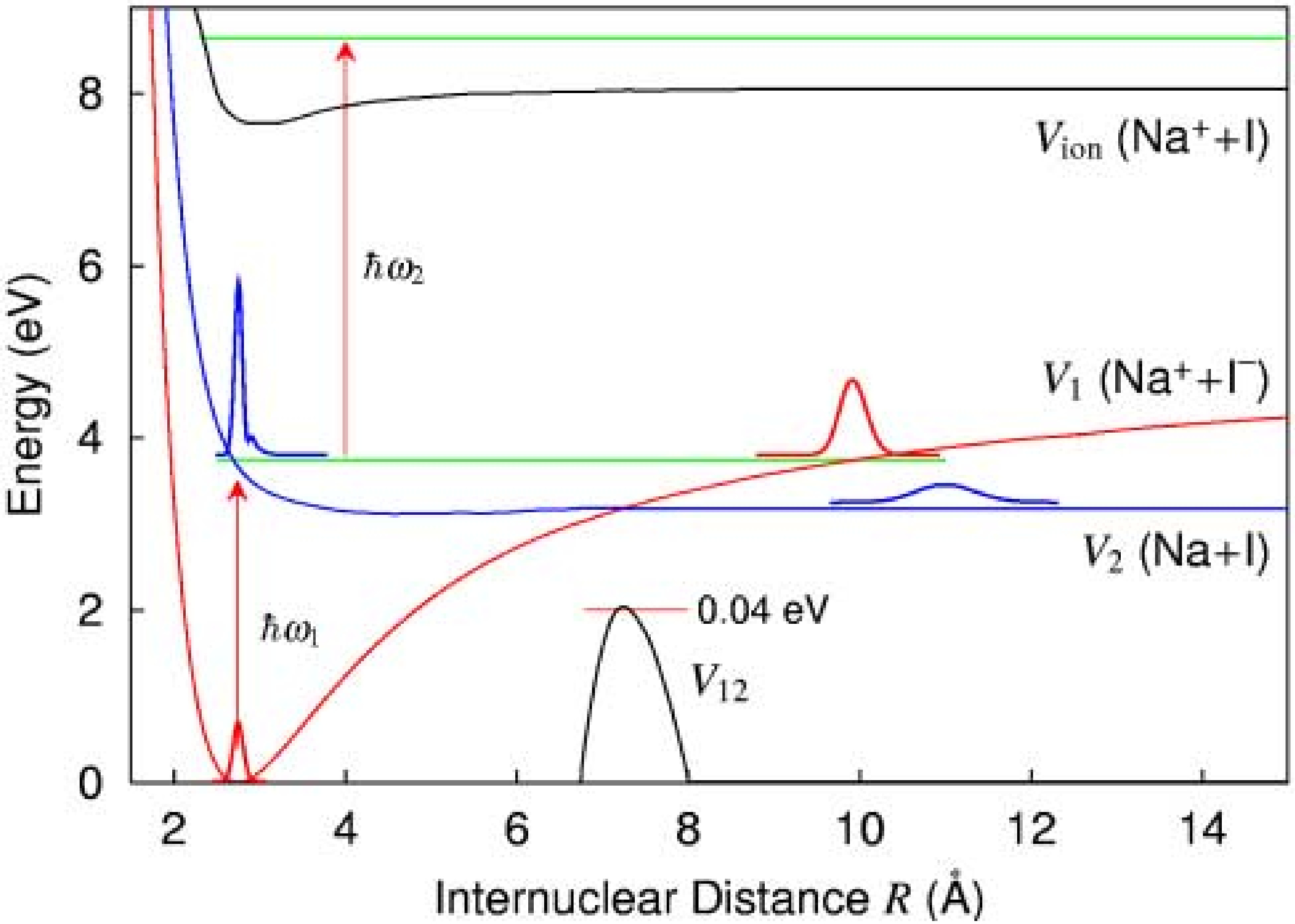
$$
\begin{aligned}
i\frac{\partial}{\partial t}\chi_{\mathbf{k}}(R,t) &= \left[T_{\rm N}+V_{\rm ion}+\frac{k^2}{2}\right]\chi_{\mathbf{k}}(R,t) \\
&+\langle\Phi_{\mathbf{k}}(R)|V_{\rm probe}(t;\hat{R},\theta_P,\omega_2;\Delta T)|\Phi_{\rm g}(R)\rangle\chi_{\rm g}(R,t) \qquad (4c)\\
&+\langle\Phi_{\mathbf{k}}(R)|V_{\rm probe}(t;\hat{R},\theta_P,\omega_2;\Delta T)|\Phi_{\rm e}(R)\rangle\chi_{\rm e}(R,t)
\end{aligned}
$$

Formulation(3): Solving the Equations

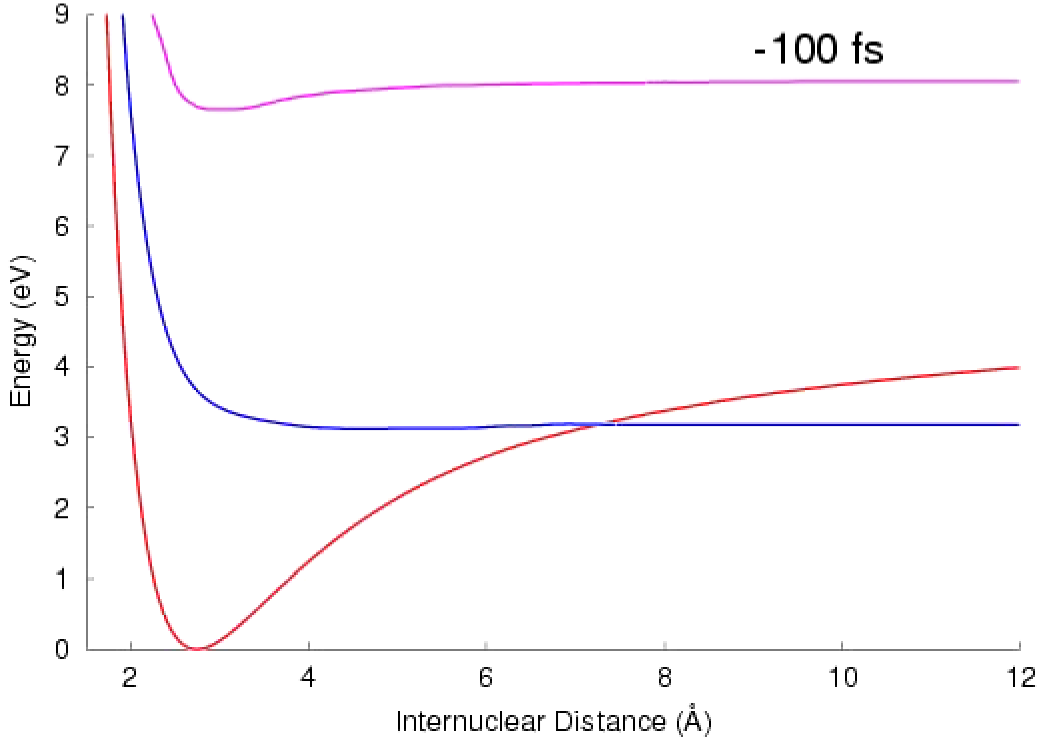
- A simple model of diabatic potentials: Adiabatic curves smoothly interpolated through avoided crossing.
- Single center expansion of scattering orbital. Iterative Schwinger method used to solve for the partial waves. $\longrightarrow$Natural inclusion of angular dependence.
- Integration over k discretized as a quadrature over N_k points.
- Split operator technique for time-propagation. Kinetic energy operator handled with FFT.
- Analytic diagonalization for pump/probe interaction.

Time-propagated vibrational wavepackets after pump-probe interaction are used to compute population corresponding to each photoelectron partial wave/discretized k (i.e. photoelectron angle and energy distribution).

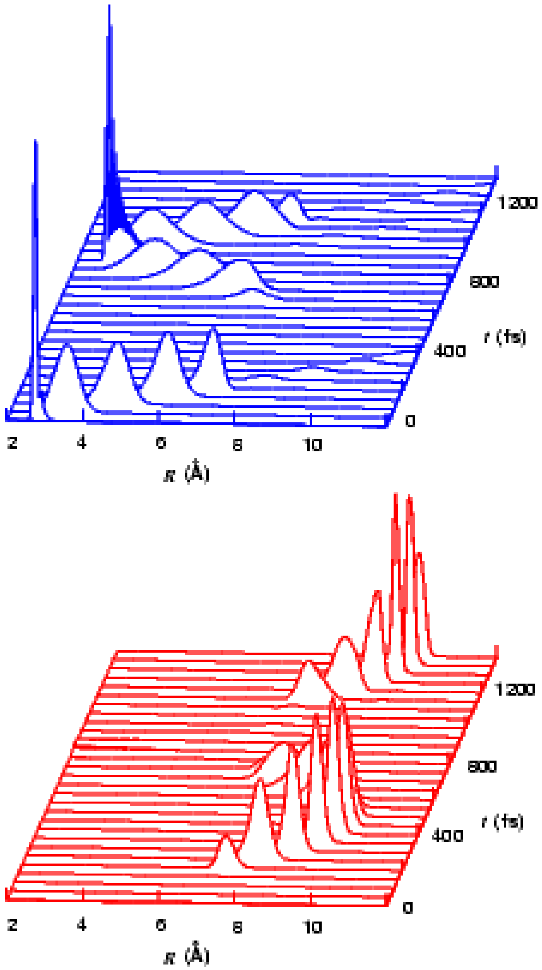
NaI Pump-Probe Scheme

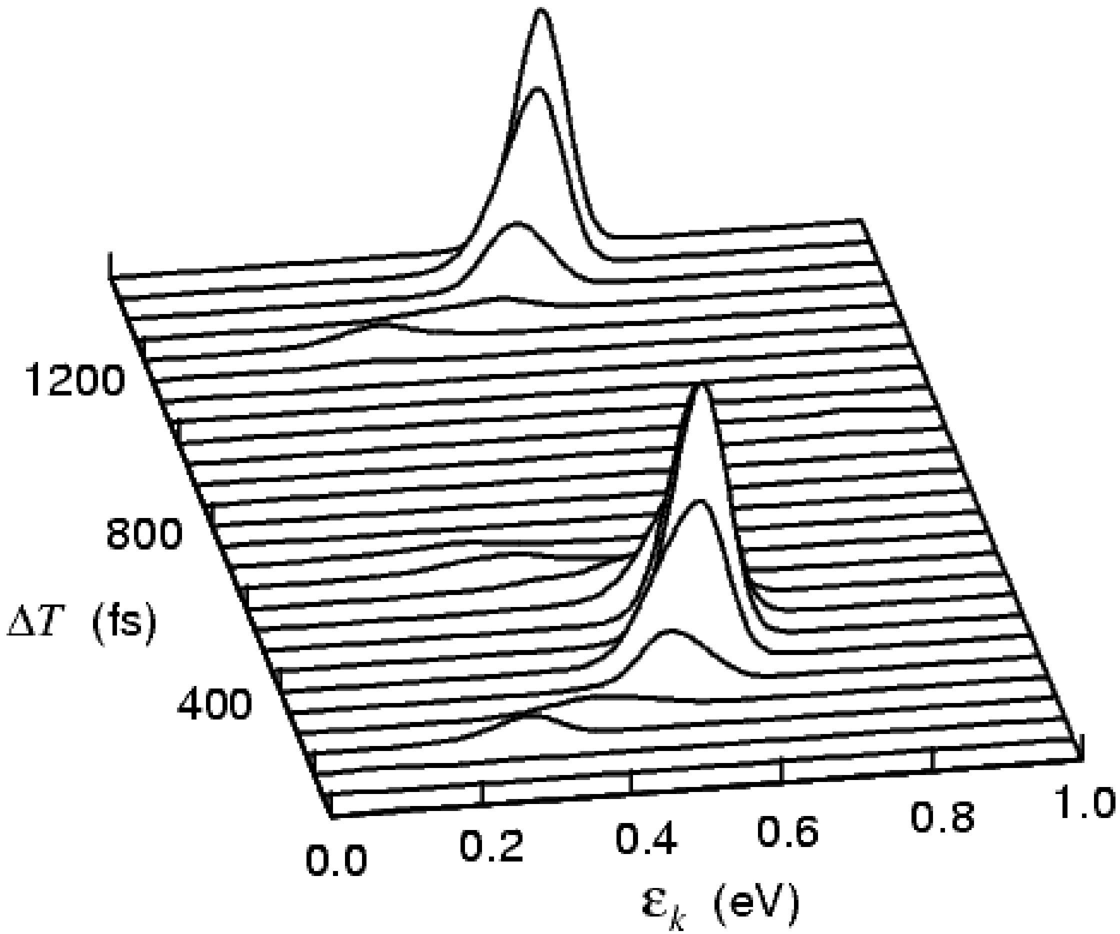


Excited State Dynamics on the Diabatic Curves

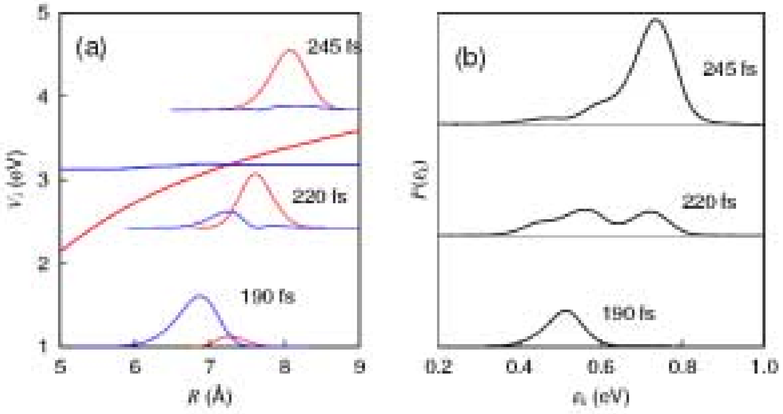


Photoelectron Kinetic Energy Spectra

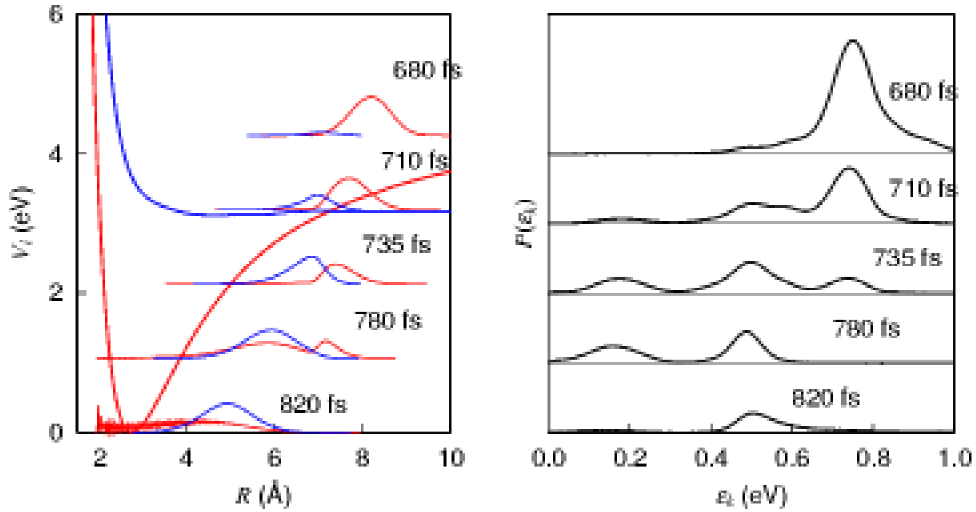




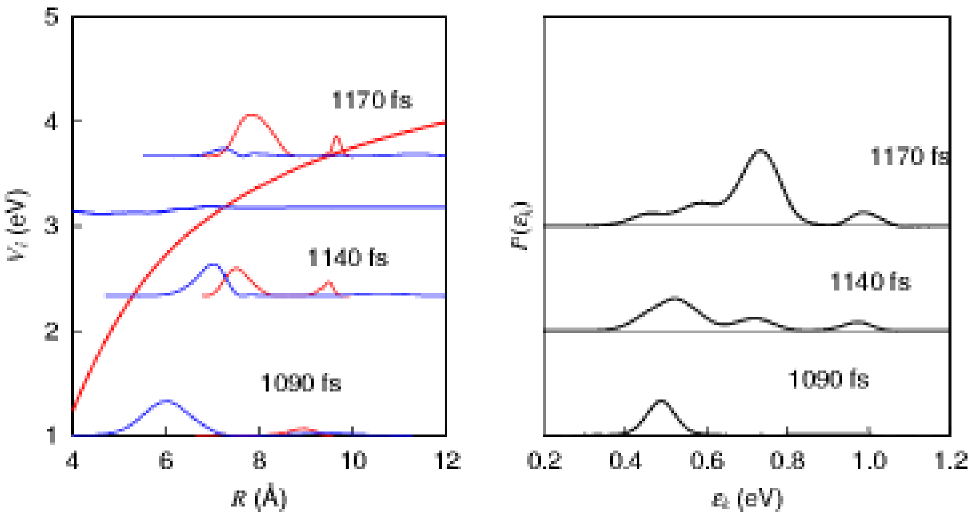
First Crossing: Transfer Among Diabatic Curves



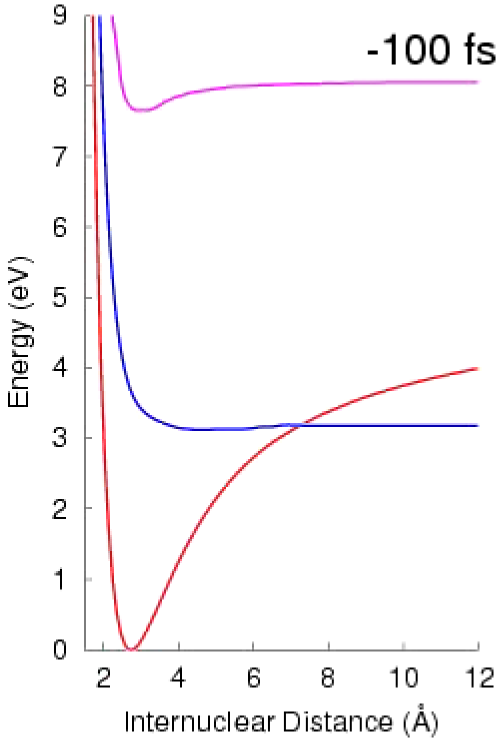
Second Crossing: Splitting Wavepacket



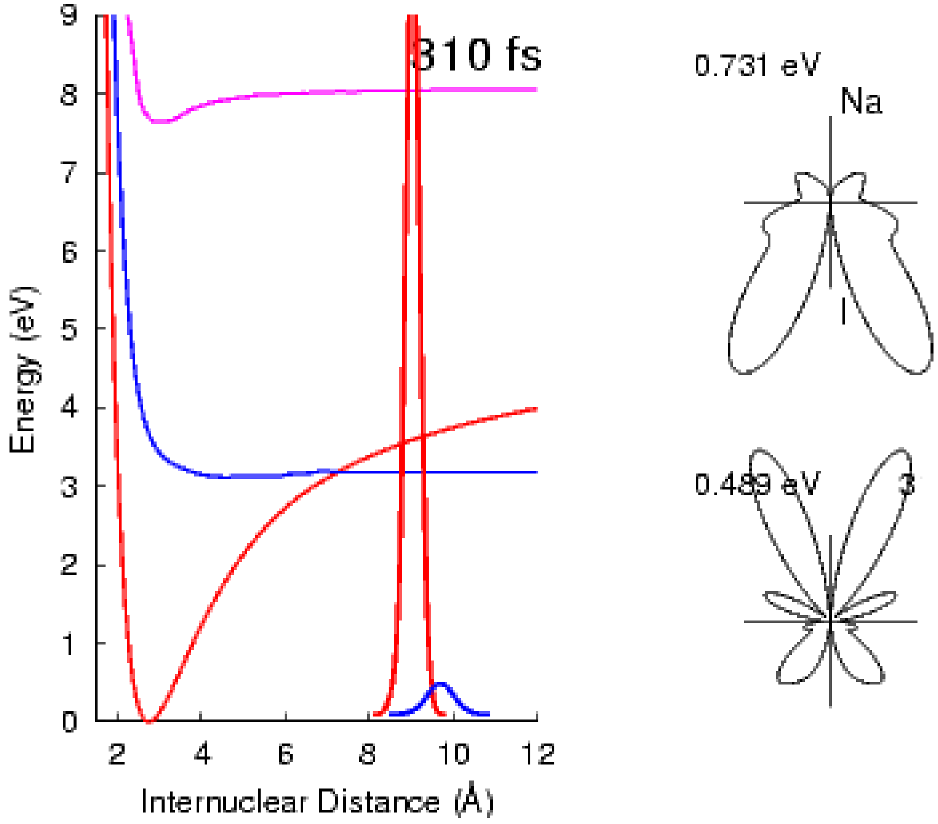
Third Crossing: Wavepacket Mixing



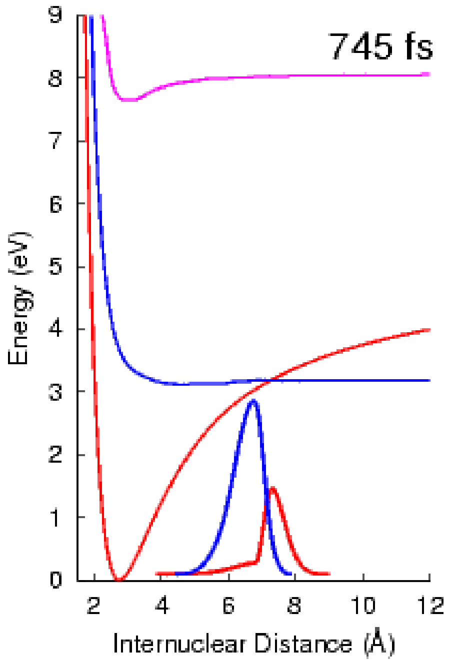
Photoelectron Kinetic Energy Spectra (in motion)

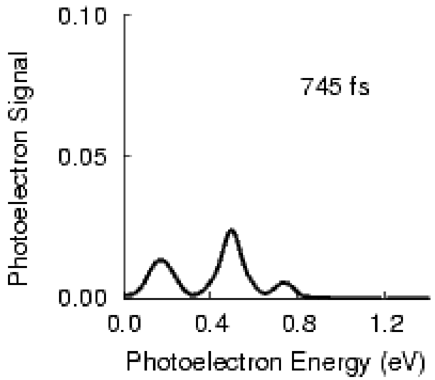


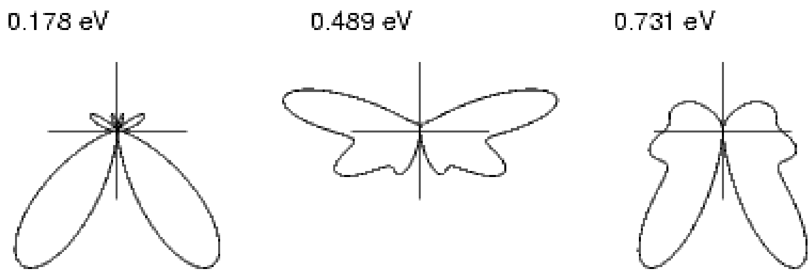
Photoelectron Angular Distributions



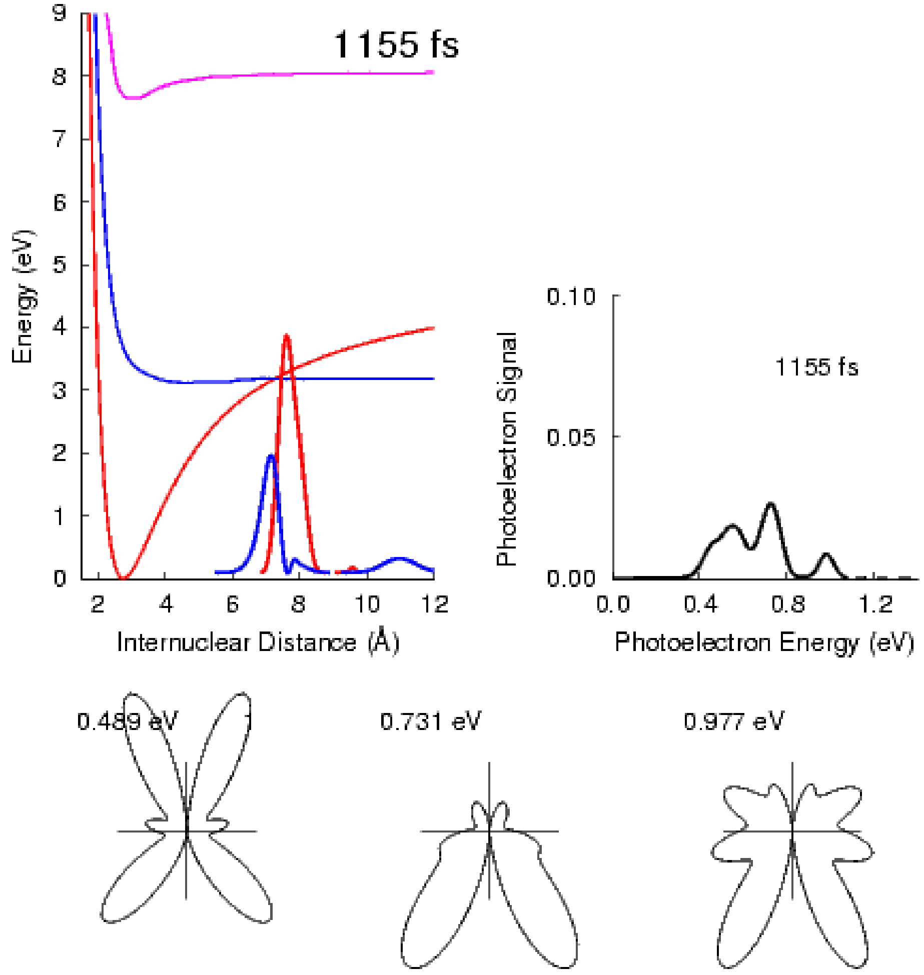
Identifying Origin of Peaks 1



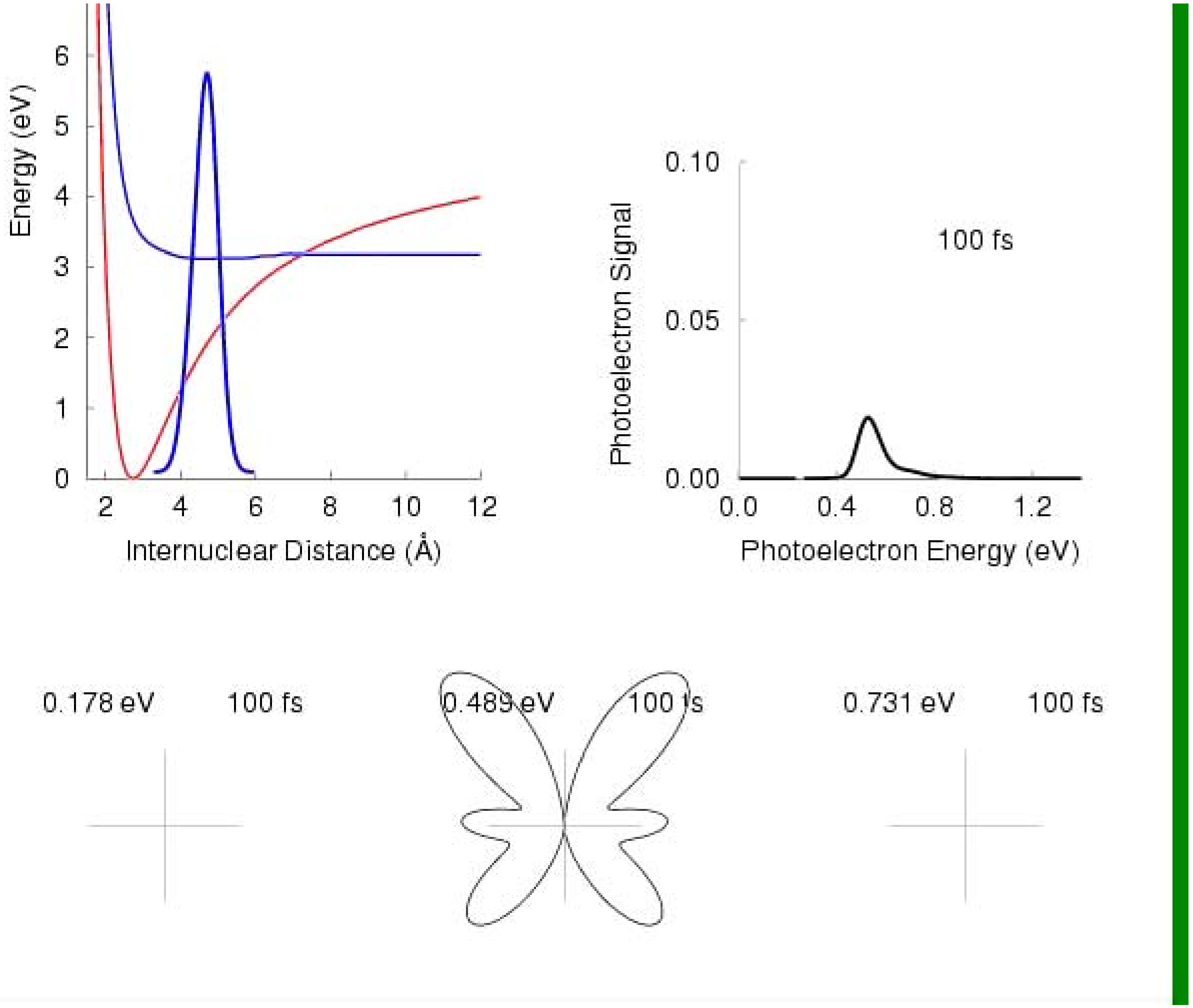




Identifying Origin of Peaks 2



Assigning Peaks with the Aid of Angular Distributions



Conclusion

Direct observation of the wavepacket passing through the avoided crossing is possible (in a favorable system)

- Femtosecond pump-probe photoelectron spectroscopy: Photoelectron kinetic energy distribution maps the position and spread of wavefunction.
- Splitting and joining of wavefunction also mapped in the energy distributions.
- Angular distribution reflects character of the ionized state. $\longrightarrow$Further clues to identify origin of signals.