Modeling Diatomic Molecular Dynamics with the Pump Probe Method

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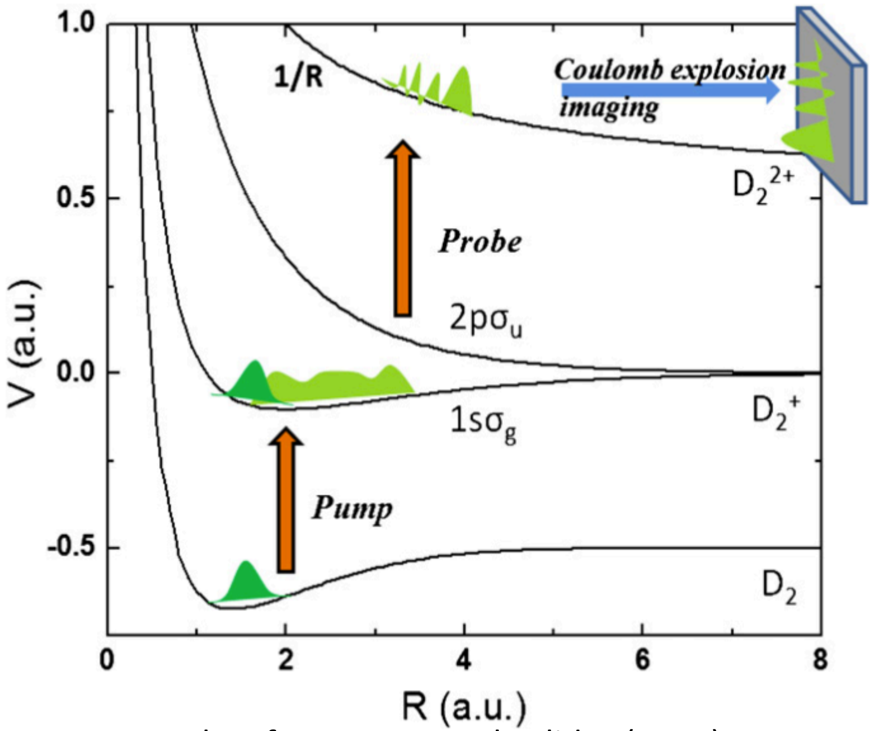
Typical Pump-Probe Schematic

- Widely used for fs + sub-fs resolution
- Pump excites neutral molecule
- Probe pulse dissociates excited molecule
- Time between pump and probe pulse is varied => KER(**τ**)



Taken from M. Magrakvelidze (2014)

Zewail, A. H. (1988). *Laser Femtochemistry. Science*

Background Theory

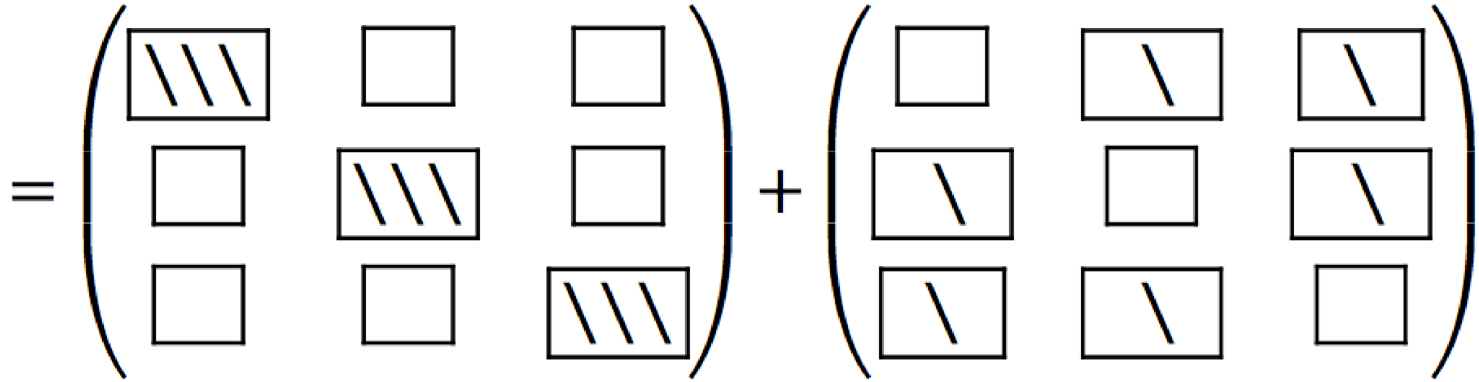
- Born-Oppenheimer approximation
  - Nuclear motion fixed with respect to electrons
  - $\psi(R, r, t) = \psi_e(r, t)\psi_N(R, t)$
  - $\widehat{H}_N = T_R + V(R) + V_{eN}$
- Franck-Condon Principle
  - Electronic transitions result in molecular vibration
  - $\psi_1(R, t = 0) = \sum_i a_i \phi_i(R)$

Time-Dependent Schrödinger Equation (TDSE)

- Total Molecular Wavefunction
  - $\phi(r, R, t) = \frac{1}{\sqrt{2}}[\psi_1(R,t)\psi_{el1}(r,t) + \psi_2(R,t)\psi_{el2}(r,t)]$
  - Project unto electronic states
- Coupled Hamiltonian
  - Two states: $-i\,\frac{d}{dt}\begin{pmatrix}\psi_1\\\psi_2\end{pmatrix} = (\hat{H} + \hat{H}_c)\begin{pmatrix}\psi_1\\\psi_2\end{pmatrix}$
  - $\hat{H} + \hat{H}_c =$ Block Matrix

Time-Dependent Schrödinger Equation (TDSE) (Cont.)

- $\hat{H} + \hat{H}_c$

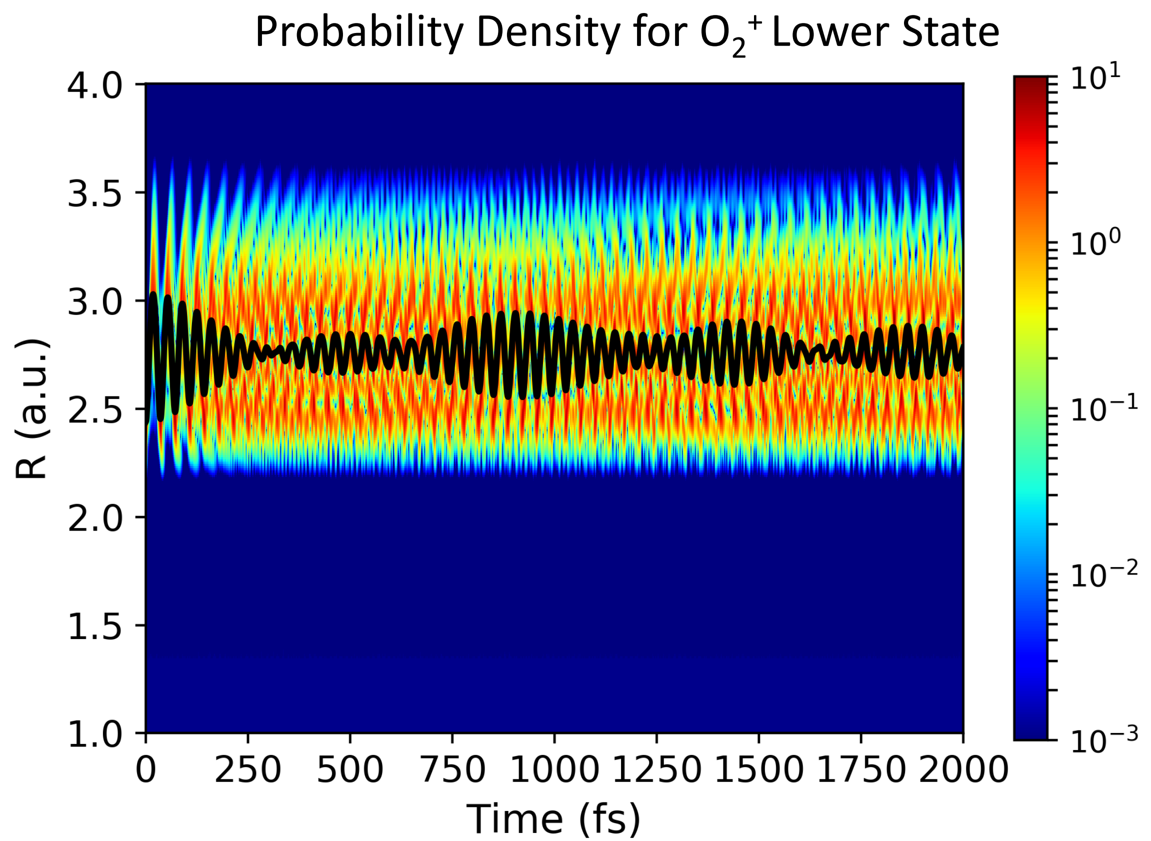


- Set of Coupled Equations:

  - $i\frac{\partial}{\partial t}\begin{pmatrix}\psi_1(R,t)\\ \psi_2(R,t)\end{pmatrix} = \begin{pmatrix} T_R + V_1(R) & d_{12} * E(t-\tau) \\ d_{12} * E(t-\tau) & T_R + V_2(R)\end{pmatrix}\begin{pmatrix}\psi_1(R,t)\\ \psi_2(R,t)\end{pmatrix}$
  - $d_{12} = \langle\psi_{el1}|r|\psi_{el2}\rangle$ (dipole coupling)

Obtainable quantities

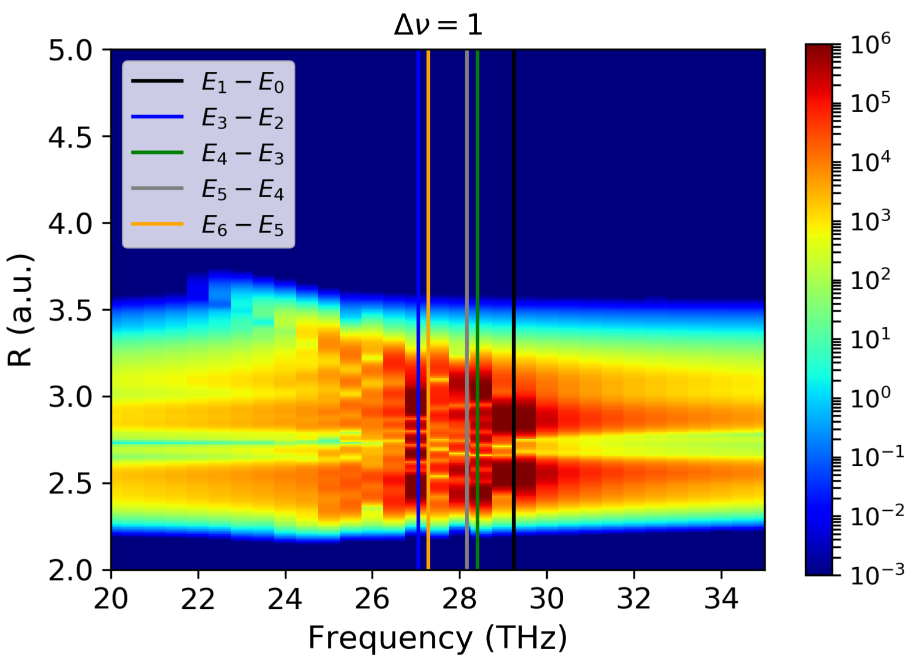
- Oscillation Period estimation
- Revival time estimation

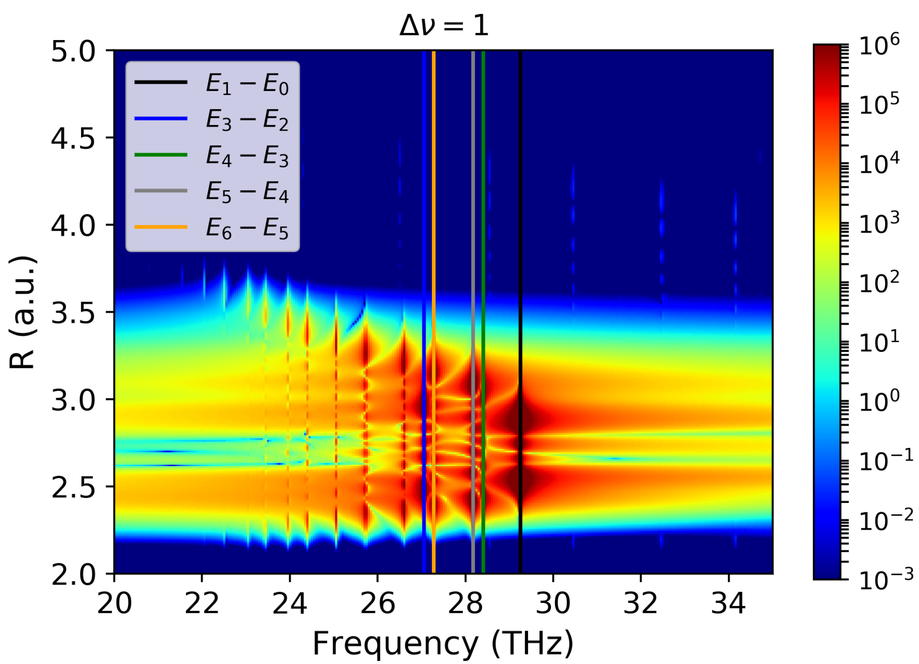


Solid Black Line = <R>

Quantum Beat Spectra

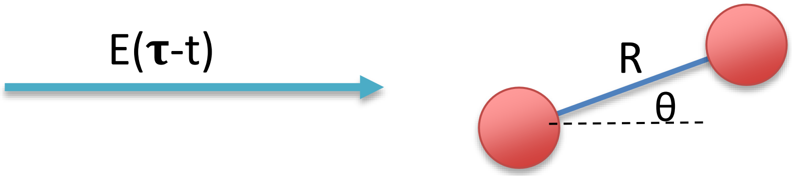
- $\rho(R,t) = |\psi_1(R,t)|^2 + |\psi_2(R,t)|^2$
- $\tilde{P}(R,\omega) = \int_0^T \rho(R,t) * W(t) * e^{-i\omega t}\ dt$
- Gives contributing vibrational energy levels/states
  - $T = 2\pi/\Delta E_\nu$
- Increase propagation time => increase frequency resolution

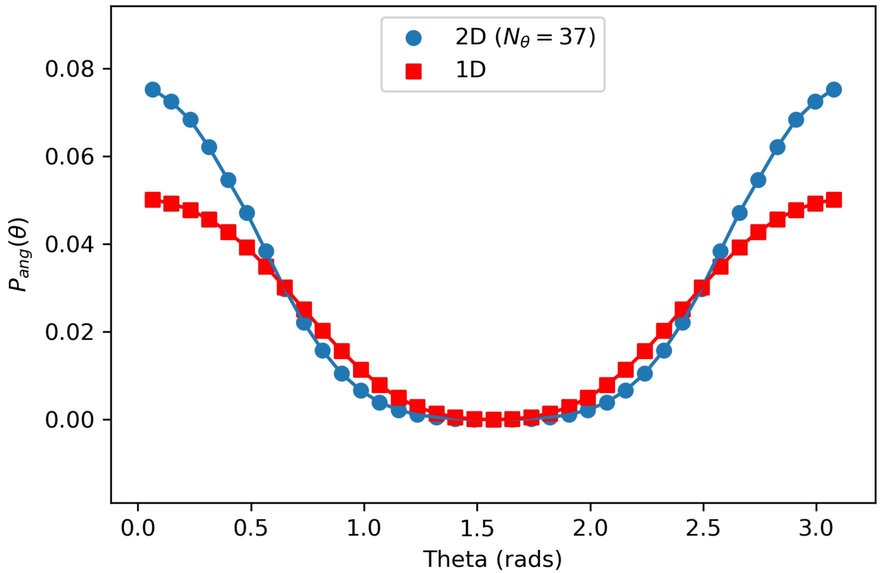




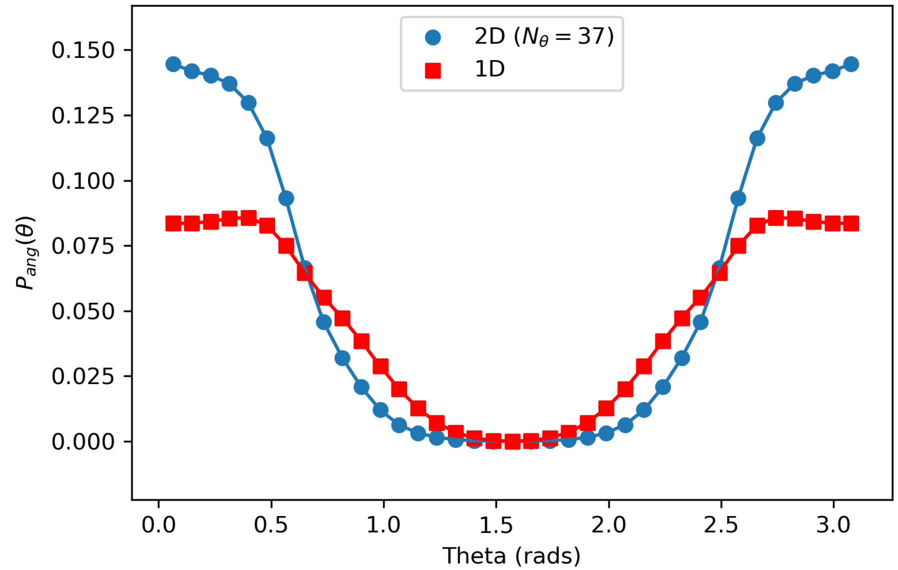
Angular Probabilities

- Dissociation probabilities
- $I_{eff} = I_0 \cos\theta$
- 2D allows for rotation
- 1D treats θ as a parameter



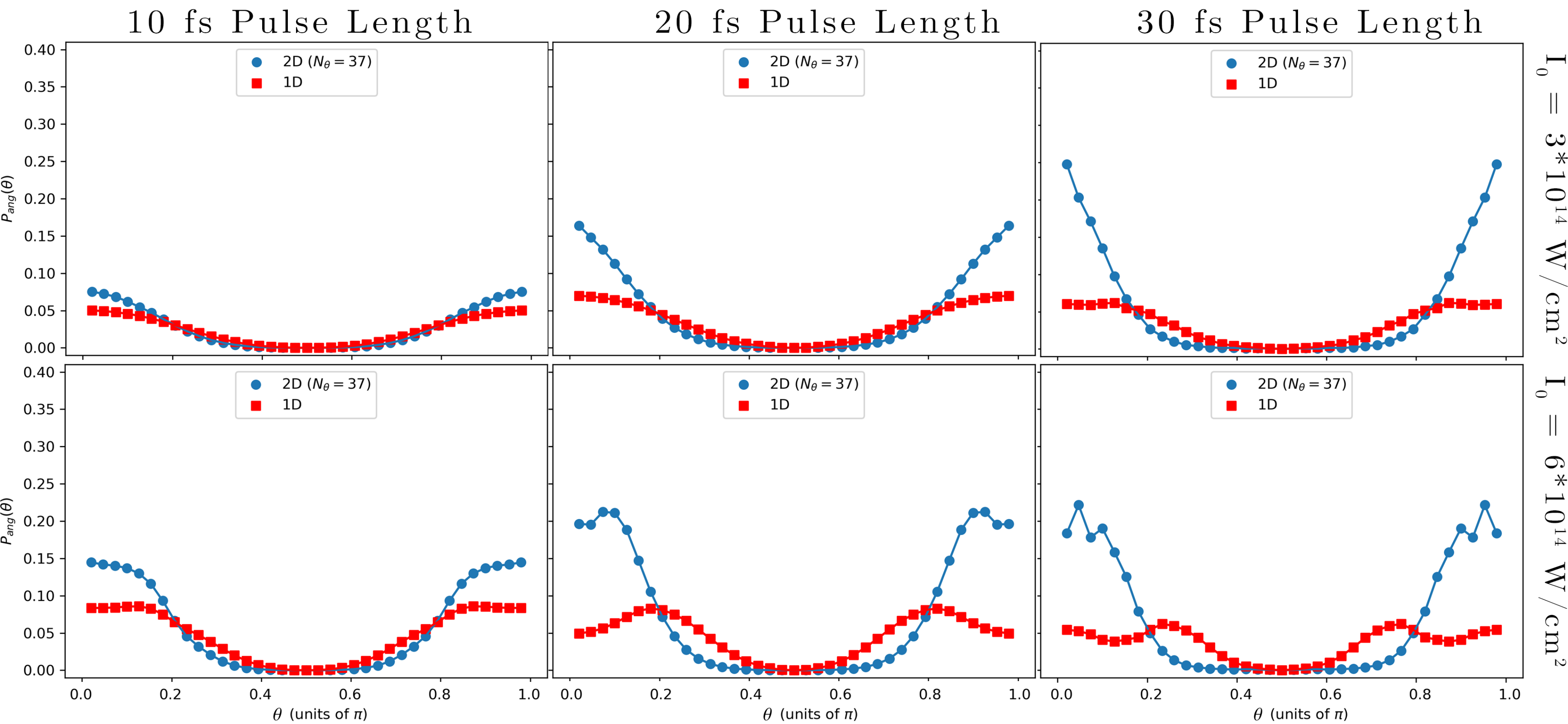


I = 3.0 * 10^14 W/cm^2



I = 4.0 * 10^14 W/cm^2

Angular Probabilities



Conclusions

- Capturing molecular dynamics
- B.O. and F. C. approximations
- TDSE
- Probability Densities and QB Spectra
- Rotational dynamics

Works Cited

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Crank-Nicholson Method

- $\hat{H} = \hat{T} + \hat{V}$ $\quad$ $\mathrm{i}\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$
- Integration => $\Psi(R,t) = \exp\left(-i\hat{H}t\right)\Psi(R,t=0)$
- $\Psi(R,t+\Delta t) = \exp\left(-i\hat{H}\Delta t\right)\Psi(R,t)$
- $\exp\left(-\left(\hat{T}+\hat{V}\right)\Delta \mathrm{t}\right) = \exp\left(-\frac{\hat{V}\Delta t}{2}\right)\exp\left(-\hat{T}\Delta t\right)\exp\left(-\frac{\hat{V}\Delta t}{2}\right)$
- In our case:
  - $\exp\left(-i\hat{H}_{tot}\Delta t\right) = \exp\left(-\frac{i\hat{H}_C\Delta t}{2}\right)\exp(-i\hat{H}\Delta t)\exp\left(-\frac{i\hat{H}_C\Delta t}{2}\right)$