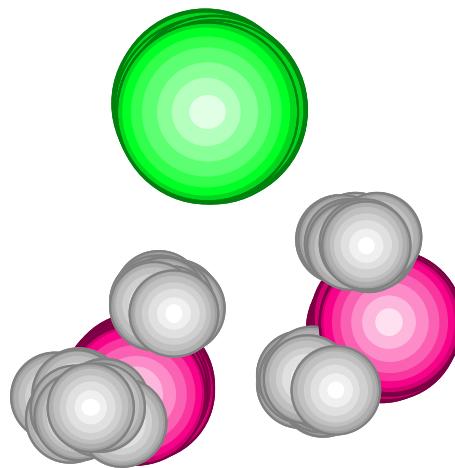


The Structure, Energetics, and Vibrational Dynamics of Aqueous Anionic Clusters

Bruce C. Garrett, Gregory K. Schenter, Liem X. Dang
Environmental Molecular Sciences Laboratory, PNNL

Gregory A. Voth

Department of Chemistry, University of Utah



Support

US DOE, Division of Chemical Sciences (OBES)

Quantum simulations of ion-water clusters: $\text{Cl}^- (\text{H}_2\text{O})_n$ and $\text{I}^- (\text{H}_2\text{O})_n$

Goal: Determine role of temperature and nuclear quantum effects on:

- Structure - atomic density distributions
- Energetics - enthalpy of formation
- Dynamics - spectra

Approach: Methods based on Feynman path integrals

- Quantum statistical mechanics for equilibrium properties (structures and energetics)
- Centroid Molecular Dynamics (CMD) for time correlation functions

Equilibrium Structural and Energetic Properties of Aqueous Ionic Clusters

Gai, Dang, Schenter, Garrett: JPC **1995**, *99*, 13303

Gai, Schenter Dang, Garrett: JCP **1996**, *105*, 8835

Schenter, Garrett, Gai, Dang: In *Advances in Classical Trajectory Methods*, Vol. 3, 1998; p. 1

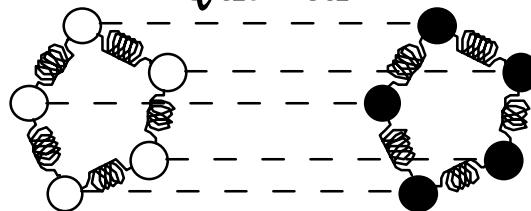
Equilibrium Statistical Mechanics Using Feynman Path Integrals

Classical



$$Q_{cl}(\beta) \propto \int dx e^{-\beta V(x)}$$

Quantum



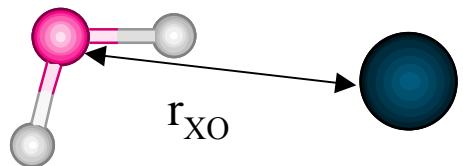
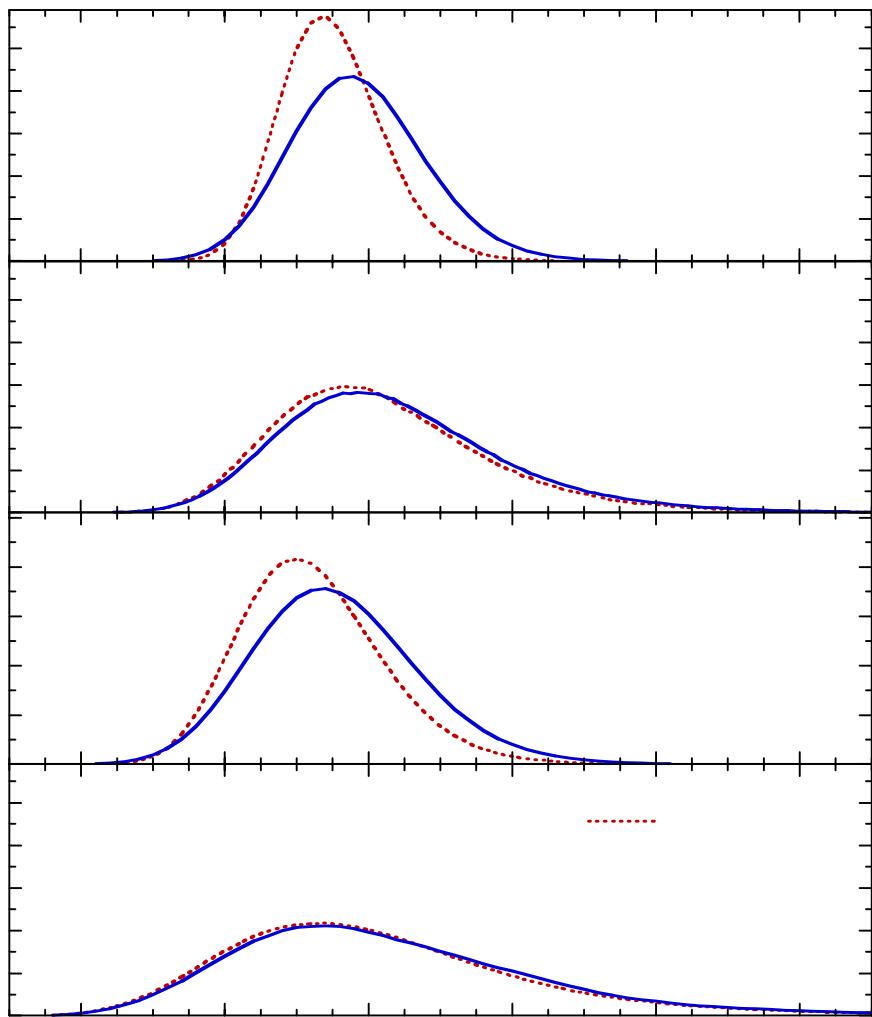
$$Q_{qm}(\beta) \propto \int \dots \int dx_1 \dots dx_p e^{-S/h}$$

$$\begin{aligned} S(x_1, \dots, x_p) = \sum_i & [(mP/2h\beta)(x_{i+1}-x_i)^2 \\ & + (h\beta/P)V(x_i)] \end{aligned}$$

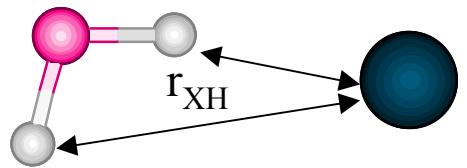
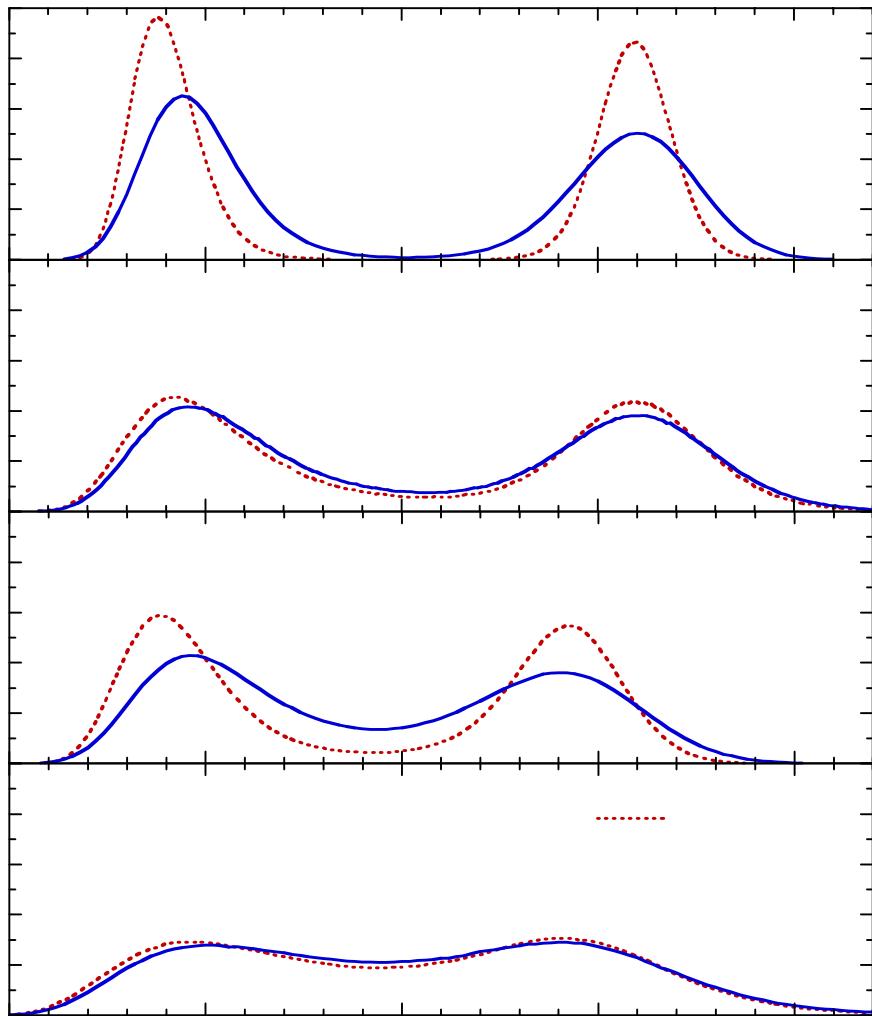
$$\langle A \rangle = \text{Tr}[e^{-\beta H} A] / Q(\beta)$$

$$U = \langle H \rangle = -\partial \ln Q / \partial \beta; \quad \rho_{AB}(r) = \langle (PN_{AB})^{-1} \sum_{j \in A, k \in B} \delta[r - r_{jk}(x)] \rangle$$

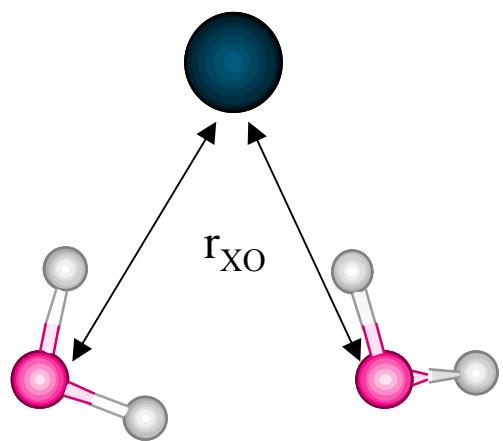
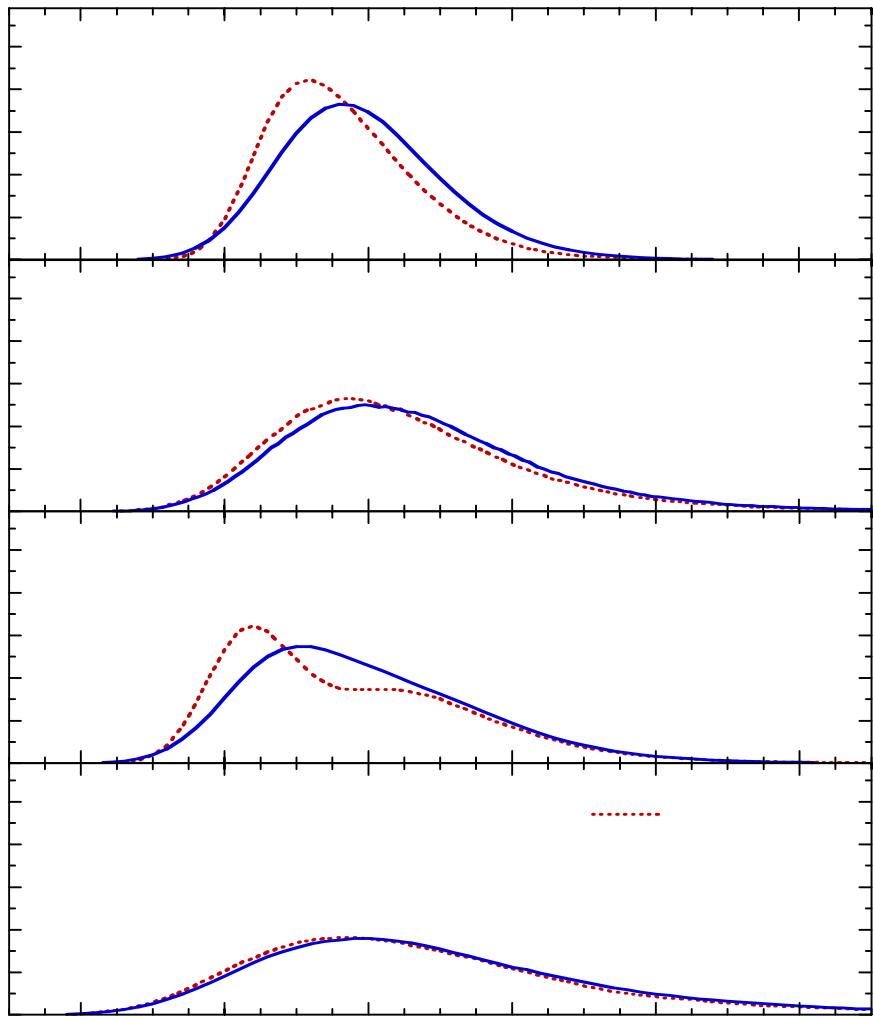
X-O Radial Distribution Functions for $\text{Cl}^- (\text{H}_2\text{O})_1$ and $\text{I}^- (\text{H}_2\text{O})_1$



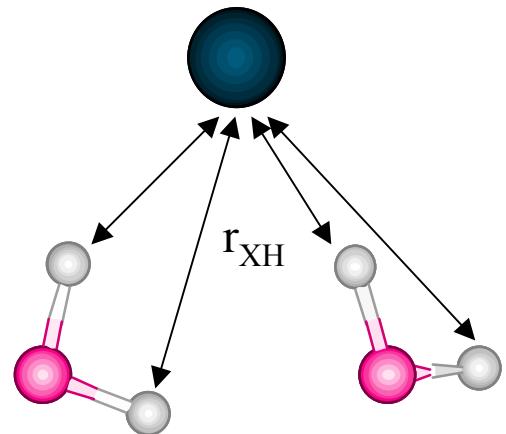
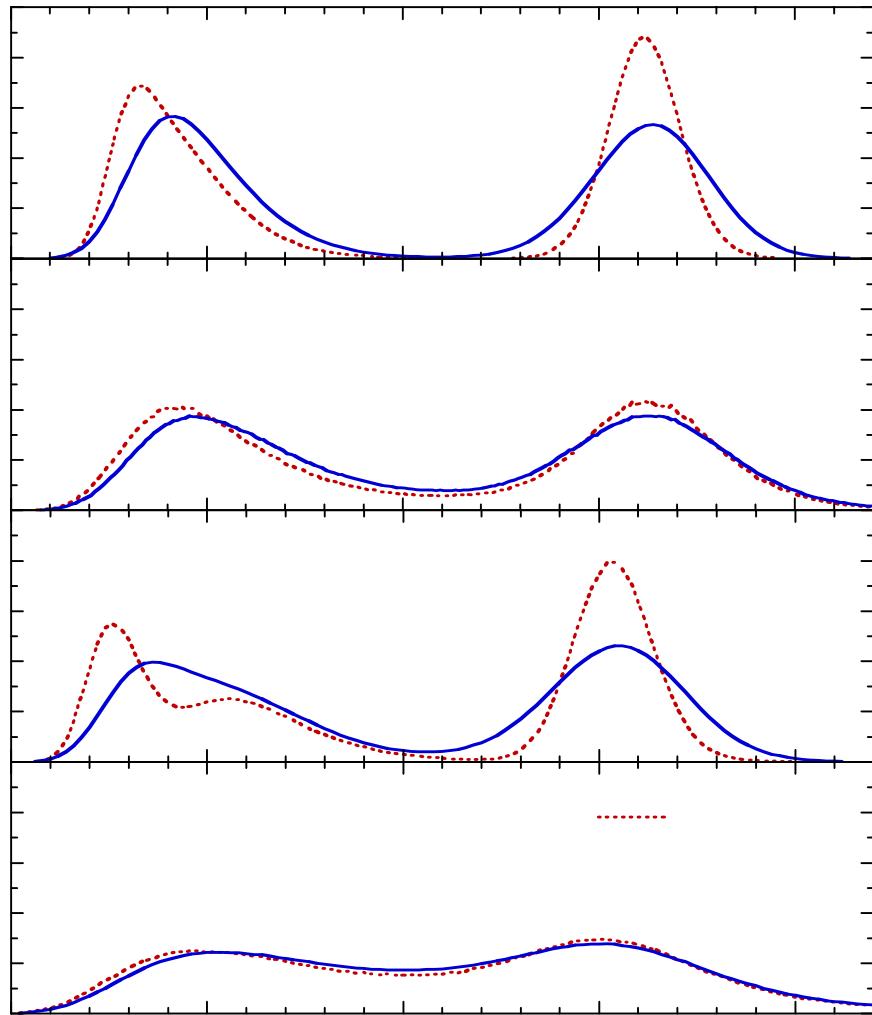
X-H Radial Distribution Functions for $\text{Cl}^- (\text{H}_2\text{O})_1$ and $\text{I}^- (\text{H}_2\text{O})_1$



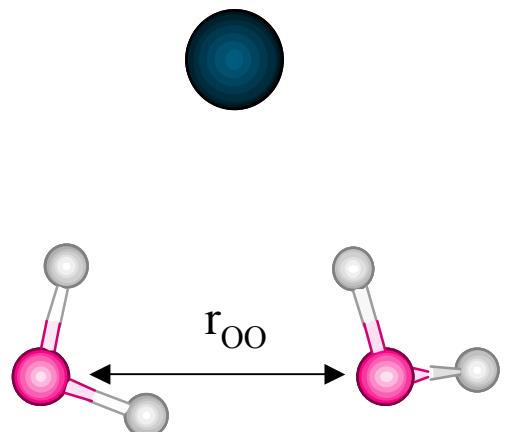
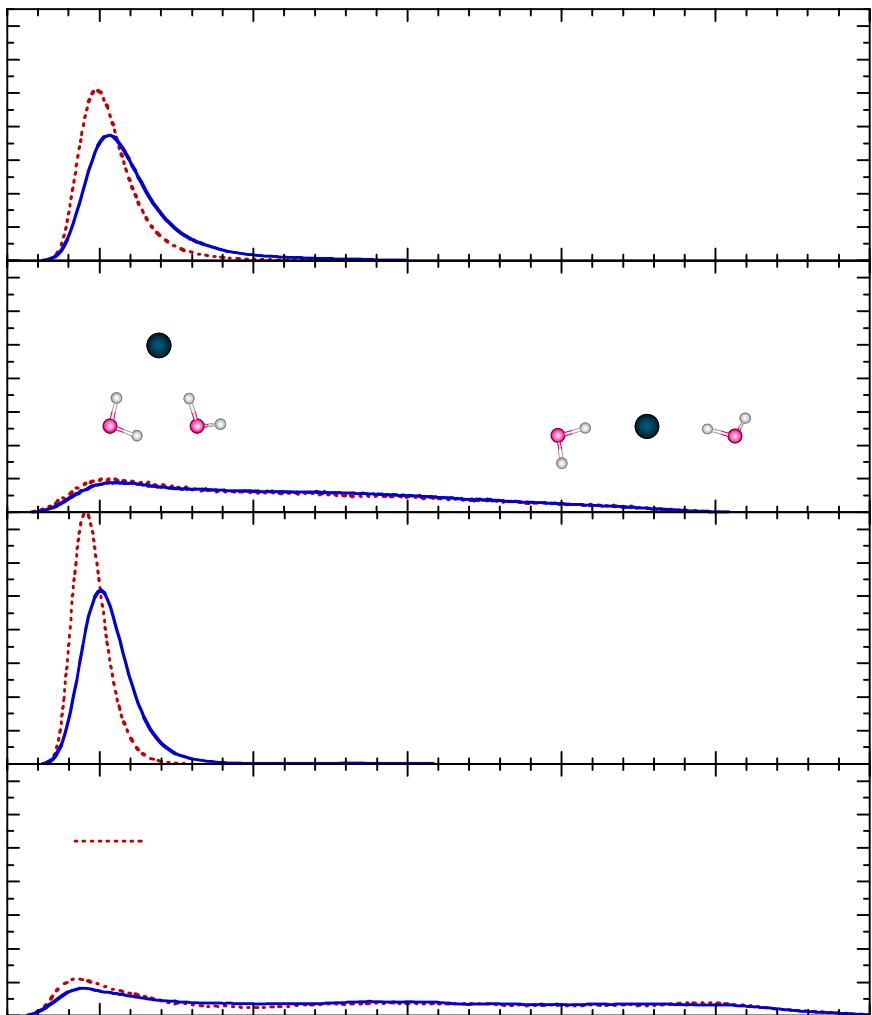
X-O Radial Distribution Functions for $\text{Cl}^- (\text{H}_2\text{O})_2$ and $\text{I}^- (\text{H}_2\text{O})_2$



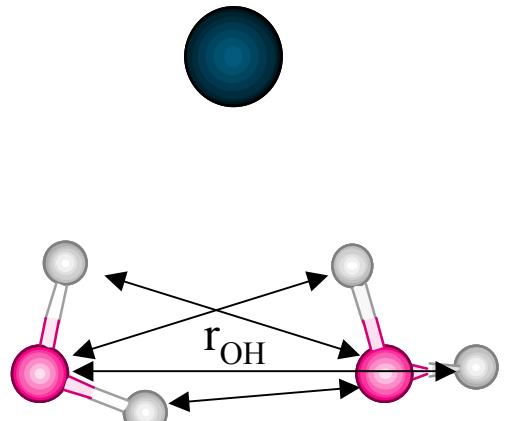
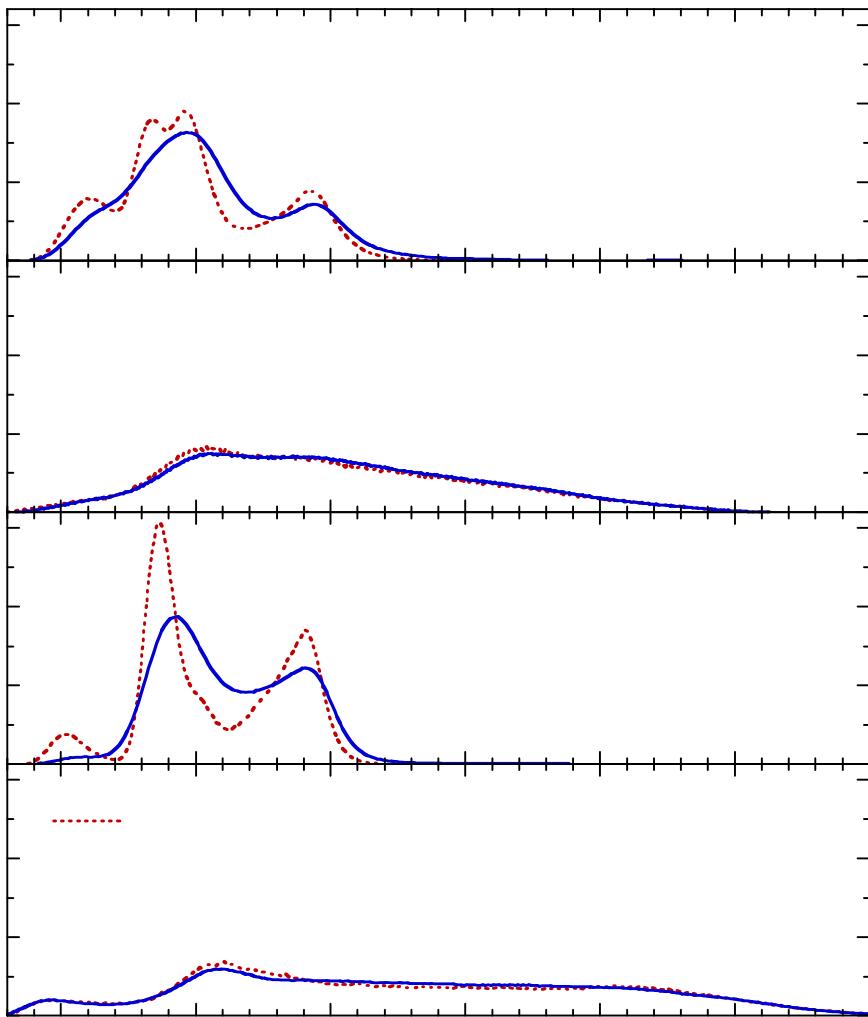
X-H Radial Distribution Functions for $\text{Cl}^- (\text{H}_2\text{O})_2$ and $\text{I}^- (\text{H}_2\text{O})_2$



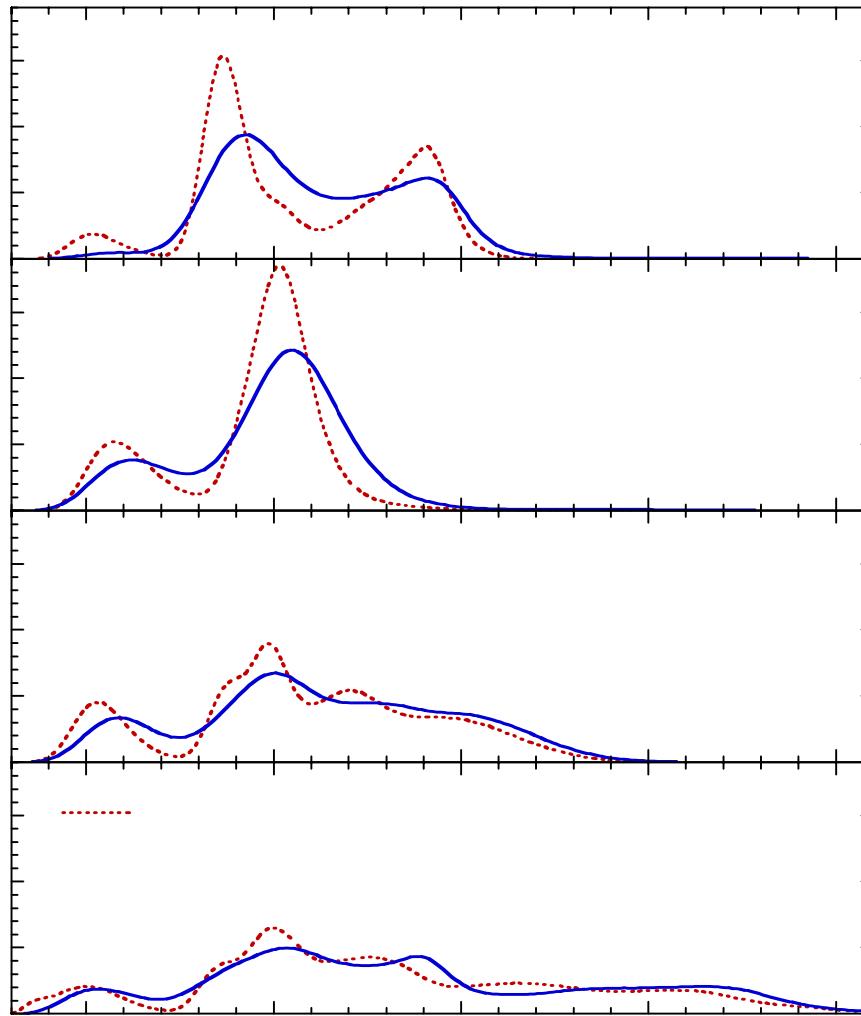
O-O Radial Distribution Functions for $\text{Cl}^- (\text{H}_2\text{O})_2$ and $\text{I}^- (\text{H}_2\text{O})_2$



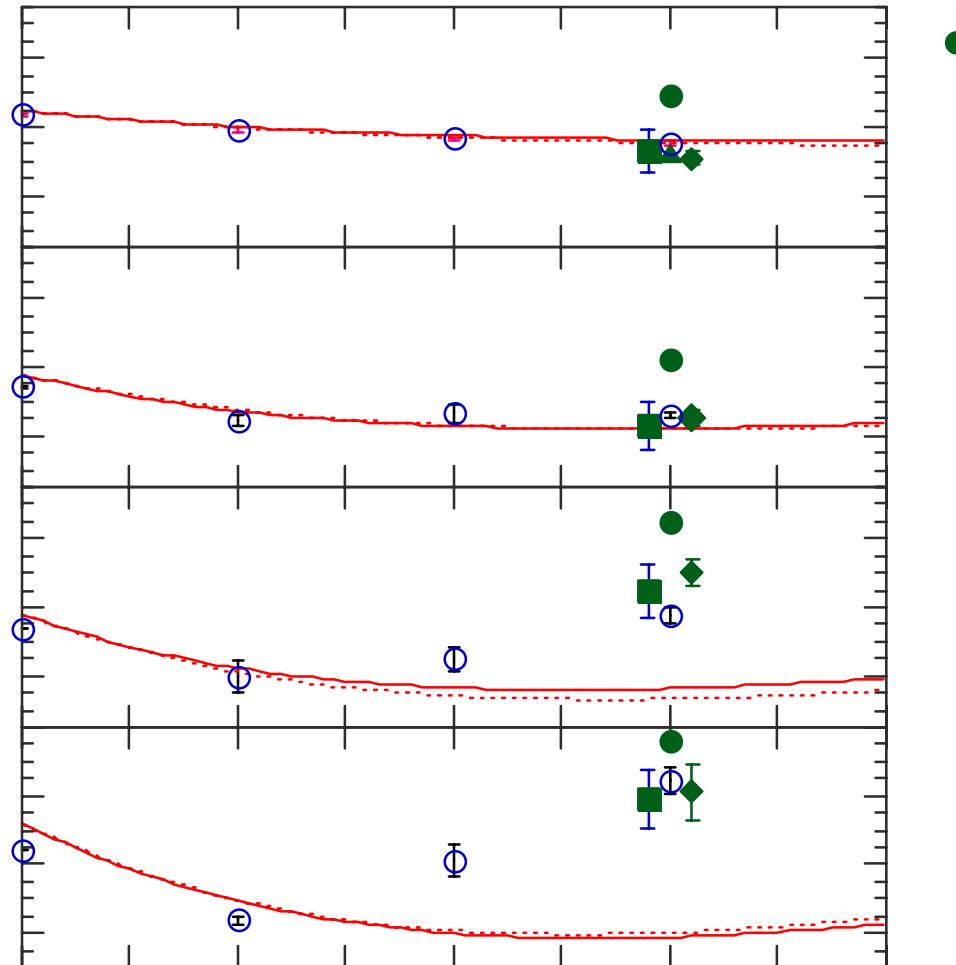
O-H Radial Distribution Functions for $\text{Cl}^- (\text{H}_2\text{O})_2$ and $\text{I}^- (\text{H}_2\text{O})_2$ at 100 and 300K



O-H Radial Distribution Functions for $\text{I}^- (\text{H}_2\text{O})_n$ at 70K



Enthalpy of Formation for $\text{Cl}^- + n(\text{H}_2\text{O}) \rightarrow \text{Cl}^- (\text{H}_2\text{O})_n$



Quantum Vibrational Dynamics of Cl⁻(H₂O)_n Clusters

Schenter, Garrett, Voth: JCP **2000**, *113*, 5171

OH Stretch Frequencies in $X^-(H_2O)_1$ Clusters

(Ayotte, Weddle, Kim, Johnson, JACS **1998**, *120*, 12361)

OH Mode	ω (cm ⁻¹)	$\Delta\omega$ (cm ⁻¹)
“Free” OH	3690	0
IHB (I ⁻)	3390	-300
IHB (Br ⁻)	3270	-420
IHB (Cl ⁻)	3130	-560

Interwater OH Stretch Frequencies

(Ayotte, Nielsen, Weddle, Johnson, Xantheas, JPCA **1999**, *103*, 10665)

OH Mode	ω (cm ⁻¹)	$\Delta\omega$ (cm ⁻¹)
OH … O (Cl ⁻)	3630	-60
OH … O (Br ⁻)	3630	-60
OH … O (I ⁻)	3620	-80
OH … O (H ₂ O dimer)	3600	-90

Theoretical Approaches to Vibrational Spectra

	Quantum Mechanics	Anharmonicity	Temperature
Harmonic	Yes	No	No spectral shifts with T
FT-VCF	No	Yes	Not adequate
FFLM	Yes, for internal vibrations only	Yes	Yes, classical for intra. vibs
VSCF-CI	Yes, but limited number of modes	Yes	T≈0K
QMC	Yes	Yes	T=0K
CMD	Yes but approximate	Yes	Yes

FT-VCF: Fourier transform of velocity correlation functions

FFLM: Frozen-Field Local-Mode (Reimers and Watts, **1984**)

VSCF-CI: Vibrational Self-Consistent-Field (Bowman, **1986**; Ratner, Gerber, **1986**)

QMC: Quantum Monte Carlo

CMD: Centroid Molecular Dynamics

Centroid Molecular Dynamics

(Cao and Voth, JCP **1993**, *99*, 10070; **1994**, *100*, 5093, 5106; **1994**, *101*, 6157, 6168;
Voth, Adv. Chem. Phys. **1996**, *93*, 135; Jang and Voth, JCP **1999**, *111*, 2357, 2371)

- Classical equations of motion for centroid coordinates on effective centroid potential $V_c(\mathbf{q}_c)$ - dynamics sample anharmonicity quantally, temperature regulated by thermostat
- Effective centroid potential includes quantum and thermal effects; formally defined by

$$\rho_c(\mathbf{q}_c) = \int \dots \int D\mathbf{q}(\tau) \delta(\mathbf{q}_c - \mathbf{q}_0) \exp\{-S[\mathbf{q}(t)]/\hbar\}$$

$$Z = \int d\mathbf{q}_c \rho_c(\mathbf{q}_c) \propto (m/2\pi\hbar^2\beta)^{1/2} \int d\mathbf{q}_c \exp[-\beta V_c(\mathbf{q}_c)]$$

$$V_c(\mathbf{q}_c) \propto -k_B T \ln [\rho_c(\mathbf{q}_c)]$$

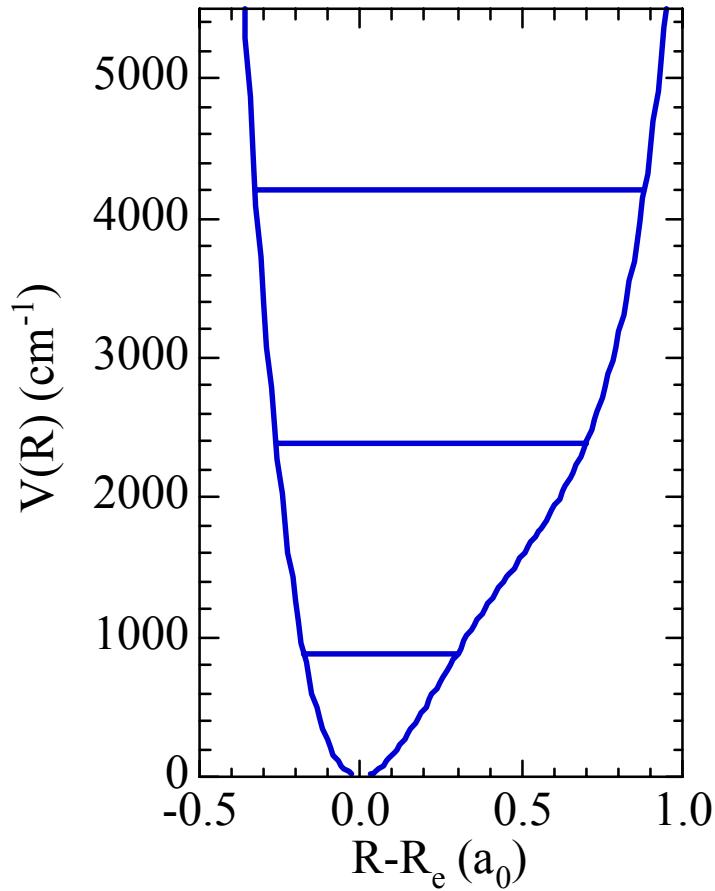
- Time correlation functions given by classical-like expression, e.g.,

$$C^*(t) = \langle \mathbf{q}_c(t) \mathbf{q}_c(0) \rangle$$

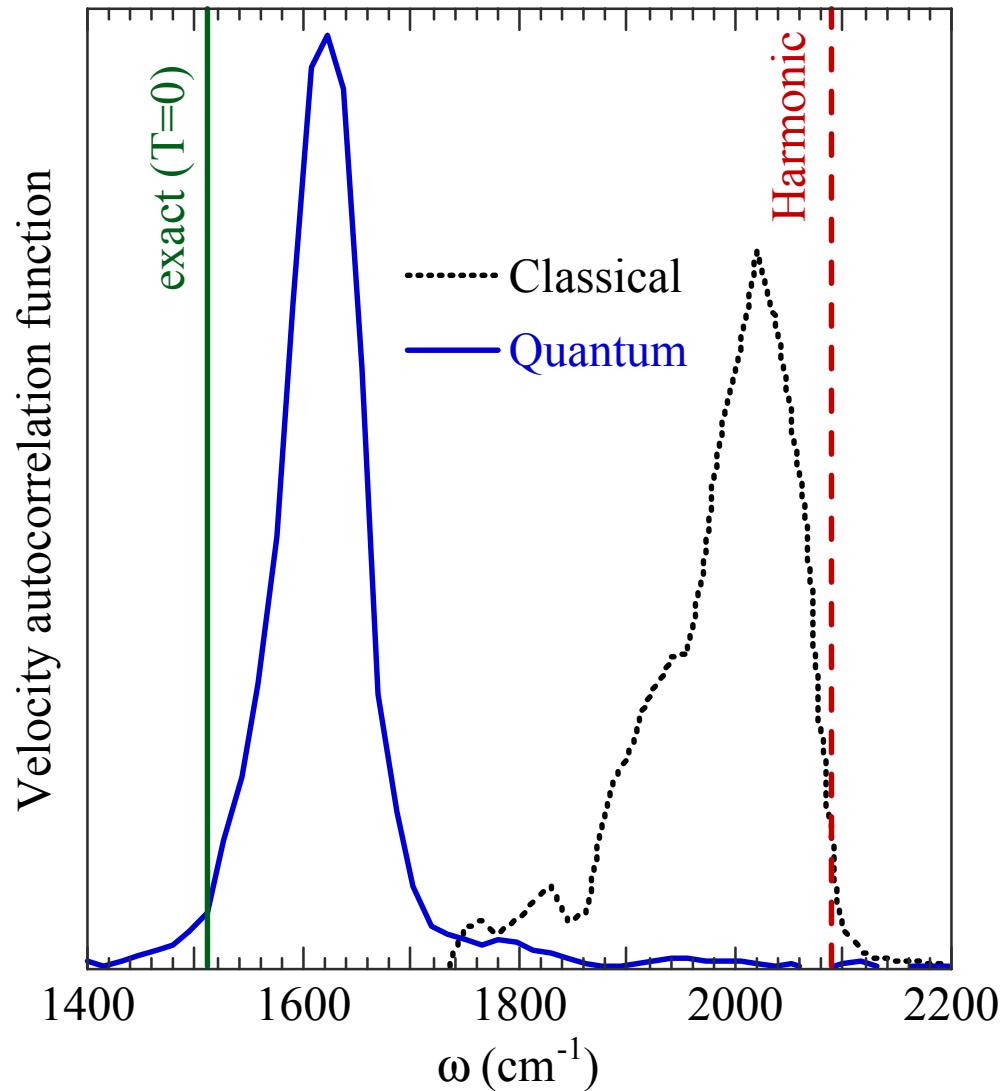
- Fourier transform given by

$$C(\omega) = (h\beta\omega/2) [\coth(h\beta\omega/2) + 1] C^*(\omega)$$

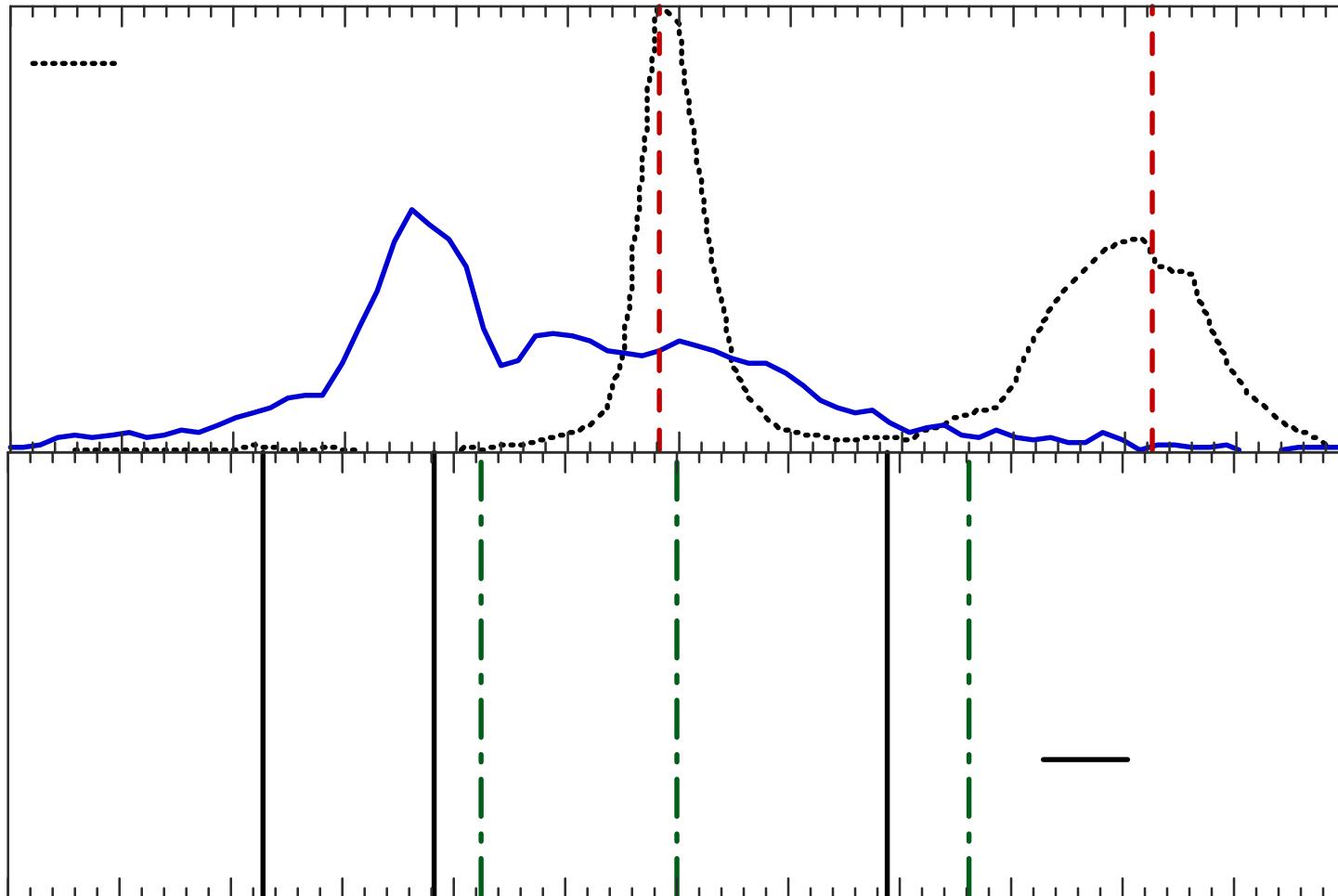
Velocity Autocorrelation Function for 1-Dimensional Model of OH Donor Stretch in $\text{F}^- \text{H}_2\text{O}$ ($T = 200\text{K}$)



Fit to OH stretch potential
from ab initio calculations
(Xantheas)



Velocity Autocorrelation Function for Cl⁻ H₂O

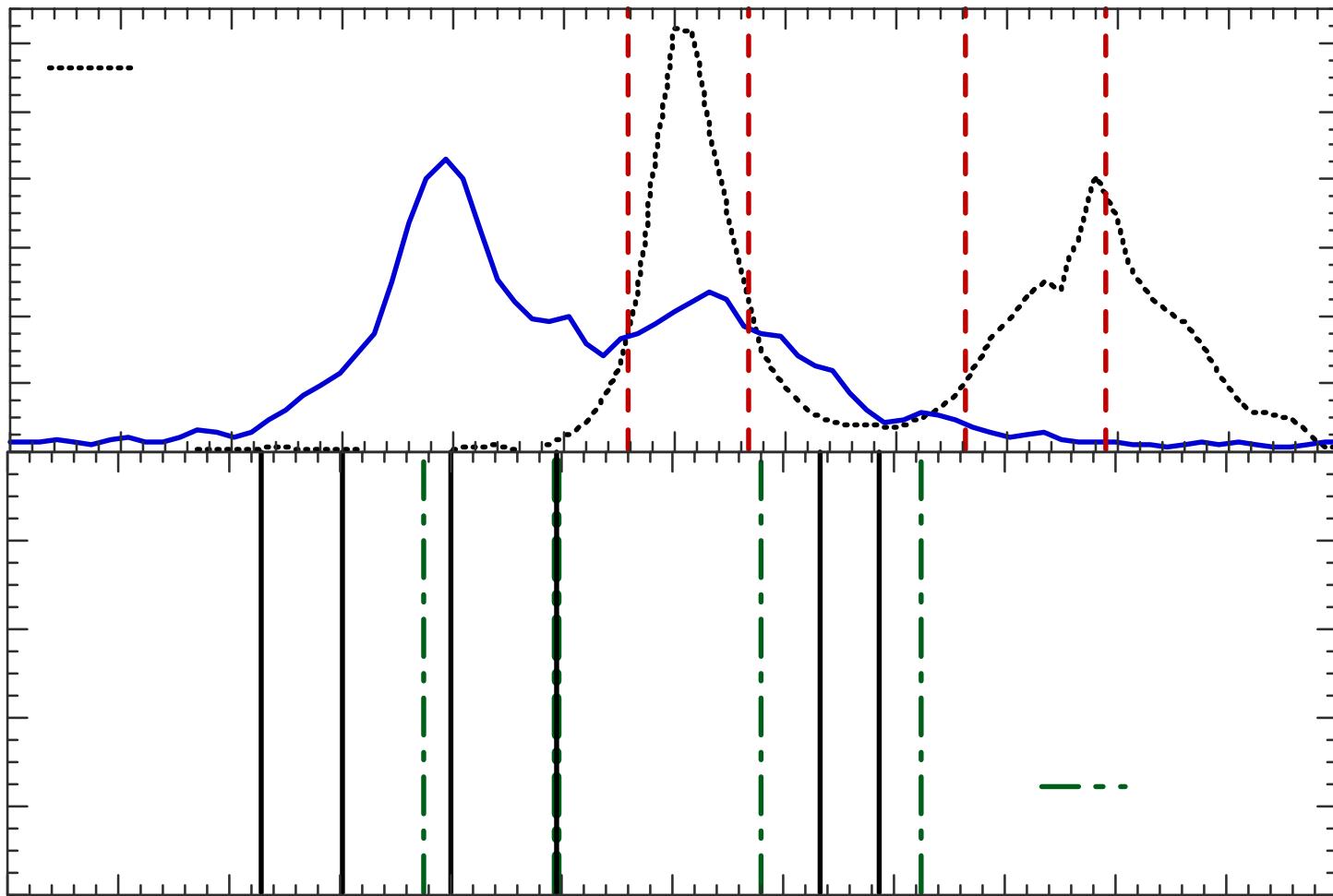


Potential: Dorsett, Watts, Xantheas, JPCA **1999**, *103*, 3351.

Experiment (low T): Ayotte, Weddle, Kim, Johnson, JACS **1998**, *120*, 12361.

Vibrational SCF + Configuration Interaction (0K): Bowman reported by Dorsett, Watts, Xantheas

Velocity Autocorrelation Function for $\text{Cl}^-(\text{H}_2\text{O})_2$



Potential: Dorsett, Watts, Xantheas, JPCA **1999**, *103*, 3351.

Experiment: Ayotte, Nielsen, Weddle, Johnson, Xantheas, JPCA **1999**, *103*, 10665.

Frozen-Field Local-Mode vibrational analysis: Dorsett, Watts, Xantheas

Summary and Conclusions

- Quantum mechanics broadens and can shift pair distribution functions although classical mechanics is adequate at room temperature and above
- Classical enthalpies poorly underestimated for $T < 200\text{K}$
- Harmonic approximate for enthalpies inadequate for clusters with 3 or more waters for $T \geq 200\text{K}$
- Fourier transforms of classical velocity autocorrelation functions and harmonic approximation to vibrational spectra agree with each other but incorrectly underestimate red shifts of OH stretches upon hydrogen bonding
- Centroid Molecular Dynamics qualitatively accounts for red shifts in OH frequencies upon H bonding to ion and provides a consistent approach to include both temperature and quantum effects