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Computational Physics and Materials Science:
Total Energy and Force Methods**

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Car-Parrinello MD Simulation Studies on Supercritical CO_2

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JNCASR

Car-Parrinello MD Simulation Studies on Supercritical CO_2

Moumita Saharay and S. Balasubramanian

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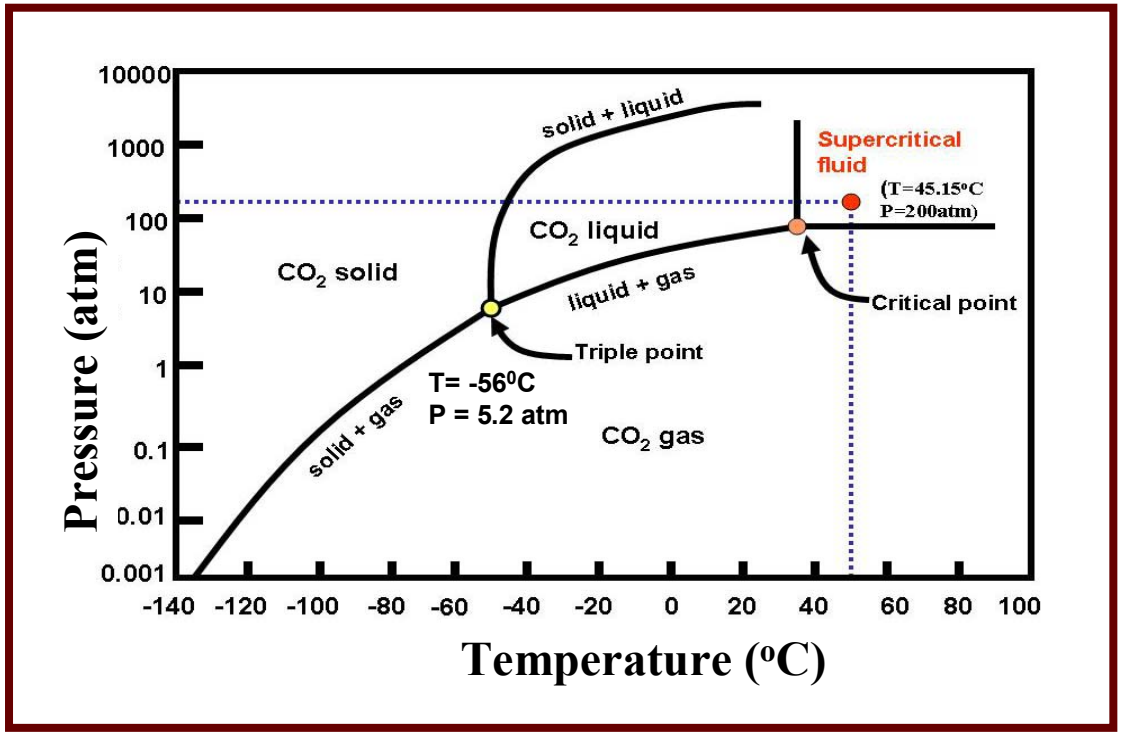
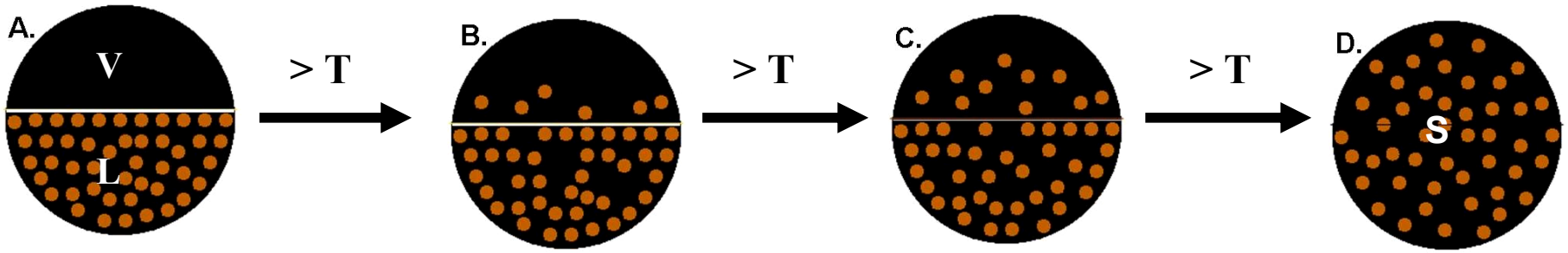
Jawaharlal Nehru Centre for Advanced Scientific Research,
Bangalore.

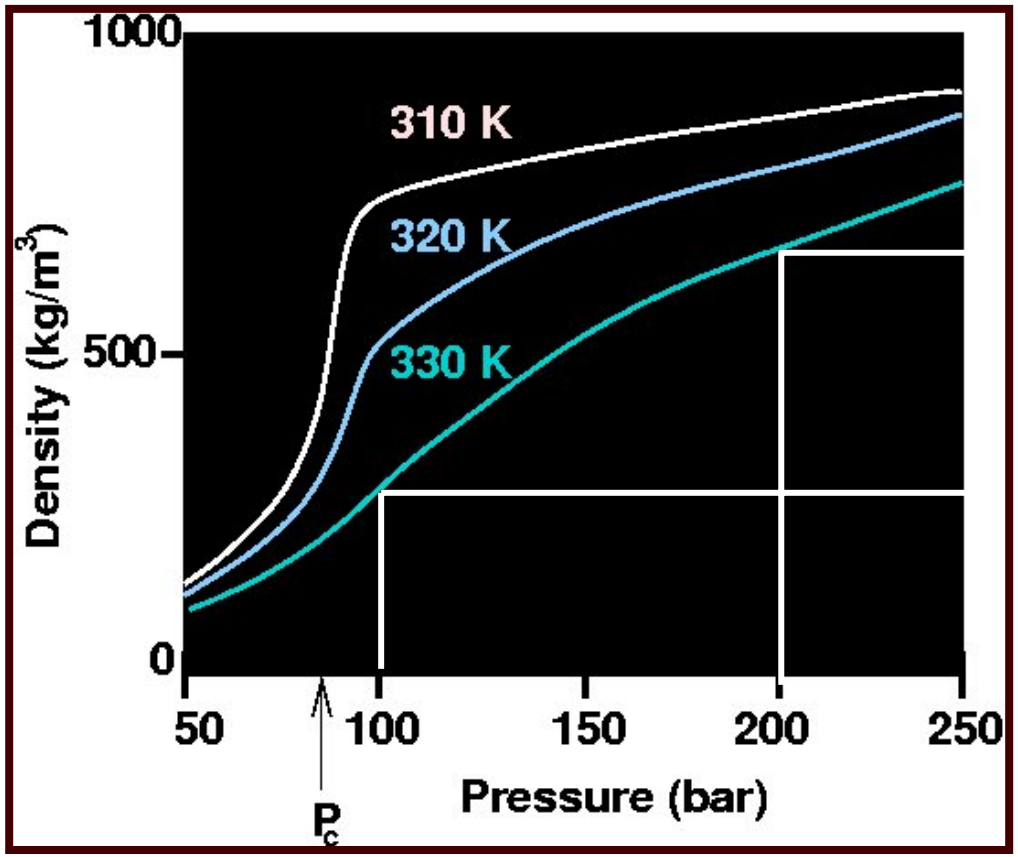
Introduction to Supercritical CO_2

Phase diagram of CO_2





Tunability of CO_2 density



Applications of $scCO_2$

- **$scCO_2$, an alternative to CFCs for dissolving PTFE**
- **$scCO_2$ replaces volatile organic solvents that could be carcinogenic – Used to make Decaf**
- **$scCO_2$: Nontoxic, recyclable, Liquid-like density, gas-like transport**
- **Nanoparticle synthesis**
- **Reaction medium for chemical synthesis (Nearly all named reactions)**
- **Binary mixture with co-solvent can enhance the solubility of polar compounds**

Our investigations

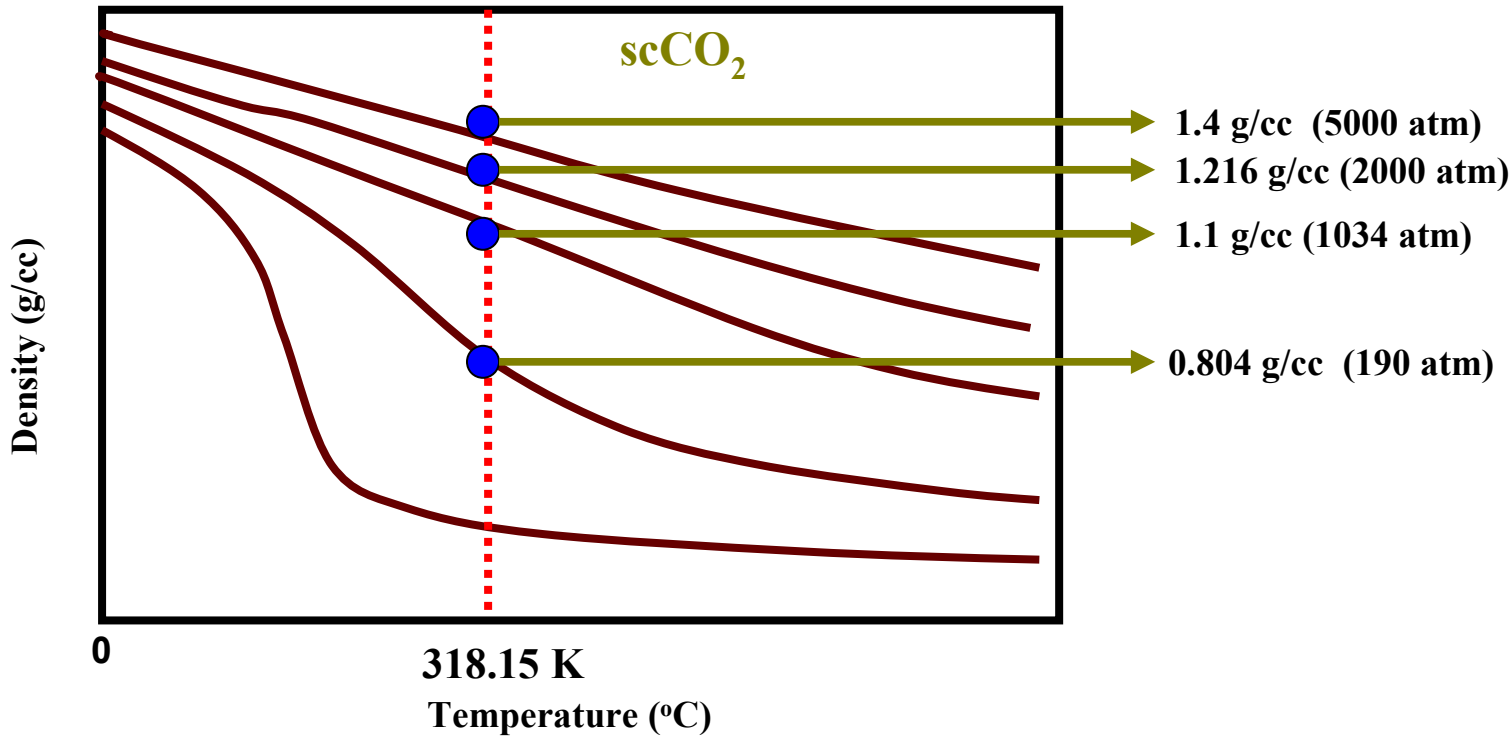
- Effect of increasing pressure and solvent tunability of $scCO_2$
- Solute-solvent interactions in Ethanol/$scCO_2$ binary mixture
- High pressure studies of binary mixture of Water (D_2O)/$scCO_2$

Effect of increasing pressure and solvent tunability of $scCO_2$

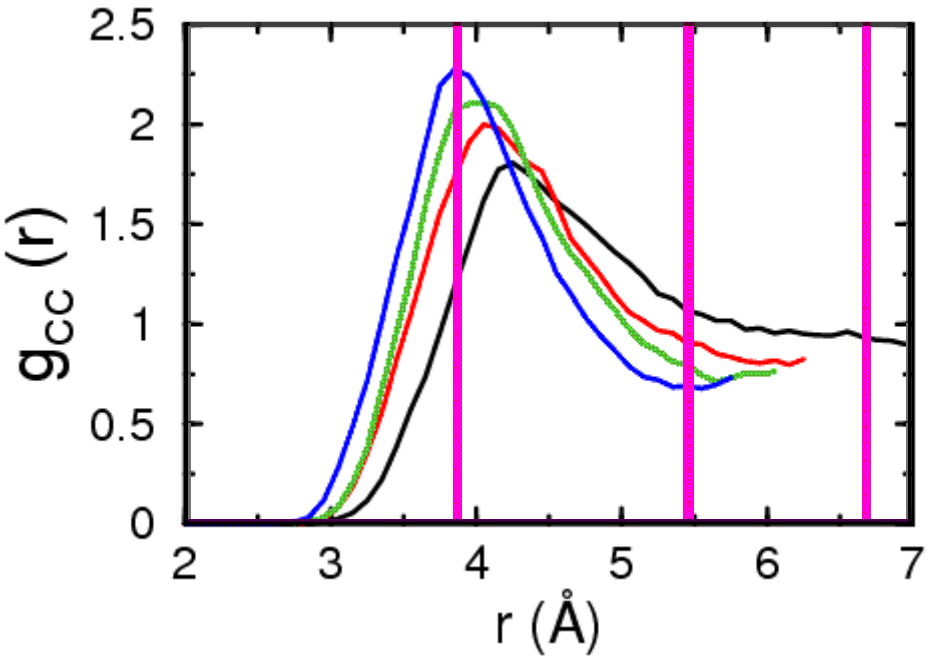
M. Saharay, S. Balasubramanian, *J. Phys. Chem. B* (2007) (In press)

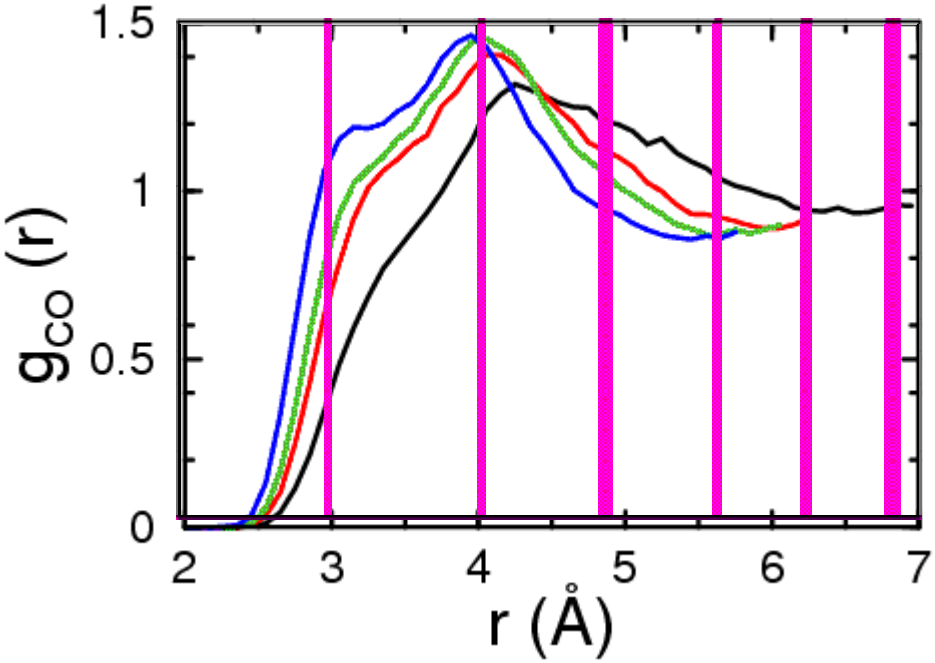
Computational details

- Kohn-Sham formulation of DFT using GGA, with BLYP exchange and correlation
- MT pseudo potential, Plane wave cutoff = 70 Ry, NVT, T = 318.15K, 32 CO_2,
- Time step = 0.096 fs, Total run length = 15 ps, Analysis = 12 ps, Equilibration = 3 ps



Pair Correlation functions



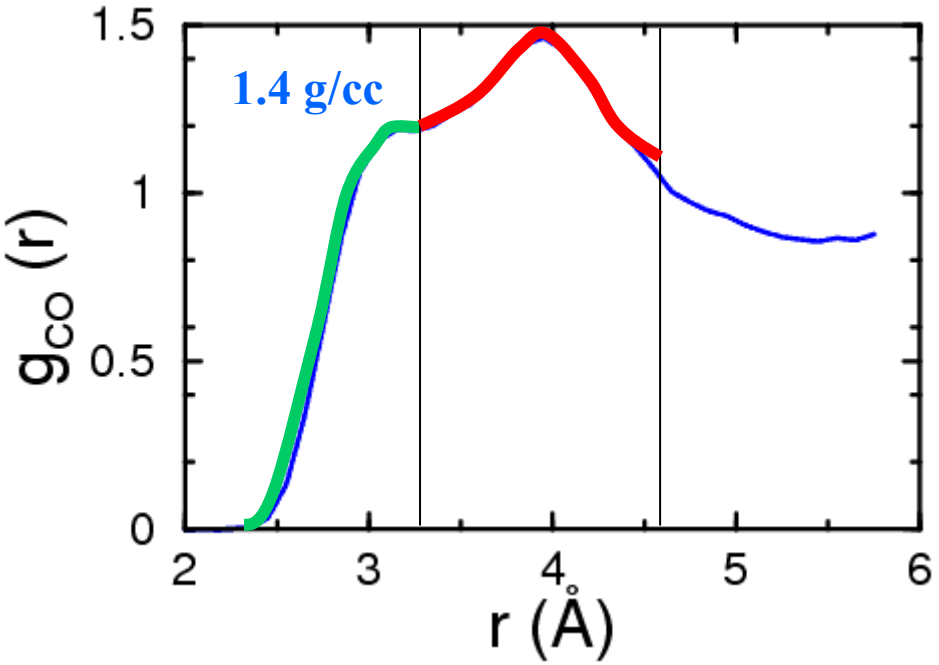


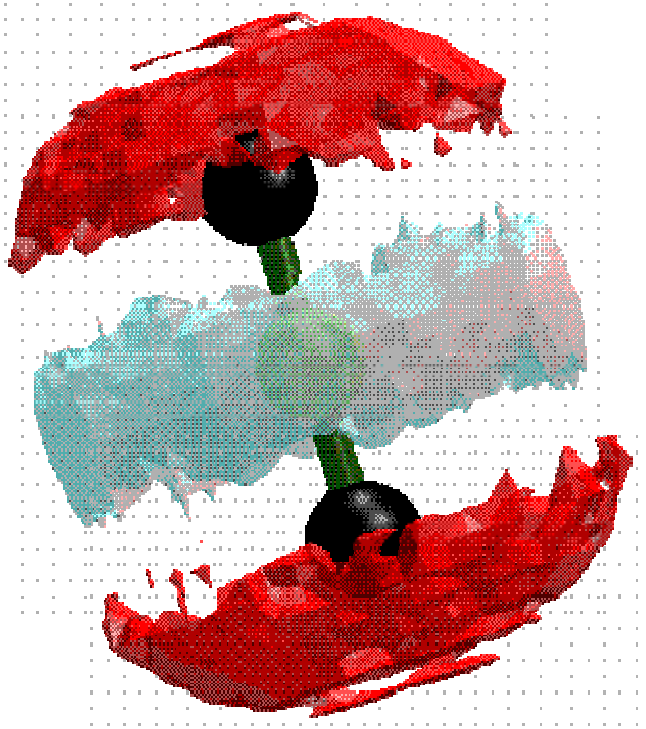
0.804 g/cc
1.1 g/cc
1.216 g/cc
1.4 g/cc

Crystal 1.76 g/cc

M. Saharay, S. Balasubramanian, J. Phys. Chem. B (2007) (In press)

Near neighbour arrangement in $scCO_2$

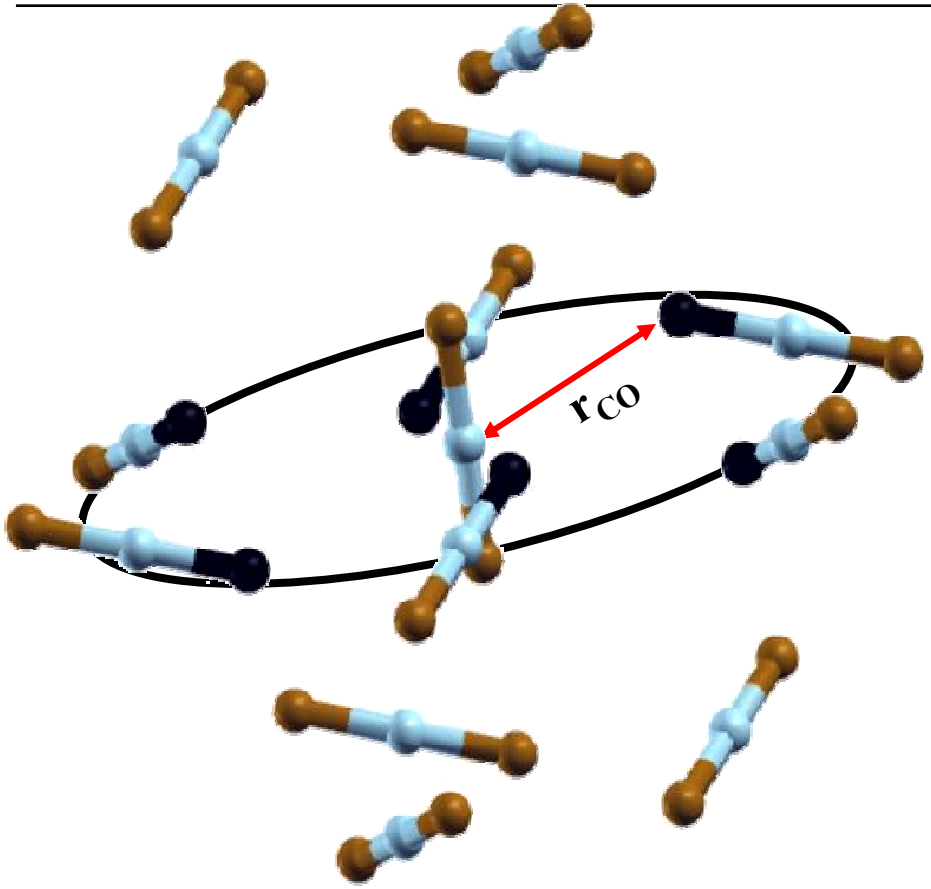


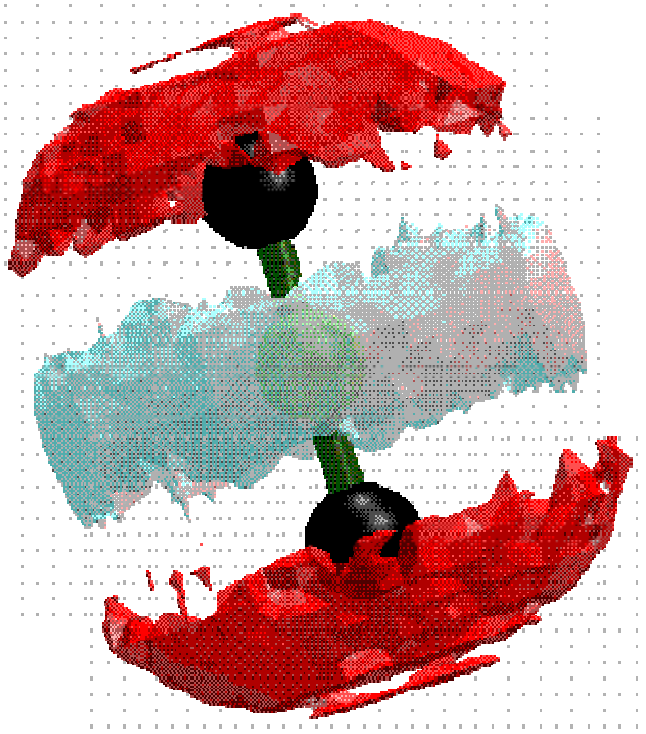


isosurface value ~ 0.07 oxy / Å^3

M. Saharay, S. Balasubramanian, J. Phys. Chem. B (2007) (In press)

Near neighbour arrangement in $scCO_2$



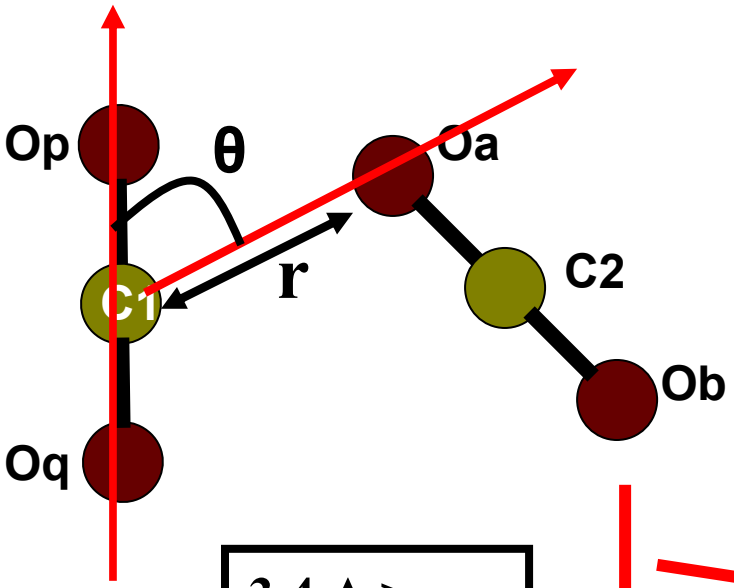


First coordination shell of CO_2 in Pa-3 crystal

isosurface value ~ 0.07 oxy / $Å^3$

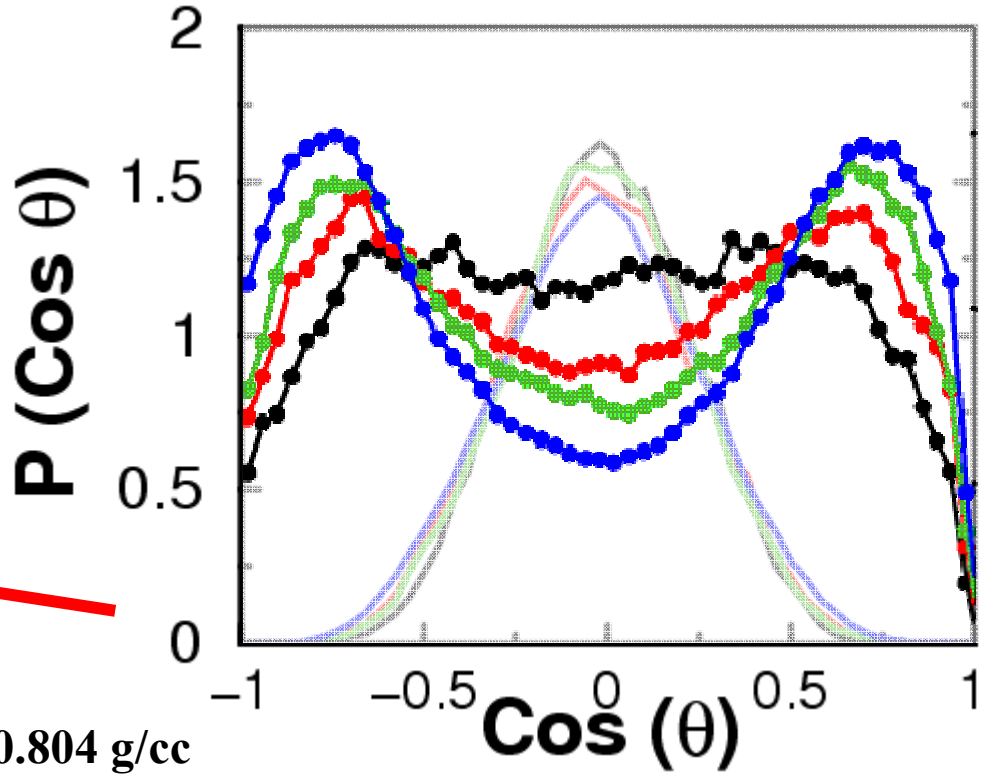
M. Saharay, S. Balasubramanian, J. Phys. Chem. B (2007) (In press)

Intermolecular angle distribution



3.4 A > r

3.6 < r < 4.3Å



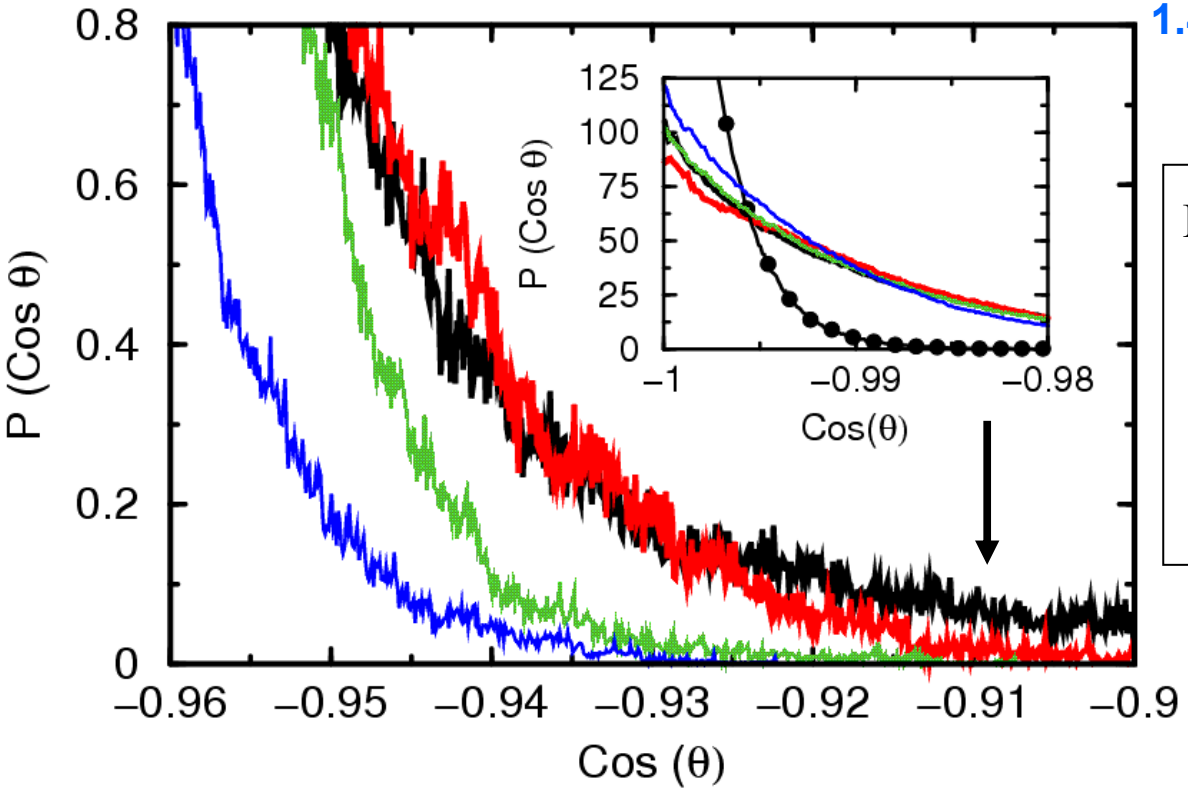
0.804 g/cc
1.1 g/cc
1.216 g/cc
1.4 g/cc

M. Saharay, S. Balasubramanian, J. Phys. Chem. B (2007) (In press)

Effect of pressure on intramolecular geometry of CO_2

Angle distribution

0.804g/cc
1.1 g/cc
1.216 g/cc
1.4 g/cc

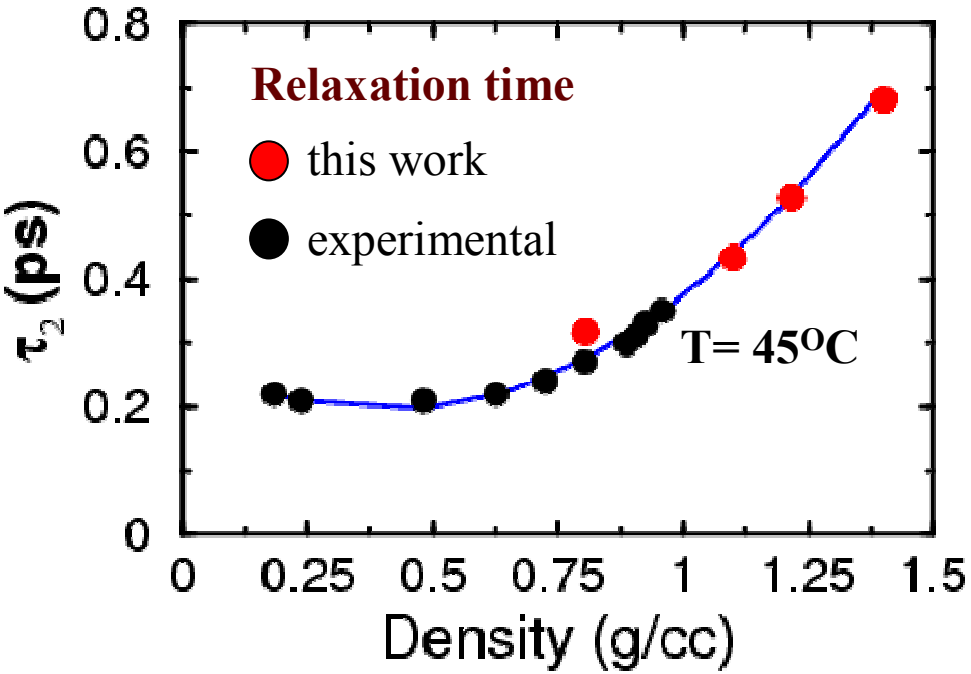


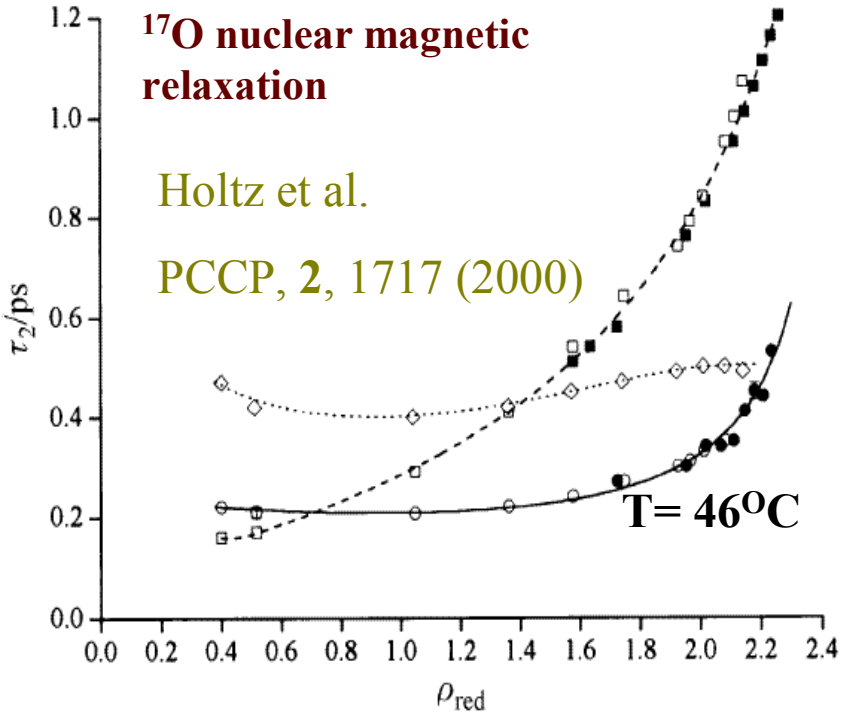
Molecule	α(Å^3)	($\alpha_{\parallel}$-$\alpha_{\perp}$) (Å^3)
HCl	2.60	0.311
CO_2	2.63	2.10

Physical Chemistry,
Berry, Rice and Ross

M. Saharay, S. Balasubramanian, J. Phys. Chem. B (2007) (In press)

Effect of pressure on dynamics of CO_2

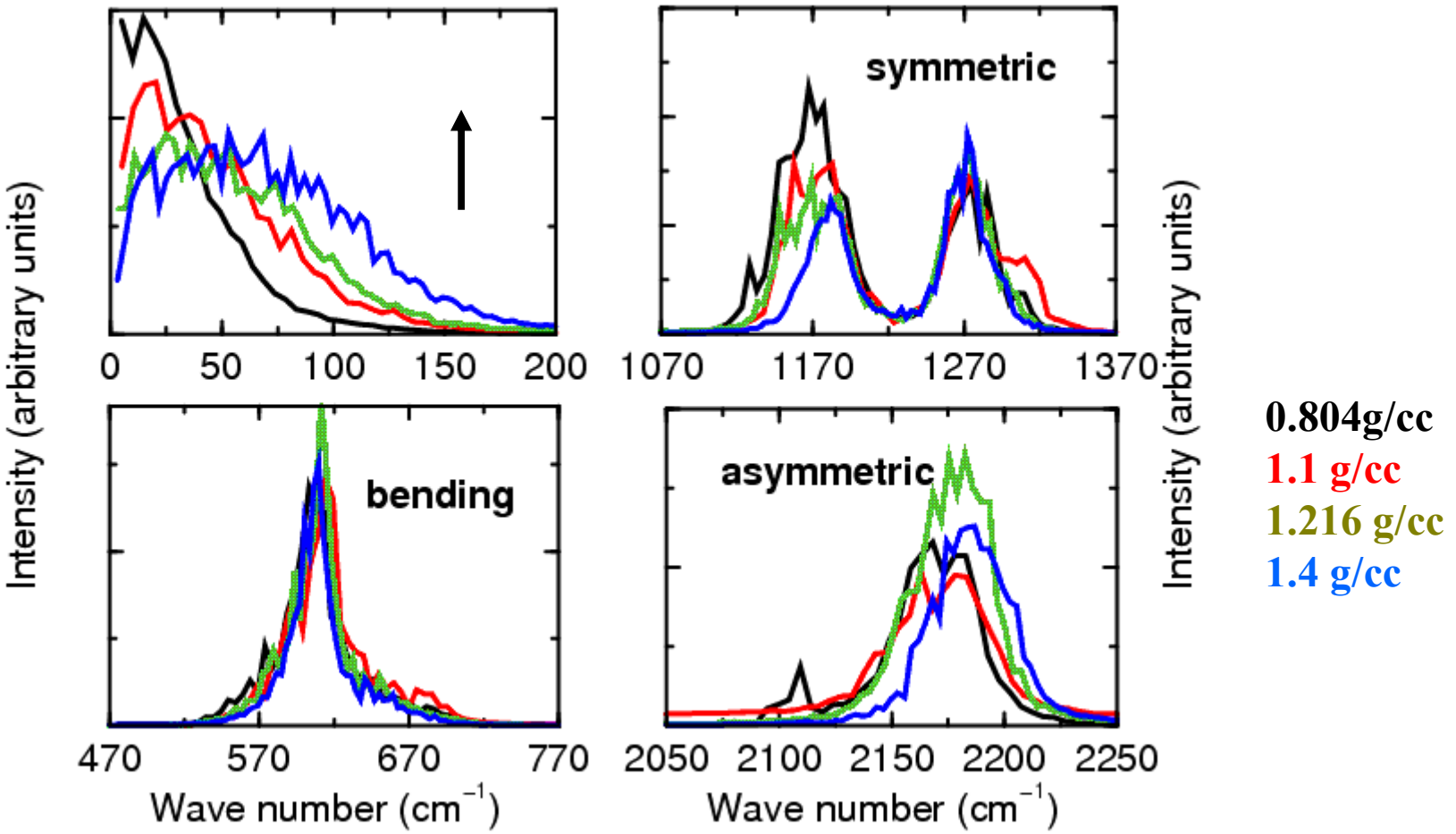




$\rho_{red} = \rho / \rho_c$

M. Saharay, S. Balasubramanian, J. Phys. Chem. B (2007) (In press)

Effect of pressure on vibrational modes



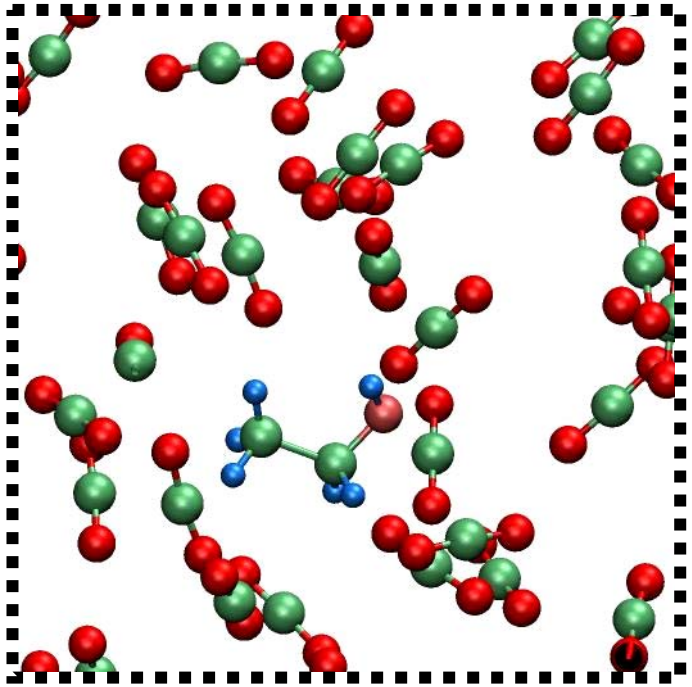
M. Saharay, S. Balasubramanian, J. Phys. Chem. B (2007) (In press)

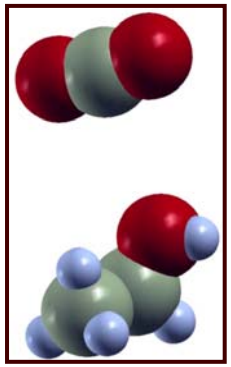
Electron Donor-Acceptor Interactions in d-Ethanol-scCO_2 Mixtures

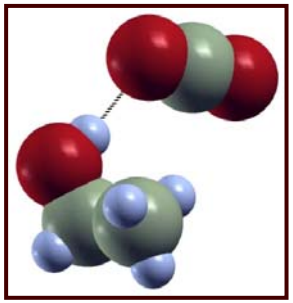
Moumita Saharay, S. Balasubramanian *J. Phys. Chem. B* 110, 3782 (2006)

Computational details

- Kohn-Sham formulation of DFT using GGA, with BLYP exchange and correlation
- MT pseudo potential, Plane wave cutoff = 70 Ry, NVT, T = 318.15K, 64 CO_2 (.7g/cc) 1 d-ethanol, 0.0154%
- Time step = 0.096 fs, Total run length = 10 ps, Analysis = 7 ps, Equilibration = 3 ps





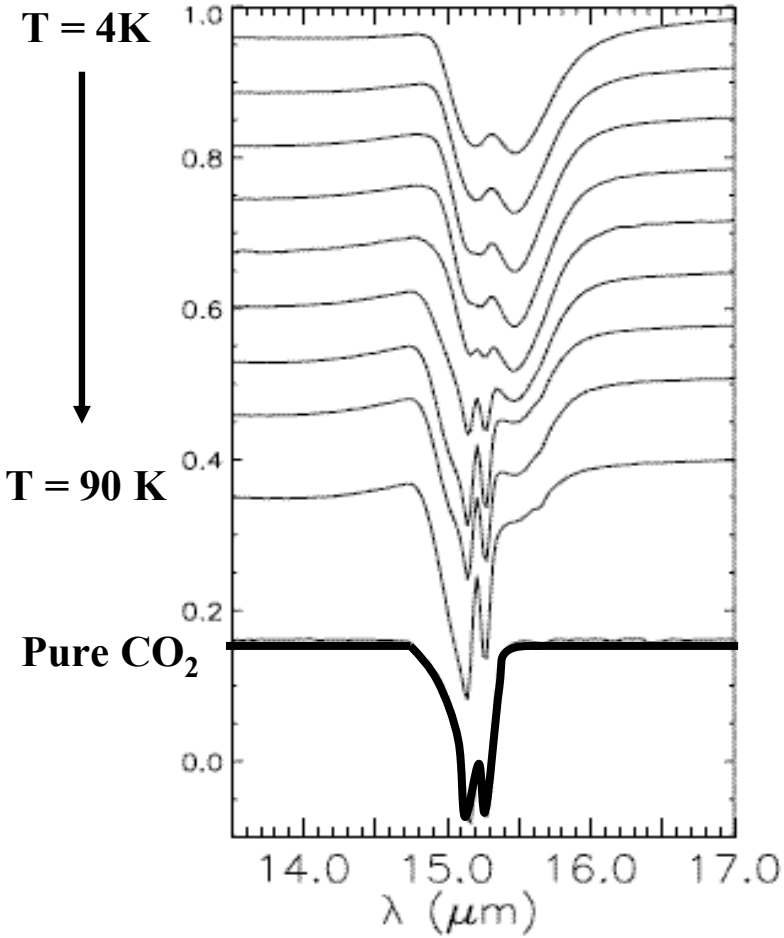


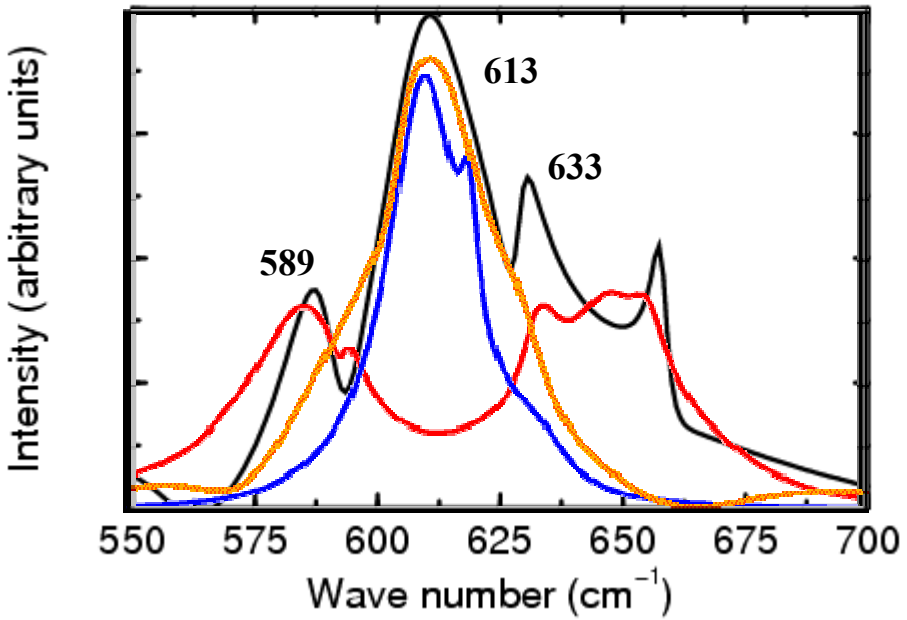
ΔE_{HYD} = -0.840 kcal/mol (CPMD)

ΔE_{EDA} = -2.627 kcal/mol (CPMD)

CO_2 Bending Mode

IR space observatory spectra, ***Astron. Astrophysics (1999)***
Spectral evolution of ice mixture composed of CO_2 and methanol





Total bending mode

Monomer

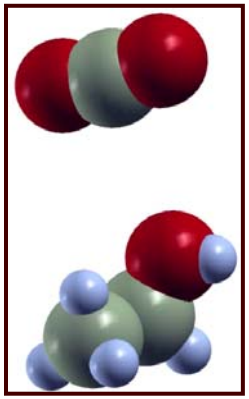
In-plane mode

Out-of-plane

2 possibilities
1. CO_2-ethanol EDA
2. CO_2-CO_2 EDA

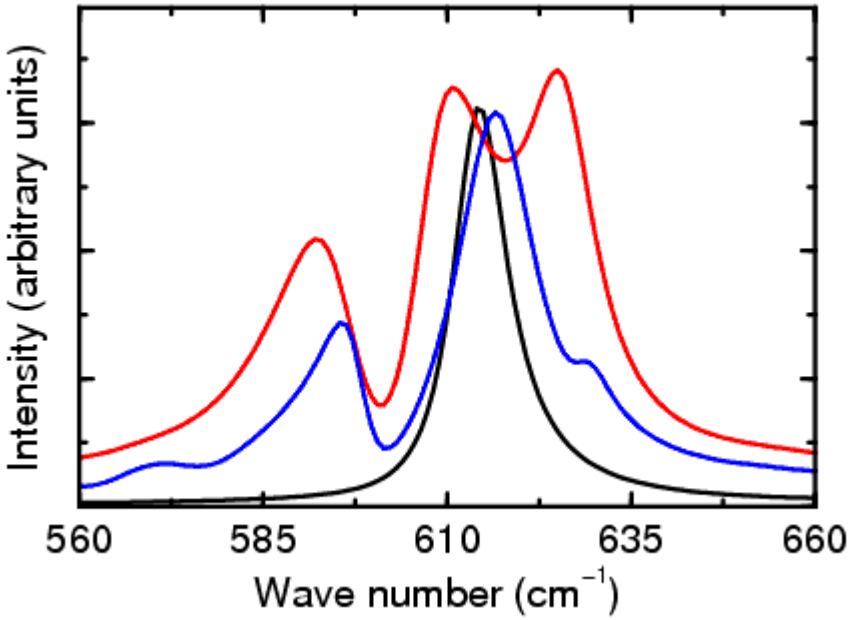
M.S. & S.B., *J. Phys. Chem. B* , 110, 3782 (2006)

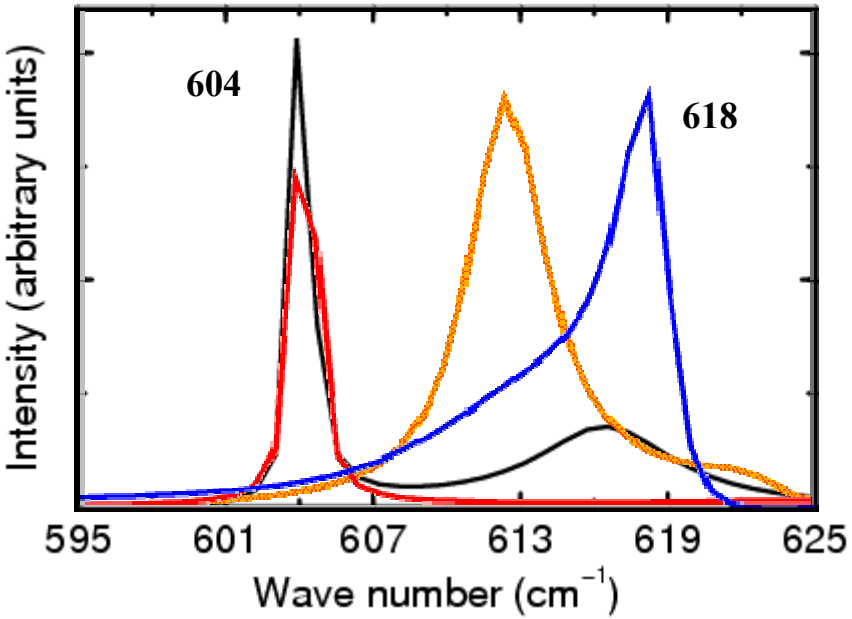
Dynamics in clusters



CO_2 bending mode in EDA complex

Bending mode for CO_2 dimer





Total EDA bending mode

Monomer

In-plane mode

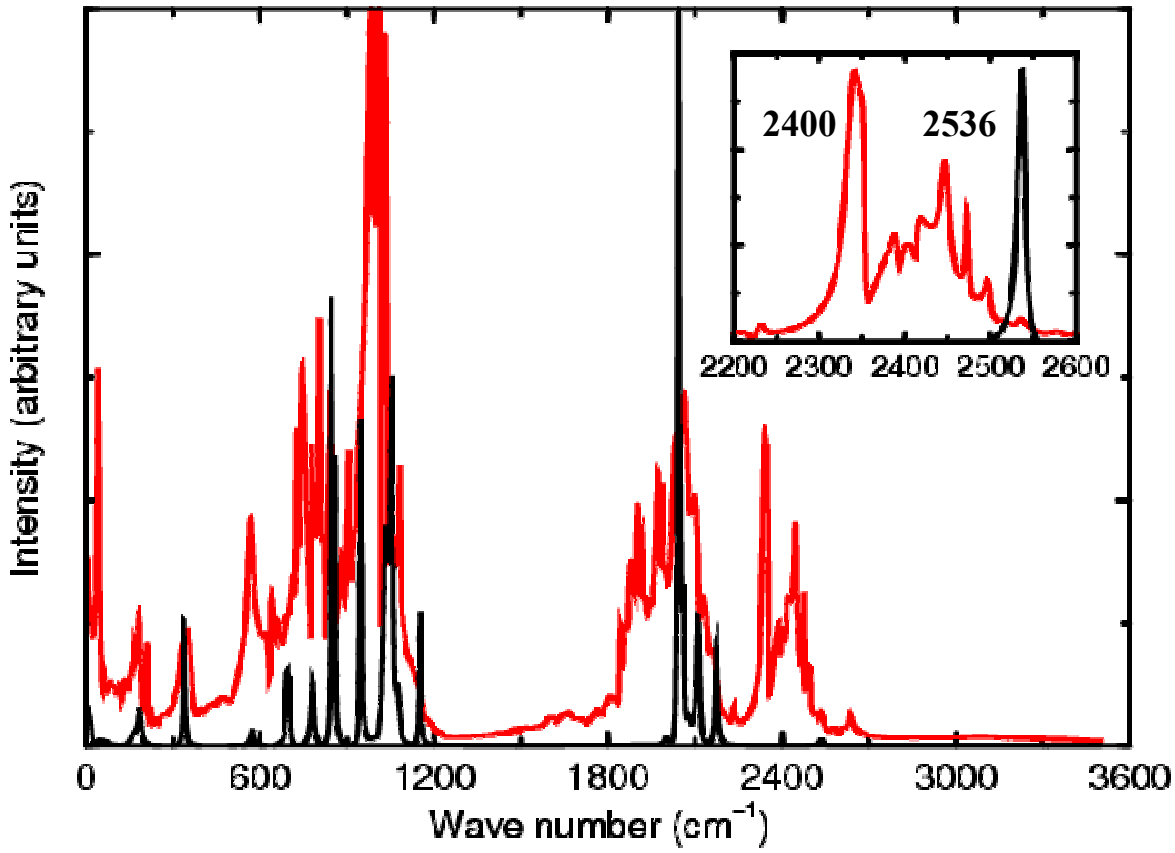
Out-of-plane

In-plane bending mode in bulk and dimer shows similar behaviour

VDOS for d-ethanol

monomer

In 1:64 system



Red shift in the OD stretching of ethanol in bulk w.r.t. isolated ethanol is due to association with CO_2

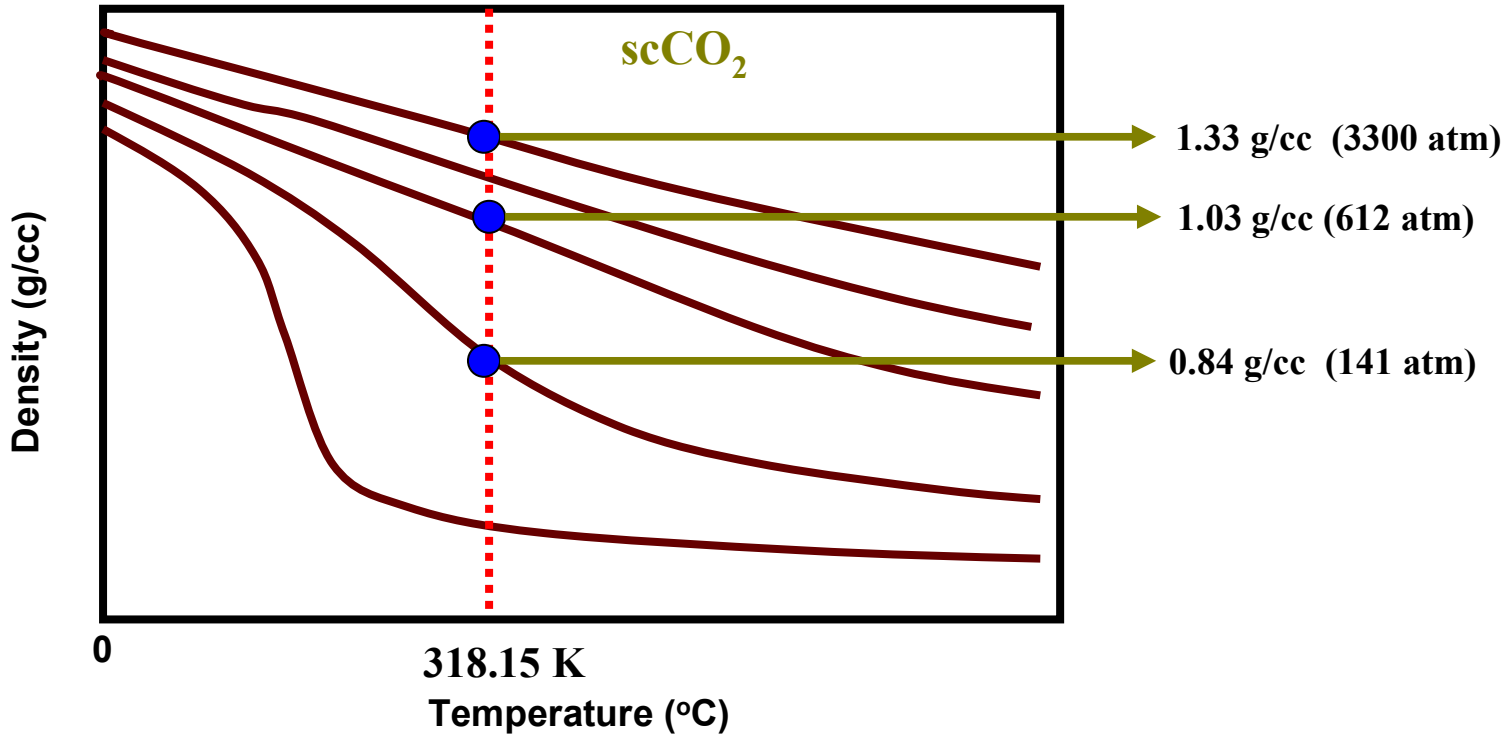
M.Saharay & S.Balasubramanian, *J. Phys. Chem. B* , 110, 3782 (2006)

High Pressure Studies on Binary Mixture of D_2O and Supercritical CO_2

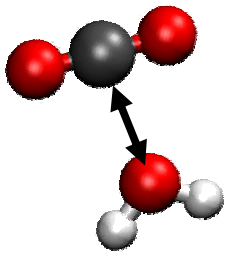
Moumita Saharay, S. Balasubramanian ***J. Phys. Chem. B***
(submitted)

Computational details

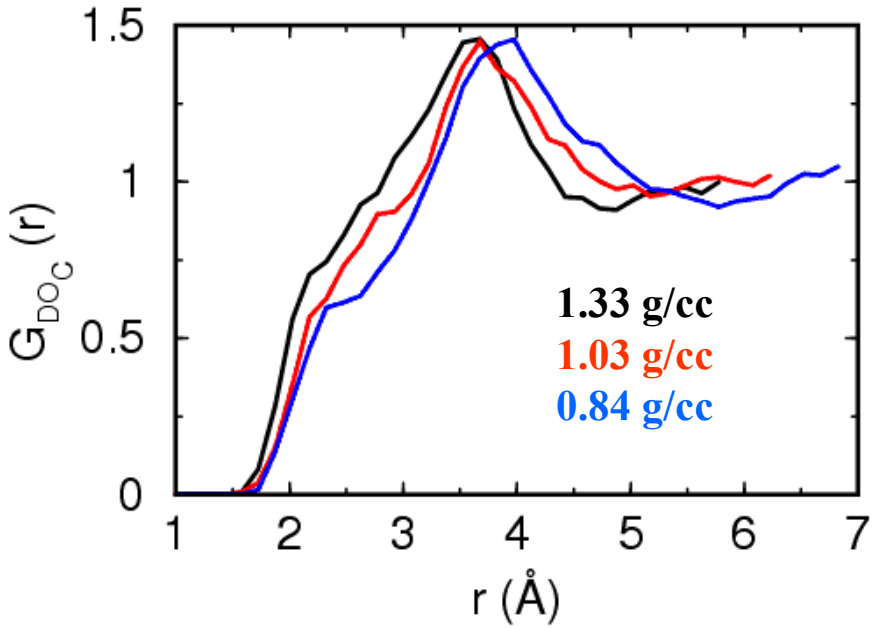
- Kohn-Sham formulation of DFT using GGA, with BLYP exchange and correlation
- MT pseudo potential, Plane wave cutoff = 70 Ry, NVT, T = 318.15K, 31 CO_2, + 1 D_2O
- Time step = 0.096 fs, Total run length = 15 ps, Analysis = 12 ps, Equilibration = 3 ps

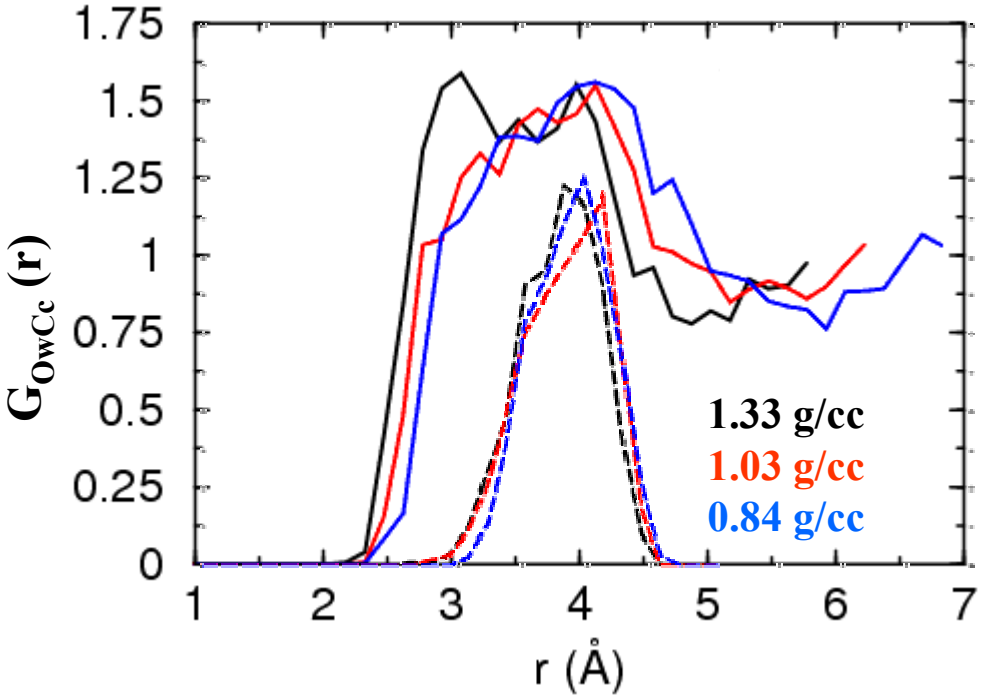


EDA vs H-bonded interaction



Signature of EDA and hydrogen-bonded interaction from pair correlation functions at different solvent densities

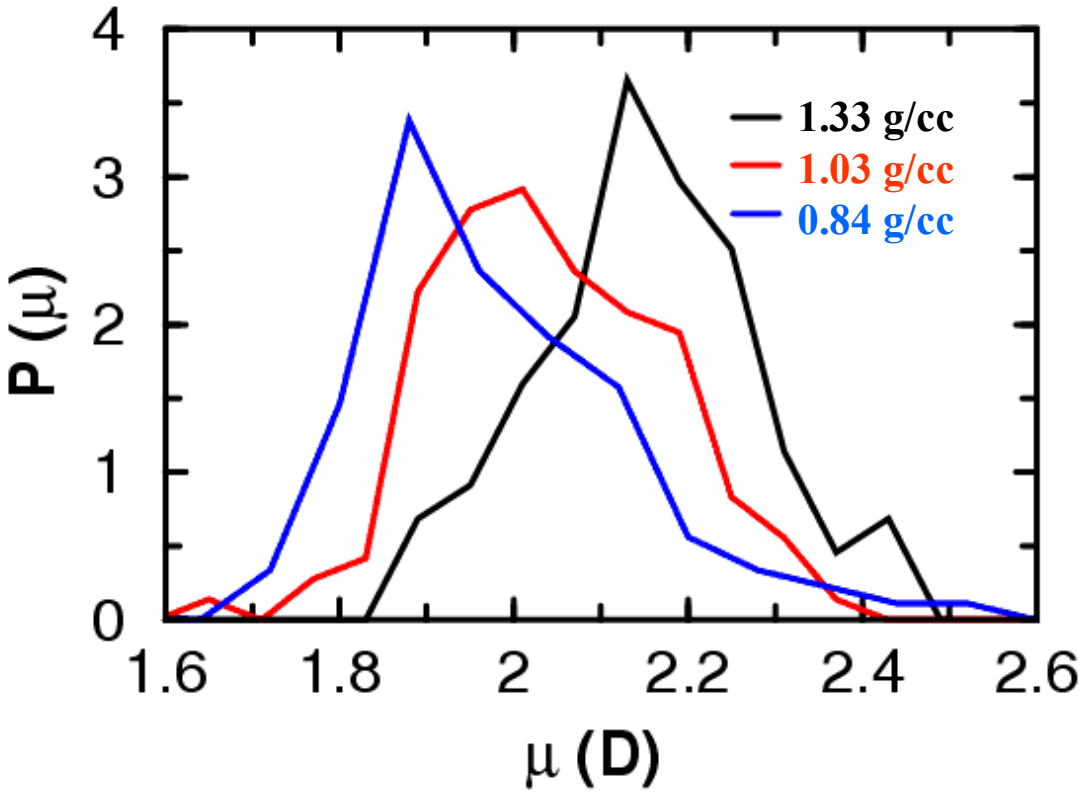




Dipole moment distribution of D_2O

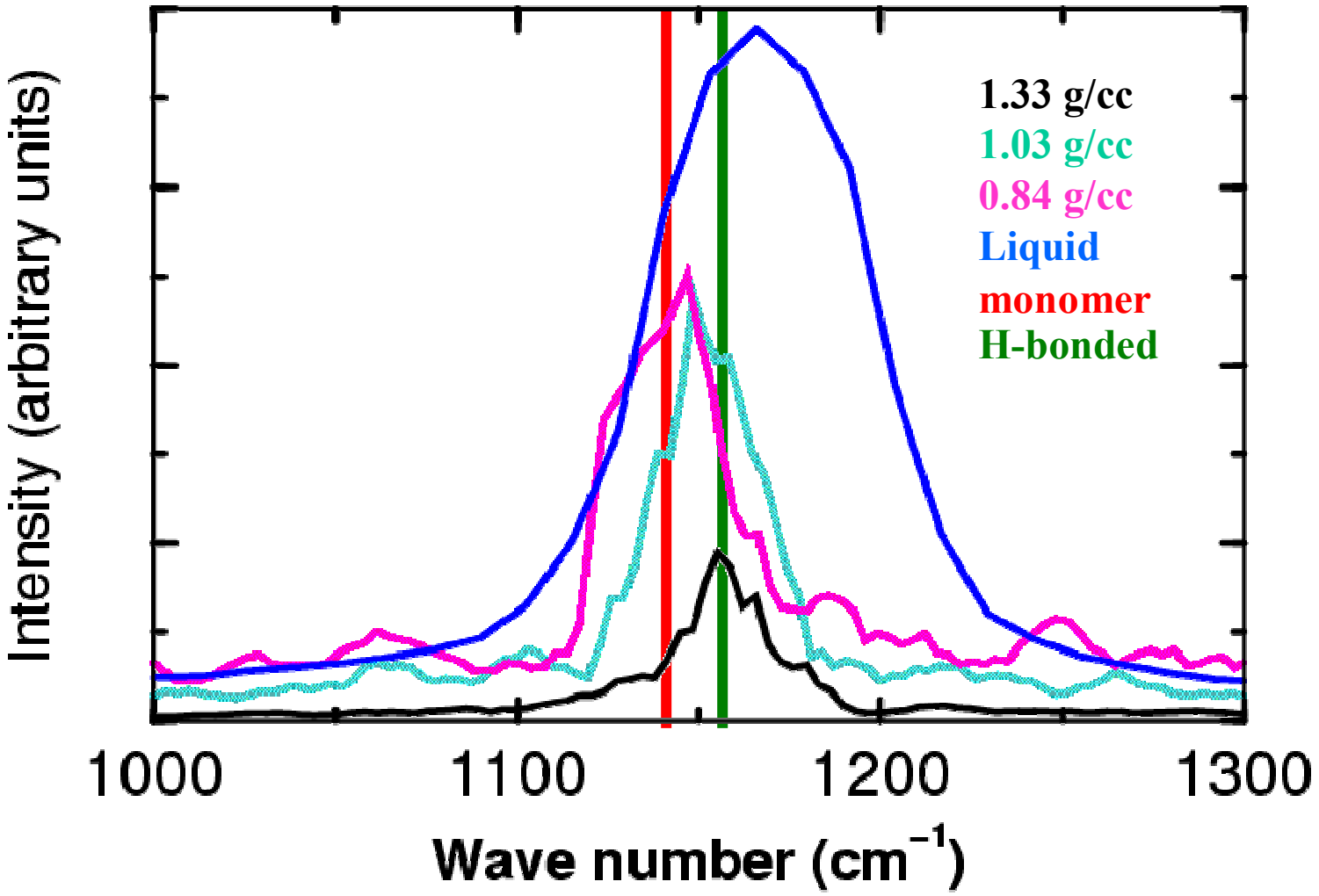
Signature of D_2O miscibility in $scCO_2$?

Possibility of increased H-bonded interaction in high density

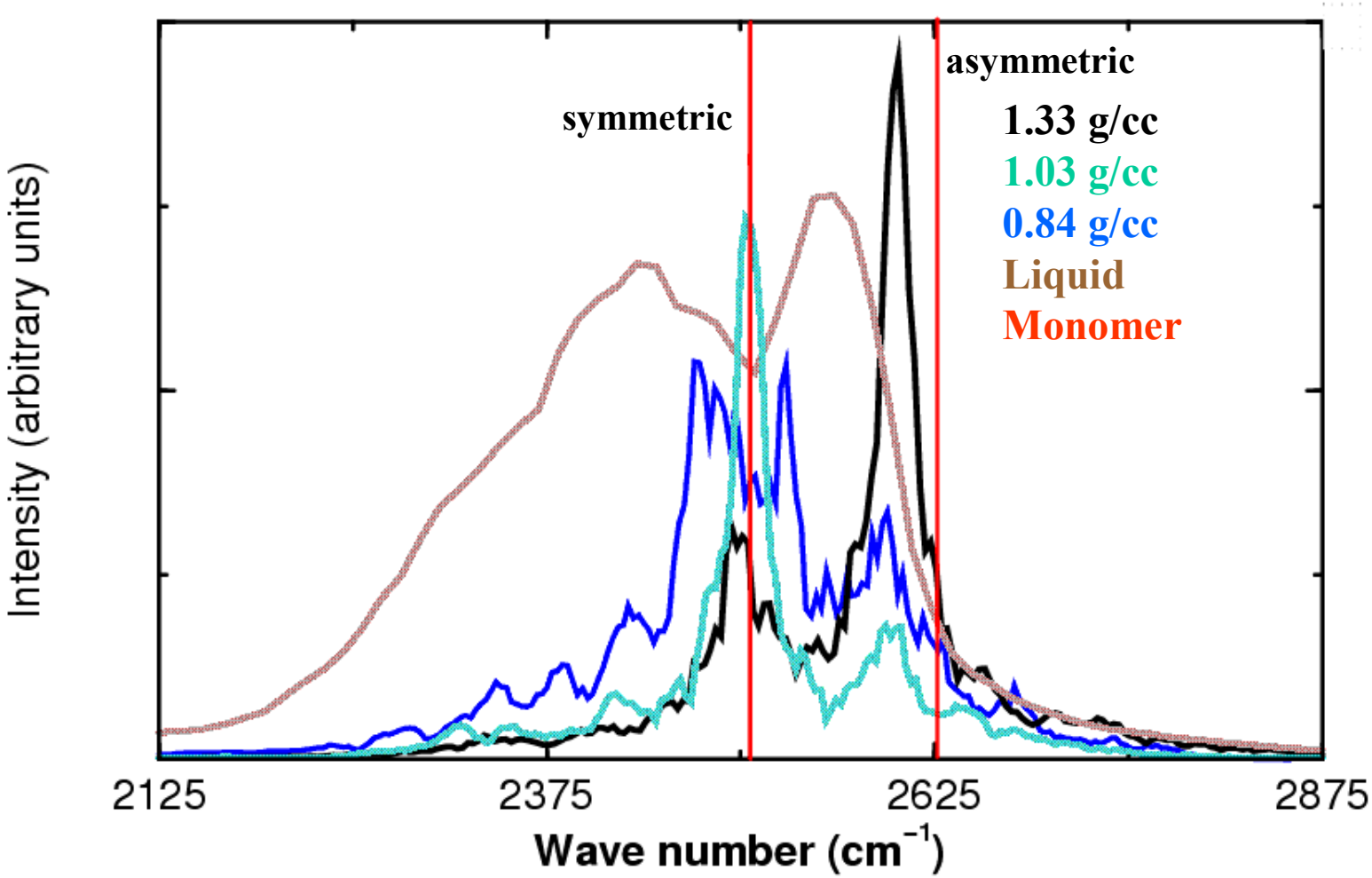


	μ
Monomer	1.85 D
Liquid water	2.66 D

Effect of pressure on bending mode of D_2O



Effect of pressure on stretching mode of D_2O



Conclusions

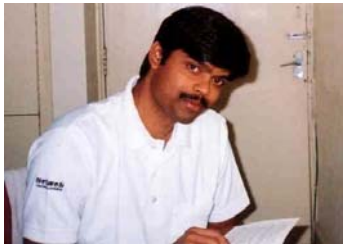
- **Structural evolution with increasing pressure : at least in the first coordination shell**
- **Deviation of CO_2 from non-linear structure decreases with increasing solvent density → effect of polarization due to near neighbor interactions**
- **CO_2 can behave both as a Lewis acid as well as a Lewis base. This attribute is responsible for its association with other CO_2 molecules as well as with ethanol in the formation of EDA complexes**
- **The degeneracy of the ν_2 mode of CO_2 gets lifted due to EDA interaction with other species**
- **Enhanced dipole moment -> Miscibility of D_2O in $scCO_2$ environment increases with system pressure**
- **Red-shift in stretching mode w.r.t. the monomer siginifies the weakening of intramolecular OD bond**

Summary

- Formation of solvation shell
- Enhanced multipole moments
- Specific solute-solvent interactions between solvent and co-solvent

Acknowledgement

Prof. S. Balasubramanian



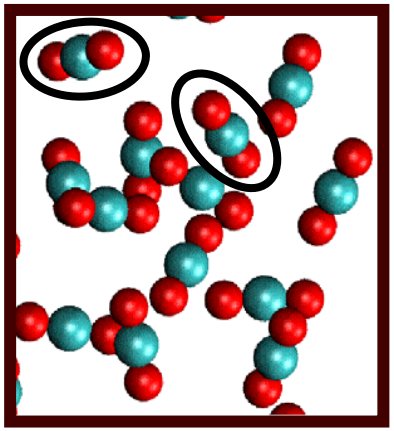
Dr. M. Krishnan

- Mr. B. L. Bhargava
- Ms. S. Saswati

CSIR, DST, JNCASR


THANK YOU

Molecular multipole moments

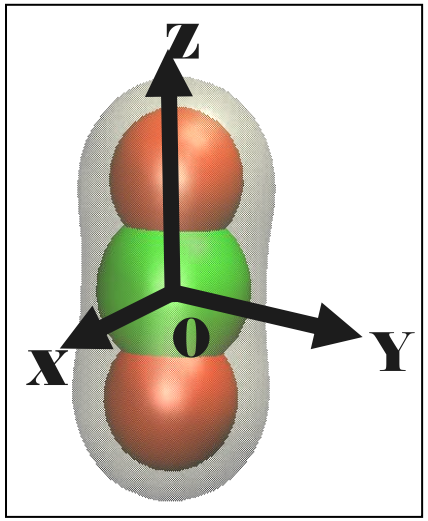


Dipole moment

$$\mu_i = 2\pi \int_{r=0}^{r_c} \int_{z=-z_c}^{z_c} \rho(\vec{r} - \vec{R}_i)\vec{r}\, r\, dr\, dz$$

μ_i = dipole moment of i-th molecule

Quadrupole moment



$$Q^i_{mn} = 2\pi \int_{r=0}^{r_c} \int_{z=-z_c}^{z_c} (3r_m r_n - r^2\delta_{mn})\rho(\vec{r} - \vec{R}_i)\, r\, dr\, dz$$

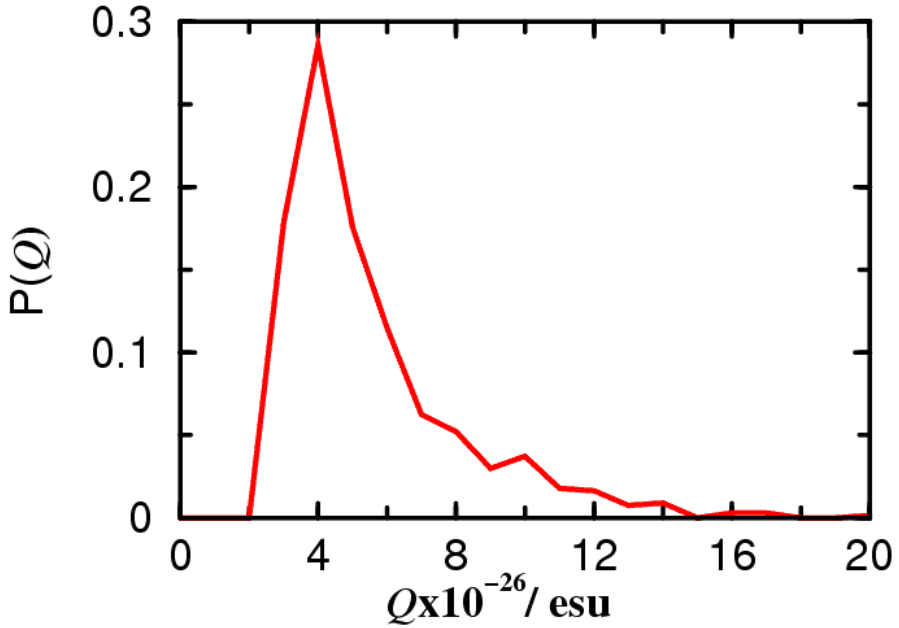
Q_{mn} = quadrupole moment component

r_c = 1.3 Å; z_c = 2.8 Å

M.Saharay & S.Balasubramanian, *ChemPhysChem*, 5, 1442 (2004)

Multipole moment distribution

Instantaneous Quadrupole moment

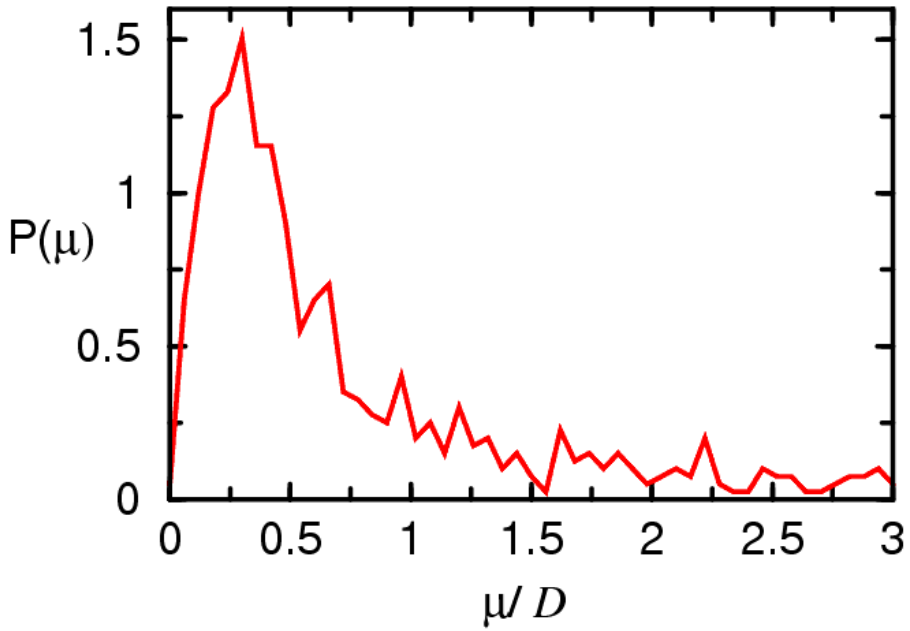


<Q> from CPMD = 6.1x10^{-26} esu

Geometry optimized value for isolated molecule from CPMD = 4.26x10^{-26} esu

Experimental value = 4.1x10^{-26} esu

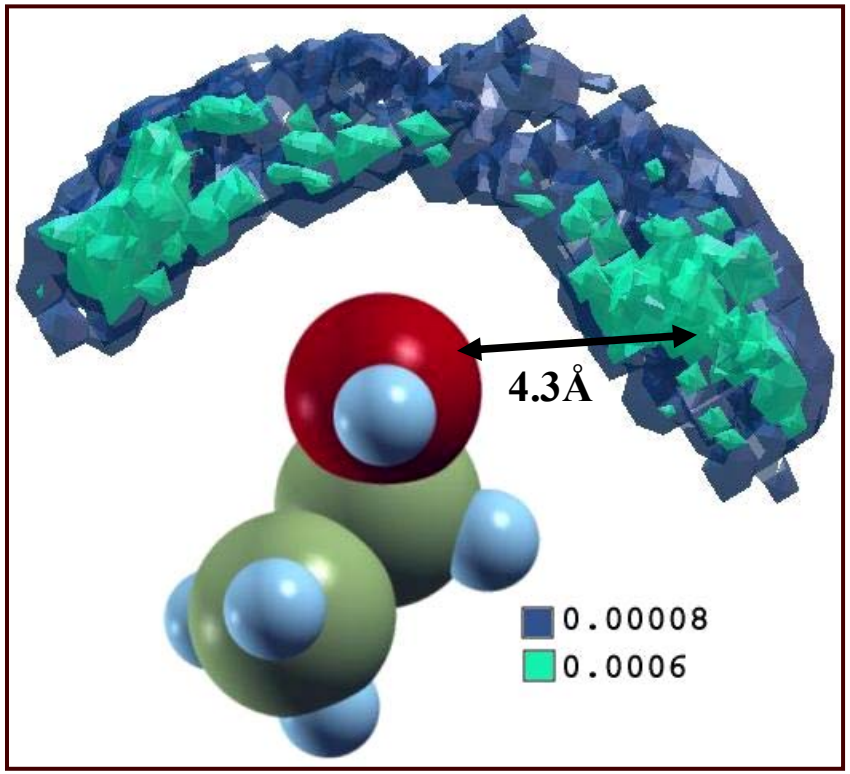
Instantaneous Dipole moment

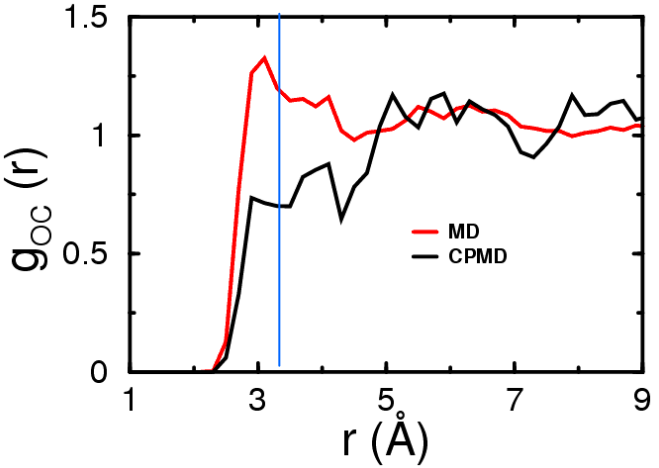


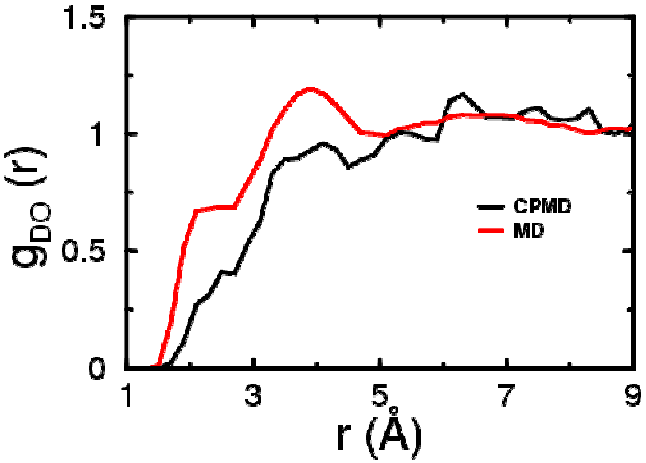
<μ> from CPMD calculation=0.85 D

M.Saharay & S.Balasubramanian, *ChemPhysChem*, 5, 1442 (2004)

Probability density map

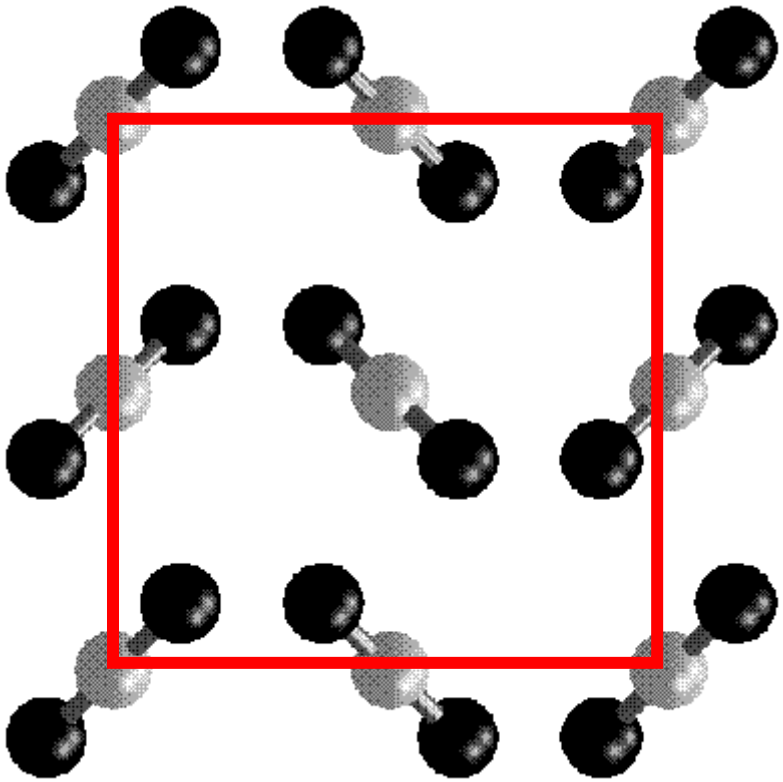






M.Saharay & S.Balasubramanian, *J. Phys. Chem. B* , 110, 3782 (2006)

Crystal structure of CO_2



PA-3 crystal structure

Density of CO_2 in crystal is 1.76 g/cc

	orientation	position
1	1 1 1	0 0 0
2	1 -1 -1	½ ½ 0
4	-1 1 -1	0 ½ ½
4	-1 -1 1	½ 0 ½

Suzuki et al. JCP, 55, 5349 (1971)

Car-Parrinello Molecular Dynamics

Kohn-Sham energy functional

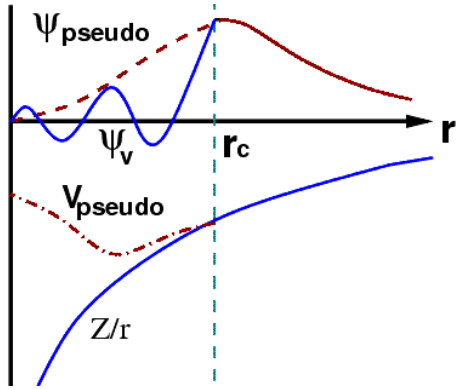
$\Psi_i(r) = \Sigma C_k^i \exp(ik.r)$

$$E[\psi_i]=2\sum_i \int \psi_i[-\frac{\hbar^2}{2m}]\nabla^2\psi_i d^3r + \int V_{ion} n(r) d^3r + \frac{e^2}{2}\int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' + E_{XC}[n(r)] + E_{ion}(R_I)$$

Norm-Conserving Pseudopotentials

$$\psi_{ps}(\vec{r}) = \psi_v(\vec{r}) \text{ for } r \geq r_c$$

$$\int_0^{r_c} d\vec{r} r^2 \psi_{ps}^*(\vec{r})\psi_{ps}(\vec{r}) = \int_0^{r_c} d\vec{r} r^2 \psi_v^*(\vec{r})\psi_v(\vec{r})$$



Equations of motion

$$L = T - V; T = \frac{1}{2}\mu \sum_i \sum_k (\dot{c}_k^i)^2; V = E[c_k^i]$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{c}_k^i} + \frac{\partial L}{\partial c_k^i} = 0 \quad (1)$$

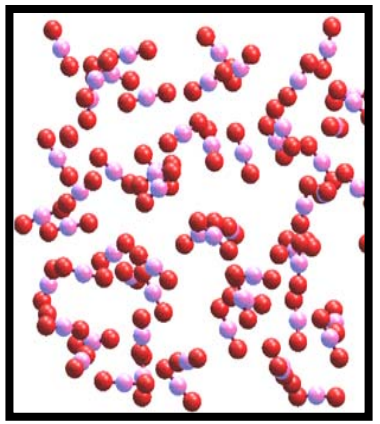
Orthonormality constraint equations

$$\sigma_{ij} = \Omega^{-1} \int_\Omega d\vec{r}\psi_i^*(\vec{r})\psi_j(\vec{r}) - \delta_{ij} = 0 \quad (2)$$

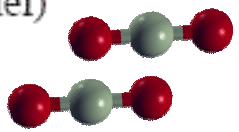
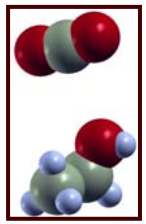
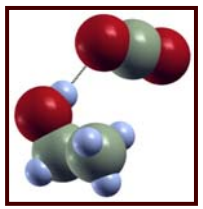
Combining (1) & (2) we get,

$$\mu\ddot{c}_k^i = -\frac{\partial E}{\partial c_k^i} - \sum_j \lambda_{ij}\frac{\partial \sigma_{ij}}{\partial c_k^i}$$

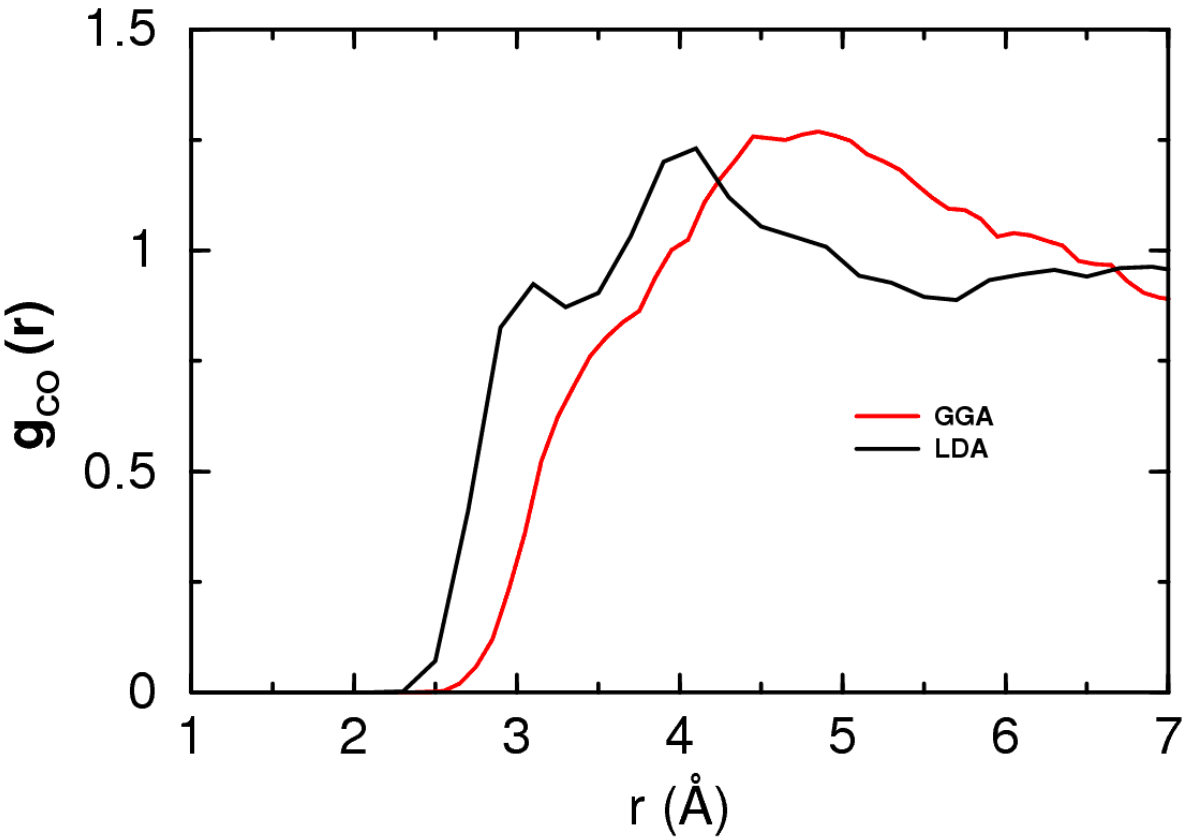
Snapshot of CO_2 molecules



Cluster geometries

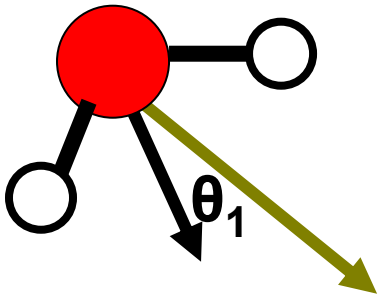
species	angle	method	bond length (Å)	dimerization energ (kcal/mol)
CO_2 monomer 	180.0 (O=C=O)	CPMD	1.176	
	180.0 (O=C=O)	Gaussian98	1.169	
CO_2 dimer (slipped parallel) 	78.9 ($O_1-C_2-O_2$)	CPMD	~1.176	−0.170
	100.9 ($C_2-O_2-C_1$)			
	84.1 ($O_1-C_2-O_2$)	Gaussian98		
	138.5 ($C_2-O_2-C_1$)	ref 29		
		Gaussian98 ref 12		−0.290
ethanol−CO_2 EDA complex 	123.1(θ_1)	CPMD	2.833 (O_e-C_C)	−2.627
	128.5(θ_2)			
	120.9(θ_1)	Gaussian98	2.746 (O_e-C_C)	−2.720
	129.7(θ_2)			
	114.7(θ_1)	Gaussian98 ref 23	2.754 (O_e-C_C)	−2.417
ethanol−CO_2 h-bonded complex 	179.4 (O=C=O)	CPMD	2.212 (O_C-H_e)	−0.840

LDA vs GGA



Weak interactions can be better understood by GGA

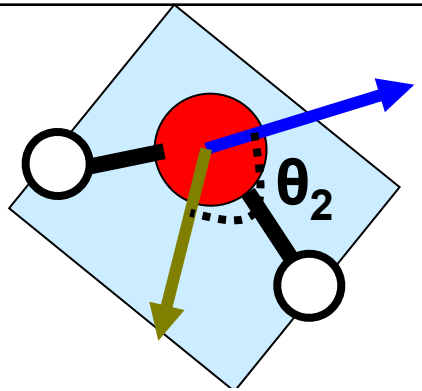
Deviation and Inclination



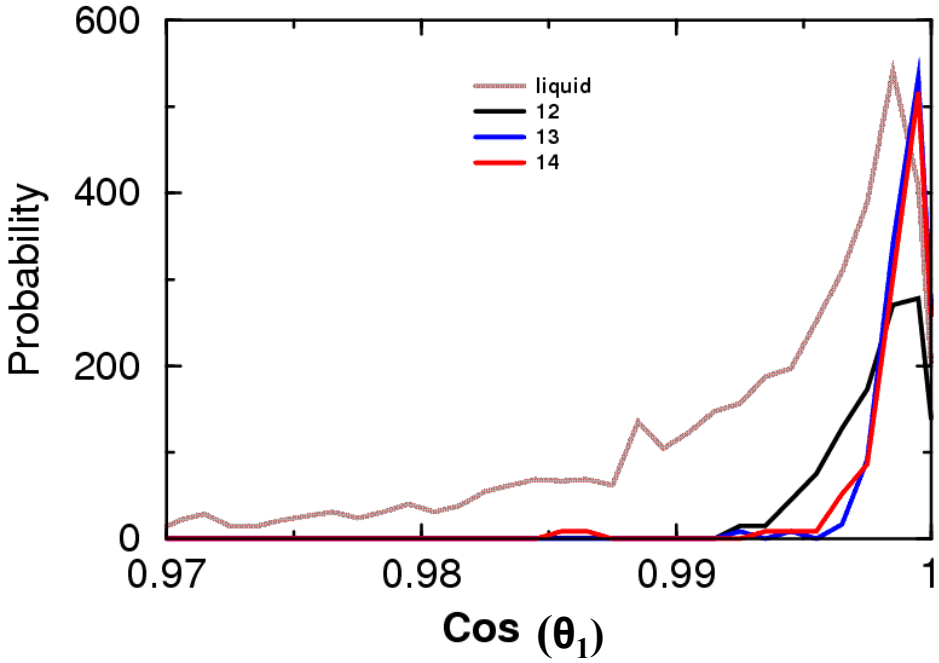
dipole

bisector

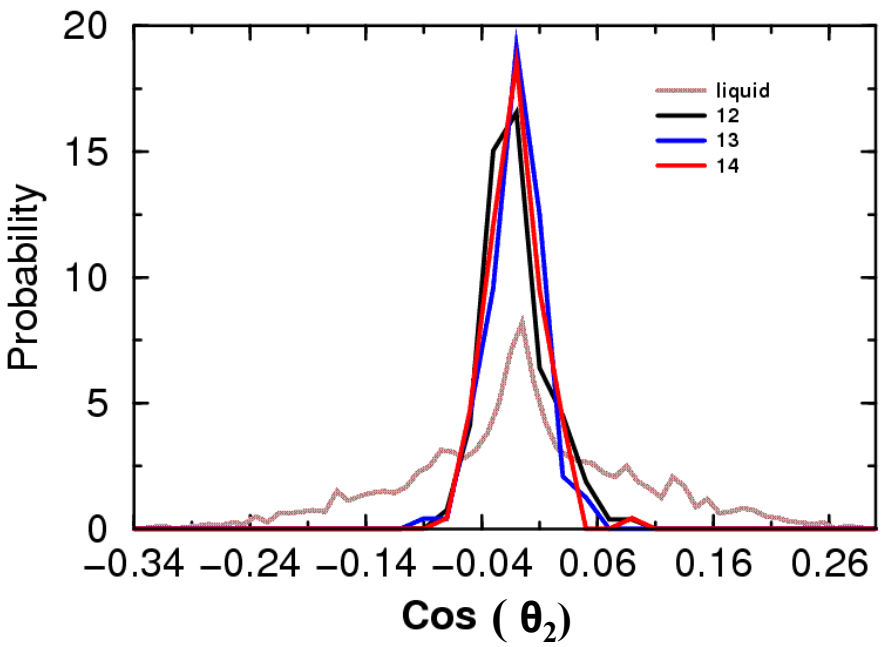
normal

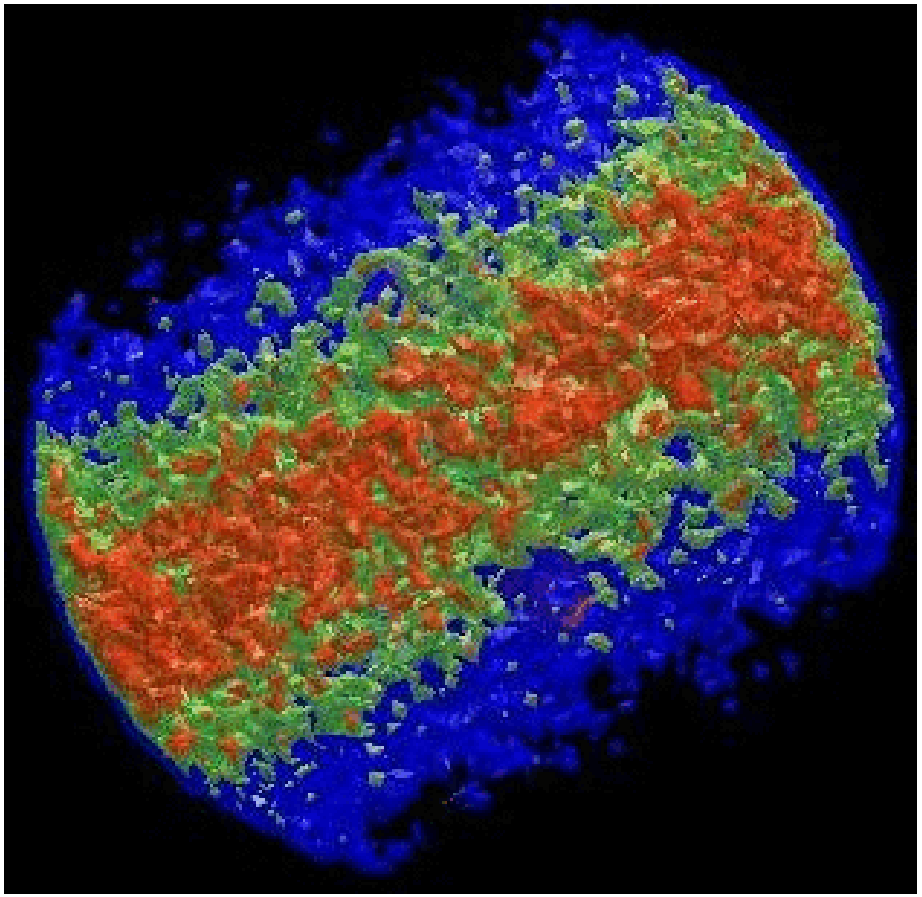


Deviation

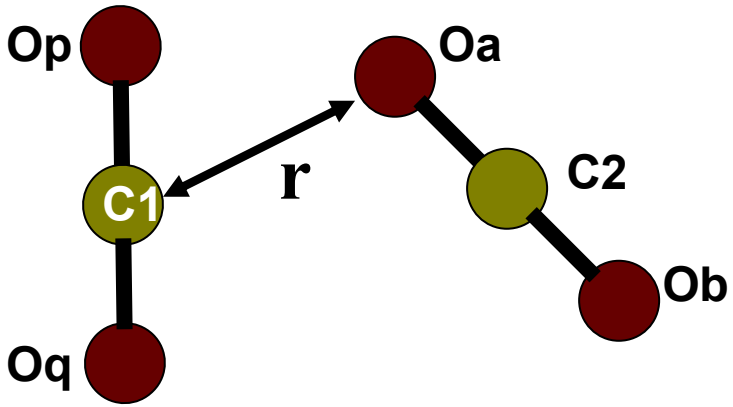


Inclination





Intermolecular angle distribution



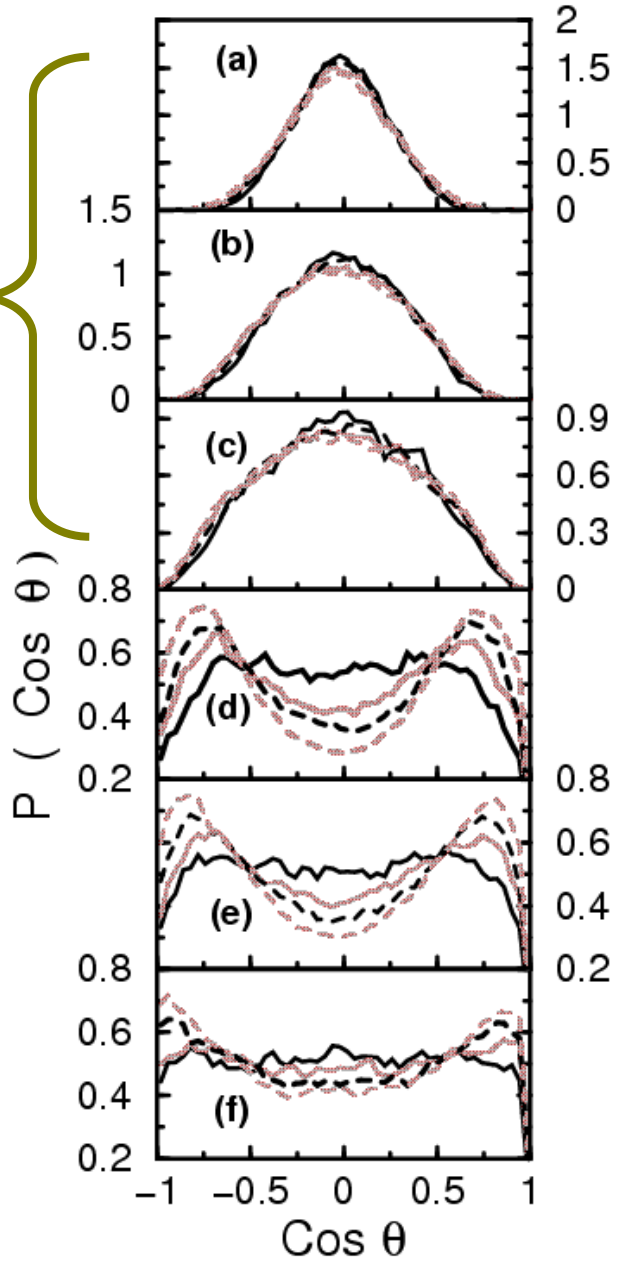
$\widehat{O_pO_q}.\widehat{C_1O_a}$ a, and d

$\widehat{O_pO_q}.\widehat{C_1O_2}$ b, and e

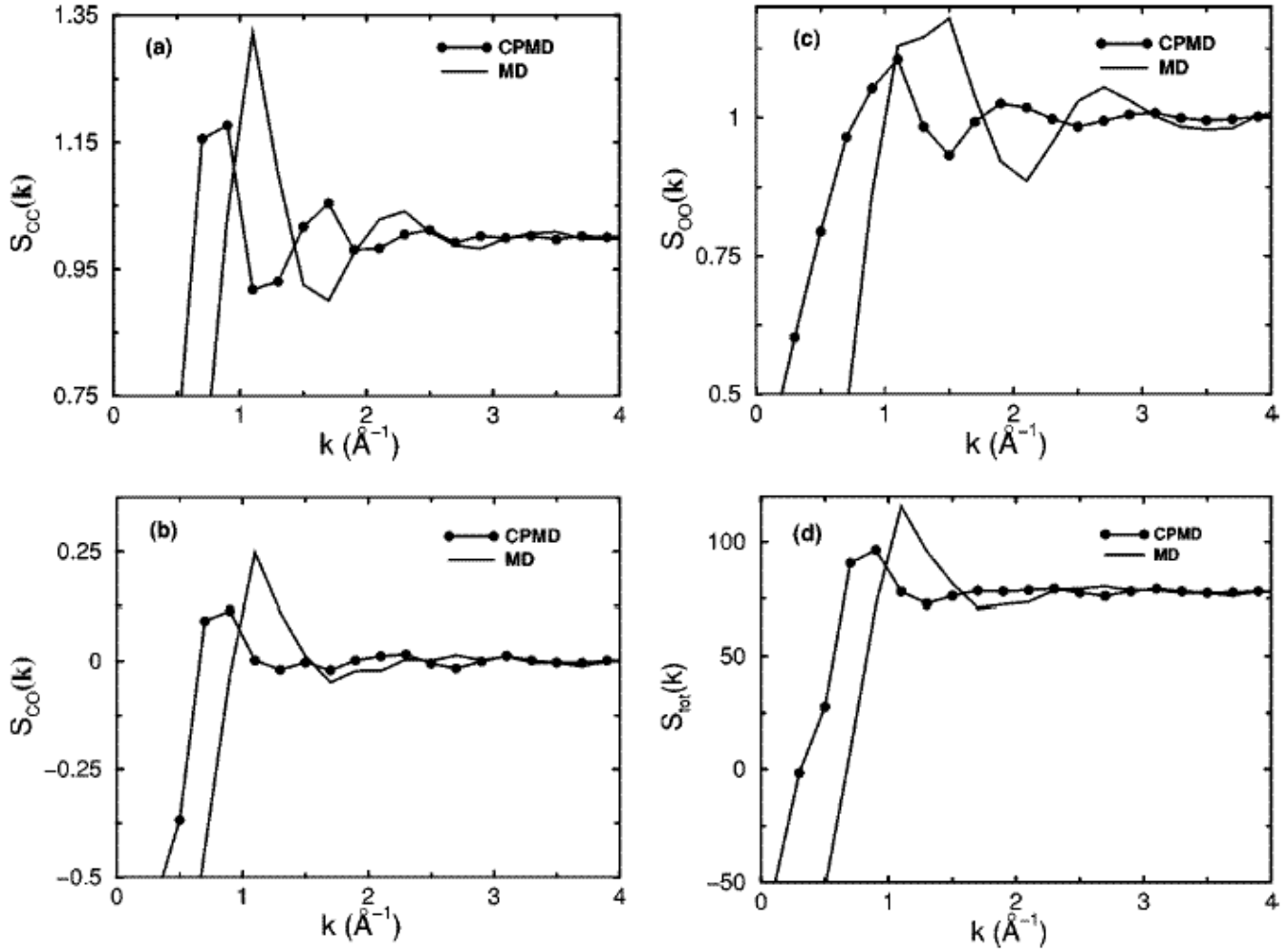
$\widehat{O_pO_q}.\widehat{C_1O_b}$ c, and f

r < 3.4Å

3.6 < r < 4.3Å



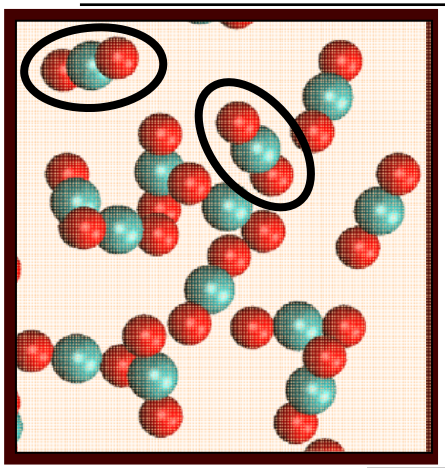
Structure factor

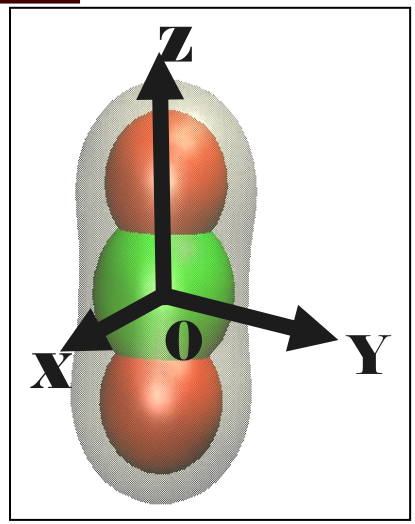


Aims

- **Is there a solvation shell ?**
- **Is polarizability important ?**
- **What is the pressure effect on solubility ?**
- **How to enhance the solubility of polar compounds ?**
- **Why does it work?**

Molecular multipole moments





Dipole moment

$$\mu_i = 2\pi \int_{r=0}^{r_c} \int_{z=-z_c}^{z_c} \rho(\vec{r} - \vec{R}_i)\vec{r}\, r\, dr\, dz$$

μ_i = dipole moment of i-th molecule

Quadrupole moment

$$Q^i_{mn} = 2\pi \int_{r=0}^{r_c} \int_{z=-z_c}^{z_c} (3r_m r_n - r^2\delta_{mn})\rho(\vec{r} - \vec{R}_i)\, r\, dr\, dz$$

Q_{mn} = quadrupole moment component

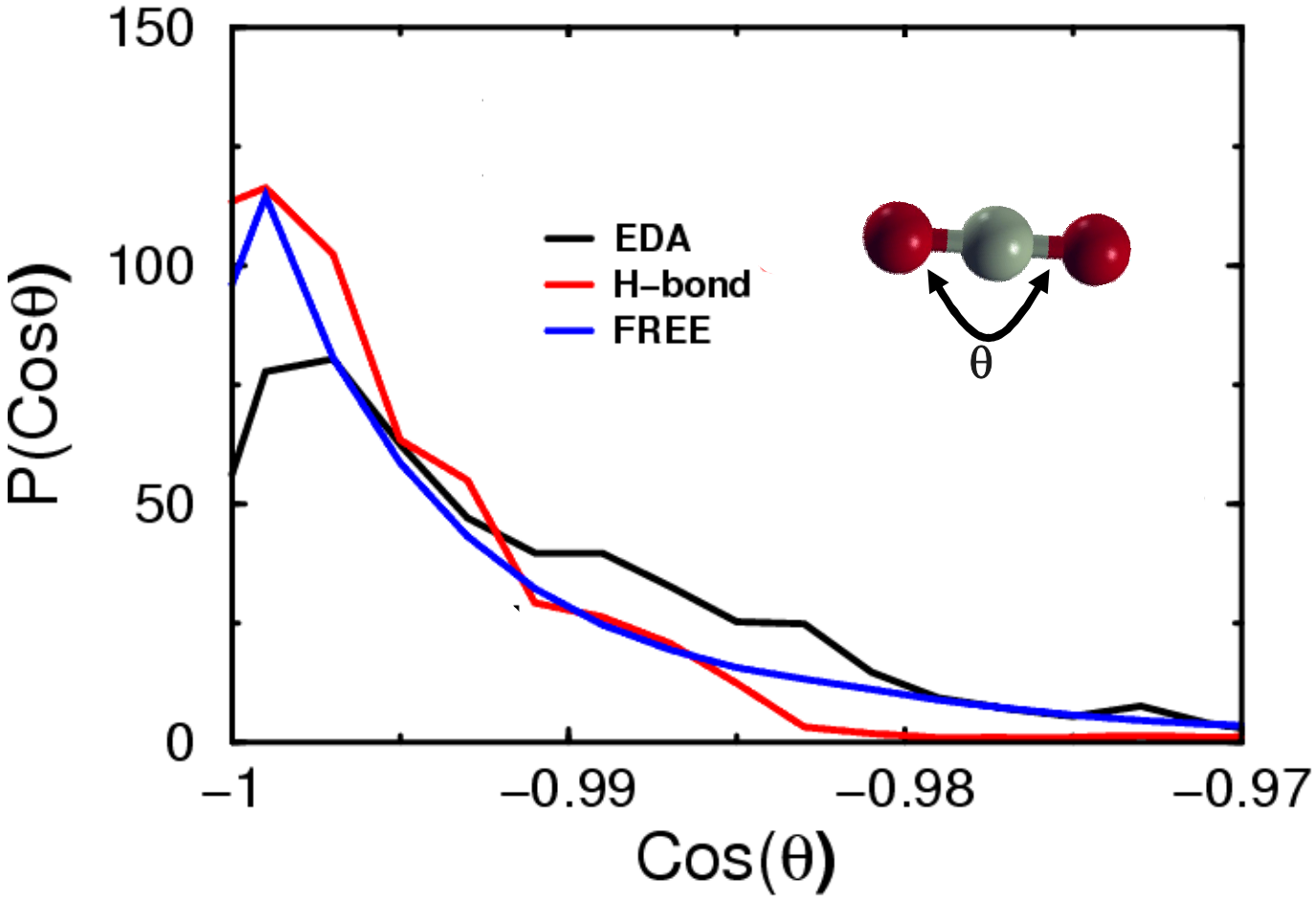
r_c = 1.3 Å; z_c = 2.8 Å

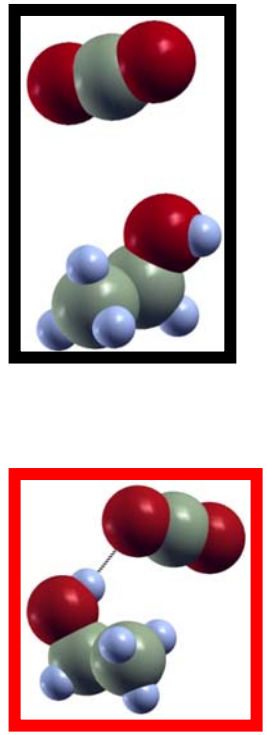
M.Saharay & S.Balasubramanian, *ChemPhysChem*, 5, 1442 (2004)

Conclusions

- **Structural evolution with increasing pressure : at least in the first coordination shell**
- **Nearest neighbors show higher probability for distorted T-shaped orientation, whereas molecules in the 2nd coordination shell are mostly orientated in slipped parallel geometry w.r.t. central molecule : → resemblance of crystal structure in high density**
- **Deviation of CO_2 from non-linear structure decreases with increasing solvent density → effect of polarization due to near neighbor interactions**
- **Increase in reorientational relaxation time with pressure**
- **Low frequency spectrum of CO_2 indicates solvent cage effect in high density → a feature of supercritical CO_2**

Intramolecular angle distribution





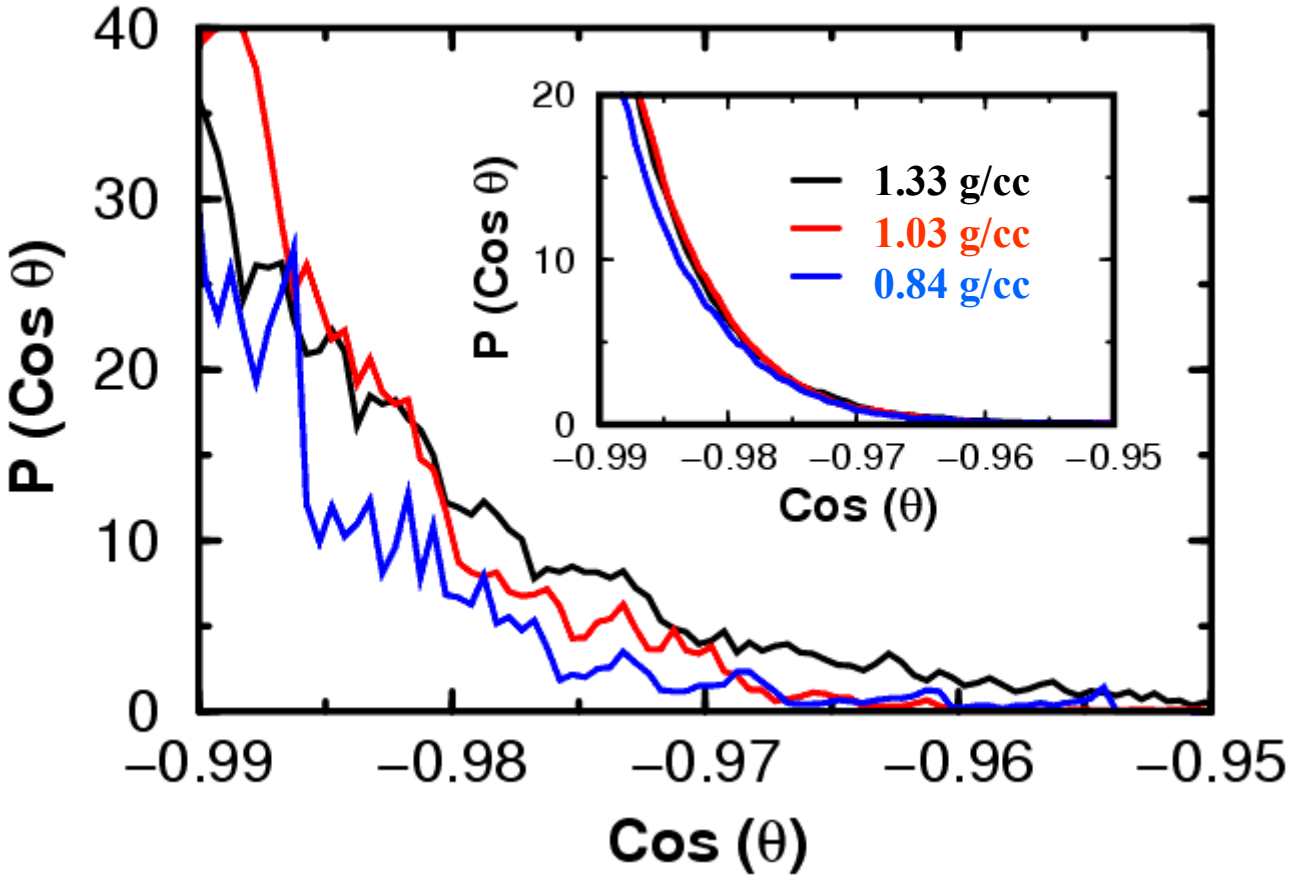
M.Saharay & S.Balasubramanian, *J. Phys. Chem. B* , 110, 3782 (2006)

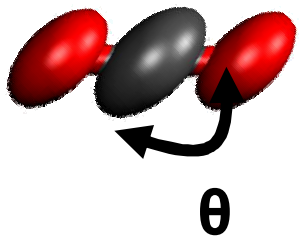
Conclusions

- **Ethanol-CO_2 EDA complex is more stable than the hydrogen bonded complex**
- **The CO_2 molecule that interacts with ethanol tends to adopt non-linear geometry more readily than the one in the neat solvent**
- **CO_2 can behave both as a Lewis acid as well as a Lewis base. This attribute is responsible for its association with other CO_2 molecules as well as with ethanol in the formation of EDA complexes**
- **The O-D stretching mode of ethanol is red shifted due to these interactions.**
- **The degeneracy of the n_2 mode of CO_2 gets lifted due to EDA interaction with other species**

Intramolecular geometry of CO_2

CO_2 (a) Interacting O_W-C_C < 2.9Å (b) Non-interacting, O_W-C_C > 3Å





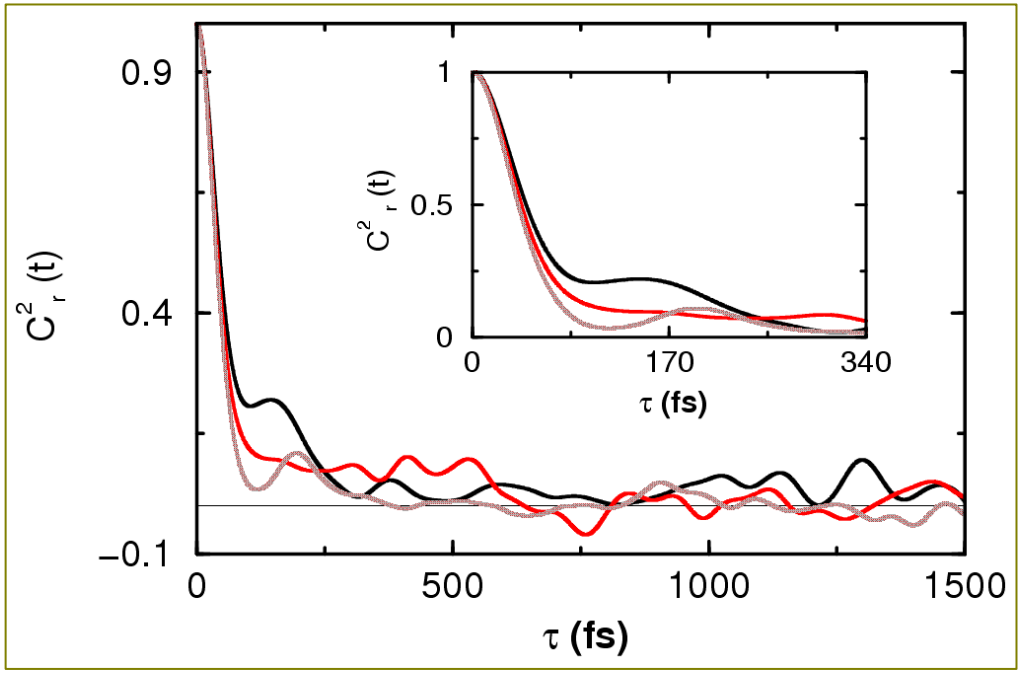
Conclusions

- Both hyd-bonded and EDA type interactions play crucial role in microscopic behavior of D_2O
- Enhanced dipole moment -> Miscibility of D_2O in $scCO_2$ environment increases with system pressure
- Blue-shift in D_2O bending mode w.r.t. the monomer -> signature of hyd-bonded interaction
- Red-shift in stretching mode w.r.t. the monomer siginifies the weakening of intramolecular OD bond

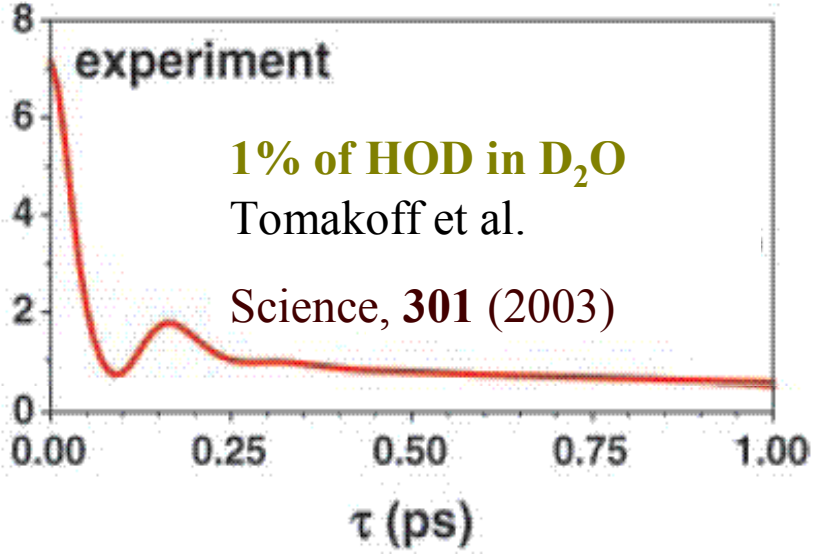
Summary

- Formation of solvation shell
- Enhanced multipole moments
- Specific solute-solvent interactions between solvent and co-solvent

Reorientational correlation function



Infrared spectroscopic measurement



1% of HOD in D_2O

Tomakoff et al.

Science, **301** (2003)

1.33 g/cc

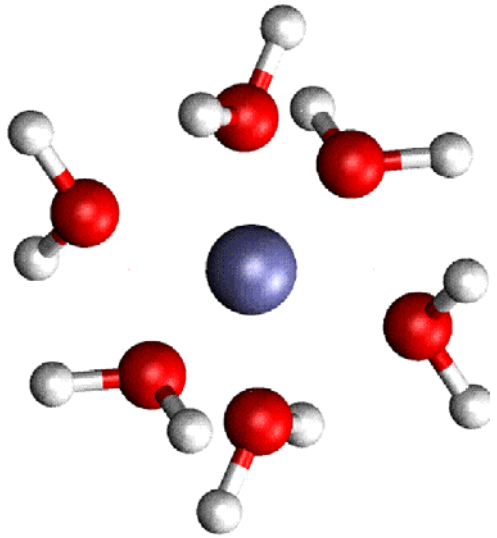
1.03 g/cc

0.84 g/cc

Solvation

3 steps for solvation :

- **creation of free space to hold the solute**
- **solvent reorganization**
- **solute-solvent interactions;**



Molecular reorganization

Molecular association can be observed experimentally by studying :

1. **Relaxation time of system as well as the probe**
2. **Spectral shifts due to association**