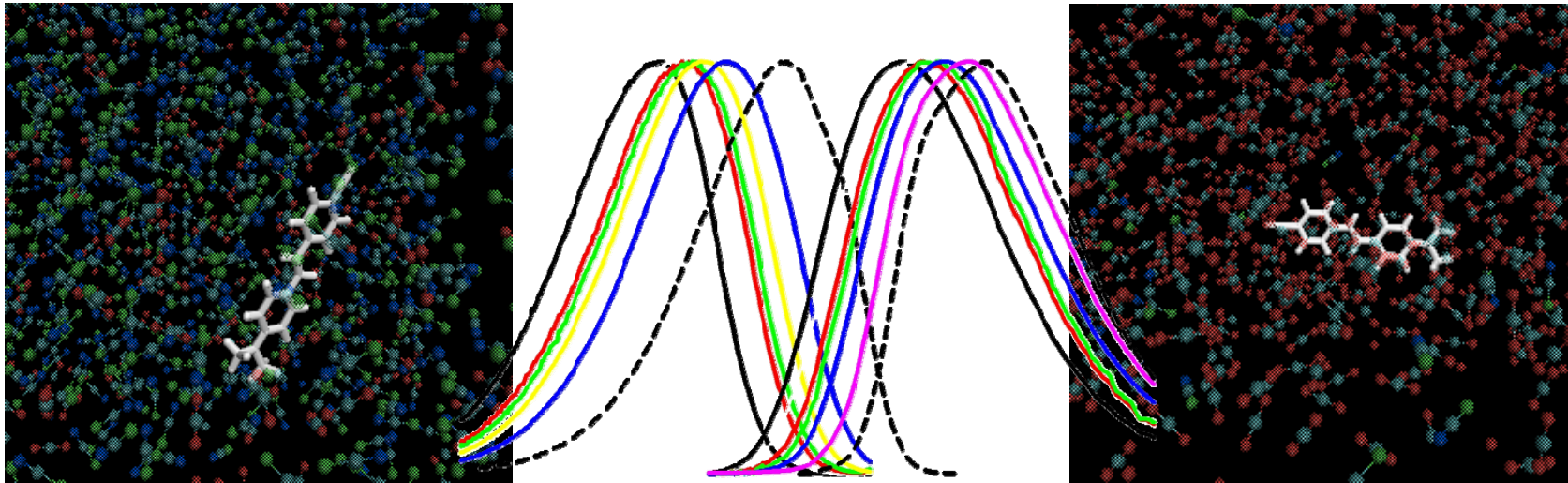


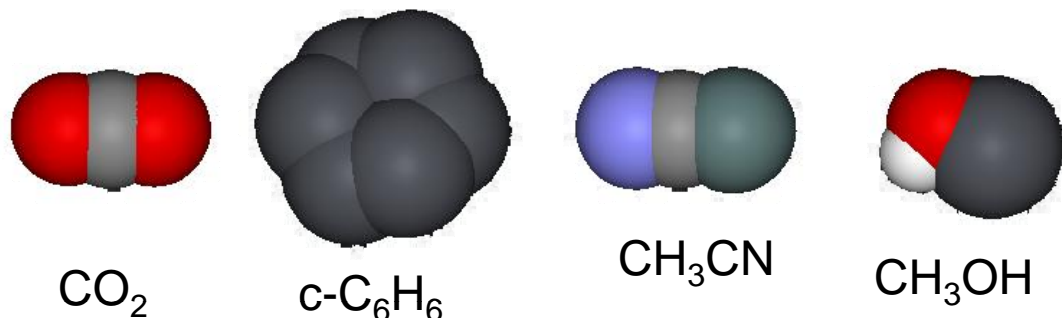
Solvatochromism and preferential solvation in CO₂-expanded liquids



**Chet Swalina, Sergei Arzhantsev, Hongping Li,
and Mark Maroncelli**

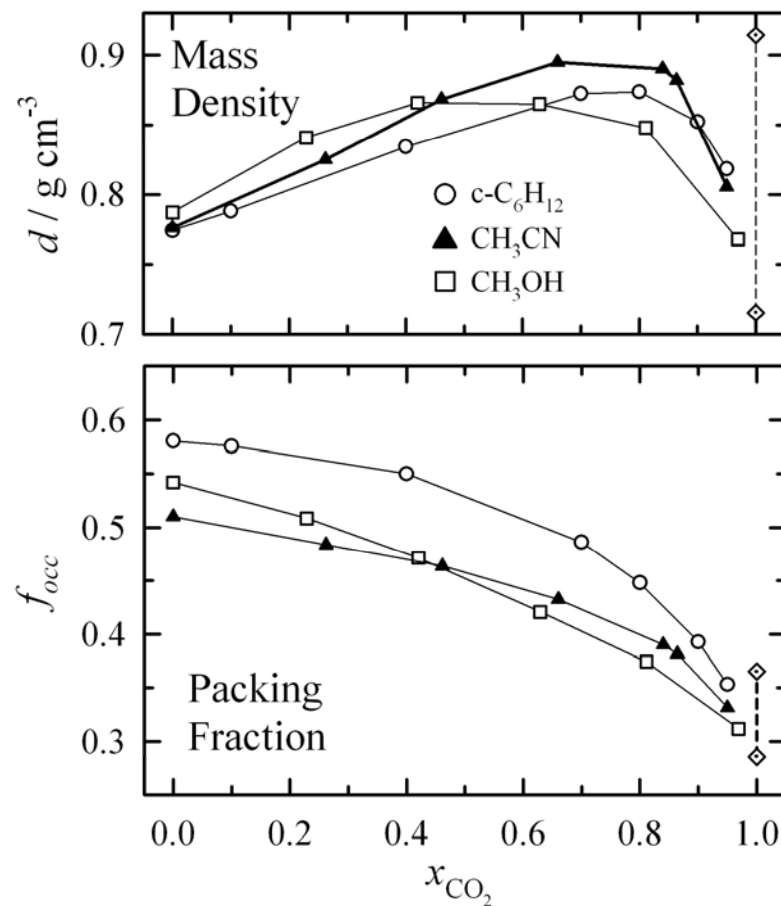
Binary CO₂ + liquid solvent mixtures

Li and Maroncelli, JPC B 110 21189 (2006)



- Simulations: LJ + Coulomb potentials. 1000 total molecules.
- Packing Fraction - fraction of total system volume occupied by vdW volumes of molecules.
- More free volume in GXL than in original liquid.

Volumetric Properties



Spectral shift and local environment

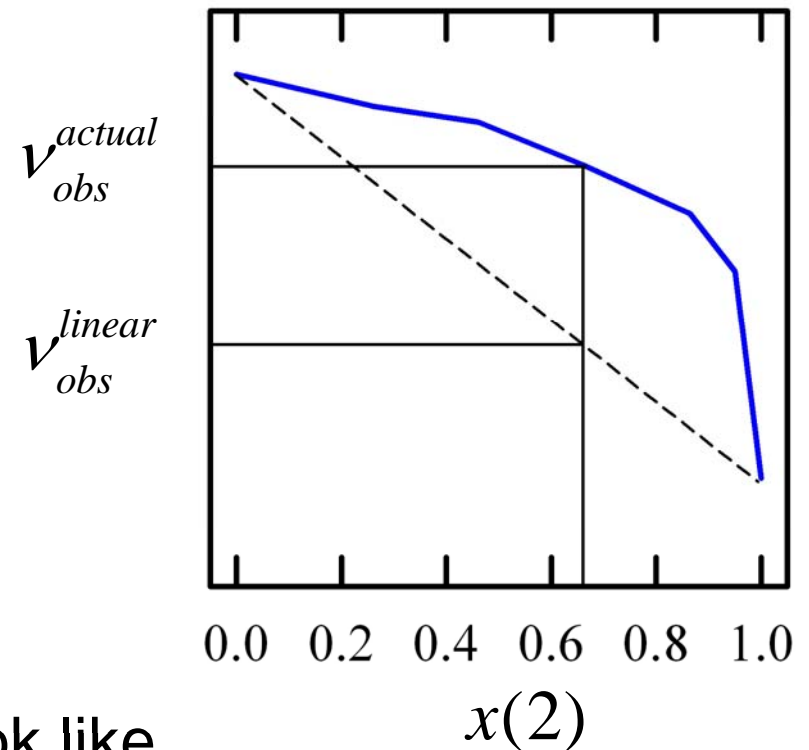
- Linear relationship between frequency and composition:

$$\nu_{obs} = x(1)\nu_1 + x(2)\nu_2$$

- Local composition of component 1:

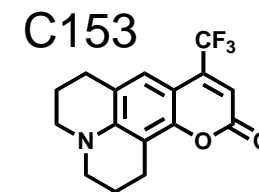
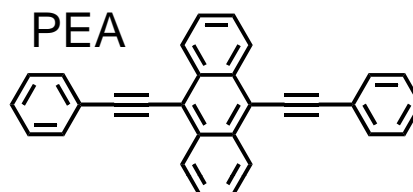
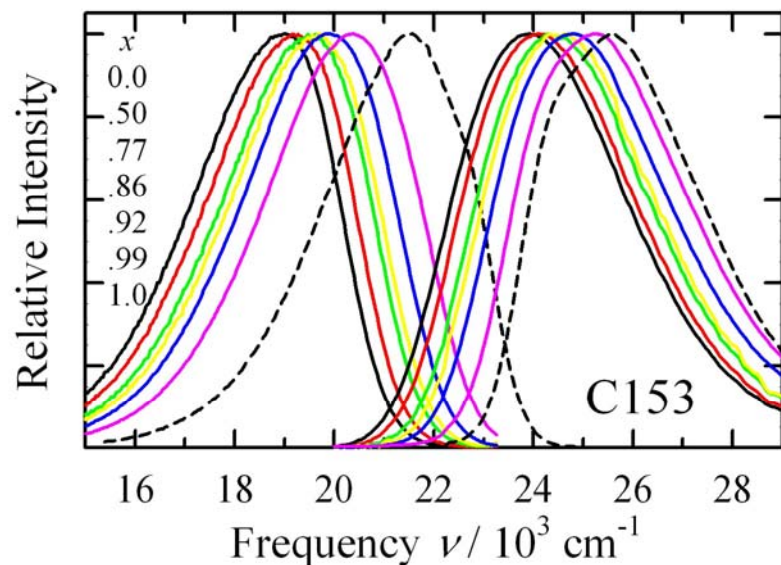
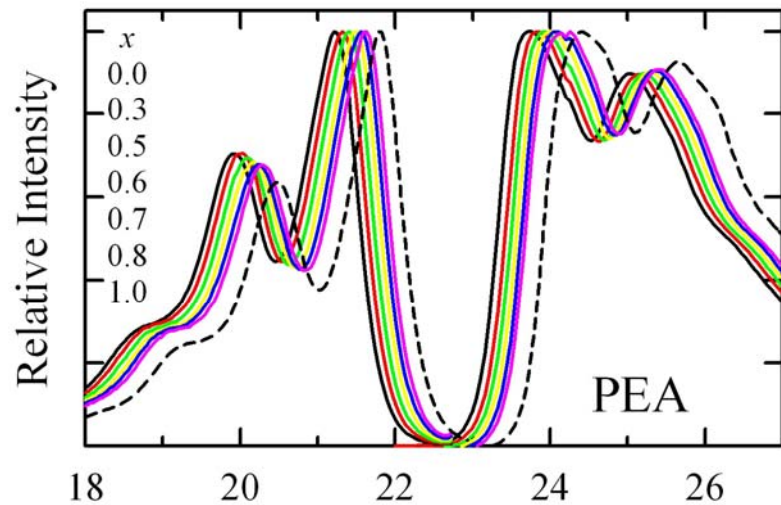
$$x_u^{\nu}(1) = \frac{\nu_{obs} - \nu_2}{\nu_1 - \nu_2}$$

- What does local environment look like compared to what spectroscopy tells us?



Absorption and emission spectra for CH₃CN + CO₂ mixtures

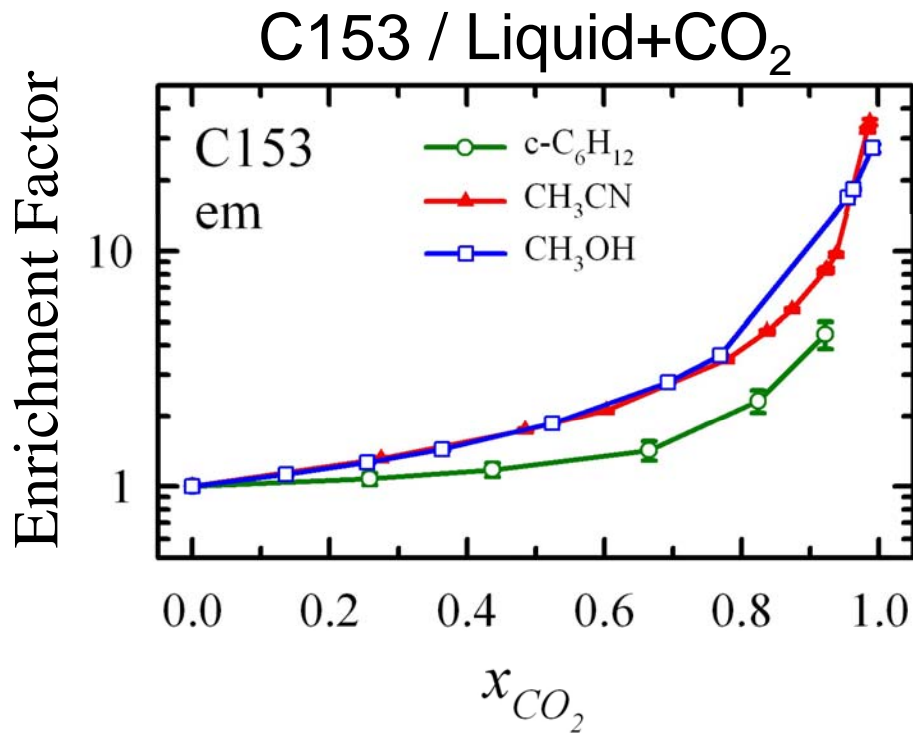
Li, et. al. JPC B 111 3208 (2007)



- CO₂ causes blue shift.
- PEA: No change in width/shape.
- Measure spectral shifts to gain knowledge of local environment.

$$\nu_{gas} - \nu$$

Spectral solvent composition



- Enrichment factors: $\frac{x_u^v(1)}{x(1)}$

- $x_u^v(1) = \frac{V_{obs} - V_2}{V_1 - V_2}$

- Spectral shifts highly nonlinear in composition.
- Unlikely that preferential solvation is this large.

Simulated spectral shifts

- Spectroscopic model:

$$h(\nu - \nu_{gas})_{abs} = f \langle U_{dsp} \rangle_0 + \langle \Delta U_{el} \rangle_0$$

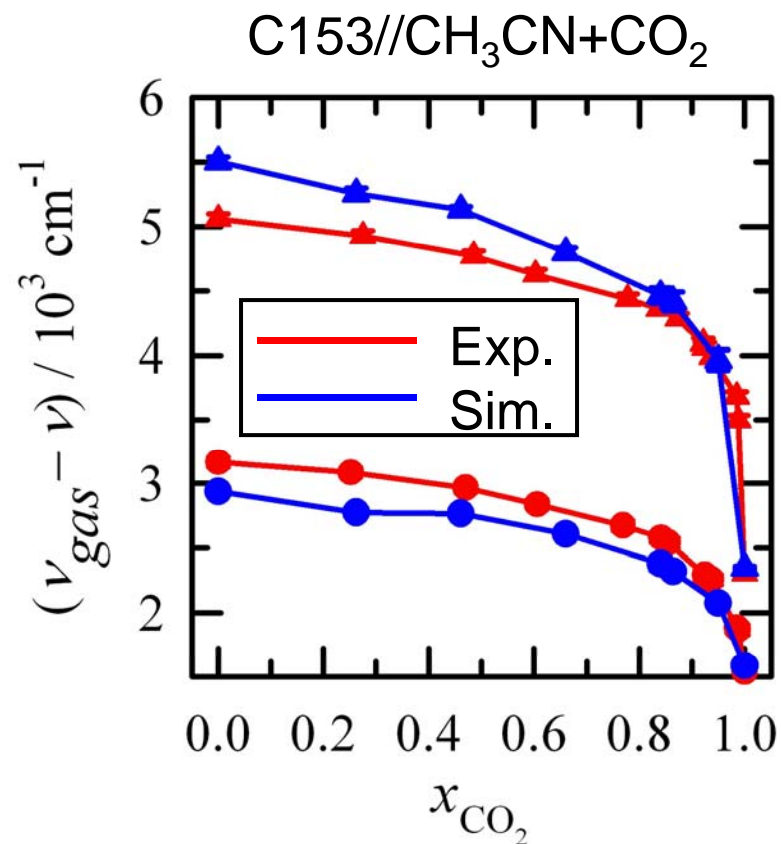
$$h(\nu - \nu_{gas})_{em} = f \langle U_{dsp} \rangle_1 + \langle \Delta U_{el} \rangle_1$$

- Quantities needed to compute

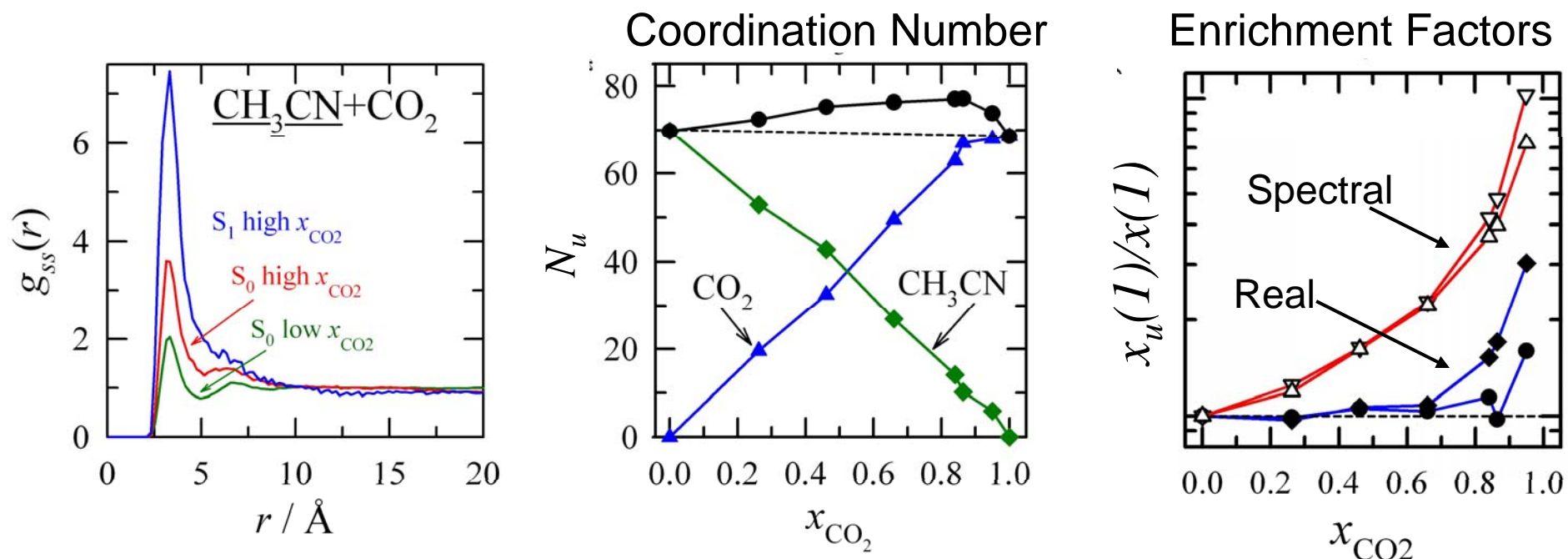
U_{dsp} and ΔU_{el}

come from force-field and electronic structure calcs.

- Model provides semi-quantitative representation of the electronic spectral shift.



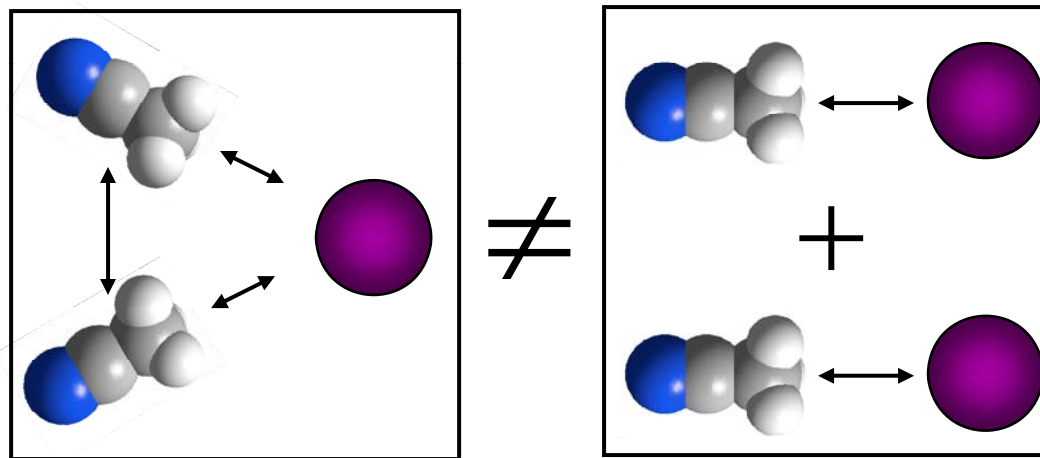
Real preferential solvation



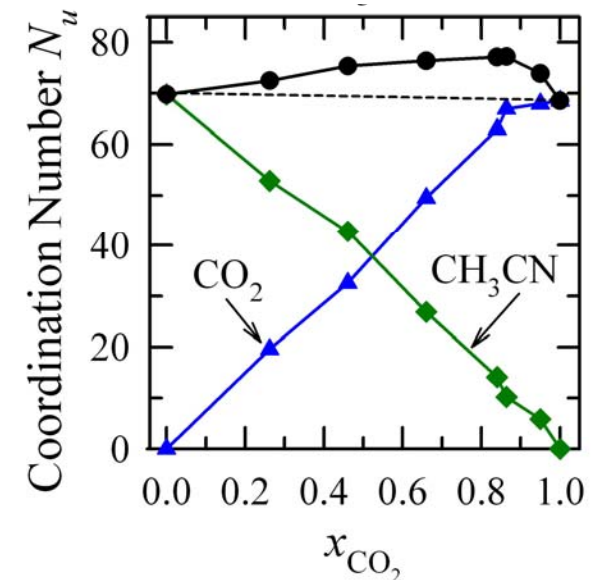
- Integrate $g_{SS}(r)$ to get local coordination numbers, N_u .
- Greater nonlinearities expected considering spectral shift trends.
- Substantial deviations from linearity at high x_{CO_2} .

Overestimation of enrichment using spectral solvent composition

- Solute-solvent U_{el} not additive.

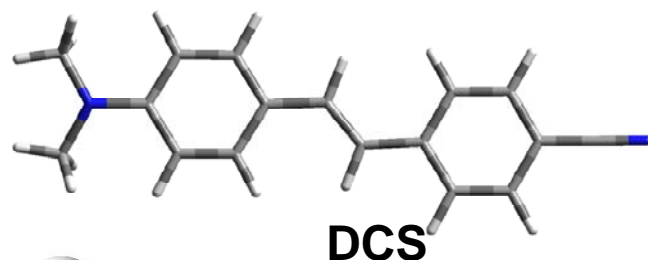


- Total coordination number varies w.r.t. composition.

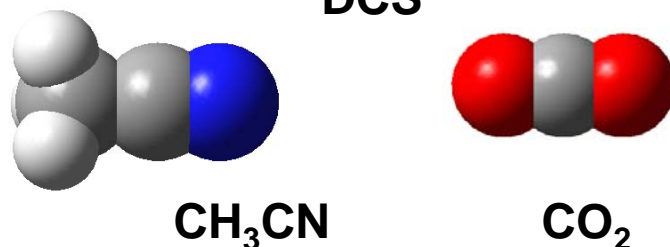


Time-resolved work

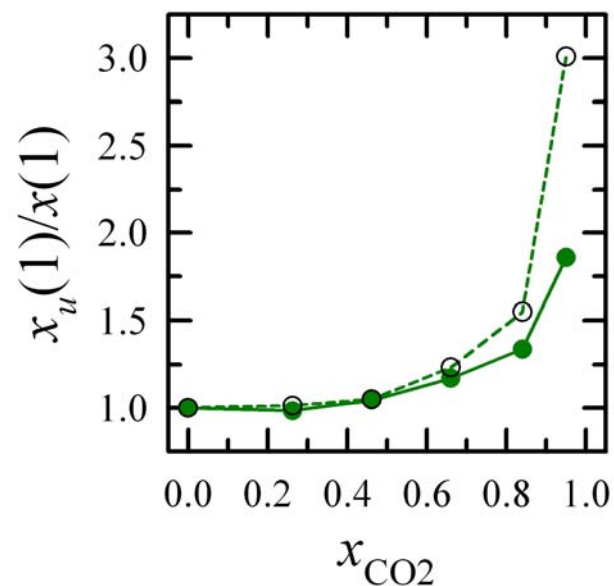
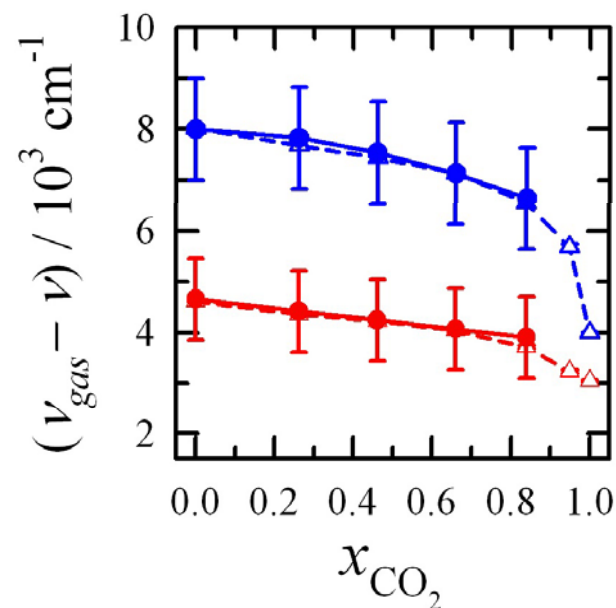
Probe:



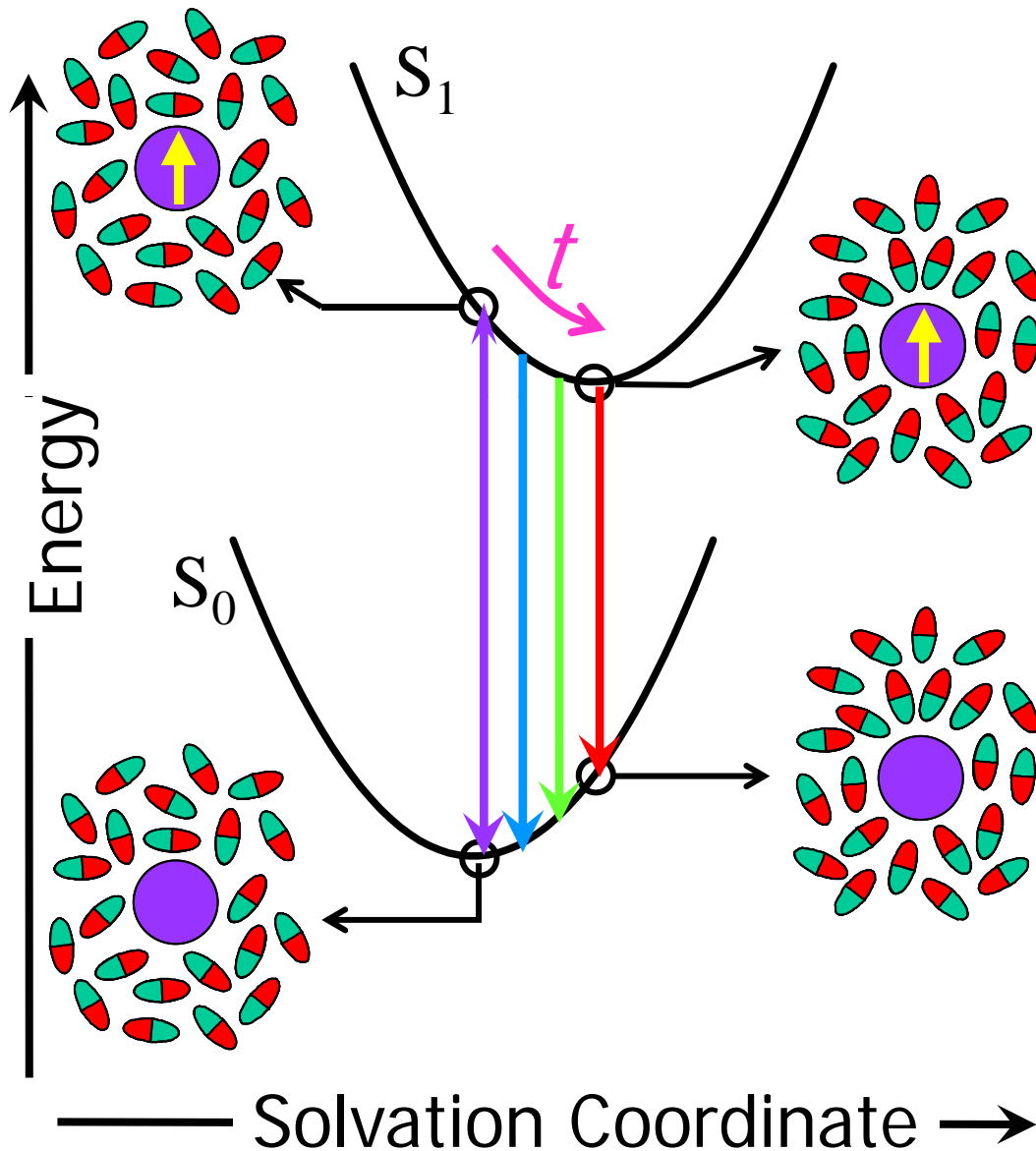
GXL:



- DCS as a solvation probe:
Arzhantsev, et. al. JPC A 110 3454 (2006)
- $\Delta\mu(S_1-S_0) = 14$ D
- Steady state spectroscopy and simulation produce similar trends to C153//ACN+CO₂:



Solvation dynamics



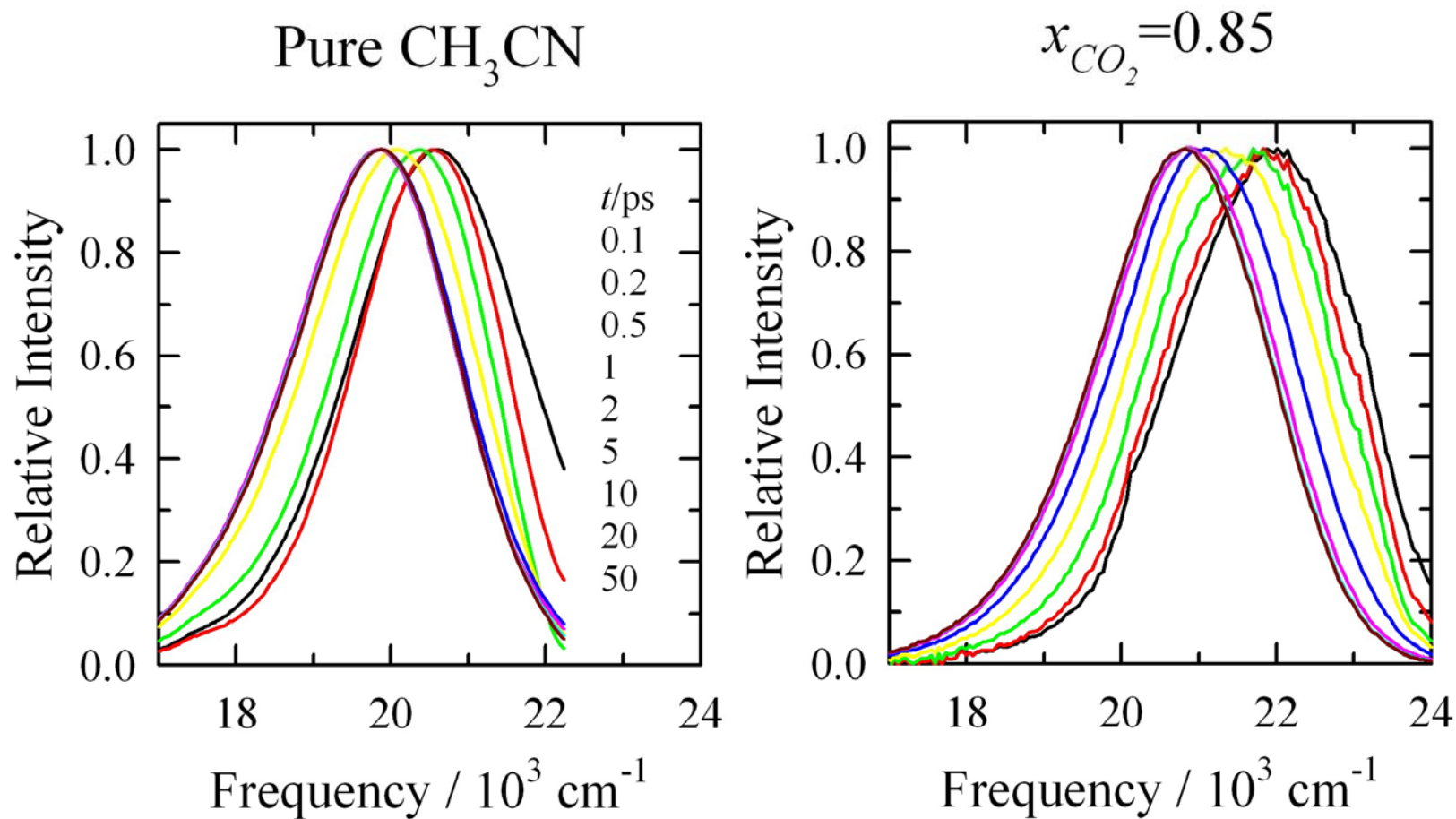
Experiment:

$$S_v(t) = \frac{v(t) - v(\infty)}{v(0) - v(\infty)}$$

Simulation:

$$C_i(t) = \frac{\langle \delta v(0) \delta v(t) \rangle_i}{\langle |\delta v(0)|^2 \rangle_i}$$

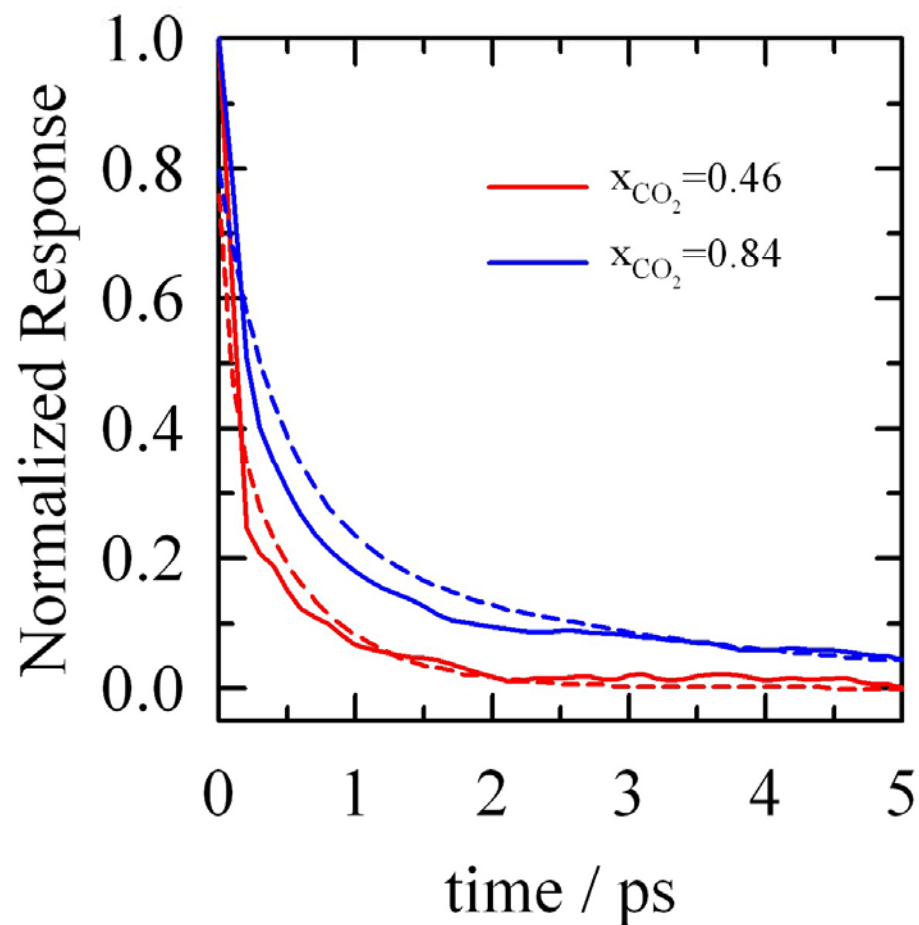
Time-resolved emission spectra



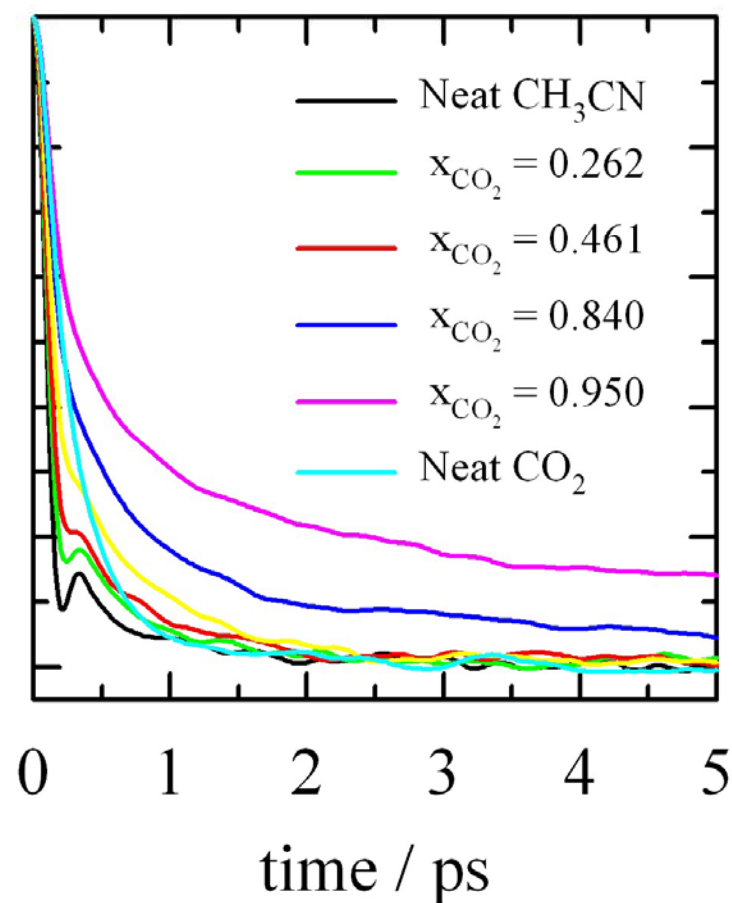
- Spectral evolution in pure CH₃CN faster than $x_{CO_2}=0.85$.
- Process occurs on 5-10 ps timescale.

Solvent response functions

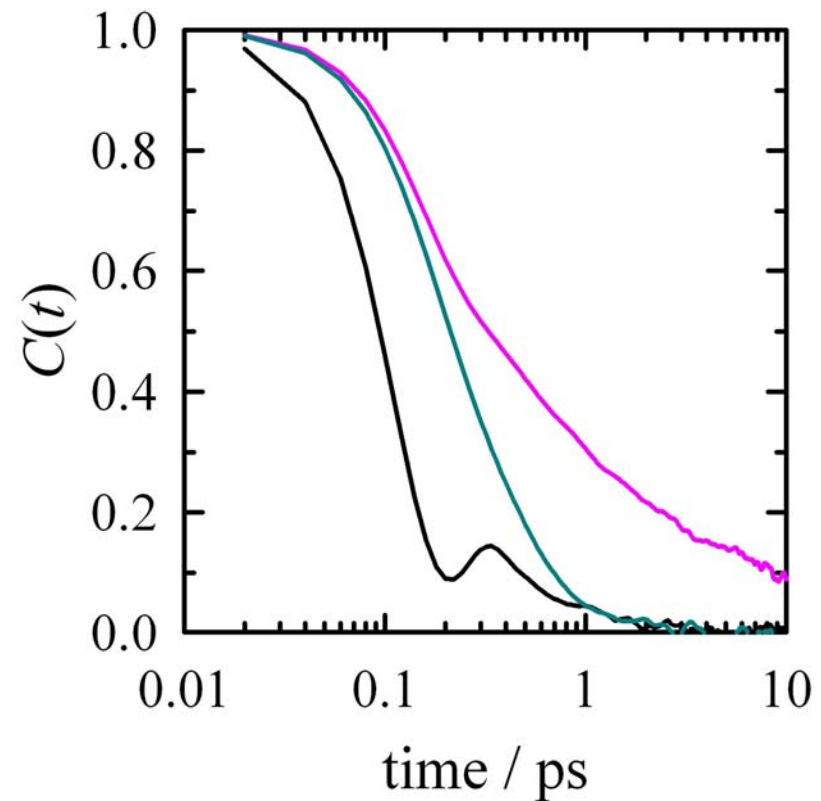
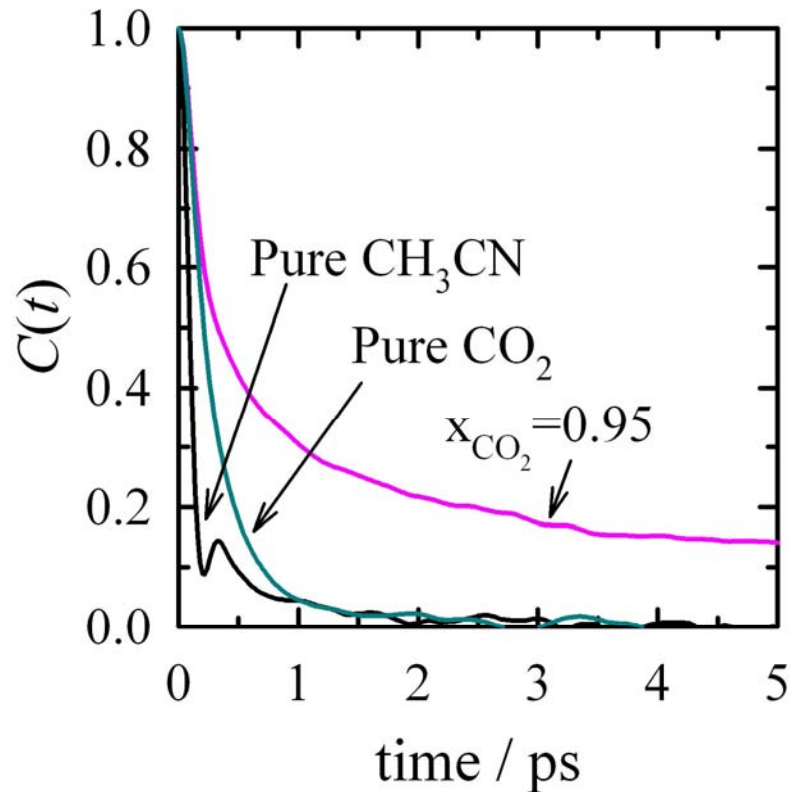
Experiment vs. Simulation



Simulation

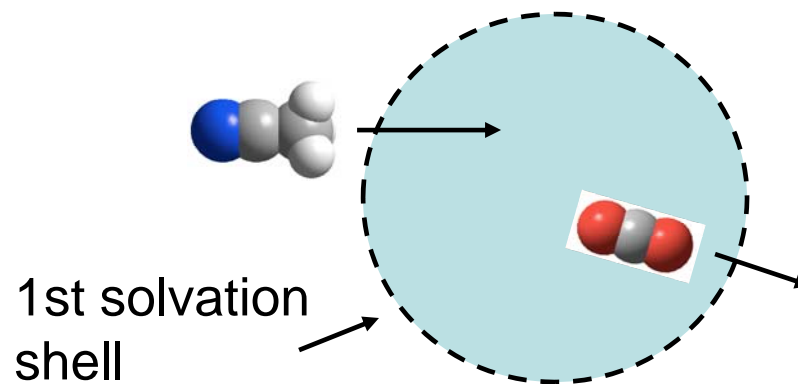
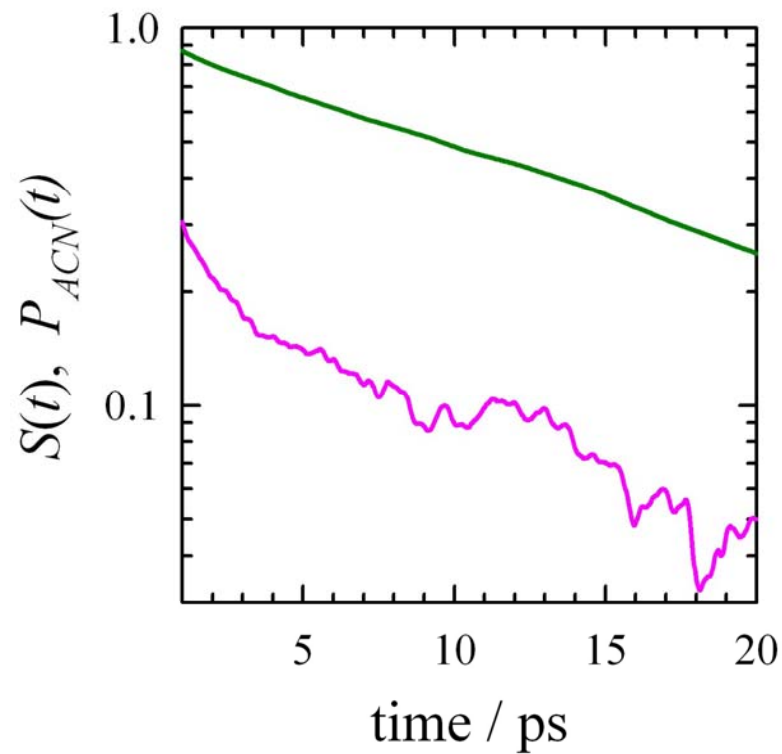
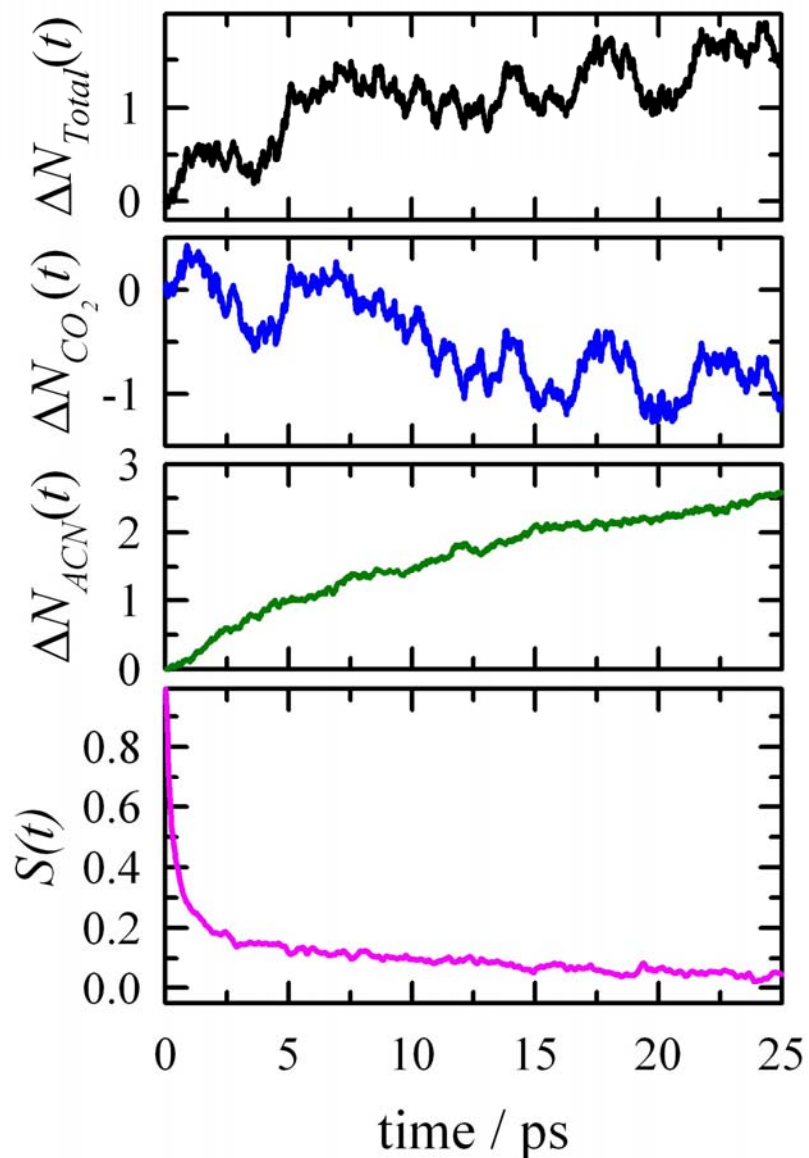


Solvation dynamics for $x_{\text{CO}_2}=0.95$



- x_{CO_2} response significantly slower compared to pure systems.
- At short times dynamics resembles neat CO_2 .
- Short-time dynamics corresponds to reorientation of solvent.

Enrichment dynamics



Conclusions

- Spectral shifts cannot be used to deduce local compositions in GXLs:
 1. Electrostatic interactions not additive.
 2. Total coordination numbers vary with composition.
- Solvation dynamics in GXL has two components:
 1. Reorientational - sub ps
 2. TD-preferential solvation - 10s of ps

Funding:

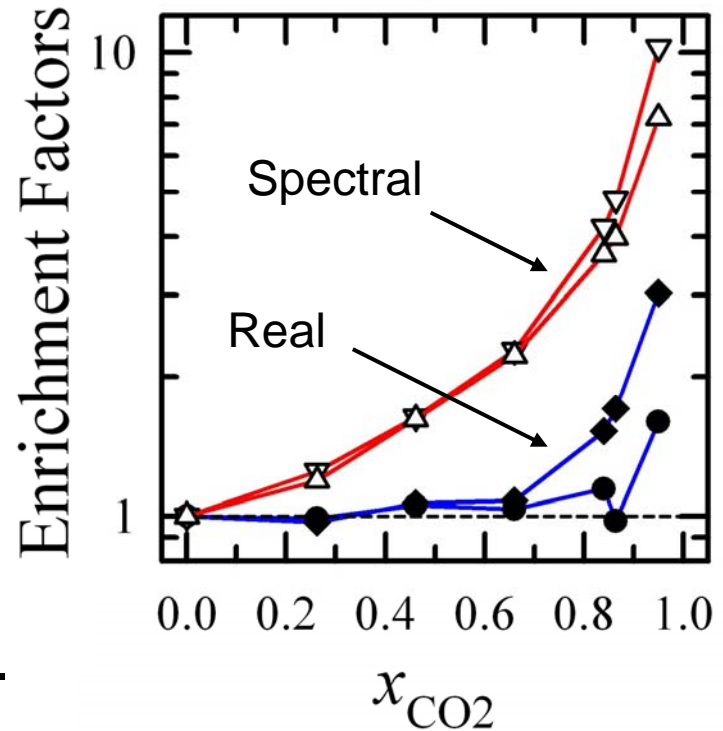
National Science Foundation, Petroleum Research Fund

Local enrichment factors

$$\frac{x_u(1)}{x(1)} = \frac{N_u(1) / N_u}{x(1)}$$

- Dynamics is diffusional.
- CH₃CN enters 1st solvation shell.
- CO₂ exits.

$$\frac{x_u^v(1)}{x(1)} = \left(\frac{v_{obs} - v_2}{v_1 - v_2} \right) / x(1)$$



$$\frac{x_u(1)}{x(1)} = \frac{N_u(1) / N_u}{x(1)}$$