Nonlinear Wave Packet Interferometry and Molecular State Reconstruction

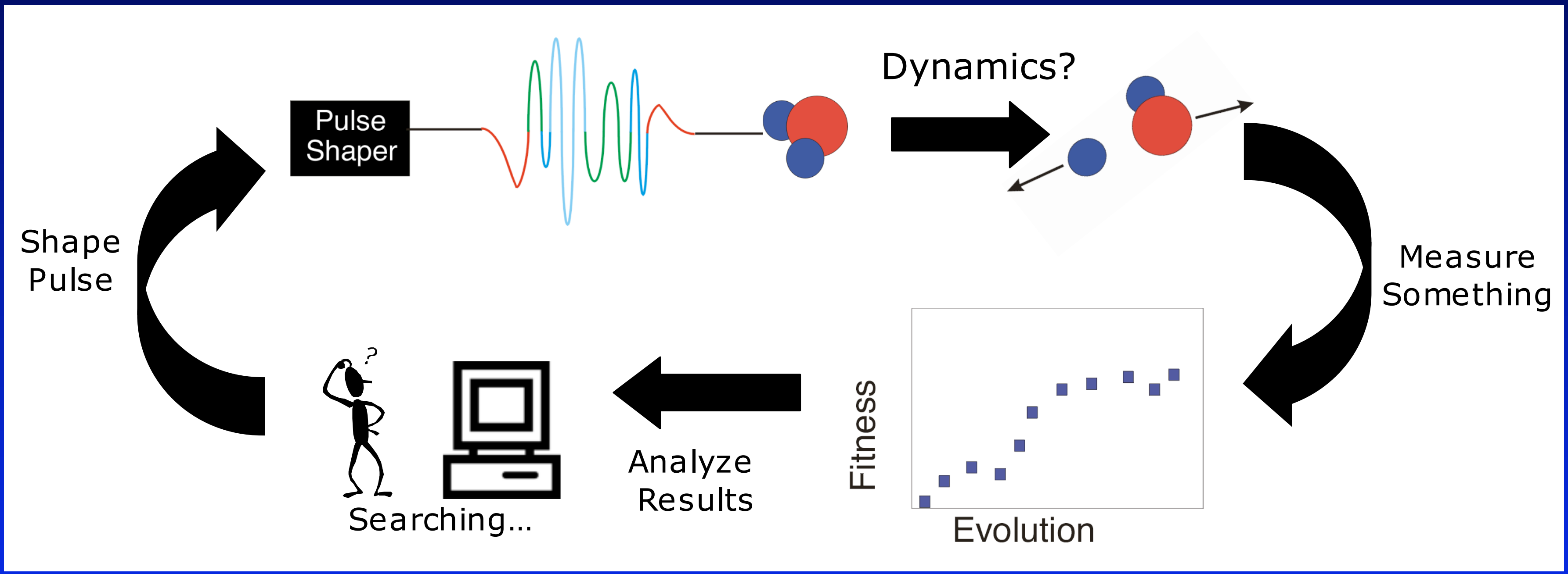
Measuring quantum dynamics with nonlinear optical spectroscopy

Travis S. Humble* and Jeffrey A. Cina
Chemistry Department and Oregon Center for Optics
University of Oregon

***Currently working with Warren Grice at Oak Ridge National Laboratory**

Coherently Controlling Chemistry

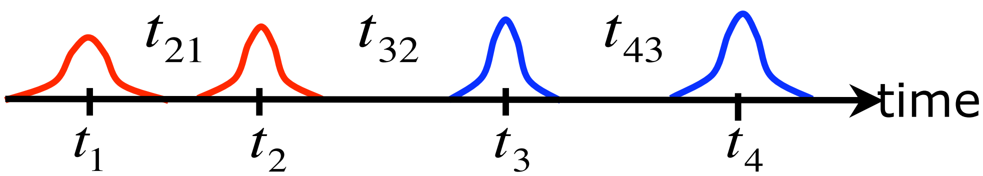
Closed-loop, feedback-controlled pulse-shaping techniques can optimize a pulse spectrum to yield a desired reaction. (Judson and Rabitz, 1993)



In lieu of solving Schrödinger's equation, we can reconstruct the molecular state by experimental determination of the expansion coefficients $c_n(t)$:

$$|\Psi(t)\rangle = \sum c_n(t)|n\rangle \qquad c_n(t) = \langle n|\Psi(t)\rangle$$

Nonlinear Wave Packet Interferometry



Two phase-locking angles:

$$\phi = \phi_2\left(\omega_L\right) - \phi_1\left(\omega_L\right) - \omega_L t_{21}$$

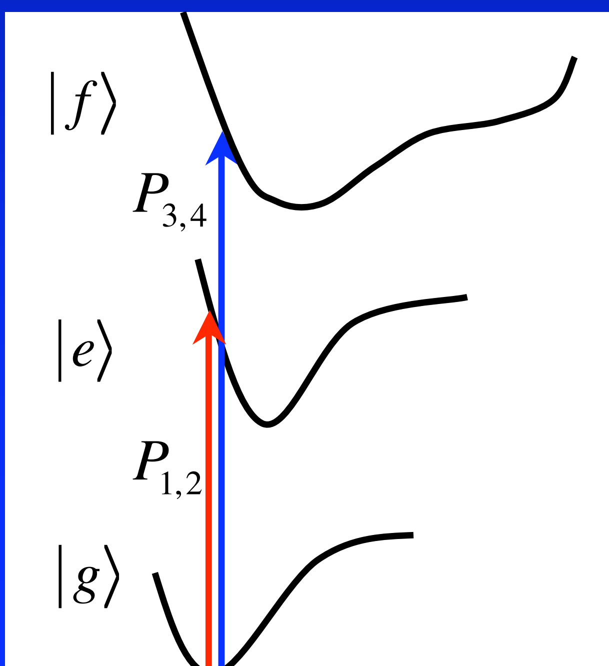
$$\phi' = \phi_4\left(\omega_L'\right) - \phi_3\left(\omega_L'\right) - \omega_L' t_{43}$$

Two pairs of phase-locked pulses:
Cina and Harris 1993, Cina 2000

Akin to four-wave mixing
with heterodyne detection

Groups: Wiersma, Jonas, Fleming,
and others

Two-color Nonlinear WPI: Each pulse-pair drives a different electronic transition.



Initial (g) and intermediate (e) levels are well characterized.

Incomplete information about final (f) level.

Hold fixed delay t_{43} during which target propagates

Scan delays t_{21} and t_{32}.

Measure f-state population.

The Electronic Population

$$P_f(\phi,\phi') = \left|\langle f | \Psi(t)\rangle\right|^2$$

3rd-order perturbation theory, collecting terms with like phase signature

$$P_f(\phi,\phi') = \sum_{m=-1}^{1} \sum_{n=-1}^{1} p_{mn} e^{i(m\phi+n\phi')} \qquad p_{-m,-n} = p^*_{m,n}$$

Only one depends on the phase-locking angle difference.

$$(\phi - \phi') \longrightarrow p_{-1,1} = \langle (421)_f | (3)_f \rangle$$

Phase-cycling measurements: Inverse Fourier transform

$$p_{-1,1} = \frac{1}{9}\Big[P_f(0,0) + P_f(0,\Delta)e^{-i\Delta} + P_f(0,2\Delta)e^{i\Delta}$$
$$+P_f(\Delta,0)e^{i\Delta} + P_f(\Delta,\Delta) + P_f(\Delta,2\Delta)e^{-i\Delta}$$
$$+P_f(2\Delta,0)e^{-i\Delta} + P_f(2\Delta,\Delta)e^{i\Delta} + P_f(2\Delta,2\Delta)\Big]$$

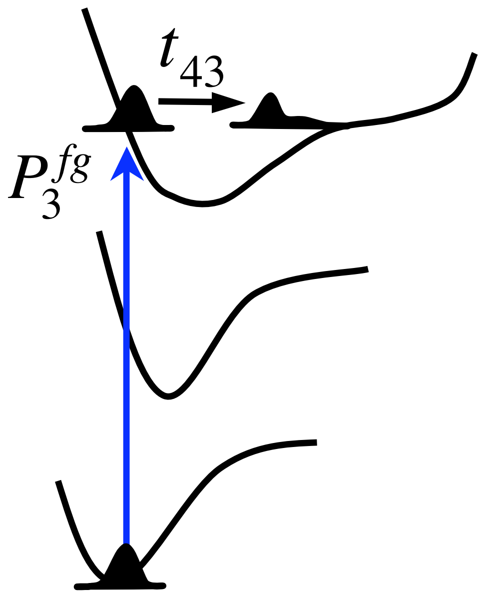
Sampling interval
$\Delta = 2\pi / 3$

Identifying Target and Reference States

From a collection of measurements $\longrightarrow \mathbf{z} = \mathbf{R}\mathbf{t}$ $\qquad \mathbf{r} = \mathbf{R}_T^{-1}\mathbf{z}$

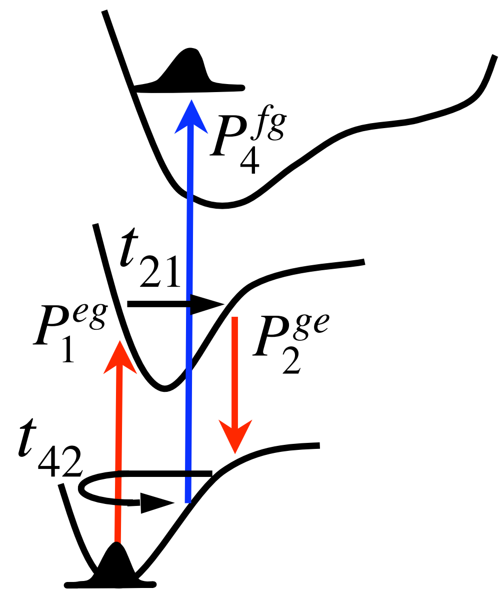
Target state

$$\left|\mathrm{tar}_3\right\rangle = \exp\left[i\phi_3\left(\omega_L'\right) + i\omega_L' t_{43}\right]\left|(3)_f\right\rangle$$



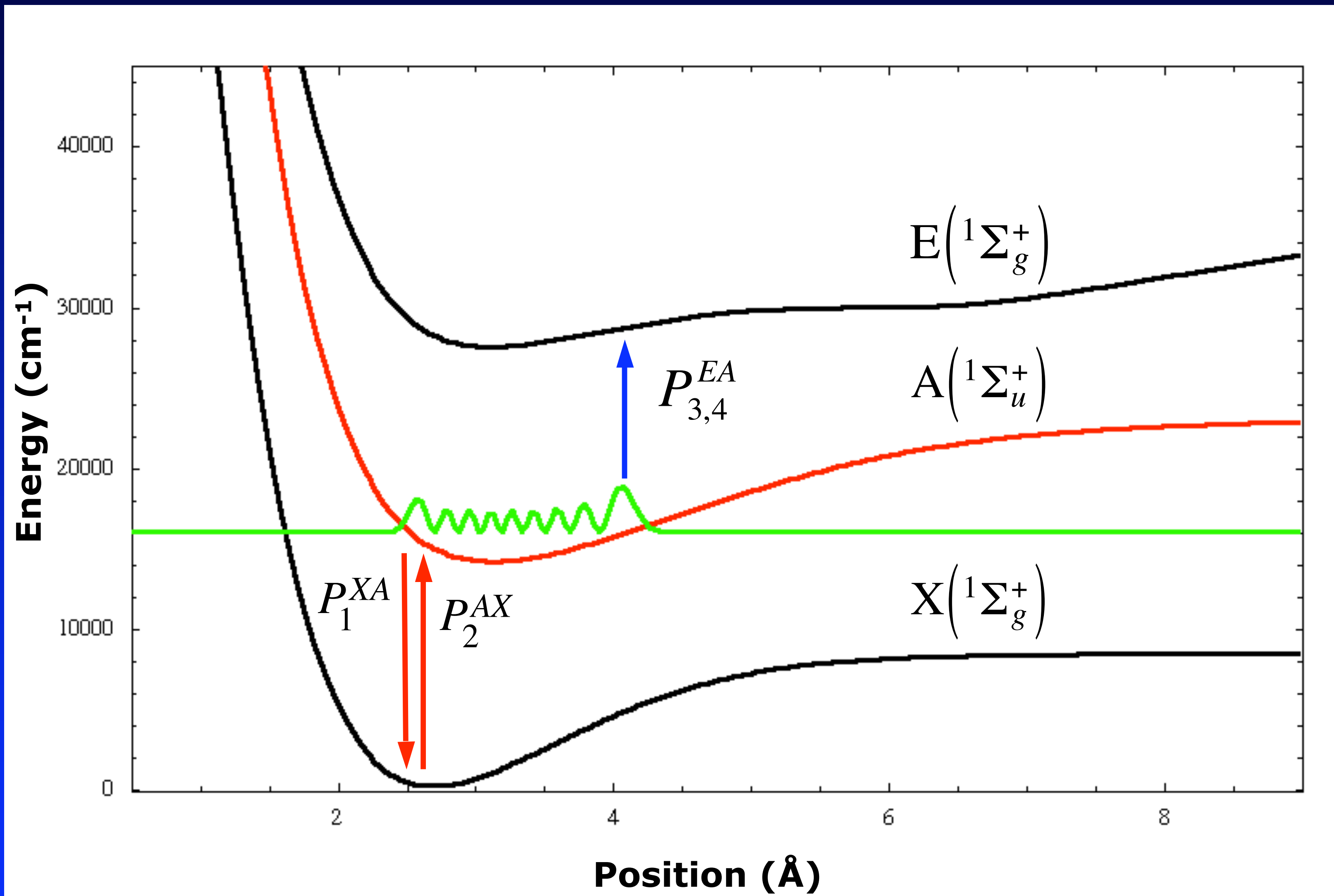
Reference state

$$\left|\mathrm{ref}_{421}\right\rangle = \exp\left[i\phi_4\left(\omega_L'\right)\right]\left|(421)_f\right\rangle$$



Reconstruction fidelity: $f = \dfrac{\left|\mathbf{r}^* \cdot \mathbf{t}\right|}{\left|\mathbf{r}\right|\left|\mathbf{t}\right|}$

Rotating and vibrating Lithium dimer



At 650 nm

$P_{1,2}^{AX}$ 23 fs FWHM

At 830 nm

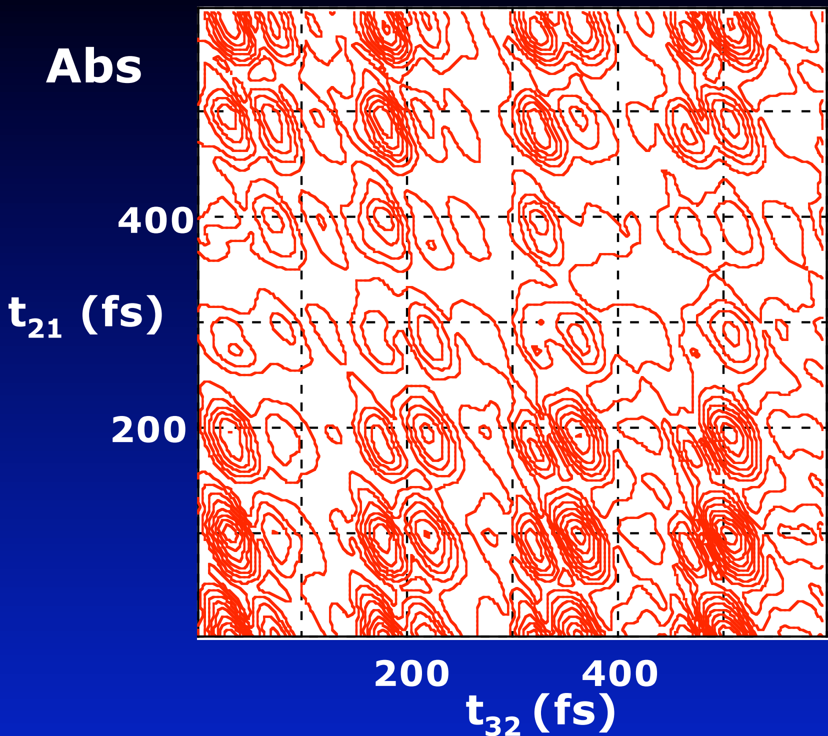
P_3^{EA} 37 fs FWHM

P_4^{EA} 14 fs FWHM

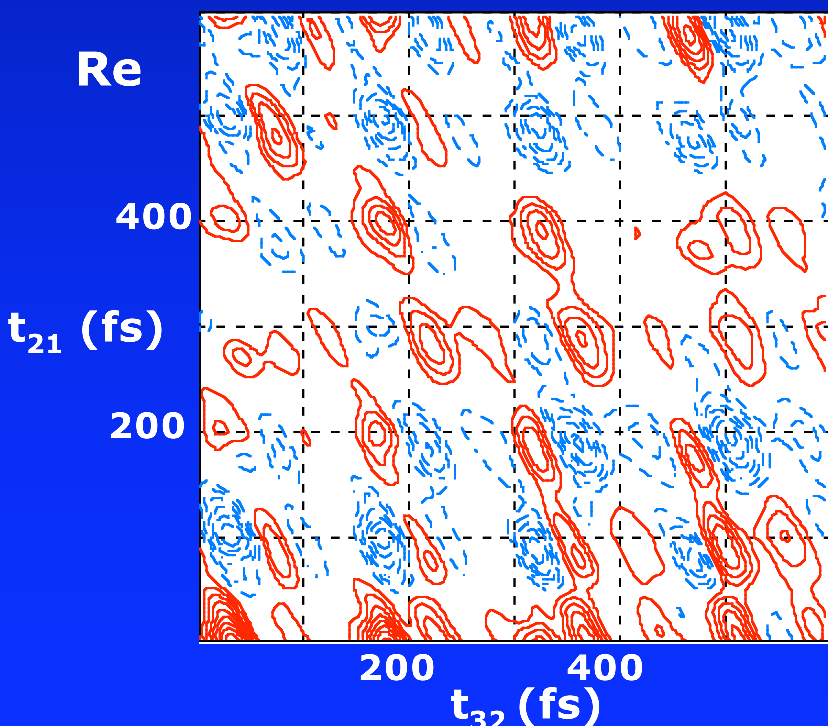
Nonlinear WPI Signal of Li_2

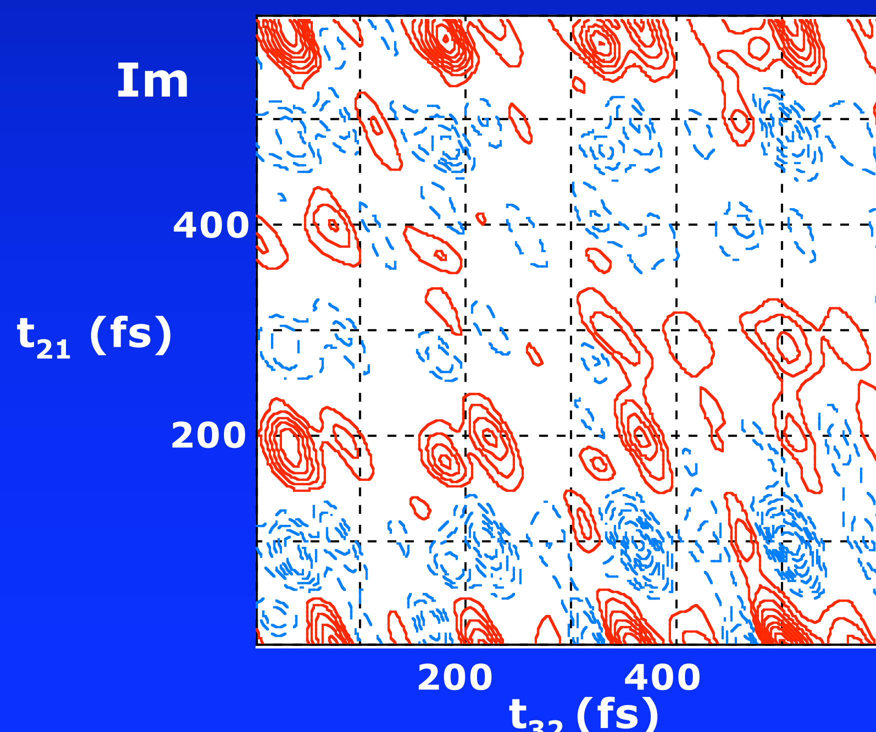
t_{43} = 18.84 ps ~ 100 τ_{Vib}

t_{21} and t_{32}: 0 to 600 fs in 4 fs steps



Positive contour
Negative contour





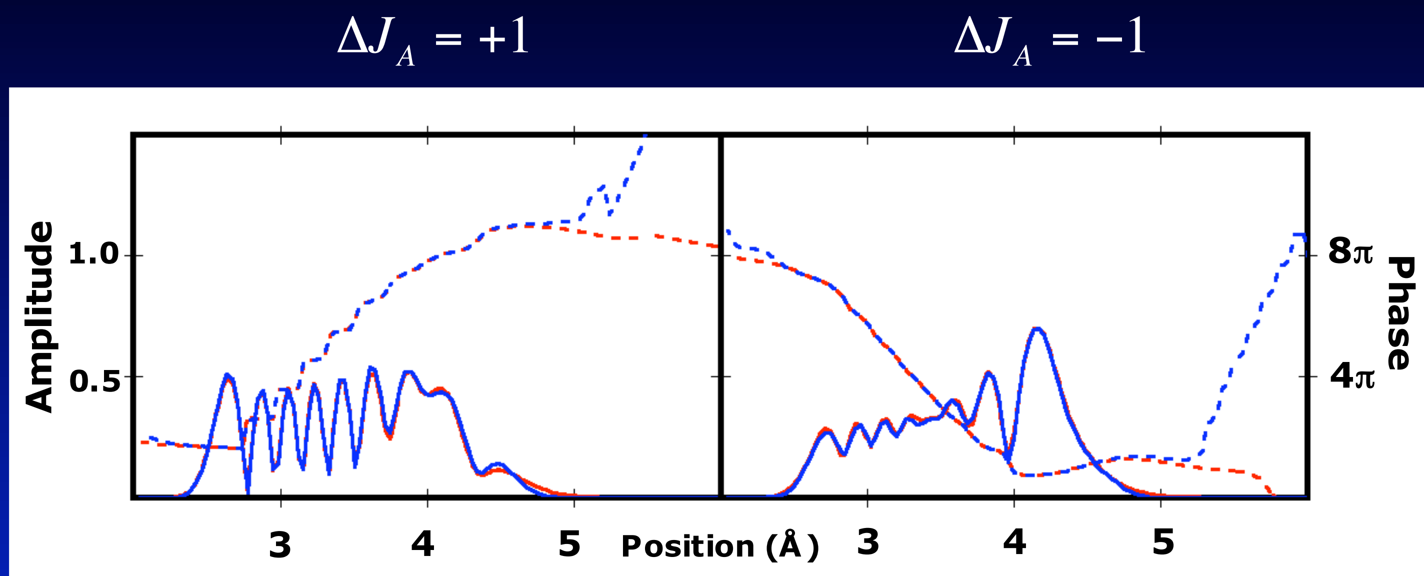
Target State Reconstruction

Added 5% Random Gaussian Noise to Signal

$$f = 0.9983$$

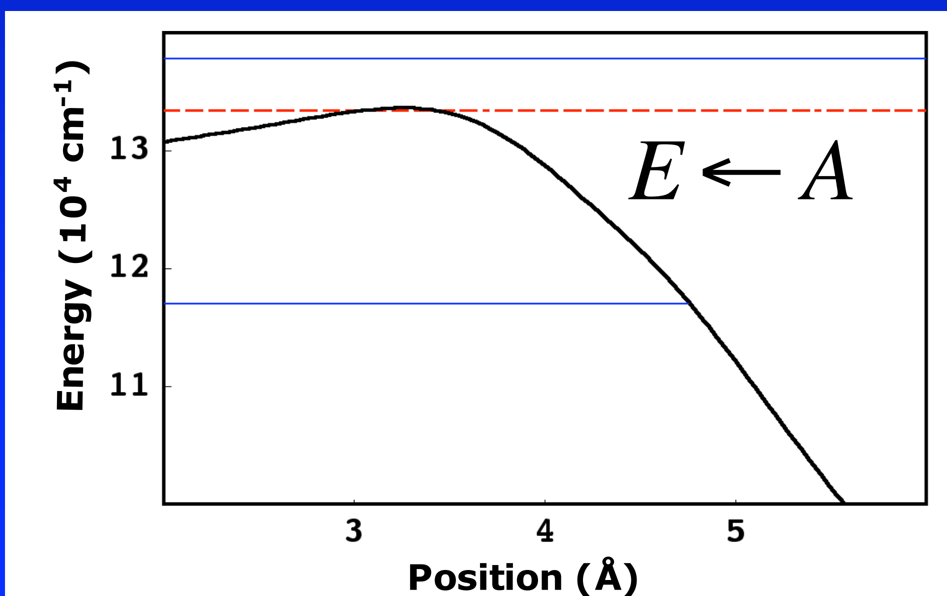
Redundant Info.

Uncorrelated noise

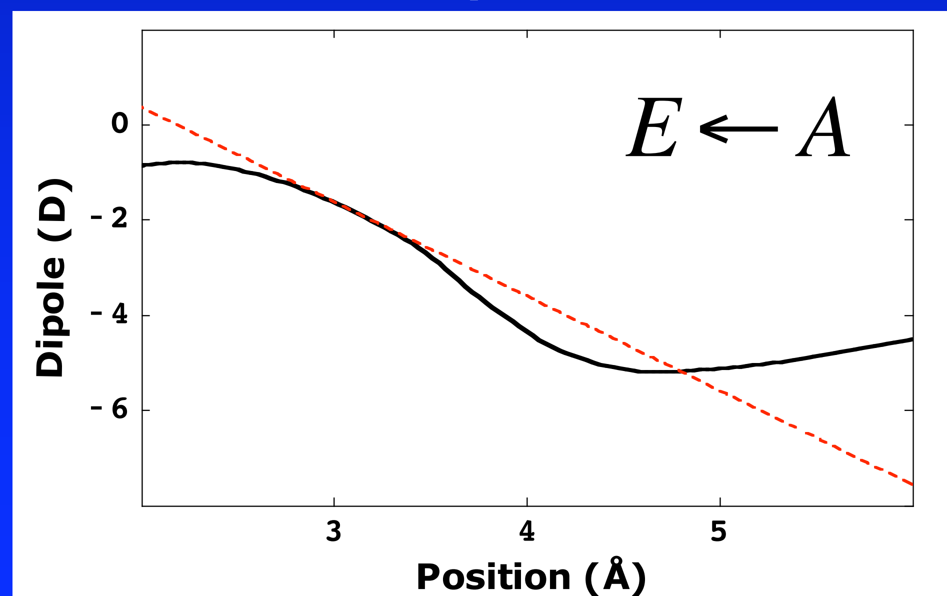


But what if we don't know much about the E surface…approximate it!

Difference Potential



Transition Dipole Moment



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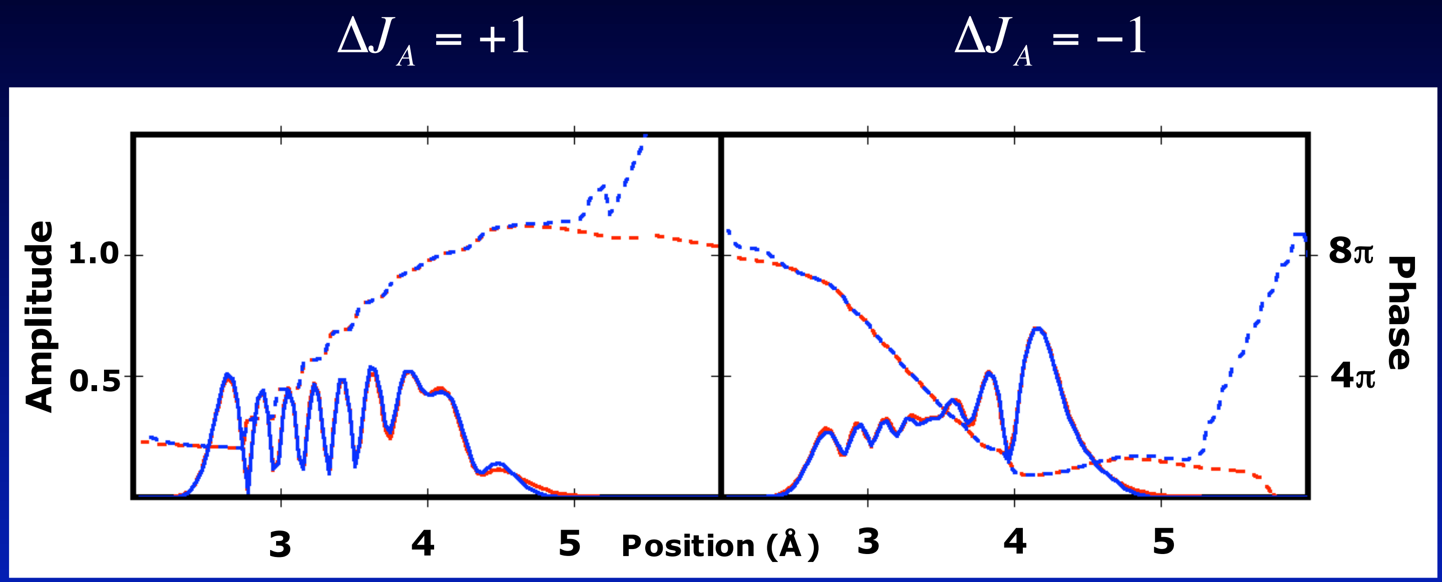
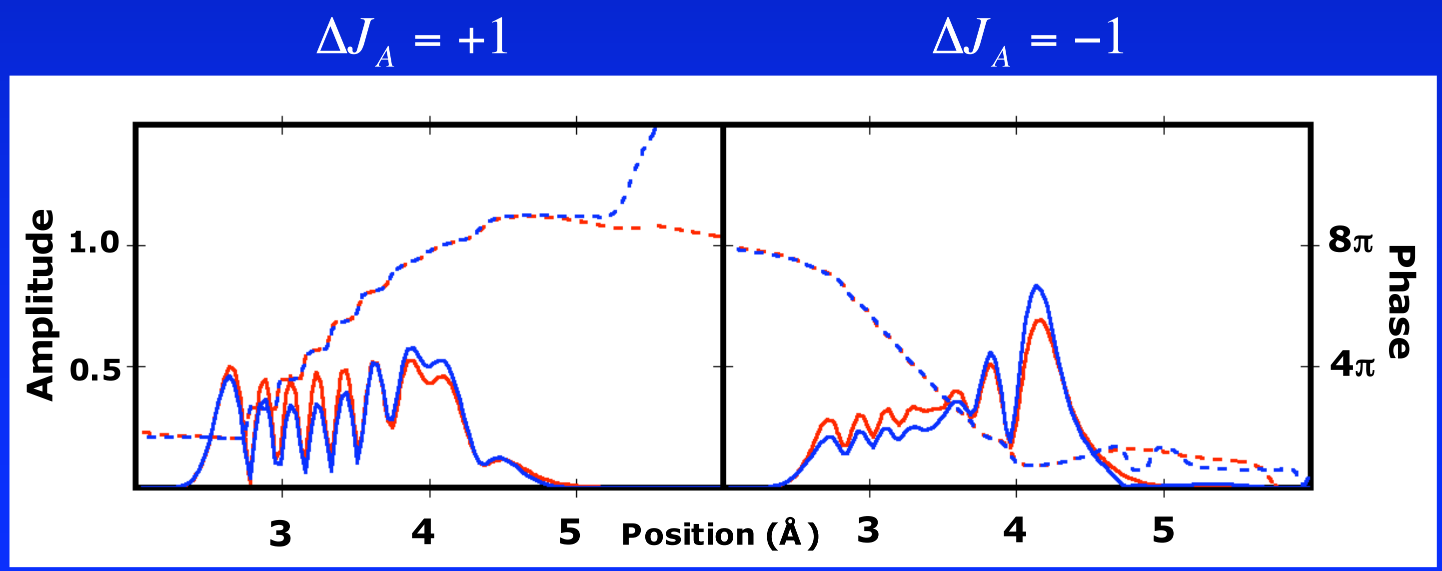


Approximate Reference Wave Packets

Constant difference potential and linear transition moment

$$f = 0.9831$$



Summary and Outlook

Molecular state reconstruction using nonlinear wave packet interferometry (WPI).

An experimental technique capable of identifying optically-prepared nuclear wave packets.

Simulations of a rotating and vibrating diatomic (Li_2) demonstrate accurate reconstructions of target wave packets, even when the target-state Hamiltonian is unknown.

Future Pursuits

- Strong-field chemistry: Explore non-perturbative matter-field interactions
- Polyatomic systems: Multiple vibrational modes and nonlinear molecules included
- Dissipative systems: A probe of system-bath coupling at the amplitude level?

For more information, please visit my web page:
http://www.ornl.gov/~hqt

The Electronic Amplitude

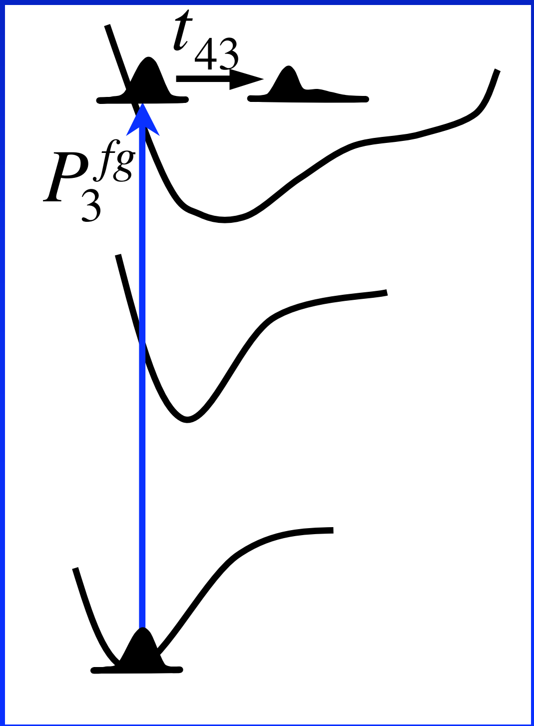
$$\left\langle f \middle| \Psi(t_4) \right\rangle = \left|(3)_f\right\rangle + \left|(4)_f\right\rangle e^{-i\phi'} + \left|(321)_f\right\rangle e^{i\phi} + \left|(421)_f\right\rangle e^{i(\phi-\phi')}$$

$$+\left|(311)_f\right\rangle + \left|(411)_f\right\rangle e^{-i\phi'} + \left|(322)_f\right\rangle + \left|(422)_f\right\rangle e^{-i\phi'}$$

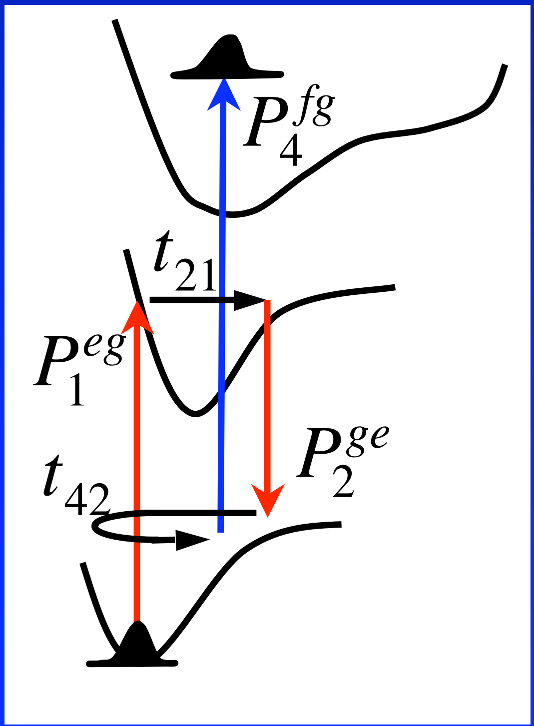
$$+\left|(333)_f\right\rangle + \left|(433)_f\right\rangle e^{-i\phi'} + \left|(443)_f\right\rangle + \left|(444)_f\right\rangle e^{-i\phi'}$$

Important Examples:

$\left|(3)_f\right\rangle$



$\left|(421)_f\right\rangle$



State Reconstruction

With a collection of interference measurements $\longrightarrow \mathbf{z} = \mathbf{R}\mathbf{t}$

$$z_m = \big\langle (421)_f \big| (3)_f \big\rangle \qquad R_{m,k} = \langle \mathrm{ref}_{421} | x_k \rangle \Delta x \qquad t_k = \langle x_k | \mathrm{tar}_3 \rangle \qquad \{x_k\},\ \Delta x$$

Interference signal — Reference matrix — Target vector — position basis

The reconstructed state: $\mathbf{r} = \mathbf{R}_T^{-1}\mathbf{z}$

Singular Value Decomposition: $\mathbf{R} = \mathbf{U}\mathbf{W}\mathbf{V}^\dagger$ Singular values $W_{jj} \geq 0$

Construct a pseudo-inverse: $\mathbf{R}_T^{-1} = \mathbf{V}\mathbf{W}_T^{-1}\mathbf{U}^\dagger$ parameterized by tolerance *T*

Best solution in the least-squares sense: reconstruction fidelity $f = \dfrac{|\mathbf{r}^* \cdot \mathbf{t}|}{|\mathbf{r}||\mathbf{t}|}$

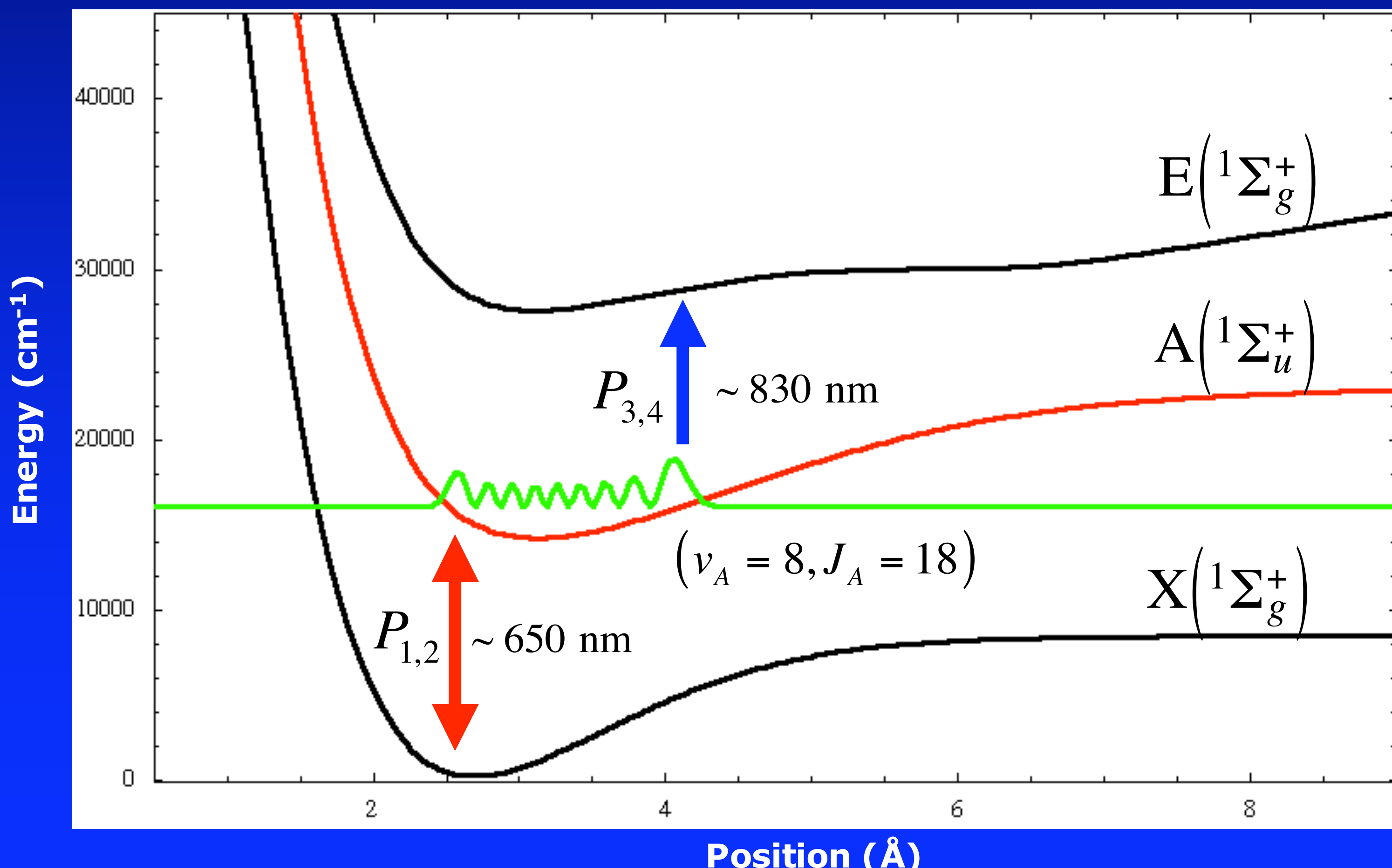
The Lithium Dimer (Li_2)

Rotational and vibrational degrees of freedom.

Accurate *ab initio* potentials and transition moments. (Schmidt-Mink et al., 1985)

E state has an anharmonic "shelf" region
Delocalized, non-rigid-rotor quantum dynamics

Recent coherent control experiments use a "**launch state**" in the **A** electronic level. (Ballard et al. 2003)



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The Rovibrational Target State

$\Delta J_A = \pm 1$ yields a superposition of two rotational states.

$$\left|\mathrm{tar}_3\left(v_A, J_A, M_A\right)\right\rangle = c_{J_A+1,M_A}\left|\chi_+\left(v_A, J_A\right)\right\rangle\left|J_A+1, M_A\right\rangle + c_{J_A,M_A}\left|\chi_-\left(v_A, J_A\right)\right\rangle\left|J_A-1, M_A\right\rangle$$

Differences due to centrifugal potential

$\Delta J_A = +1$ $\Delta J_A = -1$

Before Propagation

After Propagation For 18.84 ps $\sim 100\tau_{VIB}$