Vibrational dynamics of CO^+ in intense laser fields

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Overview

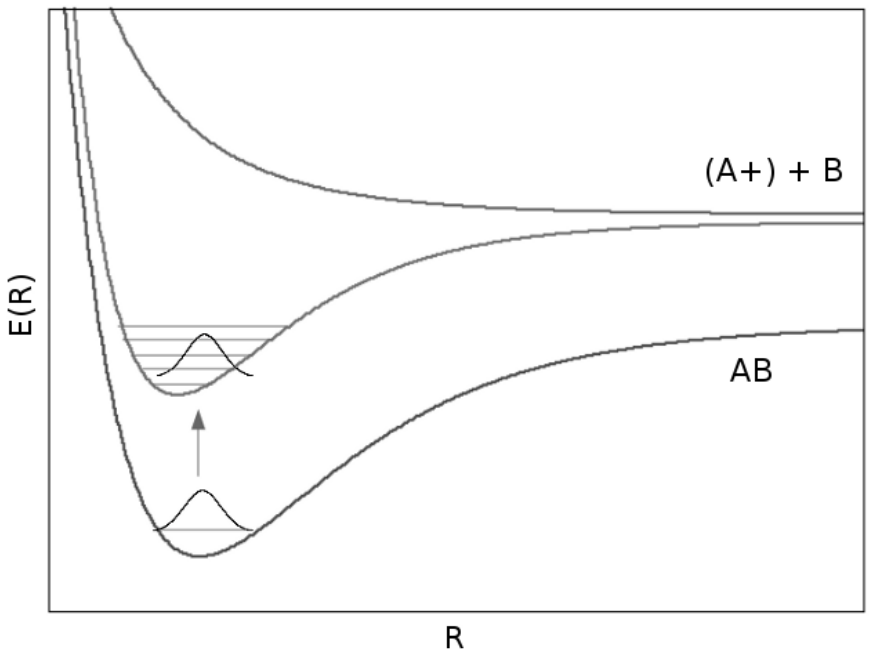
Motivation: Study nuclear vibrational motion of CO^+ and interaction of CO with laser pulses at femtosecond time scales

Outline:

- Experimental methods and prior results
- Theoretical methods
- Preliminary theoretical calculations
- Simulated experiment and results

Pump-probe spectroscopy

Pump-probe spectroscopy provides an experimental method to study vibrational nuclear motion:



1. Ionization from neutral ground state by pump pulse
   $\Psi_{\text{gr.}} \rightarrow \sum_\nu \alpha_\nu \psi_\nu e^{-i\omega_\nu t}$

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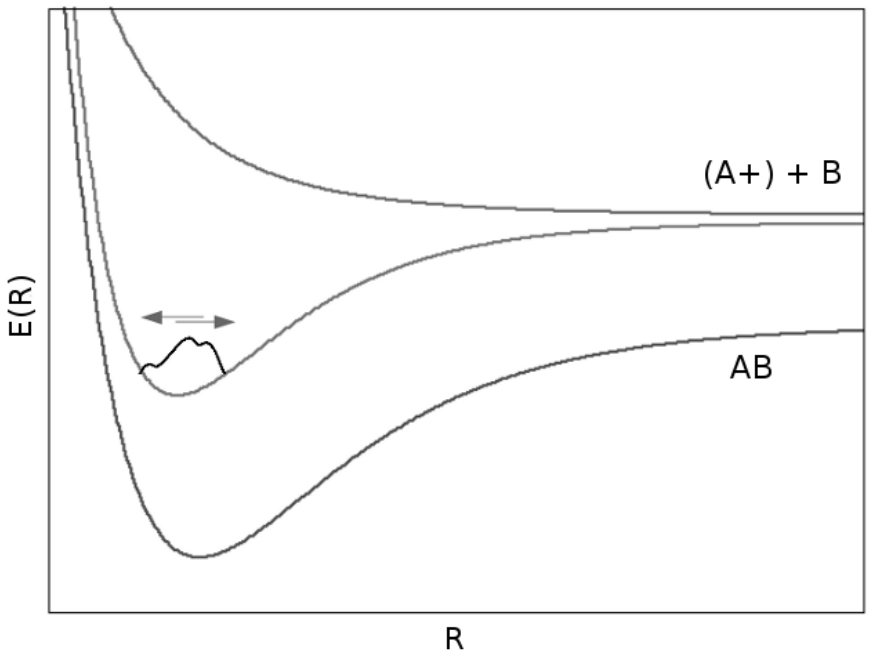
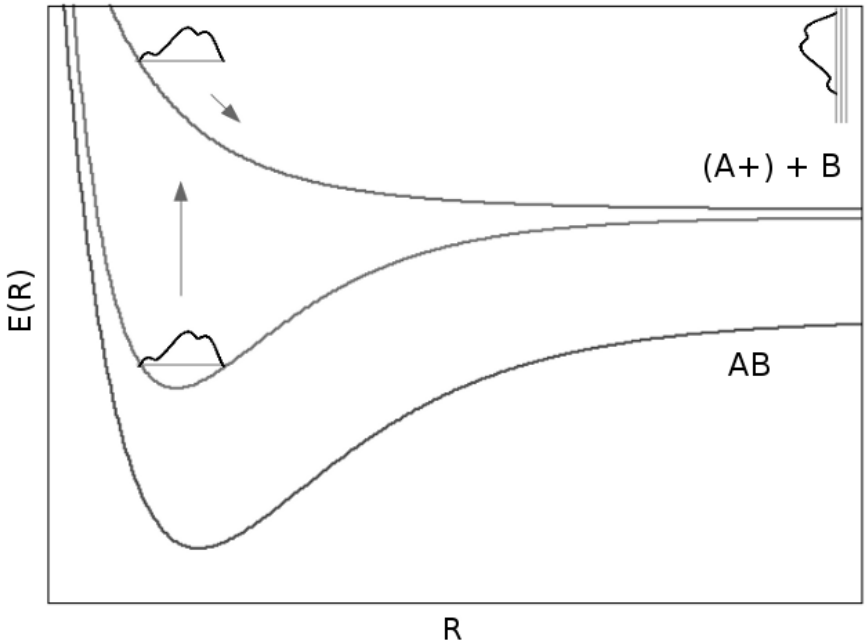


1. Ionization from neutral ground state by pump pulse
2. Wavepacket oscillation and dephasing

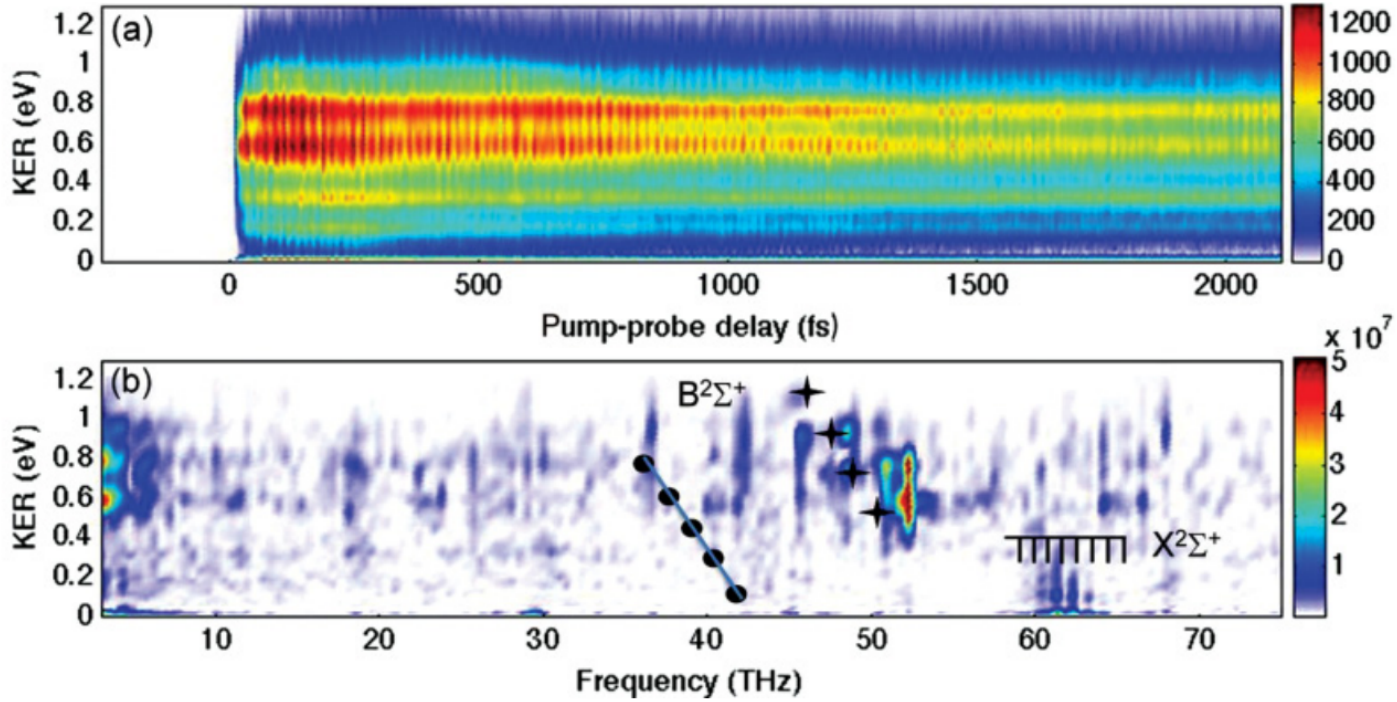
Pump-probe spectroscopy

Pump-probe spectroscopy provides a way to study vibrational nuclear motion:



1. Ionization from neutral ground state by pump pulse
2. Wavepacket oscillation and dephasing
3. Dissociation by probe pulse and imaging

Previous CO^+ experimental results



[1]

- 800 nm, ∼8 fs, 3×10^{14} W / cm^2 laser pulses
- Up to 2 ps delay between pulses

[1] De S., et al., 2011

Numerical method

- Numerically integrate the one-dimensional time-dependent Schrodinger equation:

$$\frac{\partial}{\partial t}\Psi\left(\vec{r},t\right)=-i\hat{\mathrm{H}}\Psi\left(\vec{r},t\right)$$

- Approximate solution over small time steps:

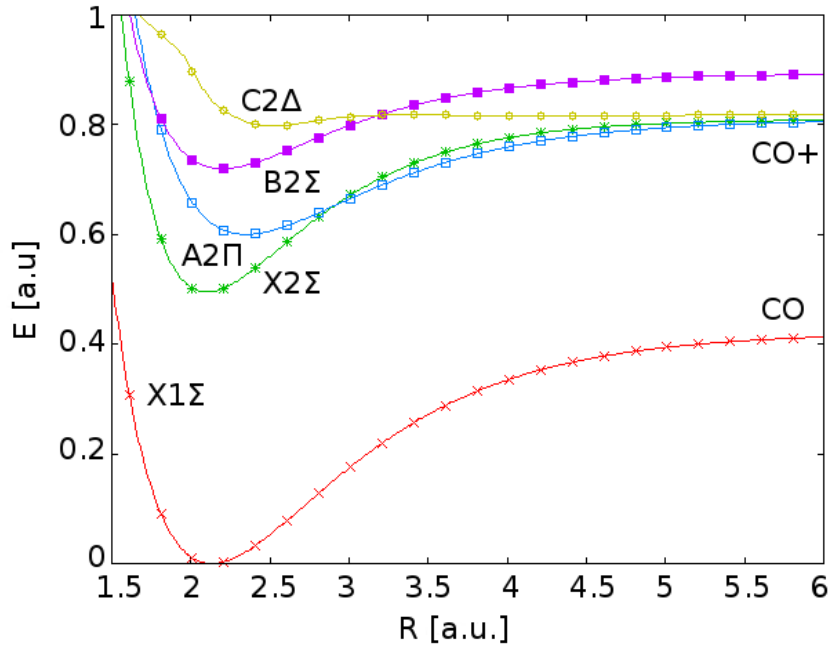
$$\Psi\left(\vec{r},t+\Delta t\right)=e^{-i\hat{\mathrm{H}}(t)\Delta t}\Psi\left(\vec{r},t\right)$$

- Cayley / Crank-Nicholson approximation on a numerical internuclear grid:

$$\Psi\left(\vec{r},t+\Delta t\right)=\frac{1-i\hat{\mathrm{H}}\left(t+\frac{\Delta t}{2}\right)\frac{\Delta t}{2}}{1+i\hat{\mathrm{H}}\left(t+\frac{\Delta t}{2}\right)\frac{\Delta t}{2}}\Psi\left(\vec{r},t\right)+\mathcal{O}\left(\Delta t^{3}\right)$$

CO^+ molecular potential curves

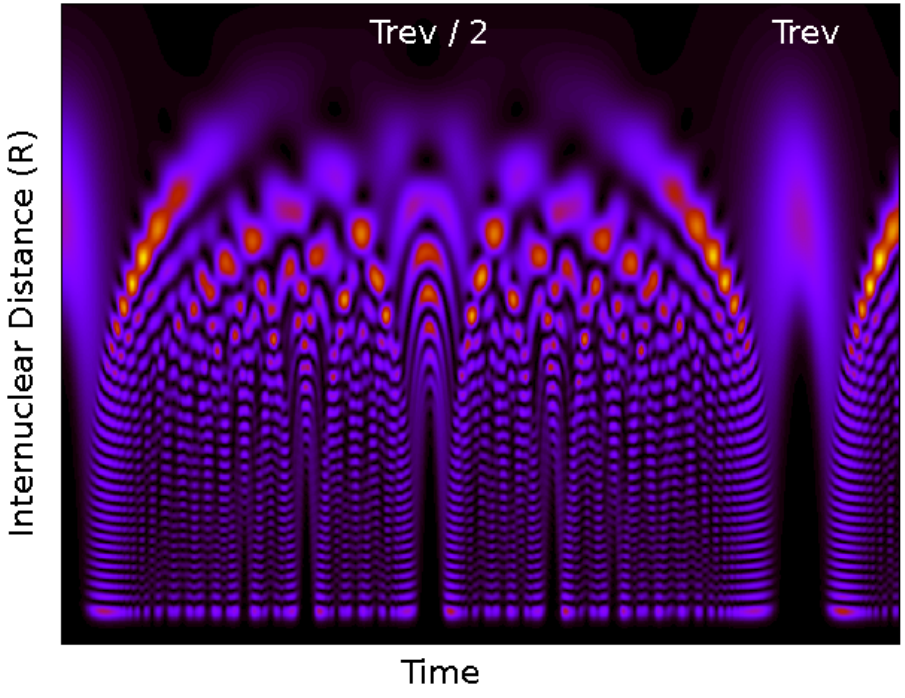
CO^+ potential curves were digitized from existing literature[2]



- 15 fs. laser pulses, up to 2 ps. delay between pulses
- Coupled $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ CO^+ states with $C^2\Delta$ state for probe pulse
- Electronic dipole couplings calculated with GAMESS quantum chemistry software

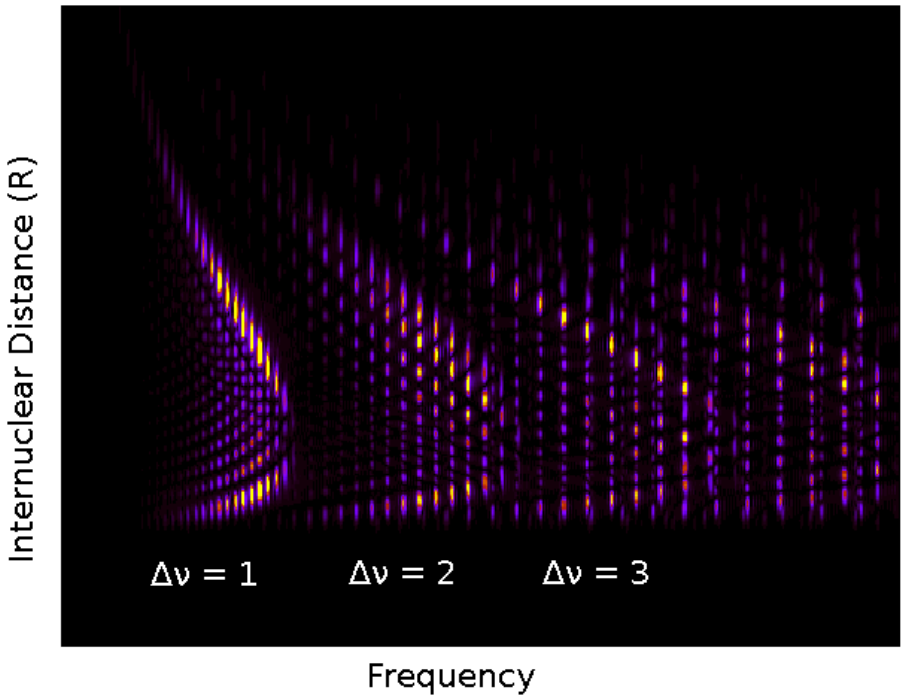
[2] Okada, K. et al., 2000

Single cation curve calculations



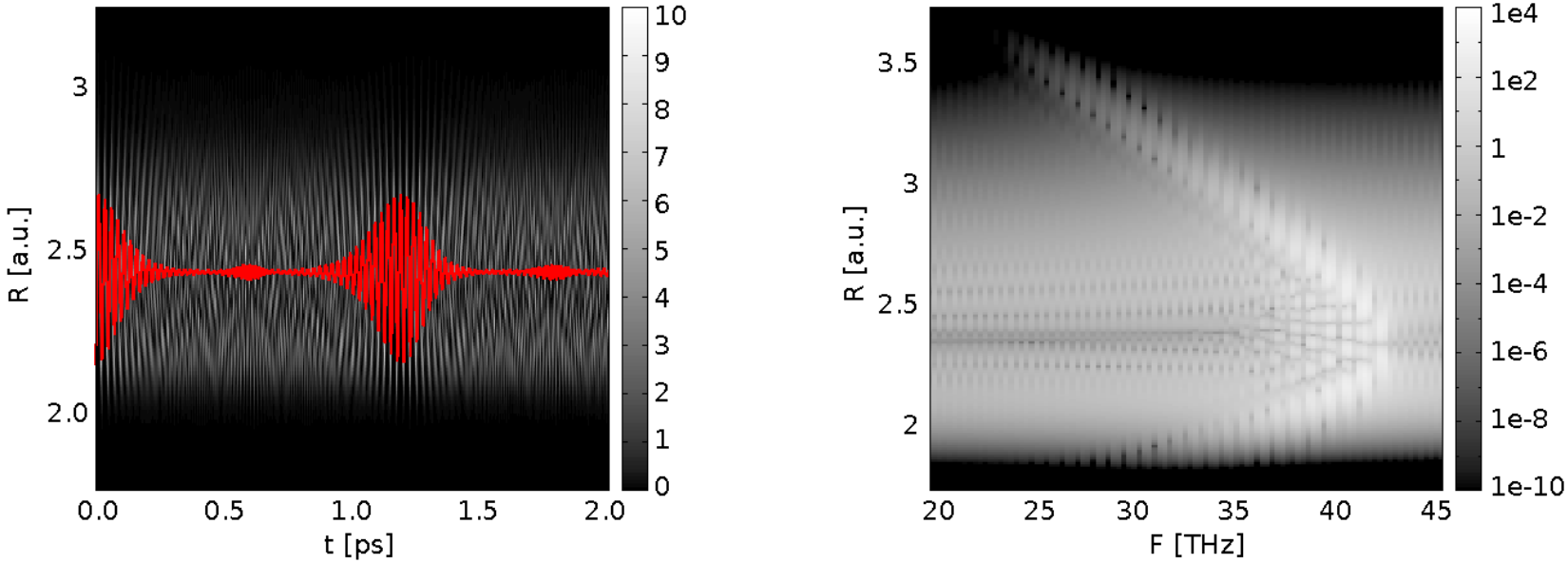
- Ionization using Franck-Condon transition
- Field-free propagation in excited CO^+ state
- Time evolution of $|\Psi|^2$ shows vibrational dephasing and revival

Preliminary single curve calculations



- Ionization using Franck-Condon transition
- Field-free propagation in excited CO^+ state
- Power spectra shows beat frequencies of vibrational energy levels

Single curve calculation example - $A^2\Pi$



- Gives information on nuclear dynamics within molecular orbital
- Provides reference for checking more complicated simulation results
- Potential curve mapping from power spectra

Dipole-coupled calculations

- Simulated simplified pump-probe spectroscopy experiment with transitions to / from coupled binding and dissociative molecular orbitals
- Dipole-coupled propagation:

$$\frac{\partial}{\partial t}\begin{pmatrix}\Psi_1\\ \Psi_2\end{pmatrix} = -i\begin{pmatrix}\hat{\mathrm{T}}+\hat{\mathrm{V}}_1 & \hat{\mathrm{D}}_{1,2}\\ \hat{\mathrm{D}}_{2,1} & \hat{\mathrm{T}}+\hat{\mathrm{V}}_2\end{pmatrix}\begin{pmatrix}\Psi_1\\ \Psi_2\end{pmatrix}$$

$$\hat{D}_{i,j} = E\left(t\right)\left\langle \Psi_i \mid R \mid \Psi_j \right\rangle$$

- Interested in dissociated portion of wavepacket after probe pulse
- Manually locate a "cutoff distance" R_c that distinguishes bound and dissociative nuclear motion

Dipole-coupled calculations

- Obtain kinetic energy release (KER) from momentum representation (Fourier transform) of dissociative wavepacket:

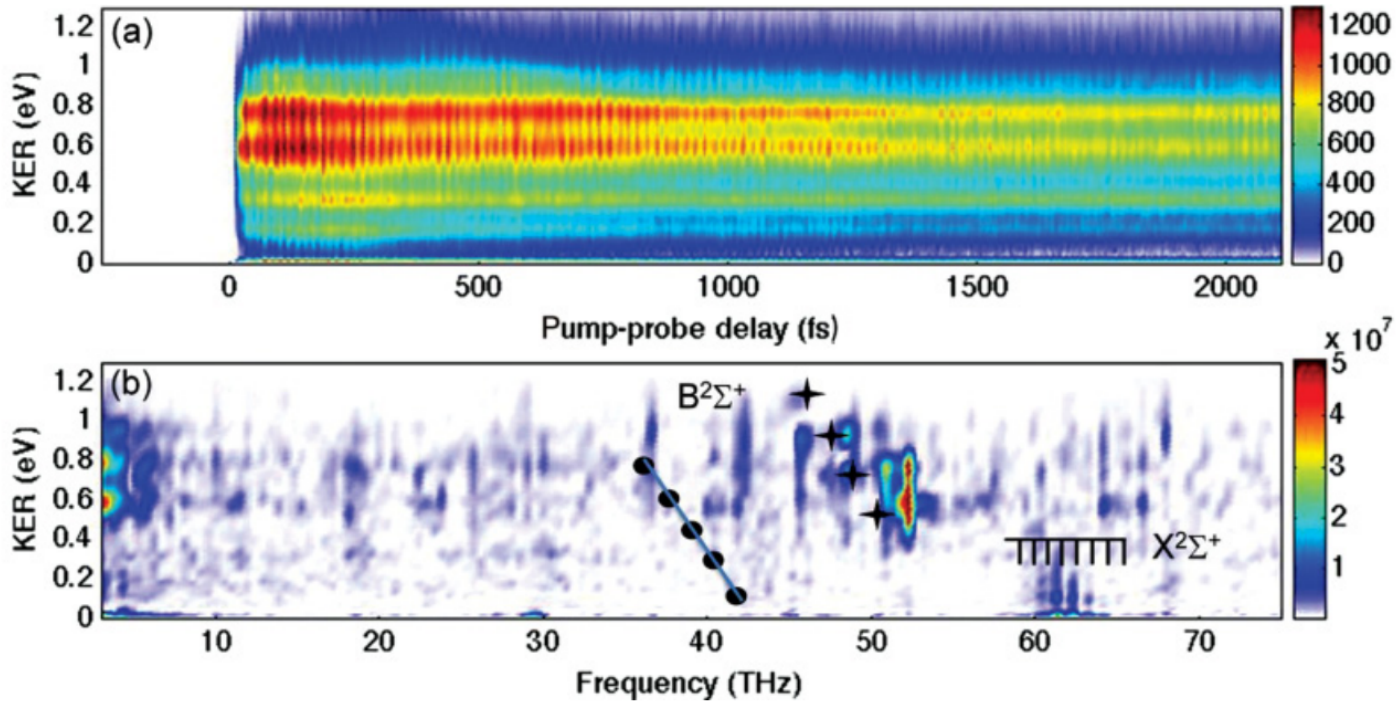
$$\tilde{\Psi}_{\text{Diss.},i}\left(P,t\right)=\int_{R_c}^{R_{max}}\Psi_i e^{-iPR}dR$$

- The energy distribution of ion fragments is related to delay time τ by:

$$C_{\text{Diss.}}\left(E,\tau\right)\propto\sum_i\left|\tilde{\Psi}_{\text{Diss.},i}\left(P,t\right)\right|^2,E=\frac{P^2}{2m}$$

- Fourier transforms of $C_{\text{Diss.}}$ give "beat frequencies" of KER

Previous CO^+ experimental results



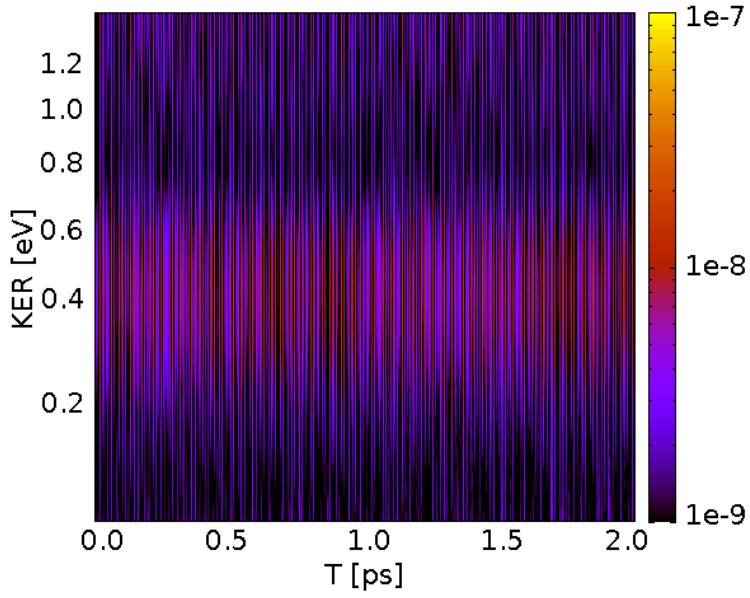
[1]

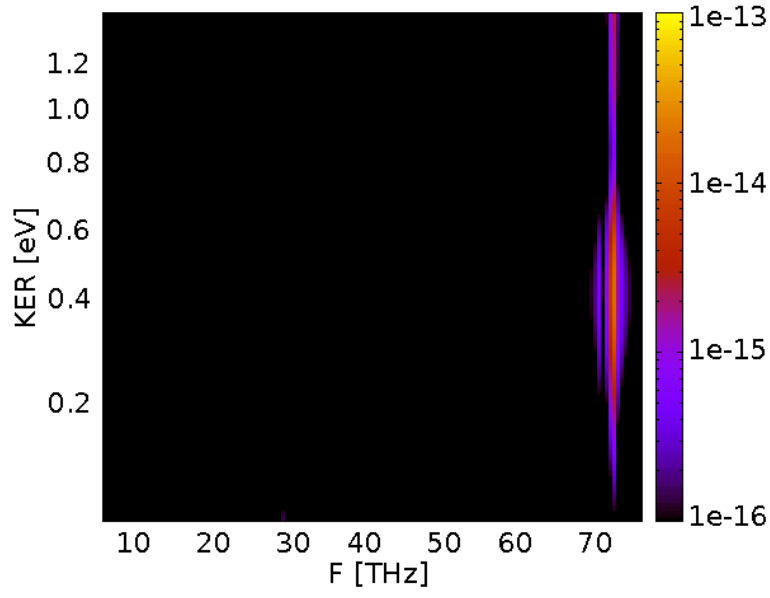
Features:

- Primary KER "streaks" between 0.4-0.6 eV and 0.6-0.8 eV, secondary streak between 0.2-0.4 eV
- Largest beat frequencies around 50 THz

[1] De S., et al., 2011

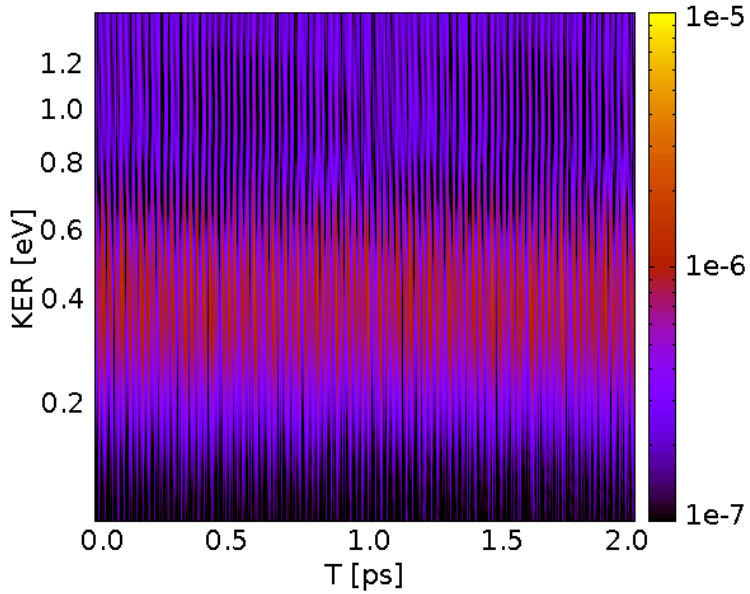
$X^2\Sigma^+$ coupled channel results

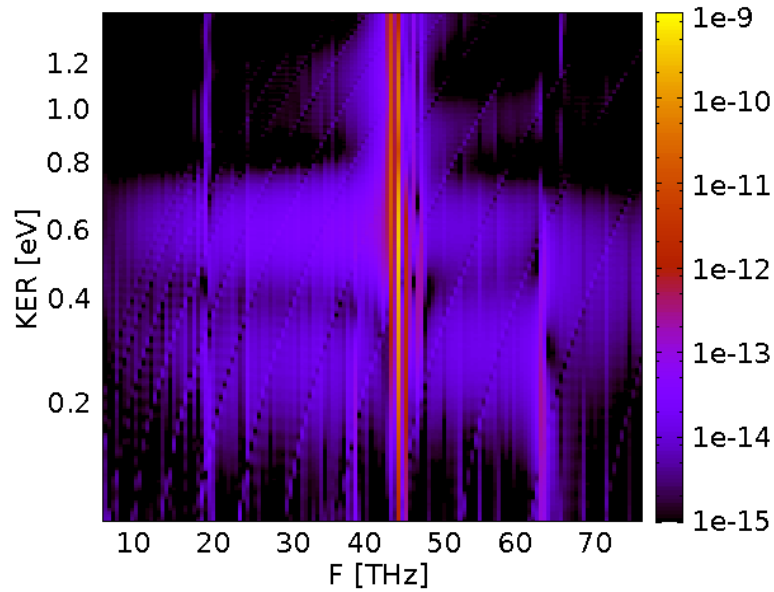




- Consistent with lower primary streak in experimental KER results
- No clear match in experimental power spectra

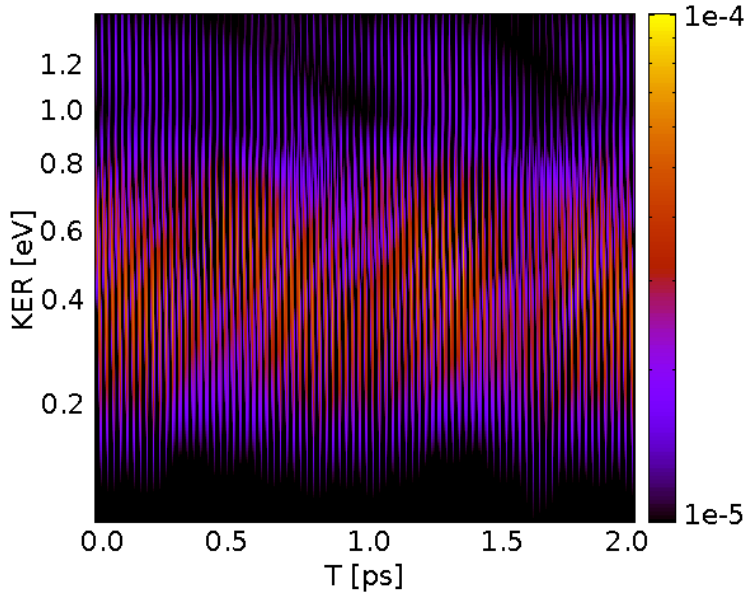
$A^2\Pi$ Results

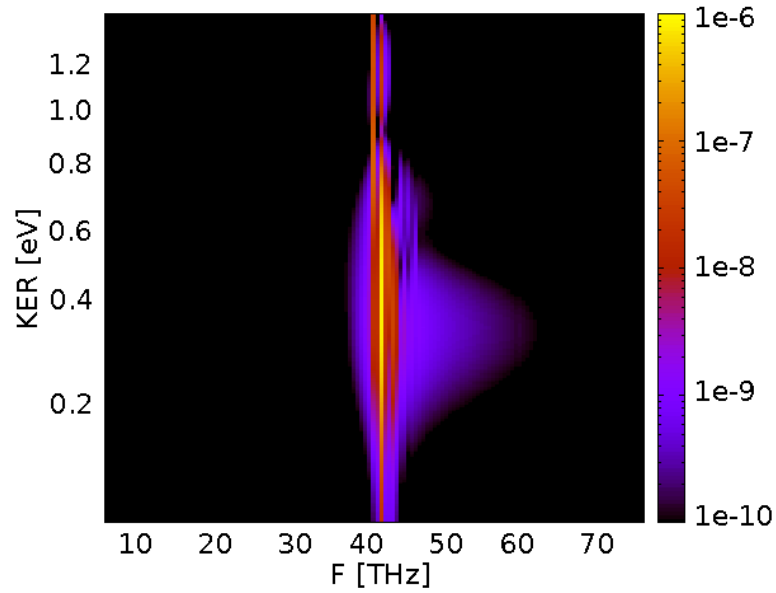




- Consistent with lower primary streak in experimental KER results
- No clear match in experimental power spectra

$B^2\Sigma^+$ Results





- In same overall KER range as experimental results, but no clear match
- No clear match in experimental power spectra

Interpretation and future work

- Coupled channel simulations fail to explain experimental KER spectra
- No low-lying CO^+ molecular potential curve explains 50 THz experimental power spectra results
- Future: more realistic simulations involving multi-coupled propagation between all low-lying potential curves
- Future: more realistic electronic transition models than Franck-Condon approximation
- Future: investigate laser-pulse dependence of KER

References

[1] De, S. et al. "Following dynamic nuclear wave packets in N_2, O_2, and CO with few-cycle infrared pulses." *Physical Review A* 84, 043410 (2011).

[2] Okada, K. and S. Iwata. "Accurate potential energy and transition dipole moment curves for several electronic states of CO^+." *J. Chem. Phys.* 112.4 (2000): p.1804-1808.