Density Functional Theory: from theory to Applications

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An Introduction to Maximally-Localized Wannier Functions

▶ The electronic ground state of a periodic system is usually described in terms of extended Bloch orbitals, simultaneous eigenstates of the periodic Hamiltonian and of the direct lattice translations.

▶ An alternative representation in terms of localized orbitals has been introduced by Gregory Wannier in 1937

▶ powerful tool in the study of the electronic and dielectric properties of materials: they are the solid-state equivalent of "localized molecular orbitals" and provide a picture of the nature of chemical bonding

▶ the charge center of a MLWF provides a kind of classical correspondence for the "location of an electron" (or electron pair) in a quantum-mechanical insulator.

E.g.: the ethylene molecule
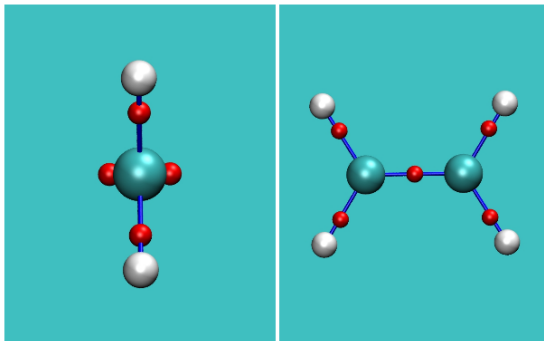
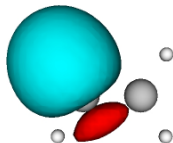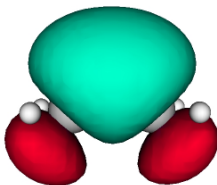| one of four C-H bond	One of two double bonds
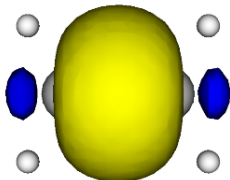
The single C-C bond	One of two *p*-like orbitals
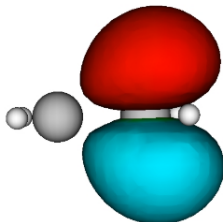
E.g.: Platinum wire
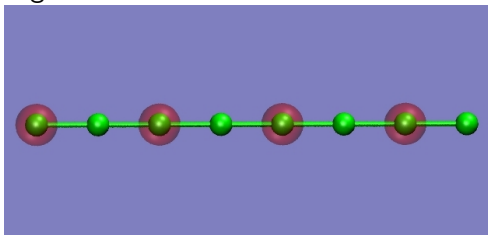
A *d* orbital centered on a Pt atom	A sigma-orbital centered between a Pt-Pt pair
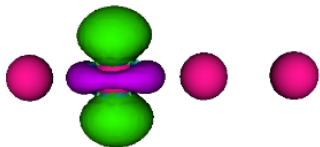
Outline
Wannier functions
Examples: Theoretical infrared spectra

Position operator in PBC
Localization functionals
Molecular dipole moments
Infrared absorption spectra
Atomic charges
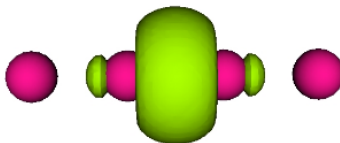
Position operator in periodic systems

The position operator is ill defined in periodic boundary conditions.
Indeed for a single particle wavefunction in periodic boundary
conditions:

$$\phi(x + L) = \phi(x) \tag{1}$$

but $x\phi(x)$ is not a periodic.

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For a non periodic system we can define the operator:

$$\langle X \rangle = \left\langle \Psi_0 | \hat{X} | \Psi_0 \right\rangle = \int x n(x) dx \tag{2}$$

where $n(x)$ is the one particle density, $\hat{X} = \sum_{i=1}^{N} x_i$ and x_i the position operator of the ith particle in one dimension.

In periodic boundary condition we can on the other end define:

$$\langle X \rangle = \frac{L}{2\pi} \, \mathrm{Im} \ln \left\langle \Psi_0 | \exp\left[i\frac{2\pi}{L}\hat{X} \right] | \Psi_0 \right\rangle \tag{3}$$

NOTE: this is not simply the expectation value of an operator, since it contains the imaginary part of the logarithm. The main ingredient is the operator $\exp\left[i\frac{2\pi}{L}\hat{X} \right]$, which is a many body operator.

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The electronic polarization corresponding to this definition of the position operator is:

$$P^{el} = \lim_{L\to\infty} \frac{-e}{2\pi} \operatorname{Im} \ln \left\langle \Psi_0 | \exp\left[i\frac{2\pi}{L}\hat{X} \right] |\Psi_0 \right\rangle \tag{4}$$

where $-e$ is the electron charge.

For a system of non-interacting particles, e.g. a crystal of lattice constant a, where periodic boundary conditions over a M linear cells ($L = ma$) are imposed, the Bloch vectors in the reciprocal cell are:

$$q_s = \frac{2\pi}{Ma}s, \qquad\qquad s = 0, 1, ..., M-1 \tag{5}$$

The one-body orbitals can be chosen to have the Bloch from:

$$\phi_{q_s,m}(x+\tau) = \exp[1q_s\tau]\phi_{q_s,m}(x) \tag{6}$$

where $\tau = la$ and m is a band index. The wavefunction can be written

$$|\Psi_0> = \mathcal{A} \prod_{m=1}^{N/M} \prod_{s=0}^{M-1} \phi_{q_s,m}(x) \tag{7}$$

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The expectation value:

$$\langle X \rangle = \frac{L}{2\pi} \operatorname{Im} \ln \left\langle \Psi_0 \right| \exp\left[i \frac{2\pi}{L} \hat{X} \right] \left| \Psi_0 \right\rangle$$

can be recasted as:

$$\langle X \rangle = -\frac{L}{2\pi} \operatorname{Im} \ln \det \mathbf{S} \tag{8}$$

where

$$S_{sm,s'm'} = \int_0^L \phi_{q_s,m}^* \exp\left[-i \frac{2\pi}{L} x \right] \phi_{q_s',m'} \, dx \tag{9}$$

Using the Γ-point only (equivalent to M=1) the matrix $S_{sm,s'm'}$ is now defined as

$$S_{n,m} = \int_0^L \phi_n^* \exp\left[-i \frac{2\pi}{L} x \right] \phi_m \, dx \tag{10}$$

and ϕ_m are the Kohn-Sham orbitals.

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Localization functionals

Wannier functions are defined in term of an unitary transformation of occupied Bloch orbitals.

The problem is their non-uniqueness.

Marzari and Vanderbilt[1] proposed a way to solve this by requiring that the total spread of the localized function should be minimal.

In one dimension the functional for the spread is

$$\Omega = <x^2> - <x>^2 = \frac{1}{(2\pi)^2} \ln |z|^2 \qquad (11)$$

where

$$z = \int_0^L \exp\left[i\frac{2\pi x}{L}\right] |\phi(x)|^2 dx \qquad (12)$$

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[1]Phys Rev B 56, 12847 (1997)

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Localization methods

The mathematical problem which defines the localization procedure is to find the unitary transformation **U** of the orbitals

$$|\tilde{\phi}_n> = \sum_i U_{in}|\phi_i> \tag{13}$$

that simultaneously minimize the spread functional Ω.

The simplest approach to parameterize the unitary transformation is the Jacobi optimization procedure and consists in a direct product of elementary plane rotations of couples of orbitals.

The transformed expectation values are obtained as

$$\tilde{z}_{I,i} = \cos(\gamma)z_{I,i} + \sin(\gamma)z_{I,j} \tag{14}$$

$$\tilde{z}_{I,j} = -\sin(\gamma)z_{I,i} + \cos(\gamma)z_{I,j} \tag{15}$$

To obtain the optimal angle:

$$\frac{\partial \Omega}{\partial \gamma} = 0 \qquad \frac{\partial^2 \Omega}{\partial \gamma^2} < 0 \tag{16}$$

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Molecular properties from WF

Maximally localized Wannier functions are used as a tool to understand the nature of the chemical bonding.

In the case of a pseudopotential approach the localized orbitals only refers to the valence electrons in the effective charge of the nuclei.

In the frame of the Kohn-Sham approach the polarization of a system is defined as

$$M_\alpha^{el} = \frac{2e}{|\mathbf{G}_\alpha|} \operatorname{Im} \ln \det \mathbf{Z}_\alpha \qquad (17)$$

where α denotes the Cartesian components and where the matrix:

$$(\mathbf{Z}_\alpha)_{kl} = <\phi_k \exp[-i\mathbf{G}_\alpha \cdot \mathbf{r}]|\phi_l> \qquad (18)$$

is defined in terms of the Kohn-Sham orbitals ϕ_k.

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For the analysis of a liquid or solid M^{el} can be approximated as a sum of molecular dipole moments μ_I^{el}.

$$M^{el} \approx \sum_I \mu_I^{el} \tag{19}$$

The expectation value of the position operator is given:

$$\mathbf{r}_k = -\frac{L}{2\pi} \operatorname{Im} \ln \mathbf{z}_k \tag{20}$$

which is just the center of a given maximally localized Wannier function (k labels the different electrons).

With this definition the electronic part of of the total dipole moment of the supercell can be approximated by

$$M^{el} \approx -2e \sum_k \mathbf{r}_k \tag{21}$$

and molecular dipole moments can be defined as:

$$\mu_I^{el} = -2e \sum_{k \in I} \mathbf{r}_k \tag{22}$$

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Infrared absorption spectra

The dipole autocorrelation function needed to calculate infrared spectra

$$C(t) = < \mathbf{M}(t) \cdot \mathbf{M}(0) > \tag{23}$$

can be decomposed as

$$C(t) = C_{SS}(t) + C_{MM}(t) + C_{SM}(t) \tag{24}$$

where

$$C_{SS}(t) = \sum_{IJ}^{solvent} < \mu_I(t) \cdot \mu_J(0) > \tag{25}$$

$$C_{MM}(t) = < \mu_0(t) \cdot \mu_0(0) > \tag{26}$$

$$C_{SM}(t) = \sum_{I}^{solvent} (< \mu_I(t) \cdot \mu_0(0) > + < \mu_0(t) \cdot \mu_I(0) >) \tag{27}$$

After Fourier transform, $C_{SS}(t)$ yields the IR spectra of the solvent, while $C_{MM}(t)$ and $C_{SM}(t)$ contribute to the spectrum of the solvent.

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- ▶ Whether or not the cross correlation term $C_{SM}(t)$ should be included in the analysis of the solvent spectrum has been answered differently by different authors.
- ▶ Care has to be taken to correct for nuclei quantum effects which have been neglected so far.

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Atomic charges

It is possible to calculate atomic charges from Wannier centers, using some approximations.

The approach is closely related to the RESP approach.

Assuming neutral molecules

$$\sum_A^{N_{at}} Z_A - M q_w = 0 \qquad (28)$$

We want a set of charges q_A which reproduce the electrostatic potential V.

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \sum_a \frac{q_w}{|\mathbf{r}_a - \mathbf{r}|} \qquad (29)$$

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The potential is sampled on many positions $\mathbf{r}_i$ outside the molecule and optimized with respect to q_A.
Reference charges q_A^0 are also included.

$$
\Omega(\{q_A\}, \lambda, \{\epsilon_\alpha\}) = \sum_i \left(\sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|} - \sum_a \frac{q_w}{|\mathbf{r}_a - \mathbf{r}|} - \sum_A \frac{q_A}{|\mathbf{R}_A - \mathbf{r}_i|} \right)^2
$$
$$
+ w \sum_A (q_A - q_A^0)^2 - \lambda \sum_A q_A - \sum_{\alpha=x,y,z} \epsilon_\alpha \left(\sum_A q_A r_A^\alpha - \mu_\alpha \right)
$$

The conditions:

$$
\frac{\partial \Omega}{\partial q_A} = 0, \qquad \frac{\partial \Omega}{\partial \lambda} = 0, \qquad , \frac{\partial \Omega}{\partial \epsilon_\alpha} = 0 \qquad (30)
$$

reduce to a system of linear equation of dimension $N_{at} + 4$.

Infrared Spectrum of Aqueous Uracil

from M.-P. Gaigeot and M. Sprik, JPC B 107, 10344 (2003)

▶ The spectrum is obtained by FT of the time correlation function of total dipole moment.

▶ Here, unlike in classical model studies, there no separation between permanent and induced dipole moments (all is contained in the total electronic polarization.

▶ The spectroscopy of aqueous solutions adds further challenges. Because of the intense IR activity of water, the signal of the hydrated solute is usually completely obscured. This is a problem in experiment, as well as computation.

▶ Motivations: Nucleic acids are exposed to water solvent in a number of biological structures. The hydration of nucleic acids of great interest and extensively investigated by infrared spectroscopy.
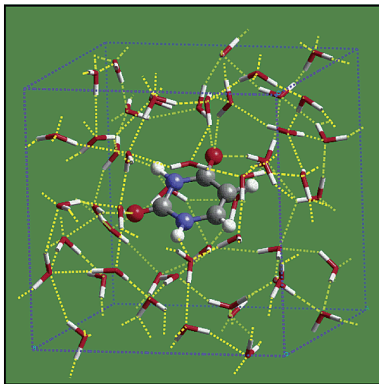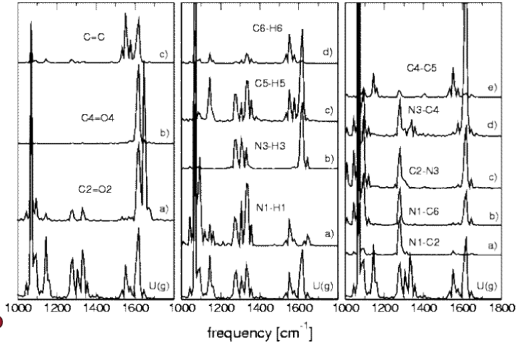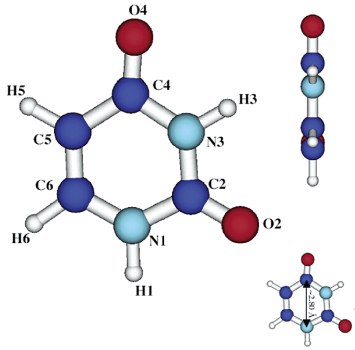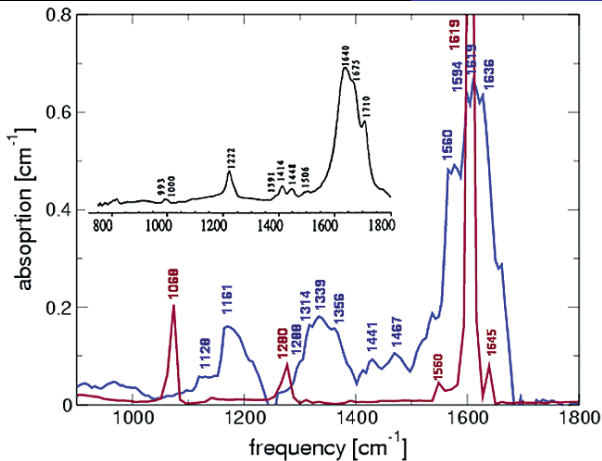
IR spectrum in vacuo (red) and in aqueous solution (blue) from CPMD at 20 and 310 K, respectively. Inset: experimental IR from ref [2]

[2] Aamouche, A.; Berthier, G.; Cadioli, B.; Gallinella, E.; Ghomi, M. J. Mol. Struct. (THEOCHEM) 1998, 426, 307.

a) Isolated U   b) Aqueous U
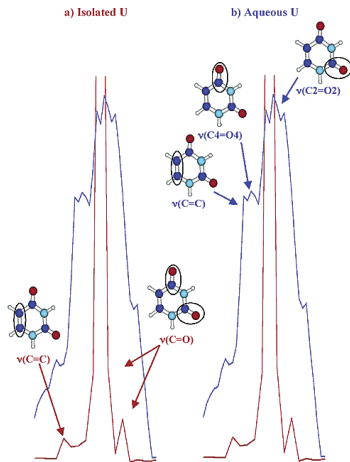
▶ 1700-1500 cm^{-1}: C-O (1620 cm^{-1}) and C-C (1150 cm^{-1}).
Bending of N-H or C-H induces vibration of adjacent C-O and C-C
bonds, signatures of bending in the 1700-1500 cm^{-1}
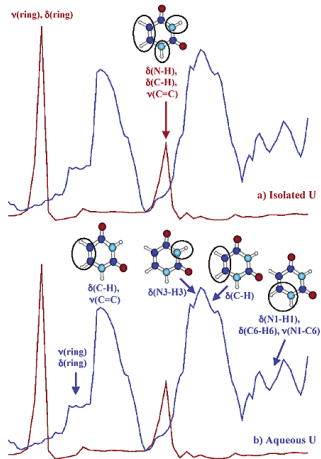
▶ The 1400-1200 cm^{-1} range is predominantly δ(N-H) and δ(CH) bending.

The IR spectrum in solution

► Substantial enhancement of the molecular dipole from 4.50 D of the isolated molecule to 7.50 D in solution (0.65 increase.)

► NO evidence of a reverse effect of the solute on the solvent. Dipole moments, even for molecules in the first hydration shell, were essentially identical to the pure liquid water values.

a) Isolated U   b) Aqueous U

ν(C2=O2)

ν(C4=O4)

ν(C=C)

ν(C=C)   ν(C=O)
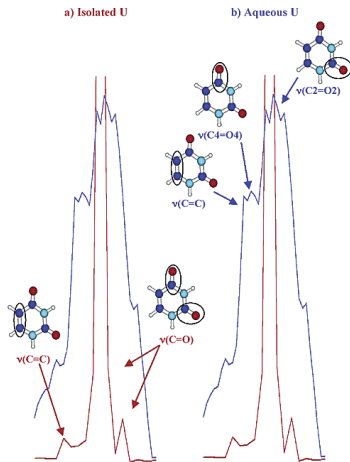
Solvation has little effect on the spectrum between 1700 and 1500 cm^{-1}.
Broadening seems the main response in this interval. C-O frequencies
red-shifted by 10-40 cm^{-1}. (consistent with H-bond)
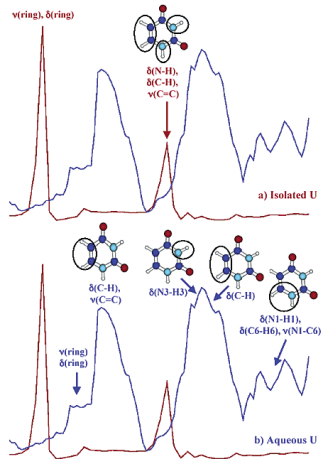
On the other hand, the number and positions of infrared active bands is completely different in the 1500-1000 cm^{-1} Vacuum: only two IR bands. Solution:five can be distinguished.

Comparison to Experiment

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▶ Overall patterns are very similar

▶ Theory and experiment are in remarkable good agreement for the main band generated by C-O and C-C stretching

▶ overall red shift in the calculation can be the BLYP functional, as well as the value of the fictitious electron mass used in the Car-Parrinello dynamics.

▶ However, the band calculated around 1330 cm-1 is too broad (assigned to N3-H3 bending motion).
(i) dynamical charges of the amide N3-H3 group are overestimated
(ii) H-bonds formed by this group to the water molecules are too strong.

Infrared Spectrum of N-methylacetamine[3]
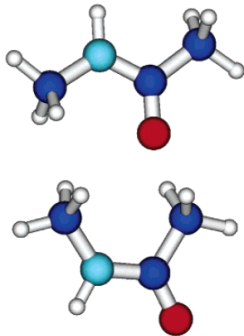
Motivations:Structural motifs such as α-helices or β-sheets can be identified by characteristic changes in position and shape of linear infrared or Raman bands, in particular the amide bands are used as structural probes The

amide I band shape is strongly affected by formation of intermolecular hydrogen bonds with the solvent.

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[3]M-P Gaigeot et al JCTC 2005, 1, 772.
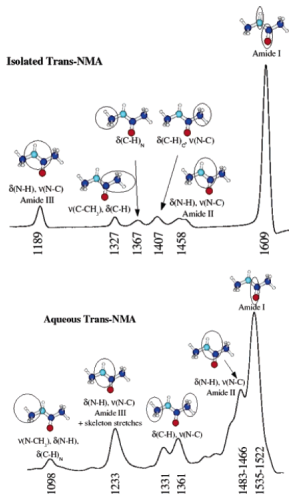
Gas-phase *trans*

The most intense IR band located at 1609 cm^{-1} is related to the amide I mode.

In the domain 1500 to 1300 cm^{-1} are 4 active bands of much lower intensity.

More intense active band at 1189 cm^{-1} is due to amide III.

Gas-phase *cis*

The cis-NMA spectrum is totally different from the trans-NMA spectrum: in particular, the number of active bands is reduced from six to four.

The most intense active band is associated with the amide I mode.

The amide I band is peaked in the two spectra (cis, trans) trans- and cis-NMA at the same frequency, and for both molecules, this band has the most intense activity of the whole spectrum.
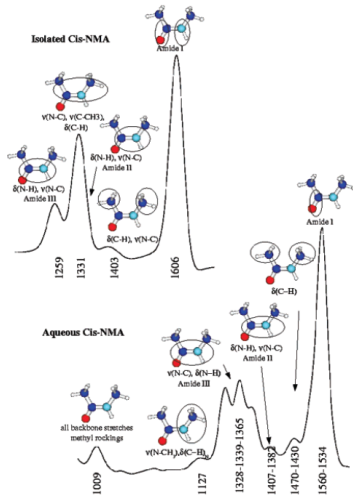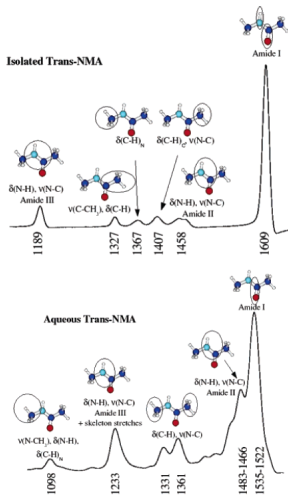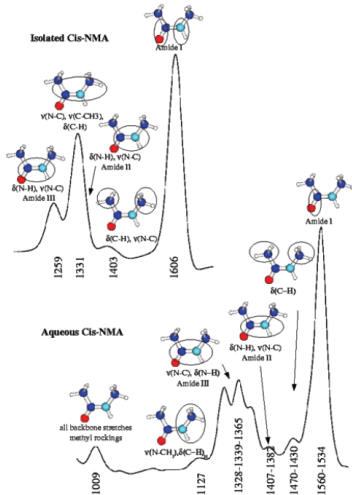
Aqueous *trans*

Red-shift of the amide I and blue-shift of amide II band reducing the 150 cm^{-1} frequency gap observed in the gas phase to 40-50 cm^{-1} in solution.

blue-shift of 40 cm^{-1} for Amide III band.

Aqueous *cis*

Amide I is 80 cm^{-1} down-shifted by the presence of the solvent, whereas amide III is blue-shifted by the same amount. The other bands keep more or less the same position.

Gas phase
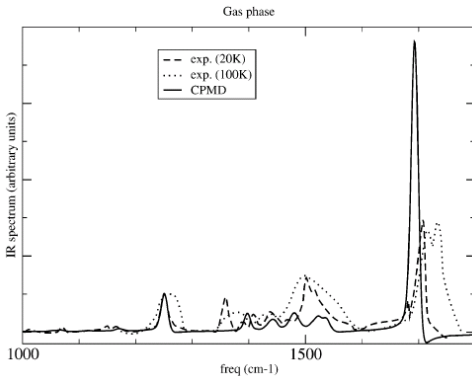
Comparison to experiments

Although band positions are systematically red-shifted (mainly due to our use of the BLYP functional), the main features, including band shapes and relative bands gaps, can be satisfactorily reproduced.
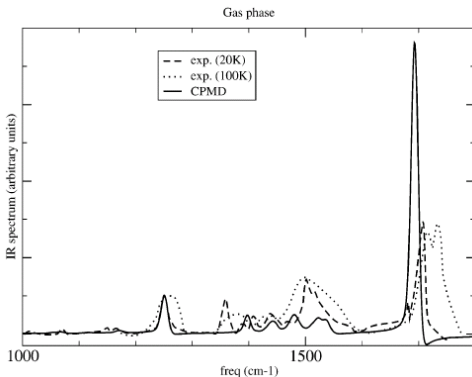
A factor of 1.064 used to adjusts exactly the position of the amide III band to the exp value of 1266 cm^{-1}. Doing so, the theoretical amide I band is close to the correct position (its intensity is overestimated). The intermediate region between 1300 and 1600 cm^{-1} is only approximately reproduced, but with correct features.

Aqueous phase
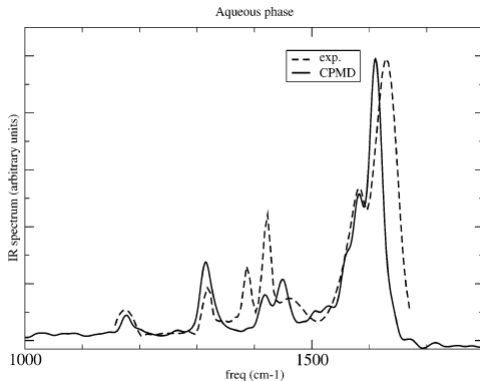
Frequencies have been uniformly scaled by a factor of 1.117 in order to align the amide III band with the experimental peak at 1318 cm^{-1}. The broad and intense double band in the 1500-1700 cm^{-1} range due to the mixing of amide I and amide II is very well reproduced.