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Triatomic Opacities from 3000-8000K

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Outline

- Goal: Triatomic Opacity
- Modern Opacity Methods
  - Discrete Variable Representation
  - Time Dependent Density Functional Theory
- Results
- Plans

Goal

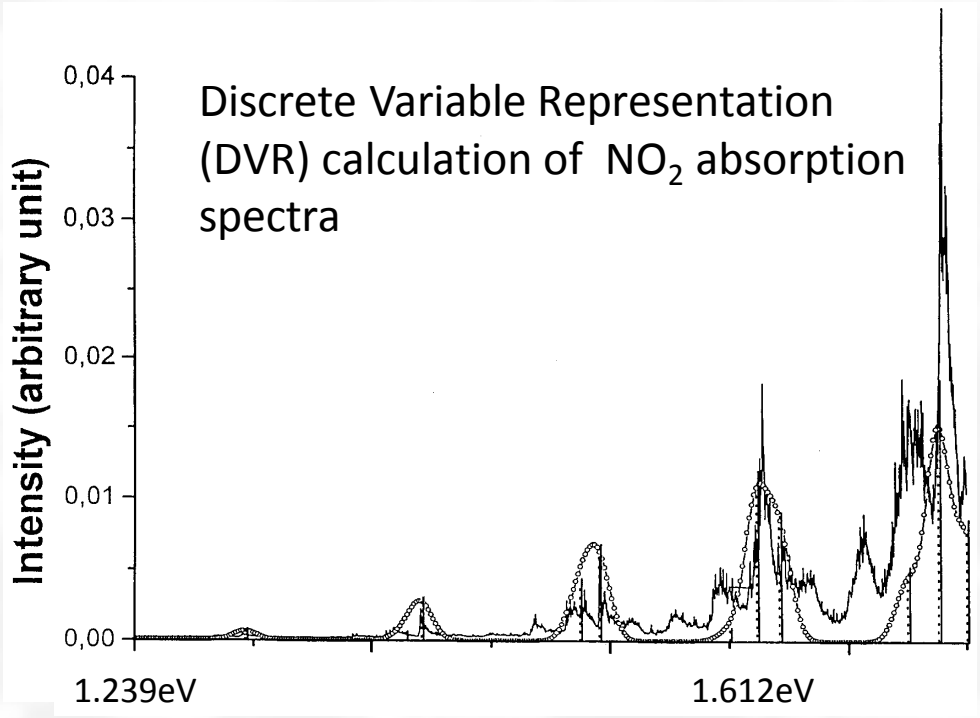
- Develop triatomic opacity calculation capability
  - Two methods
    - High-resolution spectrum
    - Interspecies effects
  - Immediate needs:
    - Visible/near-visible
    - T ϵ [3000K,8000K]
    - $\rho/\rho_0 \leq 10$
  - First case: NO_2
    - Two electronic states
    - Significant molecule
      - Large cross-section
      - Smog
      - Some experimental data

Modern methods for calculating opacity are available

- Two techniques for calculating opacities that are being implemented at SNL:
  - High-resolution single-species opacity
    - Discrete Variable Representation (DVR)
  - Interspecies (density) effects
    - Time-dependent Density Functional Theory (TDDFT)

Discrete Variable Representation (DVR) has been used to generate high resolution single-species linelists

- 1998: Transitions between two electronic states of NO_2
  - Goal was to locate energies and not to calculate intensities
  - Up to 1.98 eV with an error ~.01 eV



- 2006: DVR3D research code used for H_2O
  - 506 million transitions (>60% more lines than previous) @ 7.42 processor years
  - Within .00025eV to ~15,000 experimental transitions

DVR

- SE
  - wavefunctions -> represented by infinite basis
  - Truncate -> VBR
    - -> new Hamiltonian
  - Diagonalize Hamiltonian/Operators -> solves SE for *E*
    - (localized) Transformation
      - DVR
        - » Basis functions and quadrature points are chosen

$$H\Phi \cong (\nabla^2 + V(r))\Phi = E\Phi$$

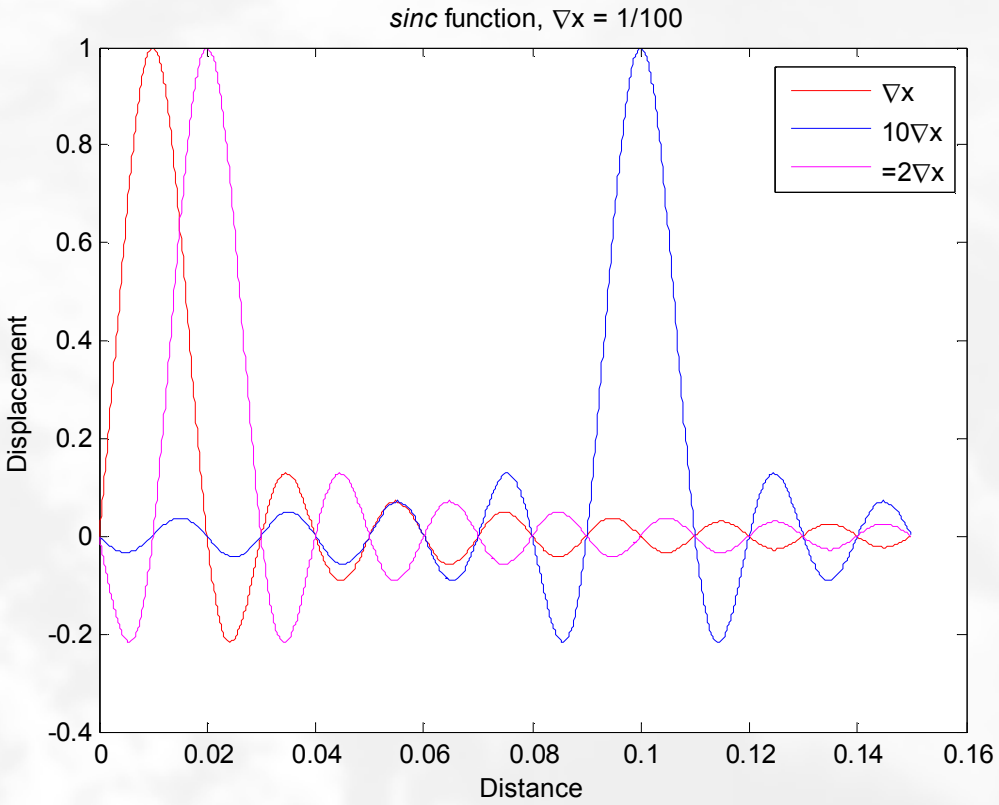
$$\Phi = \sum_i^N c_i \phi_i(r)\Theta_i(\vec{\theta})$$

$$H\Phi = \mathrm{E}\Phi \rightarrow \hat{H}\vec{c} = E\vec{c}$$

$$U^{-1}\hat{H}U = (\ddots)$$

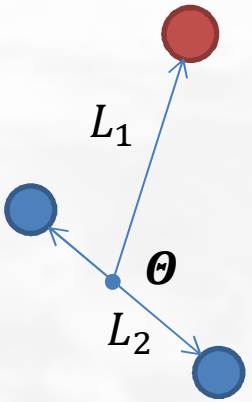
DVR

- Localization: Basis Function ↔ grid points
  - Aids in diagonalization
- Example
  - $f_n(x) = sinc\left(\frac{x-n\Delta x}{\Delta x}\right)$
    - $f_n(x) = sin\left(\frac{x-n\Delta x}{\Delta x}\right)/(x-n\Delta x)$
    - $n \in \{1,2,10\} \rightarrow x_n = \{0.01, 0.03, 0.1\}$
- Representation
  - Matrices labelled by quadrature, n



DVR

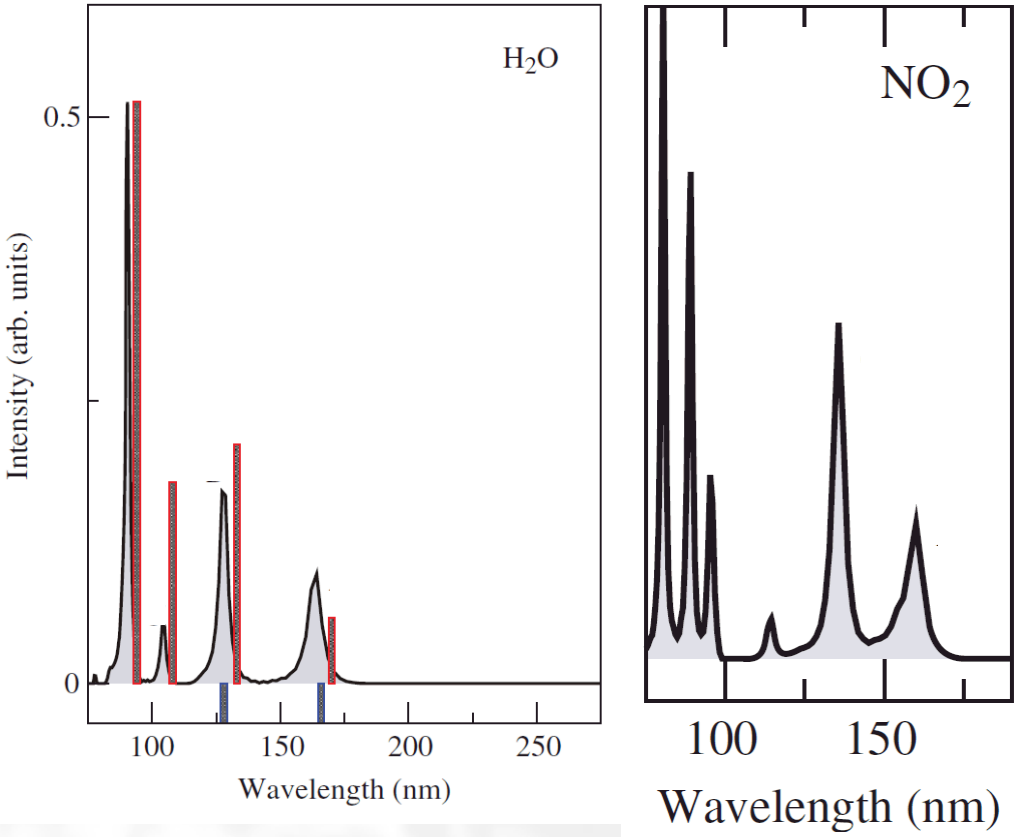
- DVR inputs
  - Potential Energy Surface
    - Evaluated at quadrature points
  - Dipole Moment Surface
    - Calculating intensity of spectra
- Highly-resolved
  - Vibrational and rotational spectra



Time Dependent Density Functional Theory can model density effects on opacity

- Codes are available
  - Gaussian 09 (commercial)
  - Octopus (research)
- Comparatively Fast
  - generate large statistics due to run times on the order of hours
- Electronic and vibronic transitions

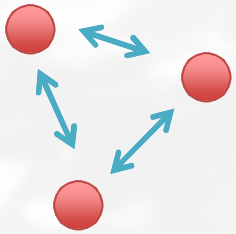
TDDFT spectra in the Far-UV (2010)

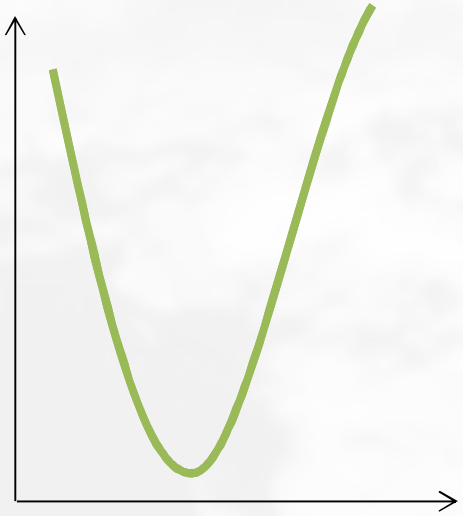


H_20: 0.1% error

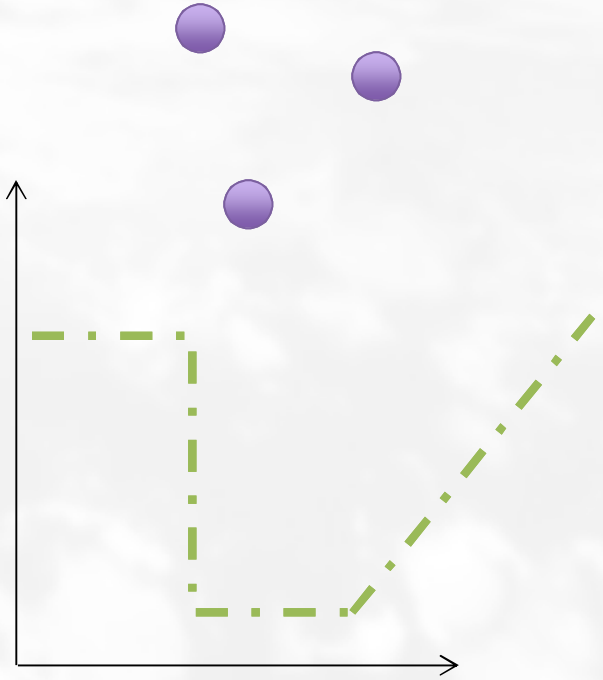
NO_2: 6.3% error

DFT





$n(r,t) \rightarrow$ observables



- N interacting e$^-$
- Φ is function of 3N spatial variables

- Non-interacting e$^-$
- Effective potential
- $n(r,t)$ function of 3 spatial variables

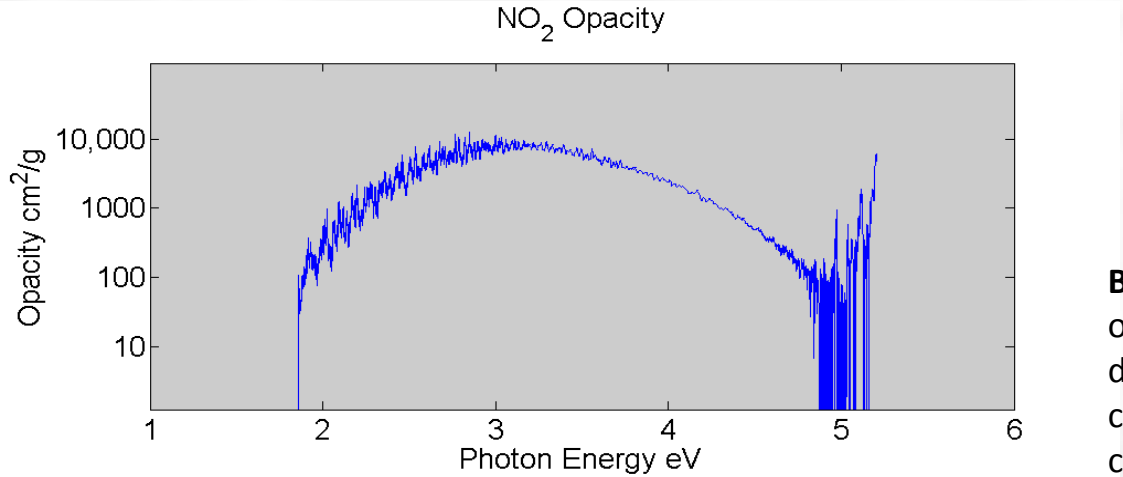
TDDFT

- $V_{eff}(r) = V_{SE}(r) + V_{DFT}(r)$
  - Last term is the only approx in DFT: *energy functional*
- DFT
  - Ground-states
- TDDFT
  - Excited states

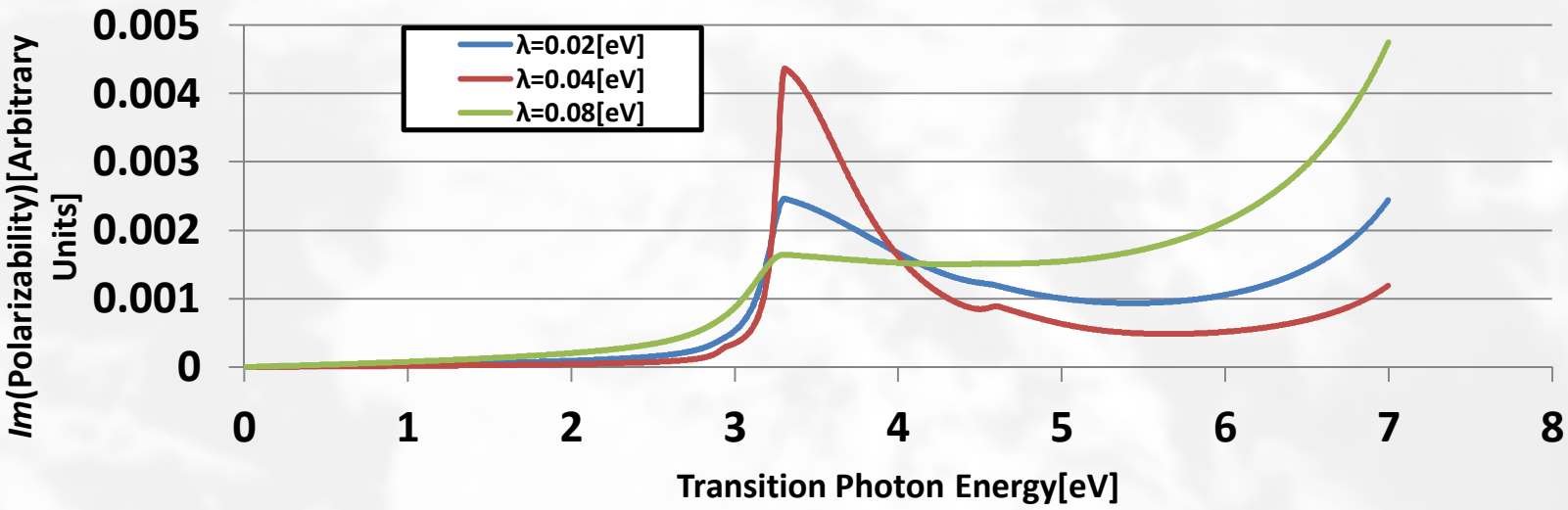
- Benefit
  - Density is a function of 3+1 variables and not 3N+1
  - Much easier to solve

Molecular excitations and molecular lines give rise to the opacity

Data source: HITRAN database @ 300K



Below: The imaginary portion of the polarizability (related directly to the absorption cross-section) of NO_2 as calculated by Gaussian TD-DFT.



Plans

- High-resolution spectra: DVR
  - Simulate temperatures up to 2000K
  - Generate and validate cross-section data
- Intermolecular effects: TDDFT
  - Generate higher temperature opacity curves for NO_2
  - Introduce interspecies effects by simulating NO_2 in the presence of other air molecules

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