Universidade de São Paulo
Instituto de Química

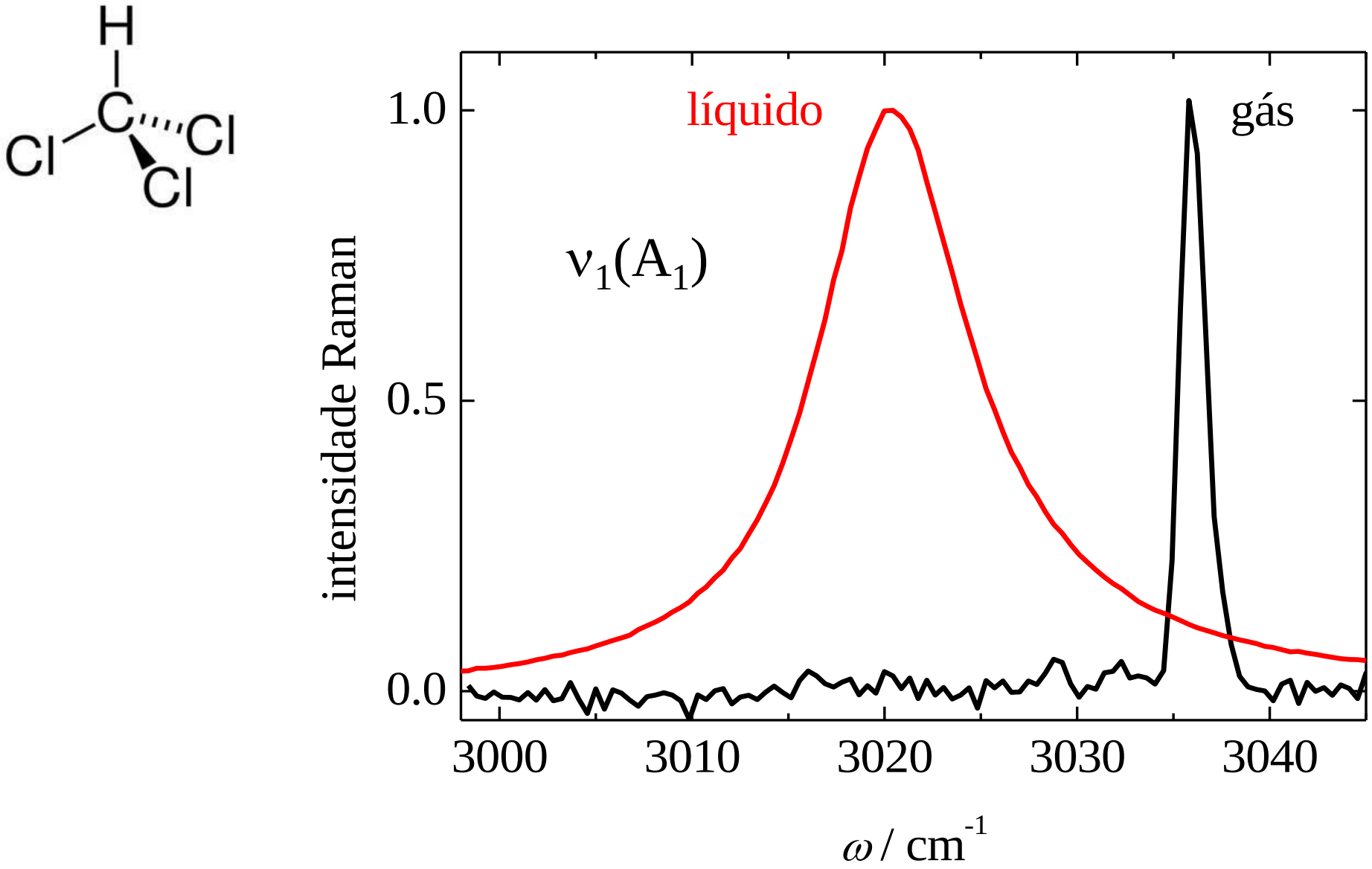
VIBROS IV

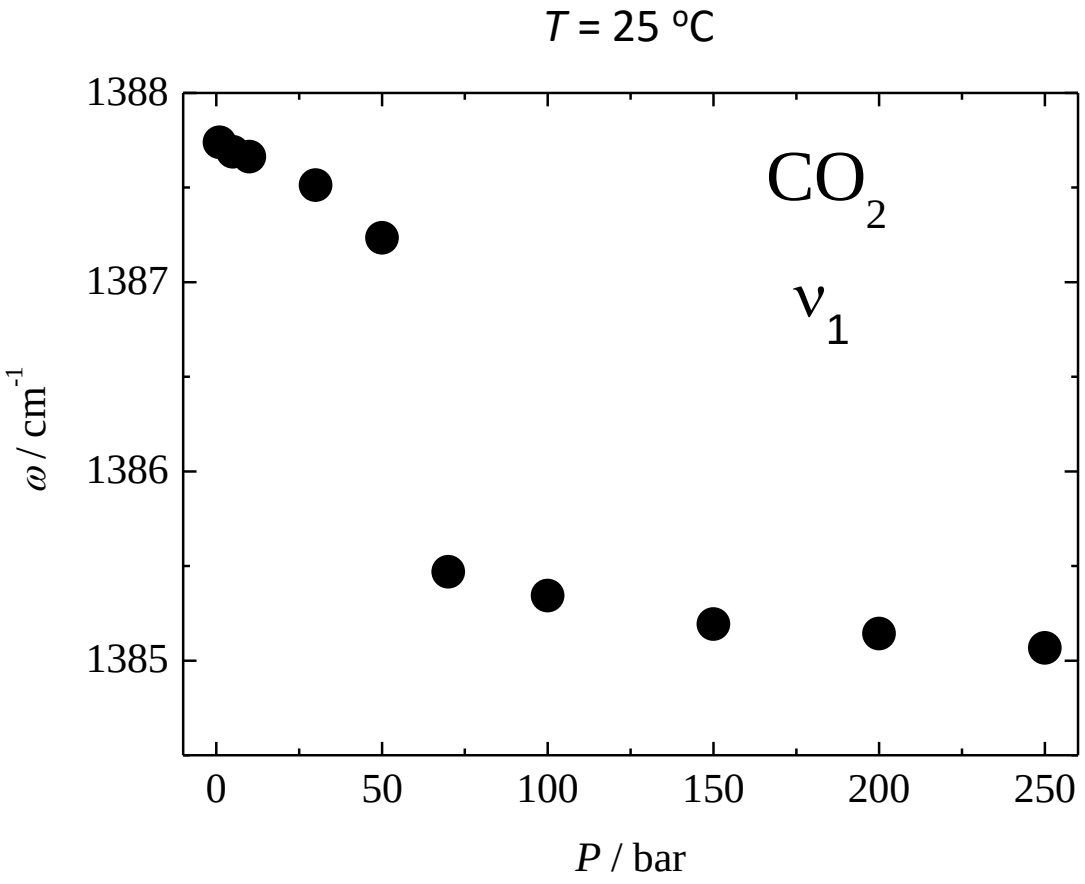
LEM
Laboratório de Espectroscopia Molecular

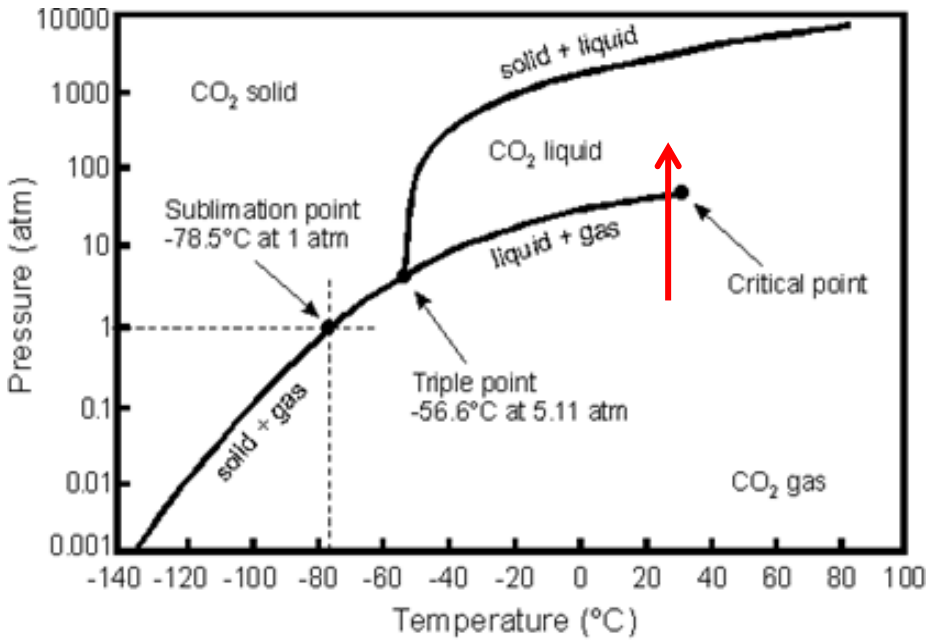
ESPECTROSCOPIA VIBRACIONAL DE LÍQUIDOS

Prof. Dr. Mauro C. C. Ribeiro

(mccribei@iq.usp.br)

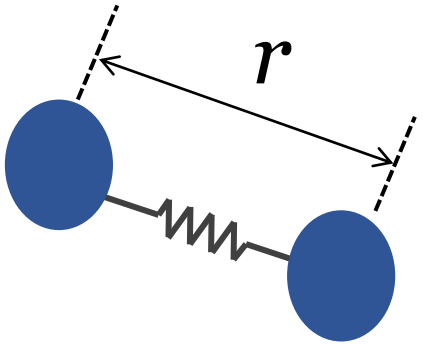

H
C
Cl
Cl
Cl
líquido
gás
$\nu_1(A_1)$
intensidade Raman
1.0
0.5
0.0
3000
3010
3020
3030
3040
ω / cm^{-1}





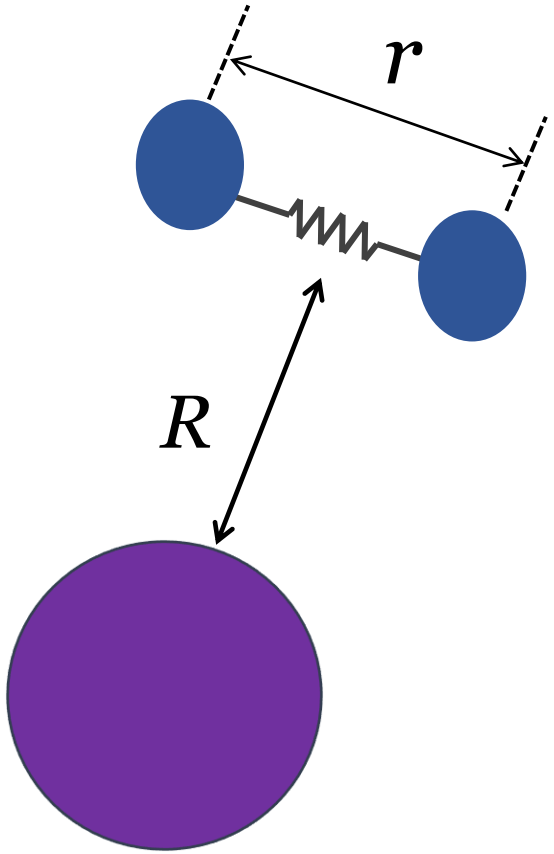
Pressure-Temperature phase diagram for CO_2.

Oscilador Harmônico



$$V(r) = \frac{1}{2}k(r - r_e)^2$$

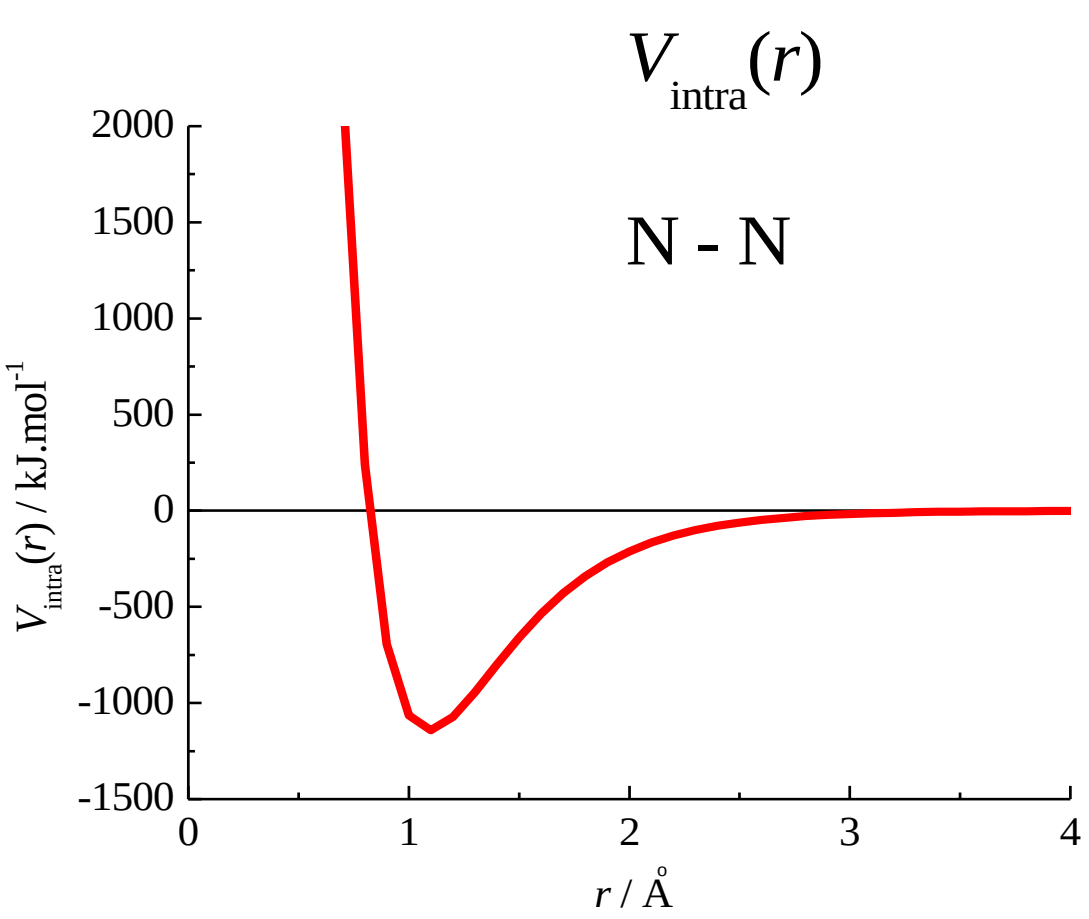
Oscilador Anarmônico

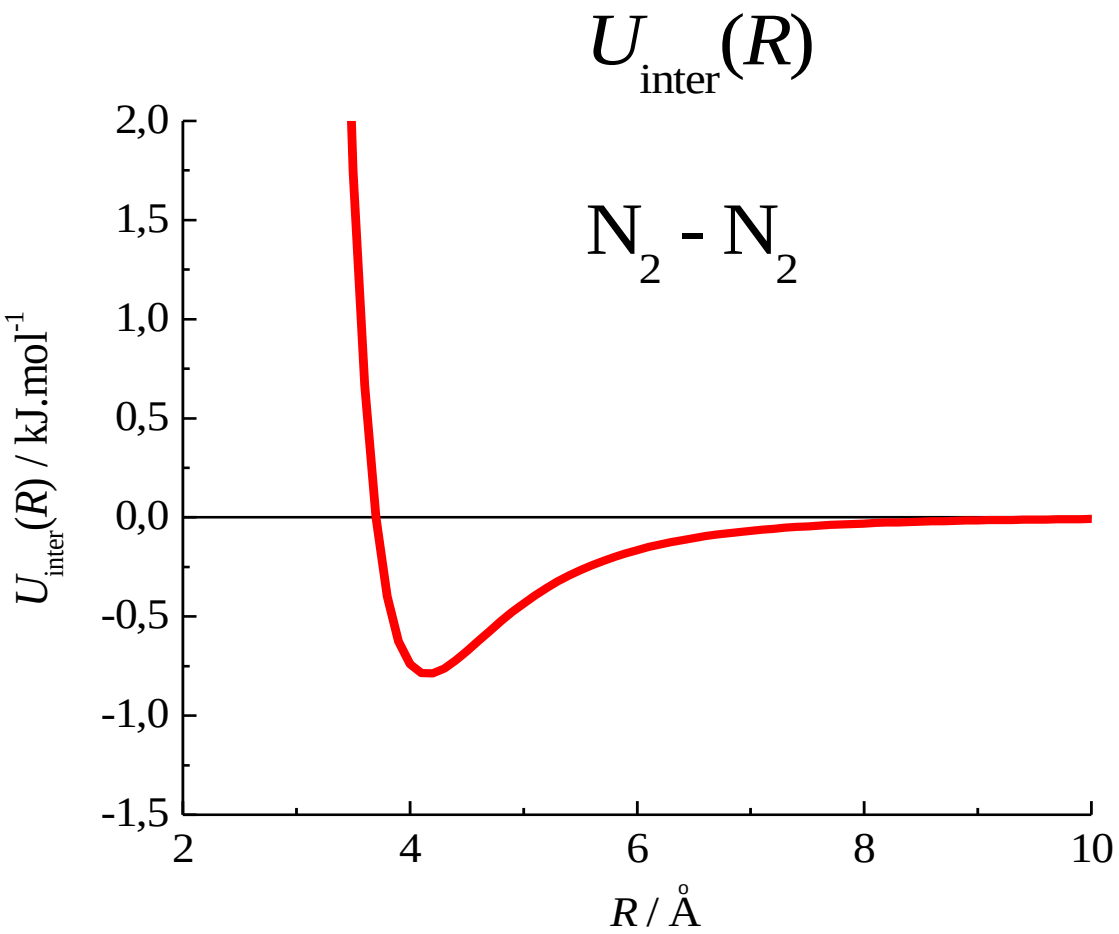


$$V(r) = \frac{1}{2}k(r - r_e)^2 + \frac{1}{6}g(r - r_e)^3 + \ldots$$

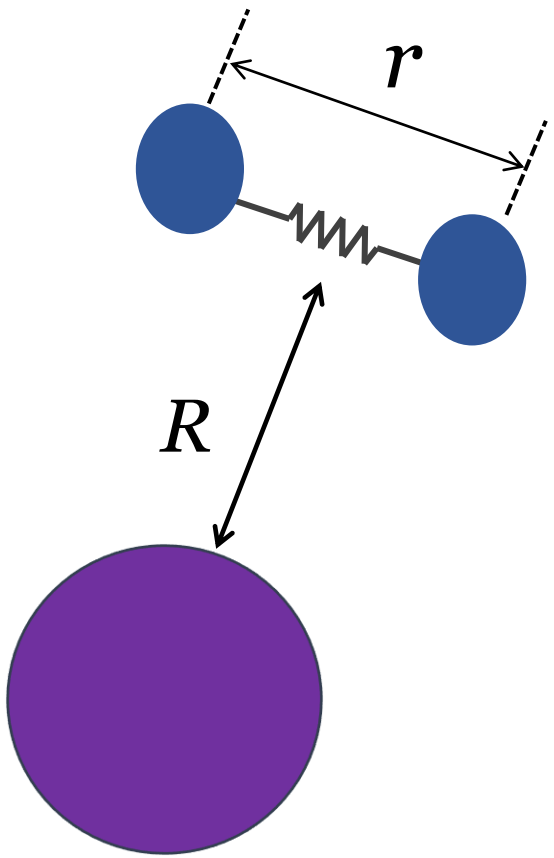
$$k = \left(\frac{d^2V}{dr^2}\right)_{r_e} \qquad \left(\frac{dV}{dr}\right)_{r_e} = 0$$

$U(R, r)$


$V_{intra}(r)$
N - N
2000
1500
1000
500
0
-500
-1000
-1500
0
1
2
3
4
$V_{intra}(r)$ / kJ.mol^{-1}
r / Å


$U_{inter}(R)$
N_2 - N_2
2,0
1,5
1,0
0,5
0,0
-0,5
-1,0
-1,5
2
4
6
8
10
$U_{inter}(R)$ / kJ.mol^{-1}
R / Å

Oscilador Anarmônico



$$V(r) = \frac{1}{2}k(r - r_e)^2 + \frac{1}{6}g(r - r_e)^3 + \ldots$$

$$k = \left(\frac{d^2V}{dr^2}\right)_{r_e} \qquad \left(\frac{dV}{dr}\right)_{r_e} = 0$$

$$\nu_o = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$$

$$4\pi^2\mu\nu_o^2 = \left(\frac{d^2V}{dr^2}\right)_{r_e}$$

$$U(R, r) = F(r - r_e) + \frac{1}{2}G(r - r_e)^2 + \ldots$$

$$F = \langle\left(\frac{dU}{dr}\right)_{r_e}\rangle$$

$$4\pi^2\mu\boldsymbol{\nu}^2 = \left(\frac{d^2(V+U)}{dr^2}\right)_{r_e'}$$

$$\left(\frac{d(V+U)}{dr}\right)_{r_e'} = 0$$

Desvio de frequência vibracional

$$\frac{\nu - \nu_o}{\nu_o} = \frac{1}{2}\left(-\frac{g}{k^2}F + \frac{G}{k}\right)$$

$$V(r) = \frac{1}{2}k(r - r_e)^2 + \frac{1}{6}g(r - r_e)^3 + \ldots$$

$$U(R, r) = F(r - r_e) + \frac{1}{2}G(r - r_e)^2 + \ldots$$

Teoria quântica do desvio de frequência vibracional

transição entre níveis vibracionais $n \rightarrow m$:

$$\frac{\nu - \nu_o}{\nu_o} = (m - n)\frac{1}{2}\left(-\frac{g}{k^2}F + \frac{G}{k}\right)$$

Educação

I_2- UMA MOLÉCULA DIDÁTICA

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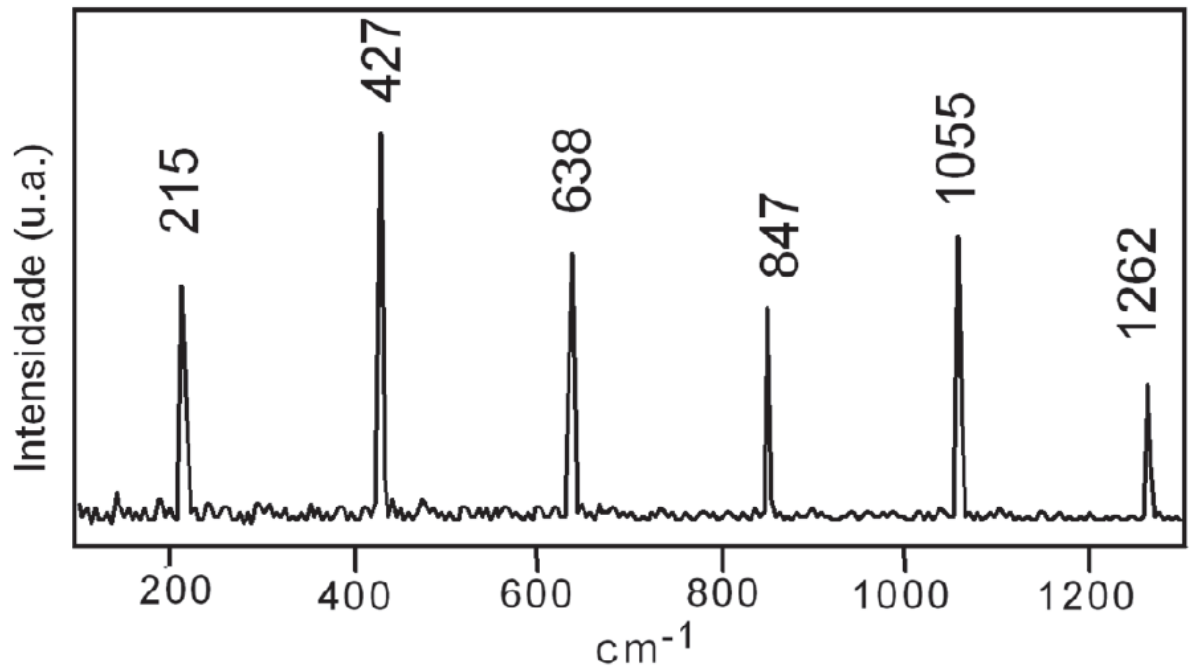
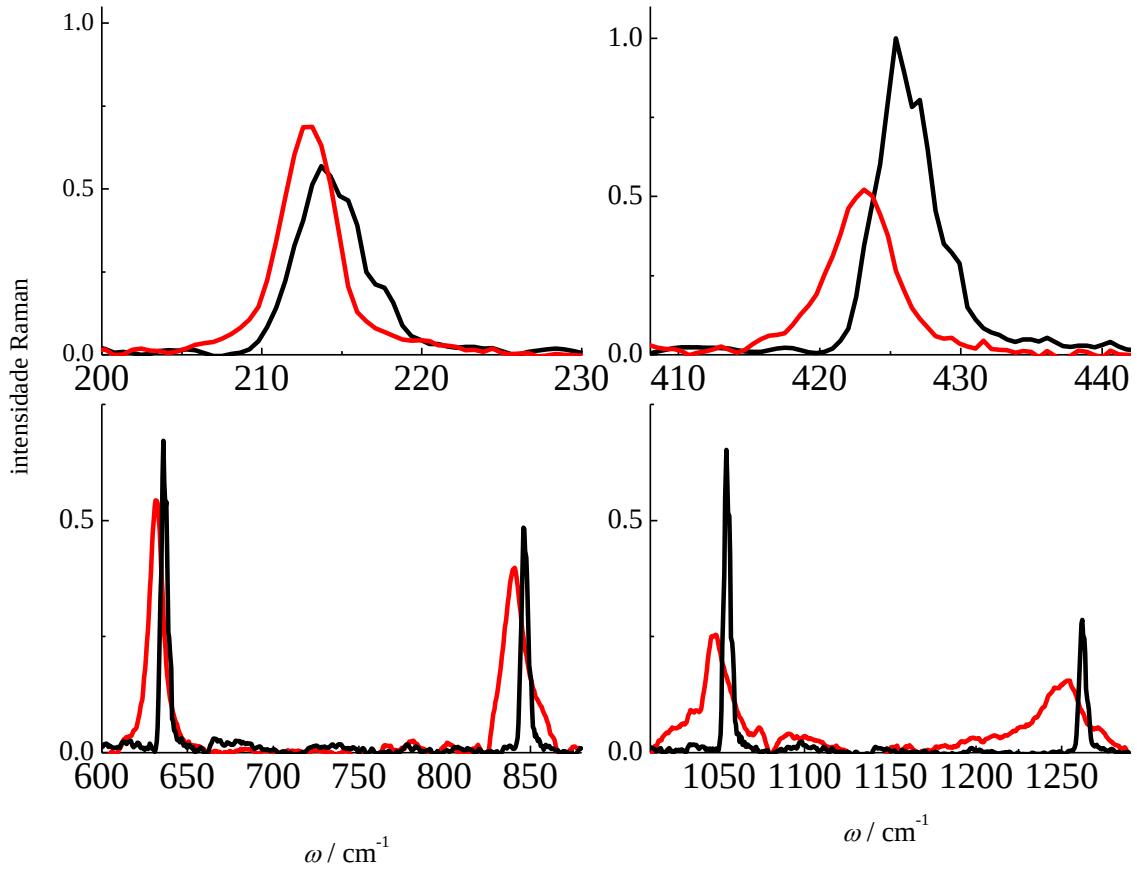


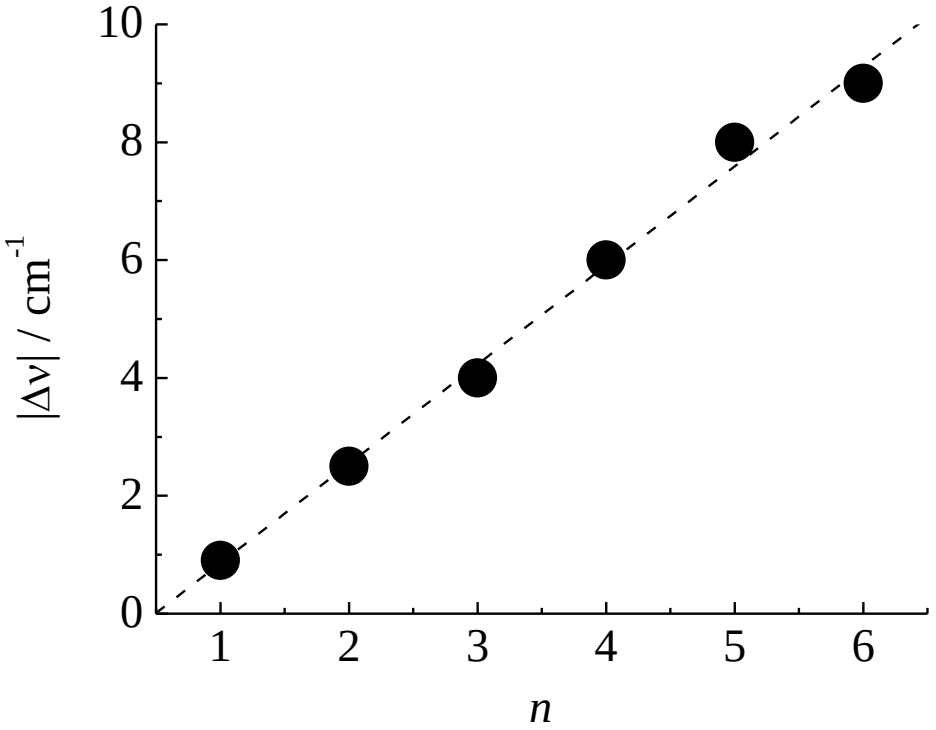
Figura 4. *Espectro Raman ressonante do vapor de iodo, excitação 514 nm, mostrando a banda fundamental (215 cm^{-1}) e algumas das harmônicas*

Desvio de frequência vibracional de I_2 em solução

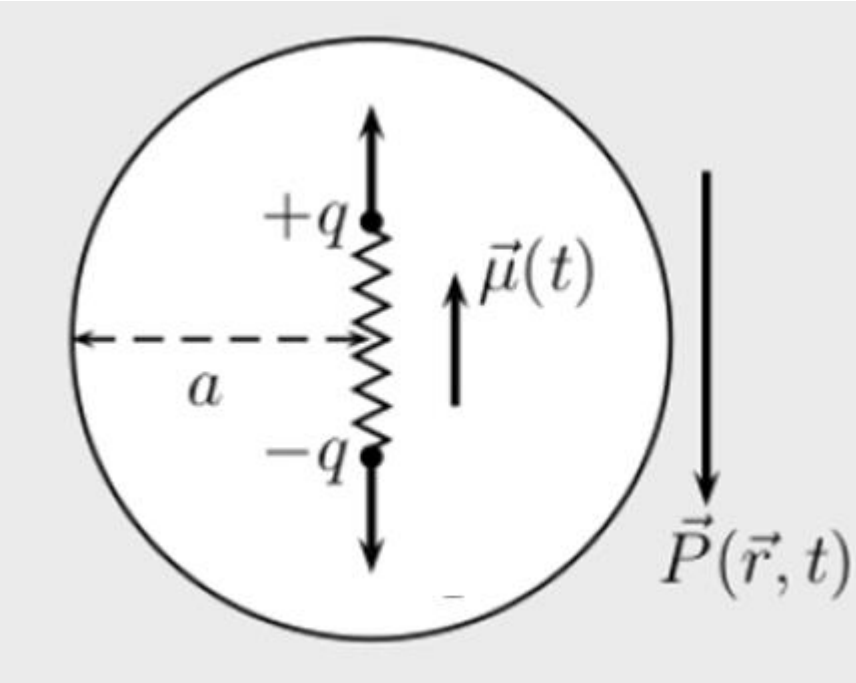
solução em *n*-hexano vapor



Δν para várias harmônicas

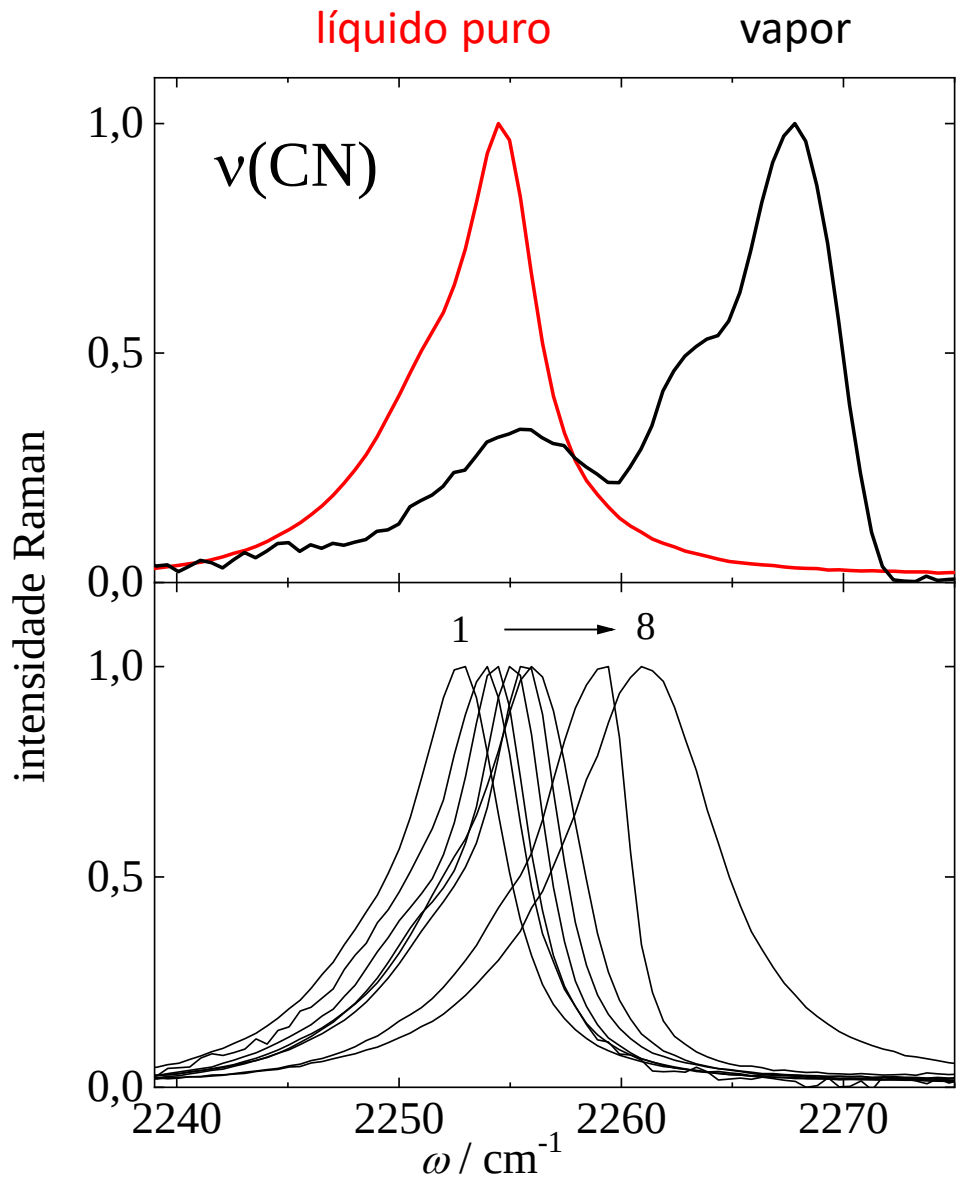


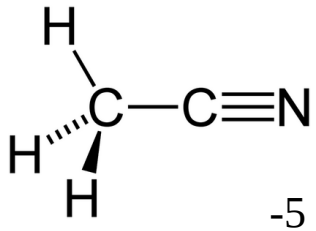
Líquido como meio contínuo

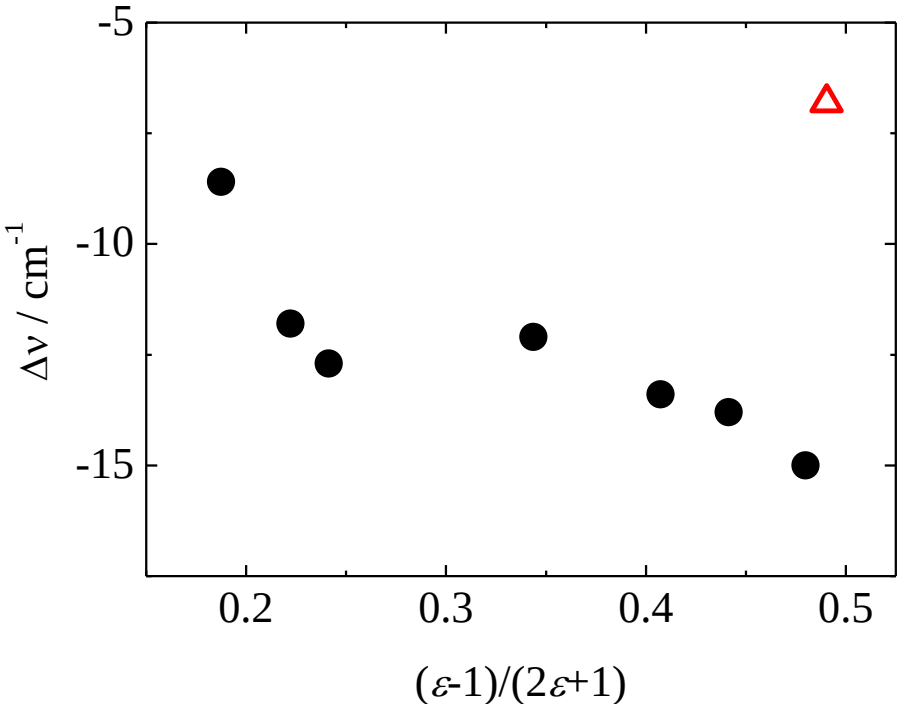


Constante dielétrica, ε

$$\frac{\Delta\nu}{\nu_o} \propto \frac{\varepsilon - 1}{2\varepsilon + 1}$$







Soluções de CH_3CN em:

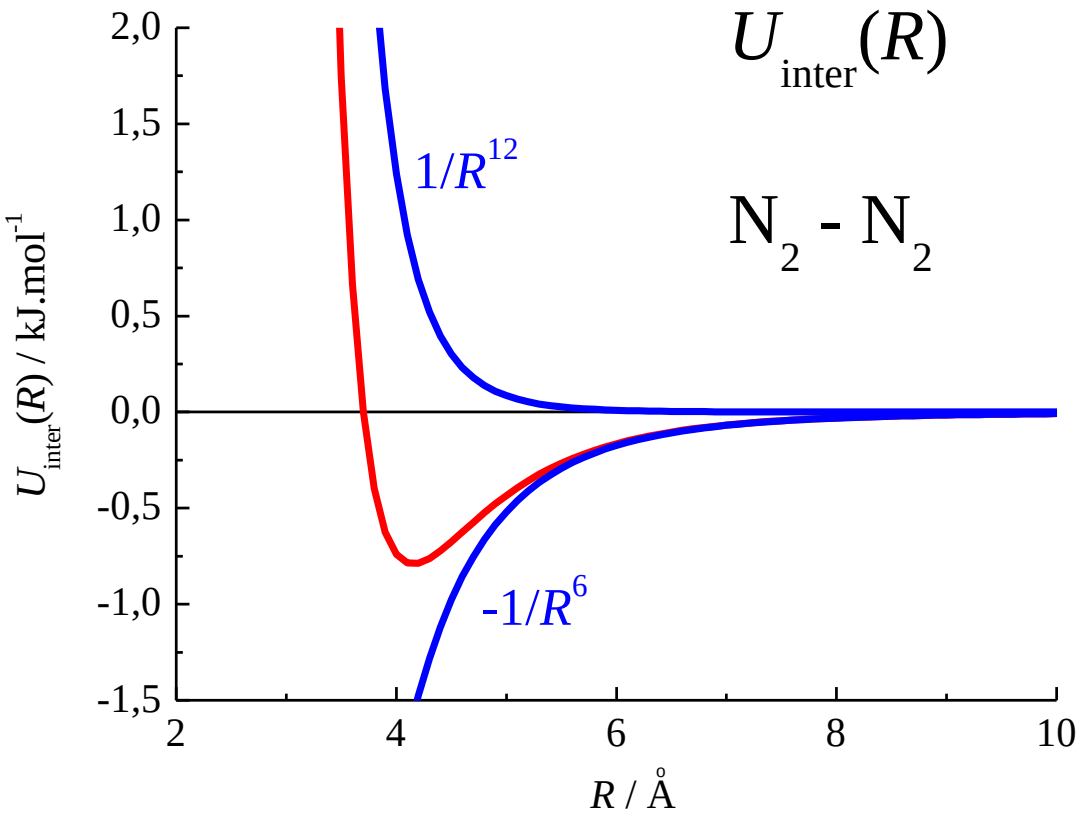
1, dimetilformamida (ε = 36,7); 2, piridina (ε = 12,3);

3, tetrahidrofurano (ε = 7,6); 4, tolueno (ε = 2,4);

5, dietiléter (ε = 4,3); 6, tetracloreto de carbono (ε = 2,2);

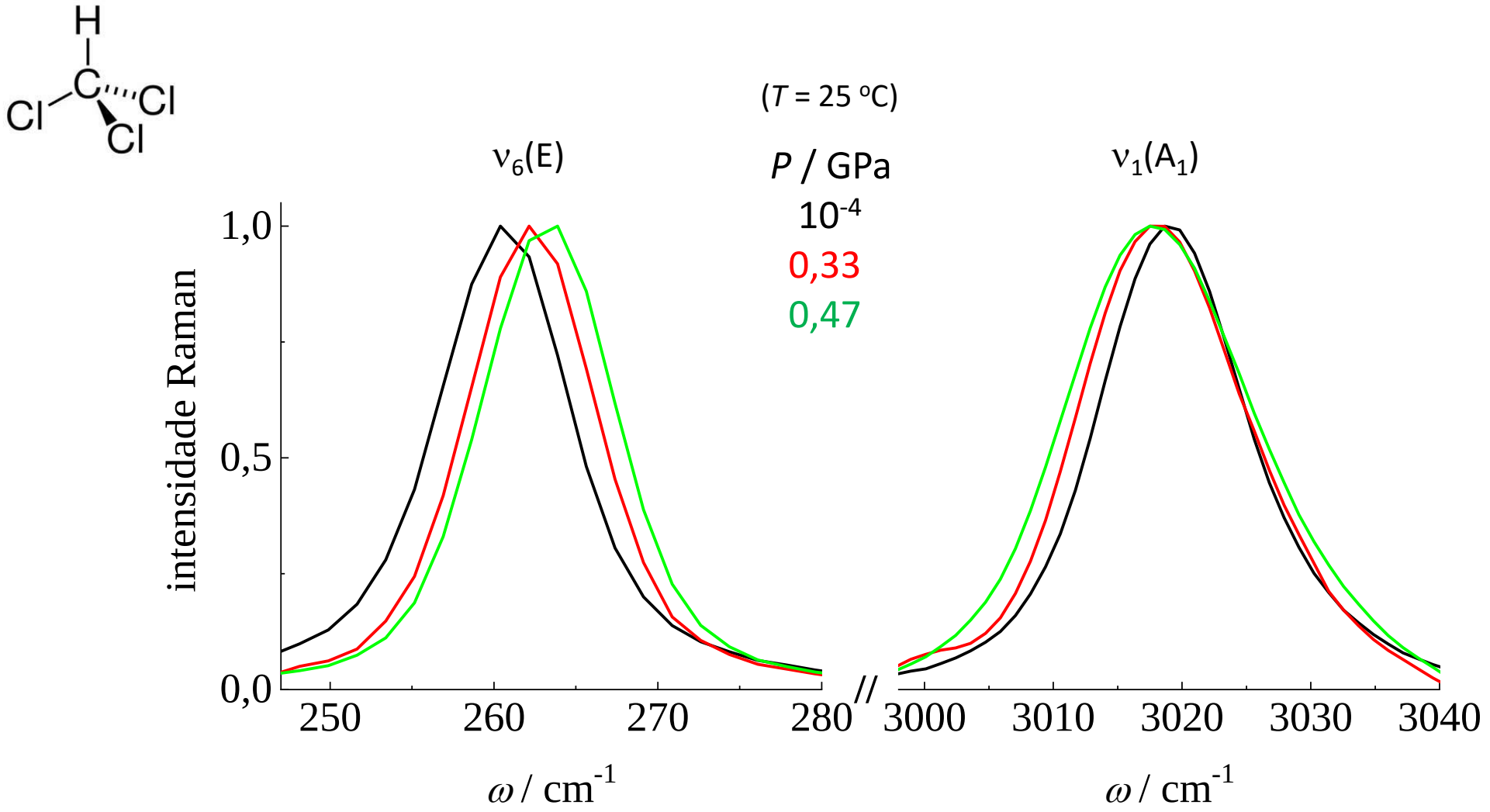
7, hexano (ε = 1,9); 8, H_2O (ε = 78,3).

Forças intermoleculares atrativas e repulsivas



$$\Delta\nu_{total} = \Delta\nu_{atract.} + \Delta\nu_{repuls.}$$

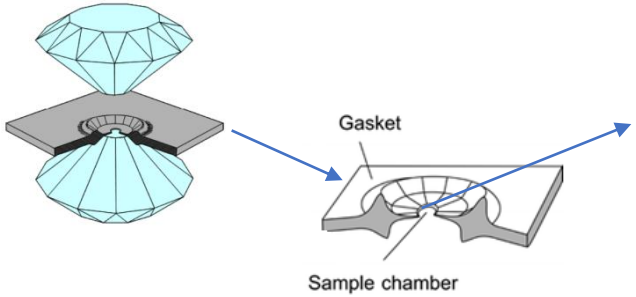
< 0 > 0

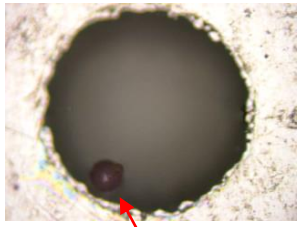


(1 GPa ≅ 10000 atm)

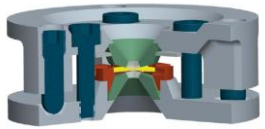
Espectroscopia Vibracional em Alta Pressão

diamond anvil cell (DAC)

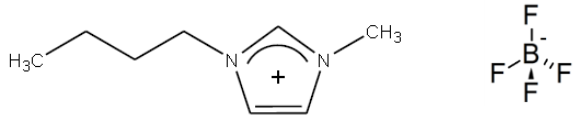


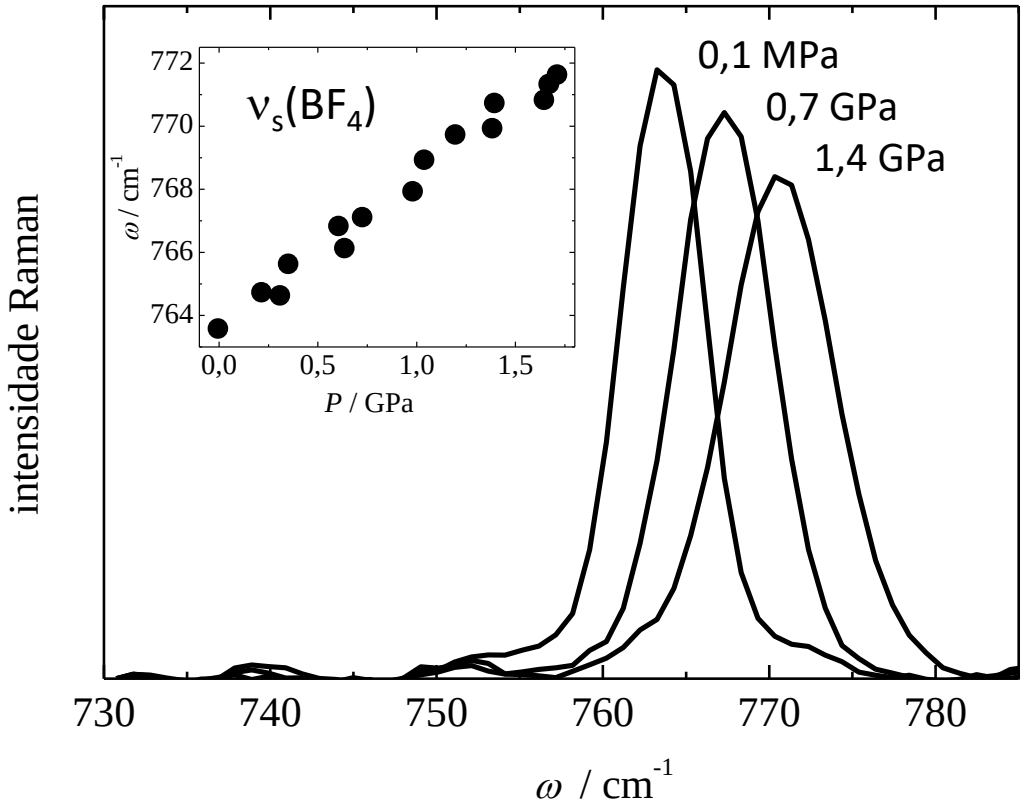


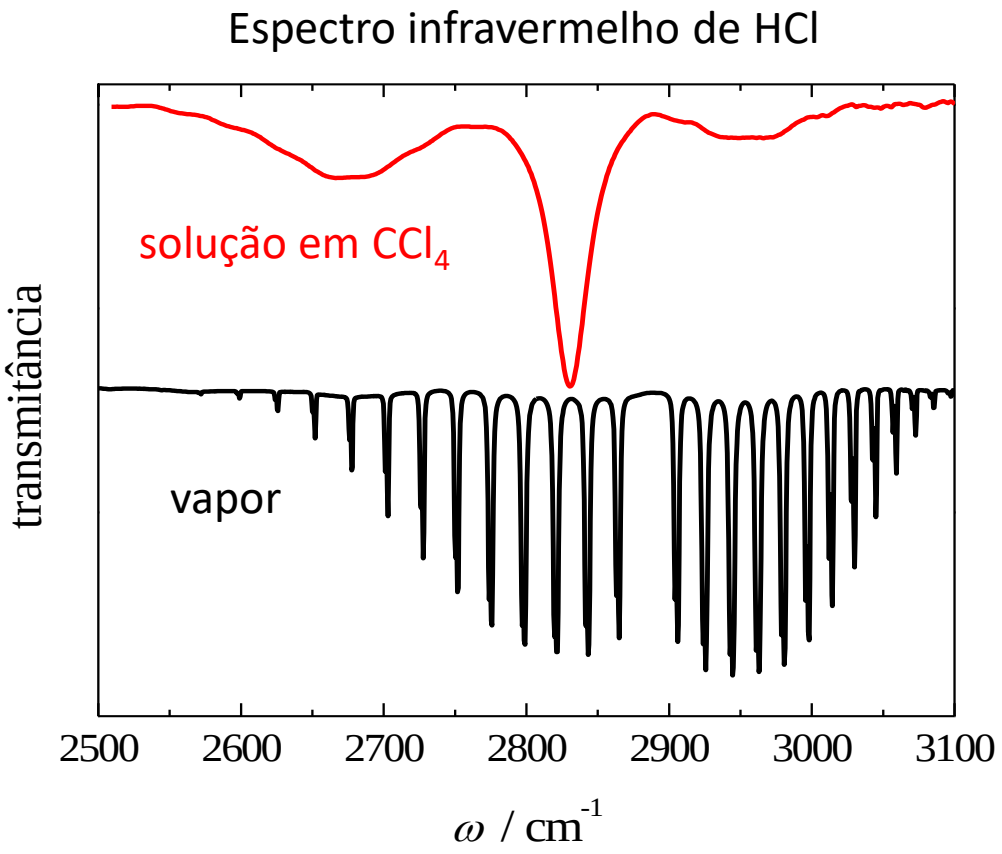
Ruby fluorescence
7.7 cm^{-1}/GPa



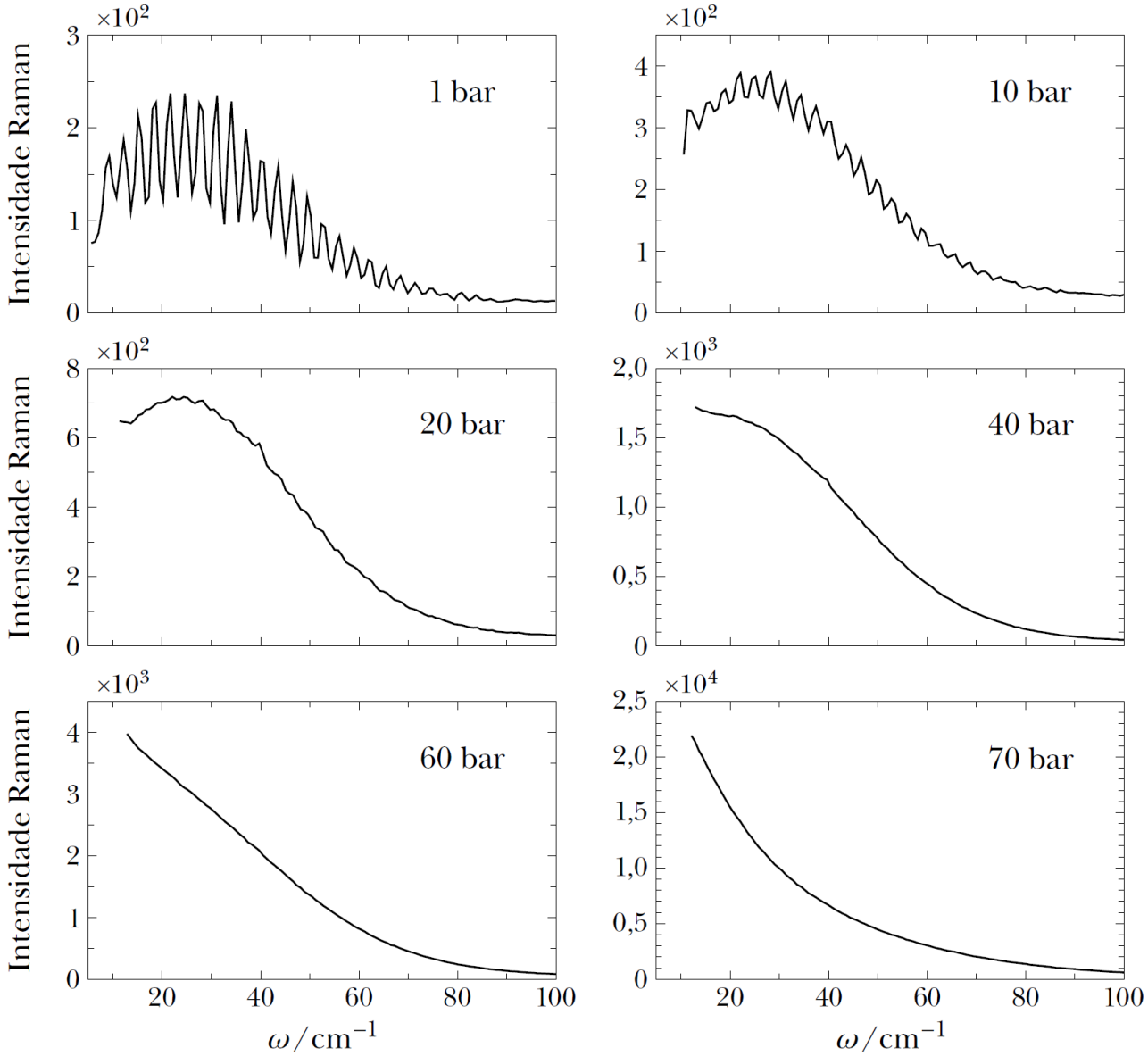
(1 GPa ≅ 10000 atm)






Espectro infravermelho de HCl
solução em CCl_4
vapor
transmitância
2500
2600
2700
2800
2900
3000
3100
ω / cm^{-1}

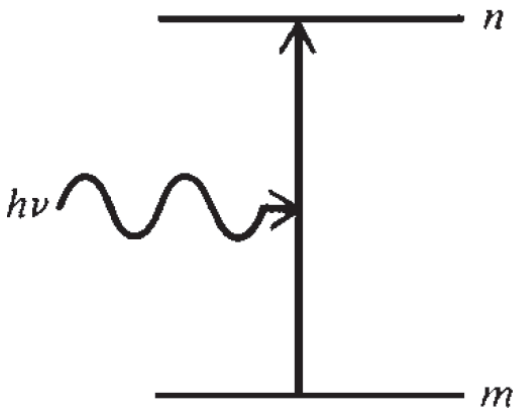
CO_2 (T = 25 ºC)


Intensidade Raman
×10²
1 bar
10 bar
×10³
20 bar
40 bar
×10⁴
60 bar
70 bar
ω/cm⁻¹

Atividade no IR

Níveis de energia do oscilador harmônico:

$$E_v = h\nu(v + \tfrac{1}{2}) \,, \quad v = 0, 1 \;\; 2, \ldots$$

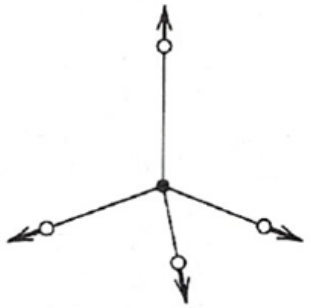


$$E_n - E_m = h\nu$$

$$\boldsymbol{\mu}[R(t)]$$

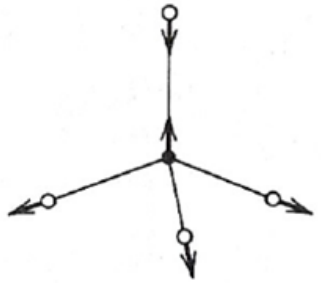
Variação do momento de dipolo elétrico com a vibração:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_e + \left(\frac{d\boldsymbol{\mu}}{dx}\right)_e x + \ldots$$



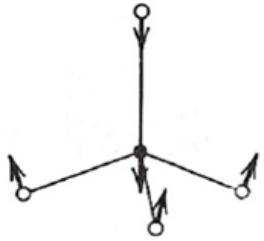
Raman

Raman



IR

Raman

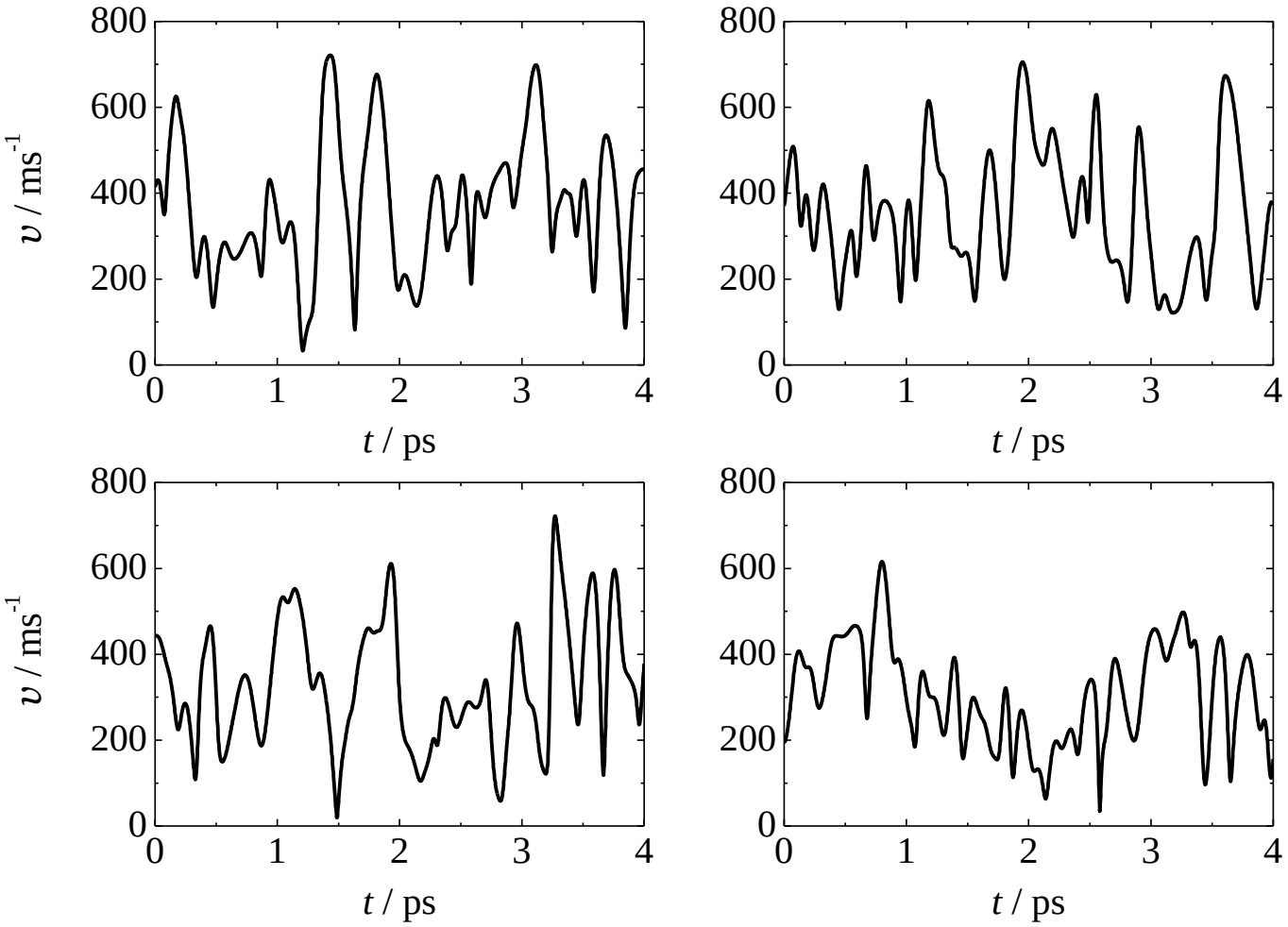


IR

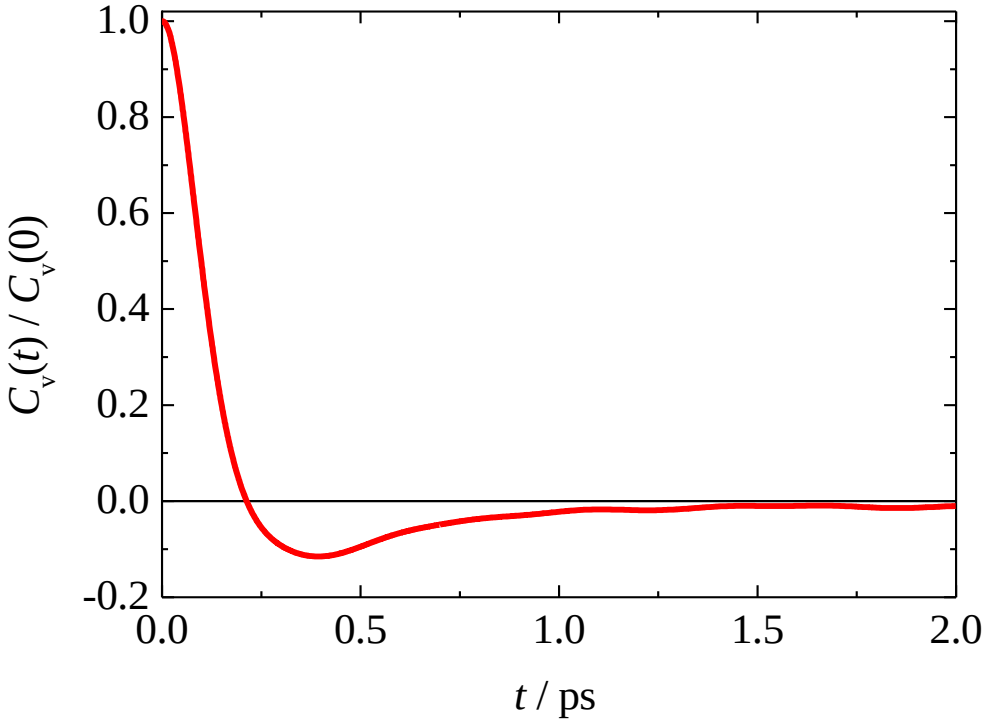
Raman

Função de Correlação no Tempo

DMSO (T = 25 ºC)



$$C_{\mathbf{v}}(t) = \frac{1}{N}\sum_{i=1}^{N} \left\langle \mathbf{v}_i(0).\mathbf{v}_i(t) \right\rangle$$



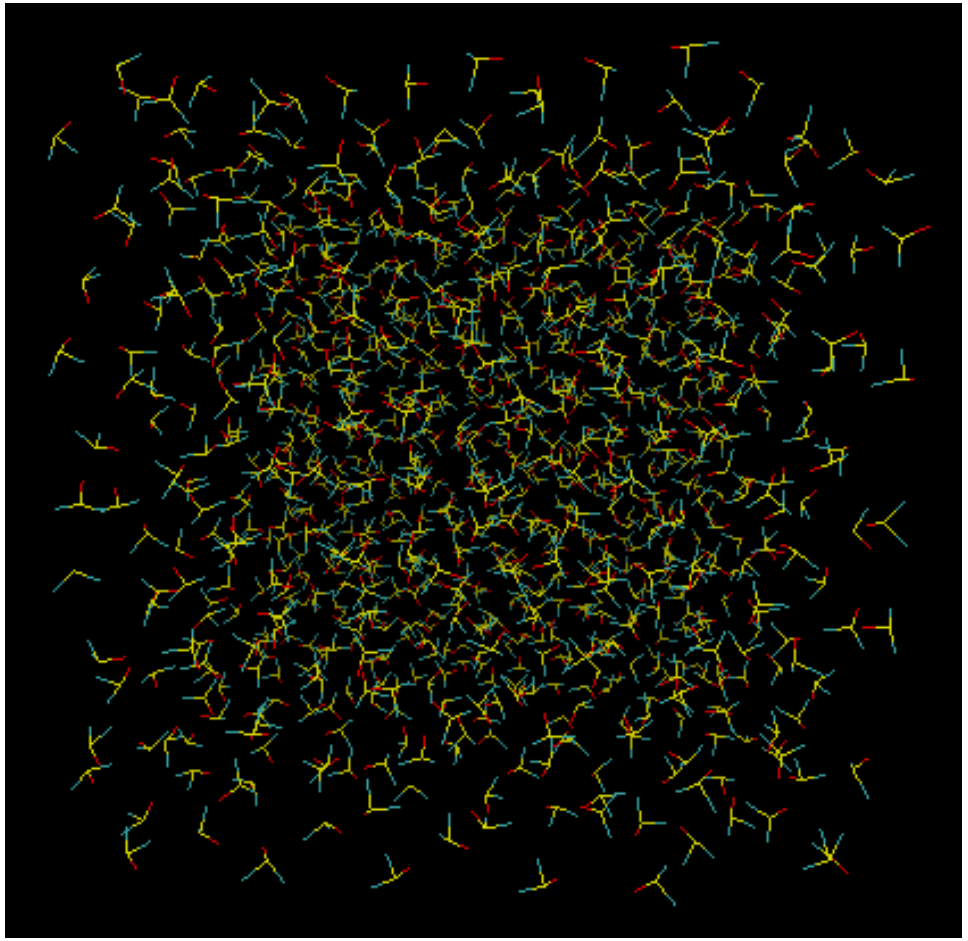
Cálculo de médias por Simulação Computacional

Simulação de líquidos por Dinâmica Molecular:

$$\mathbf{f}_i = m_i \ddot{\mathbf{R}}_i$$

$$\Downarrow$$

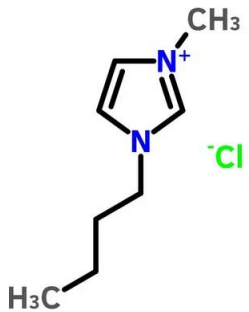
$$\{\mathbf{p}(t), \mathbf{R}(t)\} \rightarrow \{\mathbf{p}(t+\Delta t), \mathbf{R}(t+\Delta t)\}$$



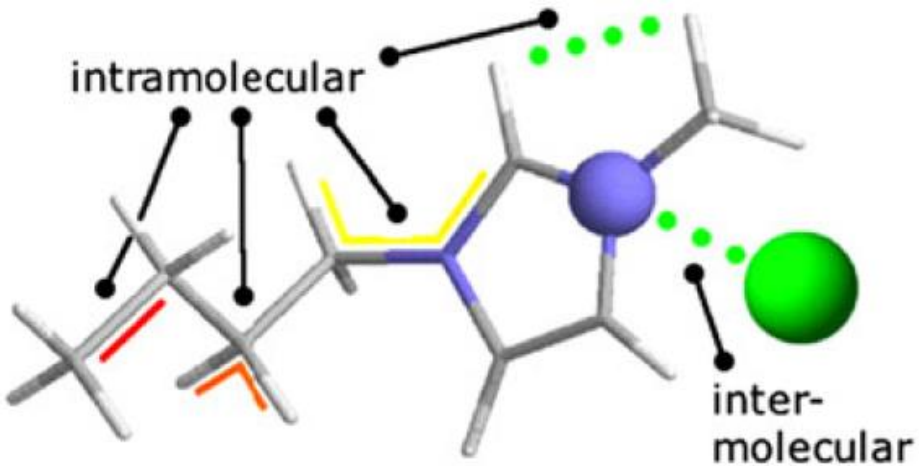
Uma configuração instantânea de DMSO líquido

$$\sum_{ij}^{\text{bonds}} \frac{k_{r,ij}}{2}(r_{ij} - r_{0,ij})^2 \quad \text{stretch}$$

$$+ \sum_{ijk}^{\text{angles}} \frac{k_{\theta,ijk}}{2}(\theta_{ijk} - \theta_{0,ijk})^2 \quad \text{bend}$$



1-butyl-3-methilimidazolium chloride

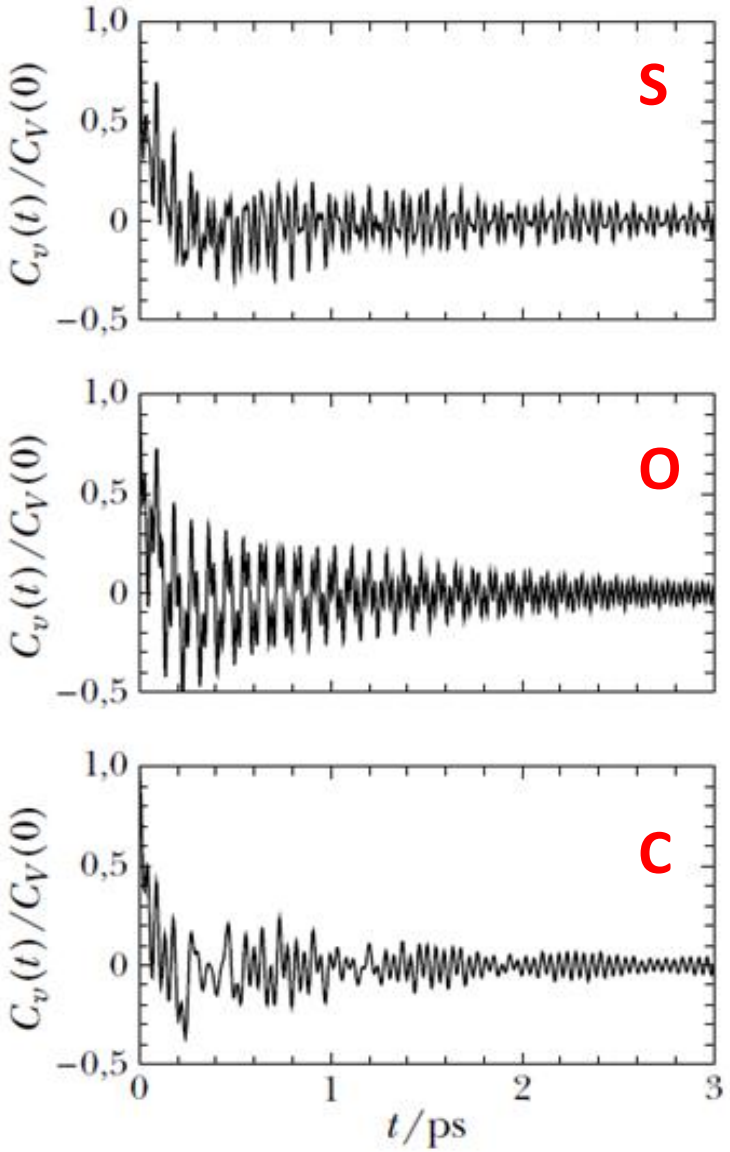


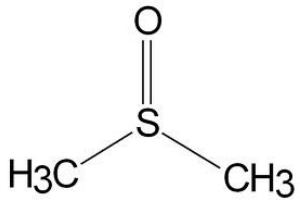
$$+ \sum_{ijkl}^{\text{dihedrals}} \sum_{m=1}^{4} \frac{V_{m,ijkl}}{2}[1 + (-1)^m \cos(m\,\varphi_{ijkl})] \quad \text{torsion}$$

$$+ \sum_{i}^{\text{atoms}} \sum_{j \neq i} \left\{ 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}} \right\} \quad \text{Lennard Jones + Coulomb}$$

J. N. G. Lopes, A. A. H. Pádua, *Theor. Chem. Acc.* **131**, 1129 (2012)

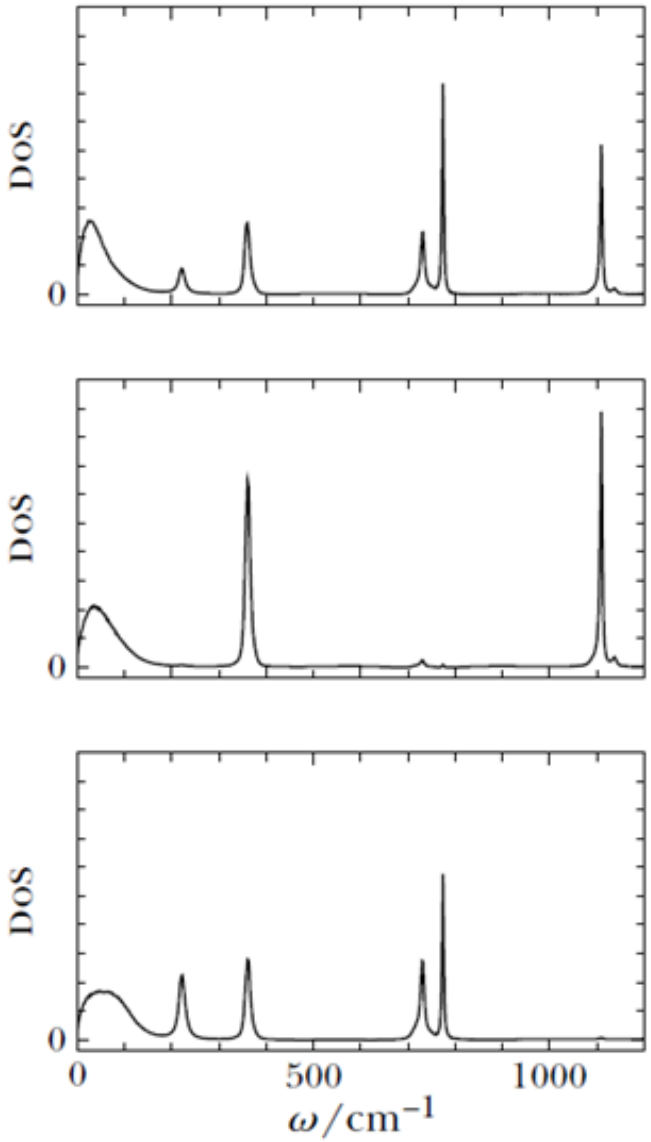
Função de correlação de velocidade





Transformada de Fourier

$$C(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C(t) e^{-i\omega t} \mathrm{d}t$$



Espectro IR e a Função de Correlação de Dipolo

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \mathbf{M}(0).\mathbf{M}(t) \rangle \; e^{-i\omega t} \mathrm{d}t$$

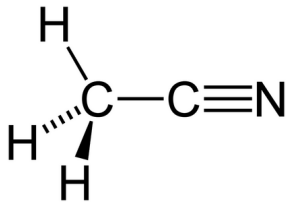
$$\mathbf{M}(0).\mathbf{M}(t) = \left(\sum_{i=1}^{N} \boldsymbol{\mu}_i(0) \right) \left(\sum_{j=1}^{N} \boldsymbol{\mu}_j(t) \right)$$

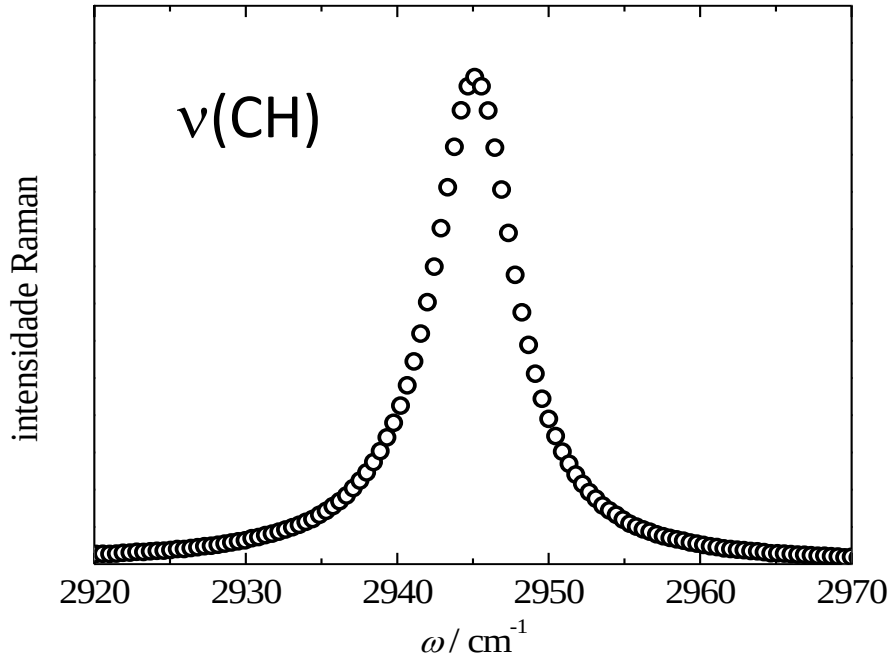
quando não há correlação entre $\boldsymbol{\mu}_i$ e $\boldsymbol{\mu}_j$

$$\langle \mathbf{M}(0).\mathbf{M}(t) \rangle = \langle \sum_{i=1}^{N} \boldsymbol{\mu}_i(0).\boldsymbol{\mu}_i(t) \rangle$$

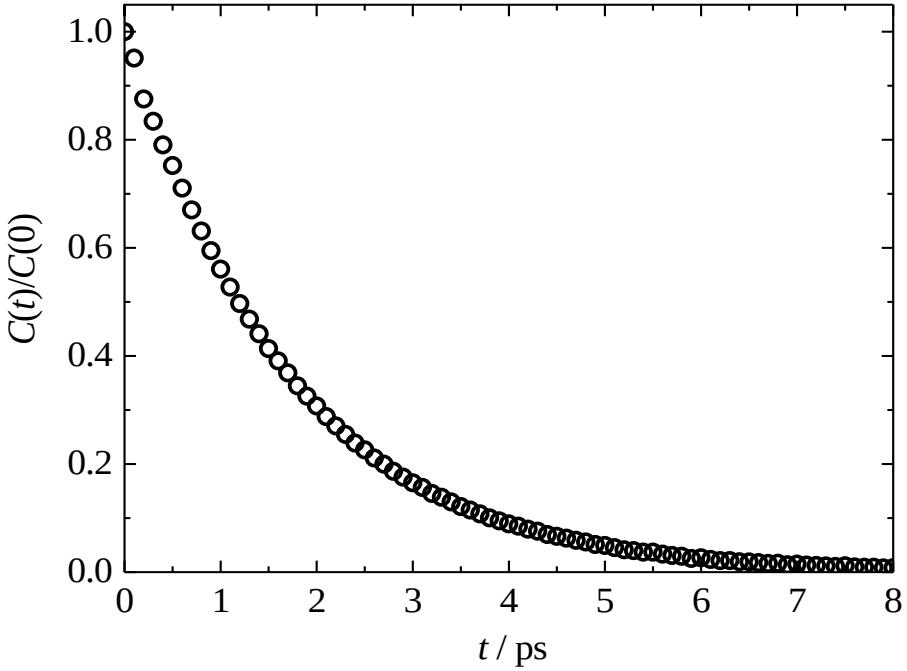
Vibração de molécula isolada: $\boldsymbol{\mu}_i(t) = \left(\frac{\mathrm{d}\mu}{\mathrm{d}Q} \right)_e Q(t) \propto \cos(2\pi\nu t)$

D. A. McQuarrie, *Statistical Mechanics*, Univ. Sc., 2000





Transformada de Fourier

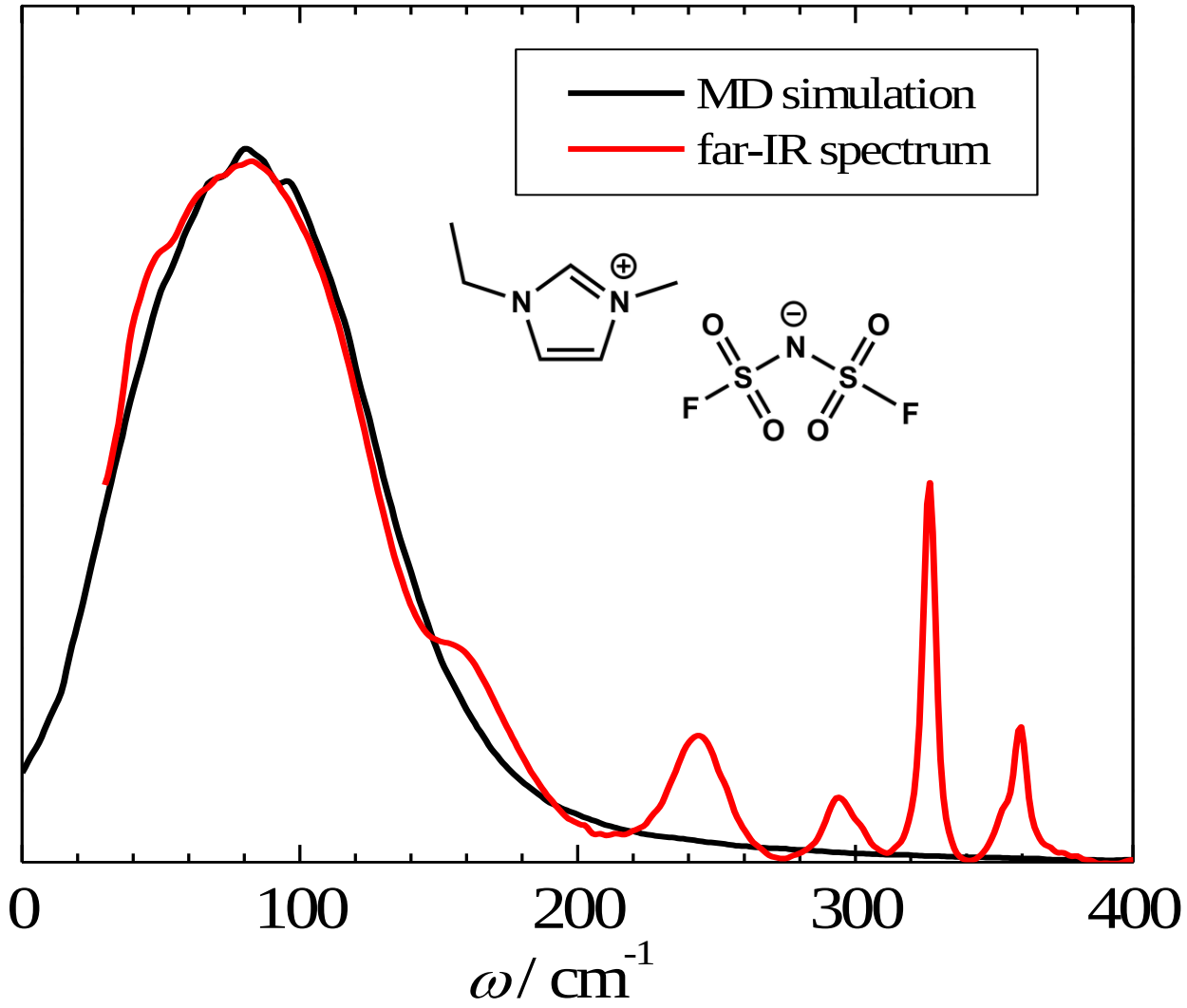


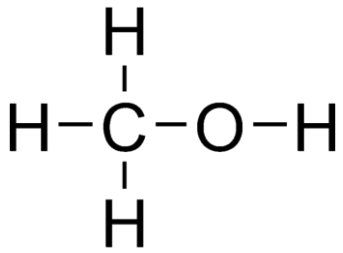
Espectro no Infravermelho Distante (far-IR)

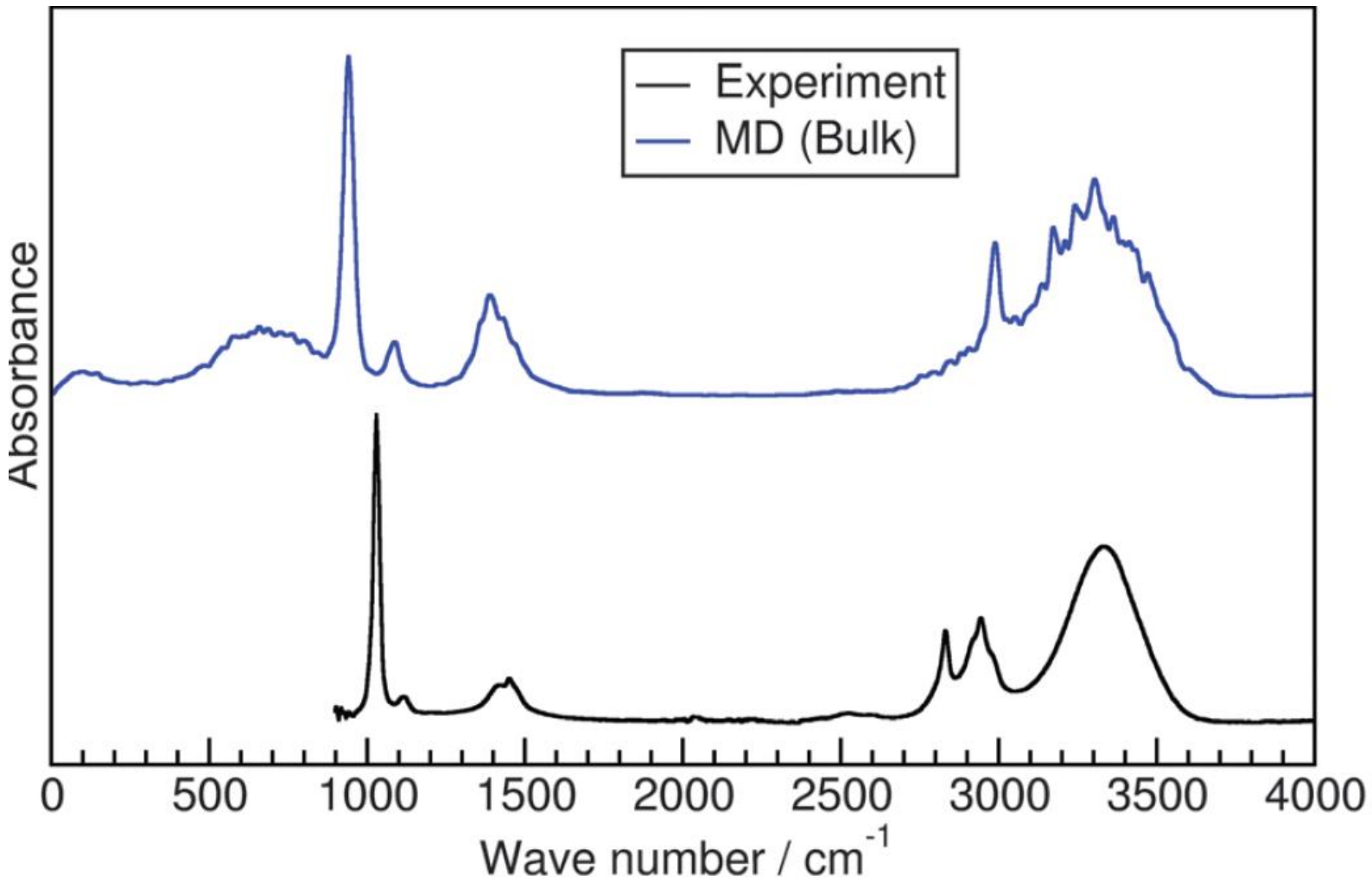
Função de correlação no tempo de corrente de carga:

$$C_{\mathbf{J}}(t) = \langle \mathbf{J}(0).\mathbf{J}(t) \rangle$$

$$\mathbf{J}(t) = \sum_i q_i \mathbf{v}_i(t)$$

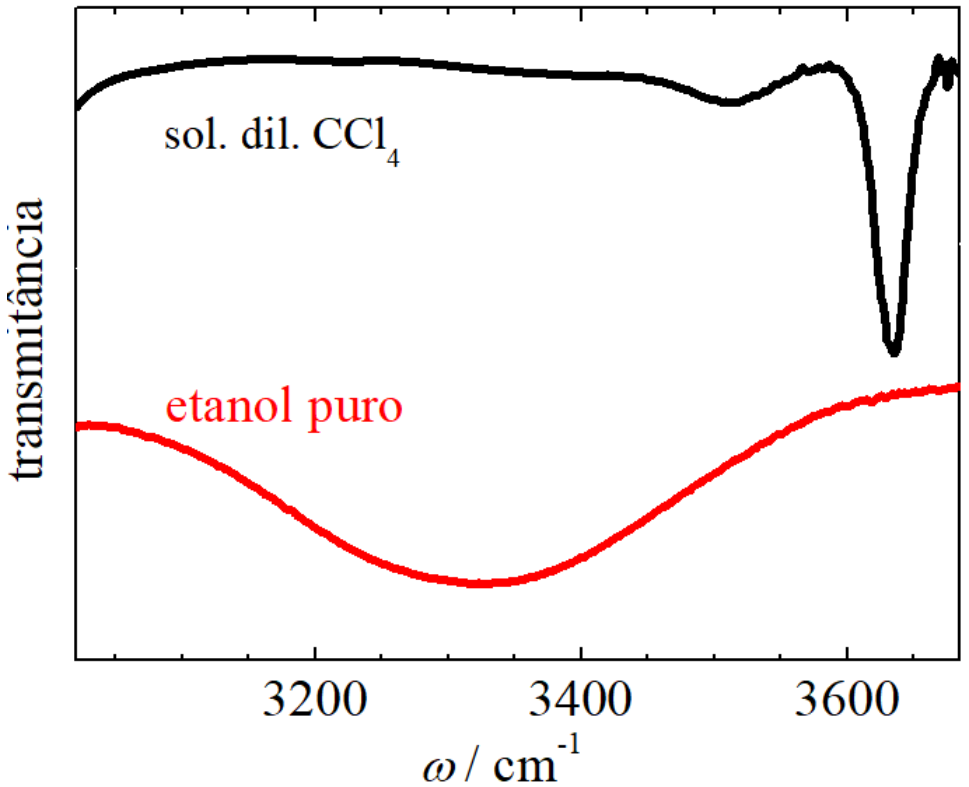


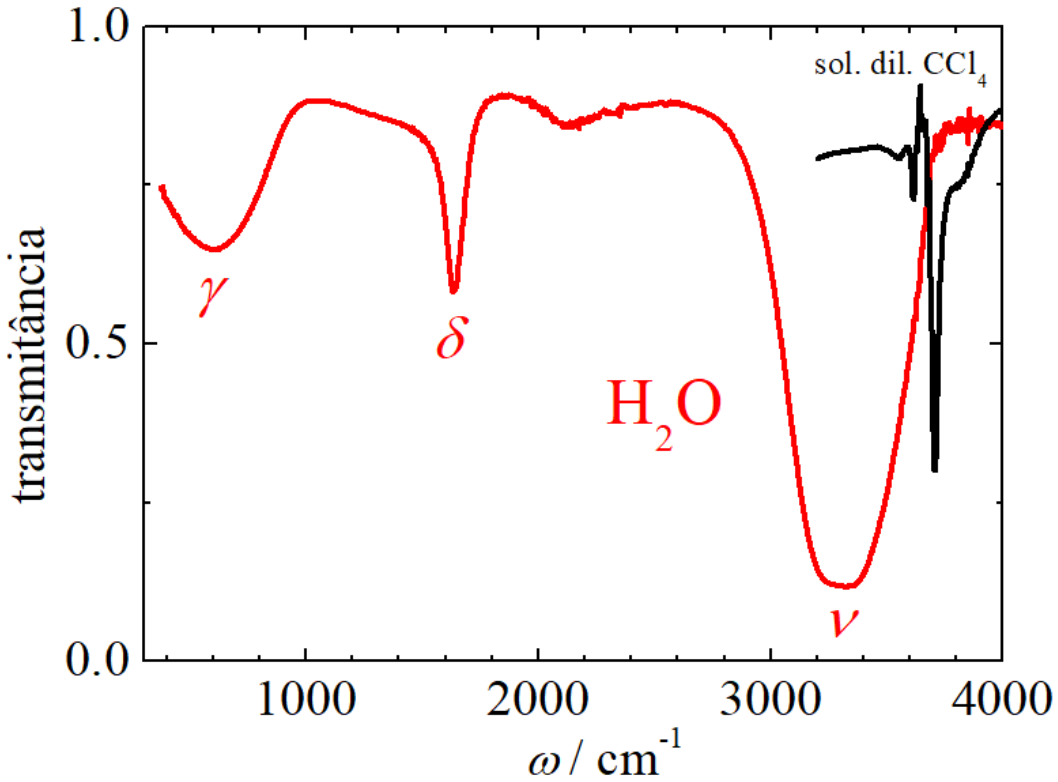


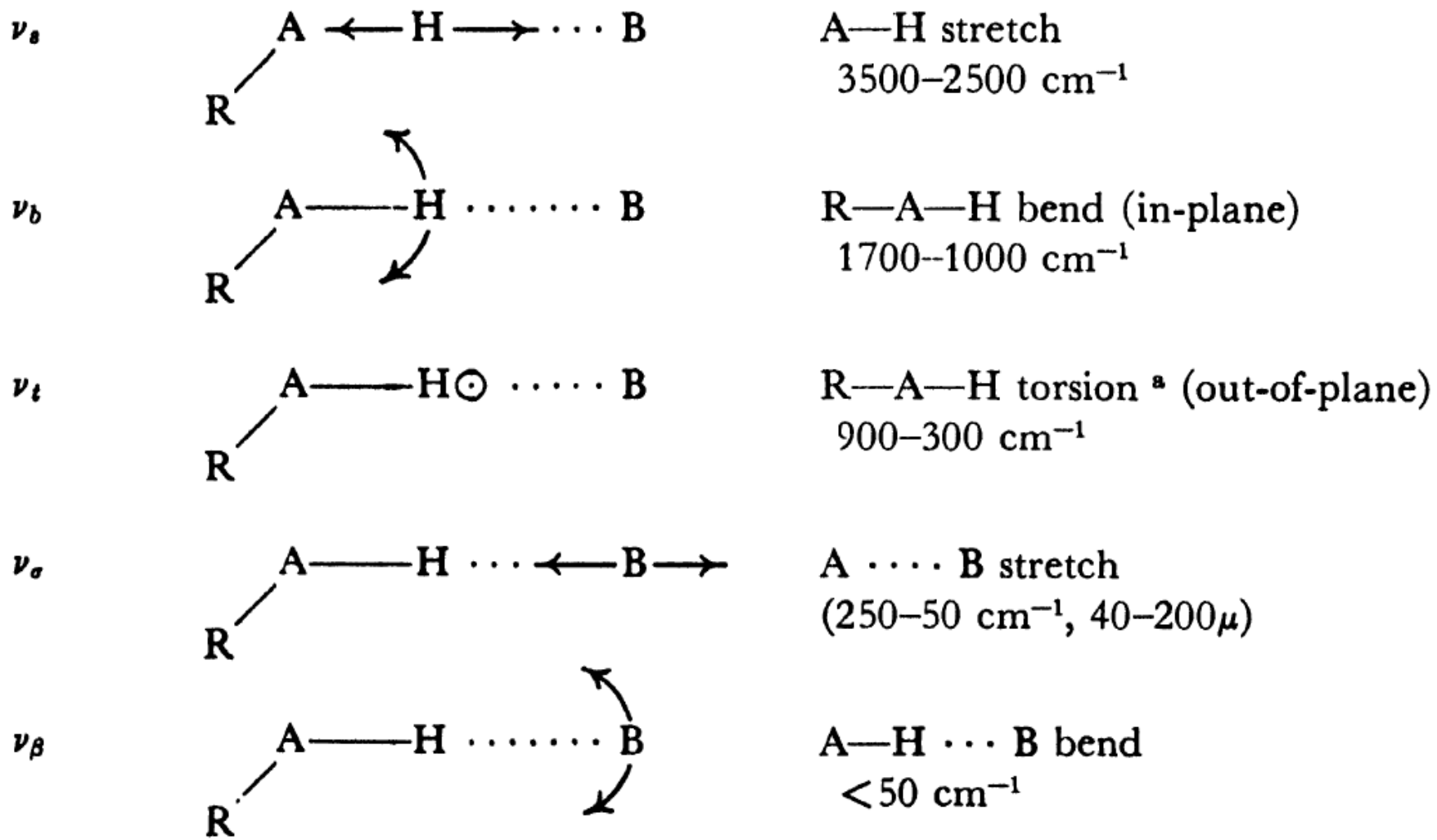


M. Thomas, M. Brehm, R. Fligg, P. Vohringer, B. Kirchner, *Phys. Chem. Chem. Phys.* 15, 6608 (2013)

Espectroscopia Infravermelho e Ligação de Hidrogênio



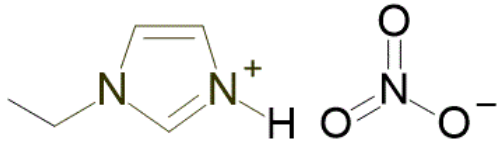




[a] The symbol ⊙ indicates a vibrational movement of the hydrogen atom perpendicular to the RAB plane.

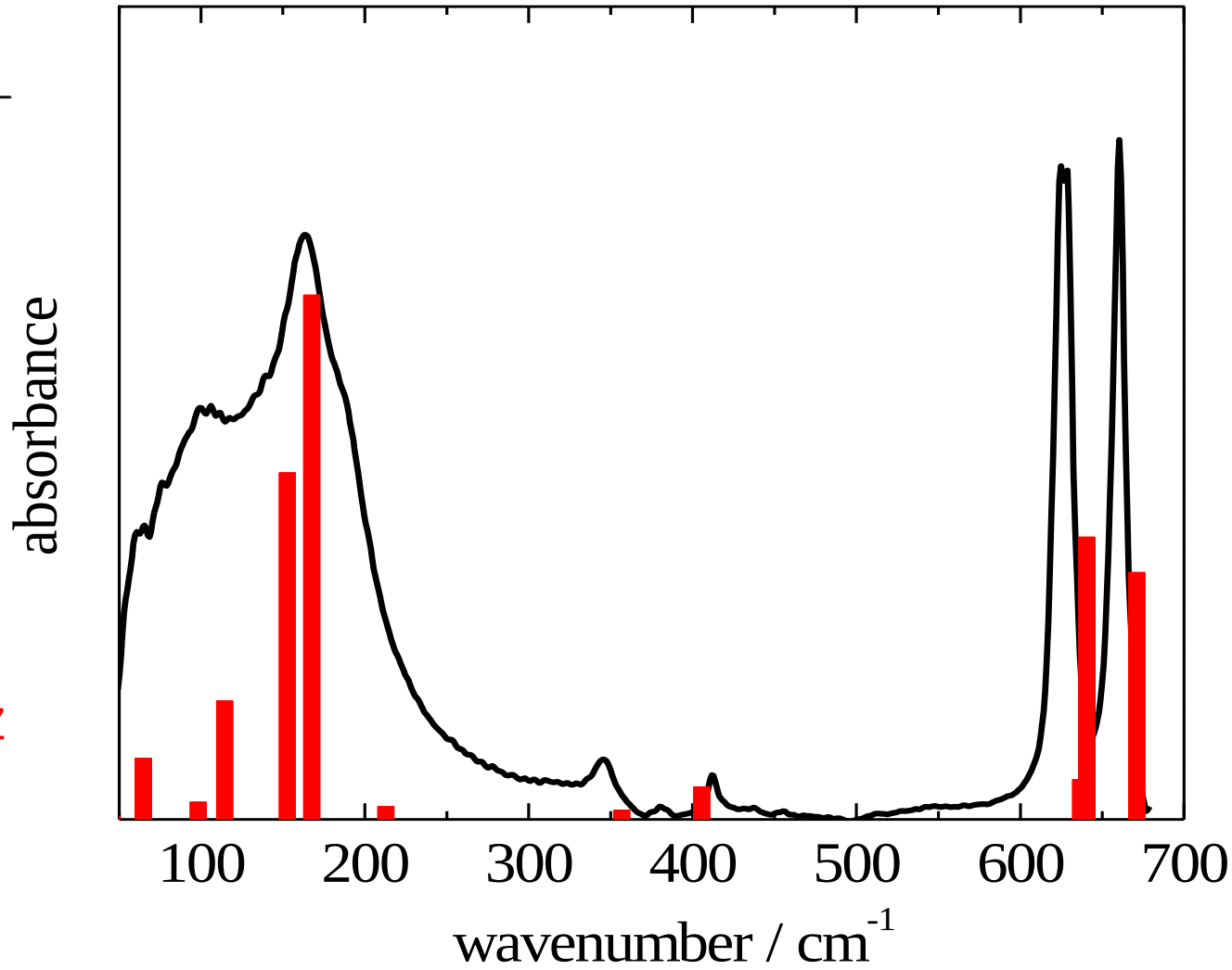
G. C. Pimentel, A. L. McClellan, *The Hydrogen Bond*, Freeman Co., 1960

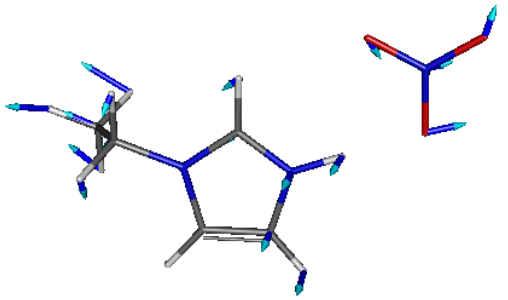
Espectro no Infravermelho Distante (far-IR)



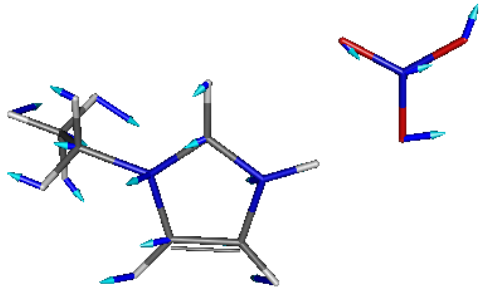
1-ethylimidazole nitrate

DFT
B3LYP-D3/aug-cc-PVDZ
CPCM, $\varepsilon = 24.3$



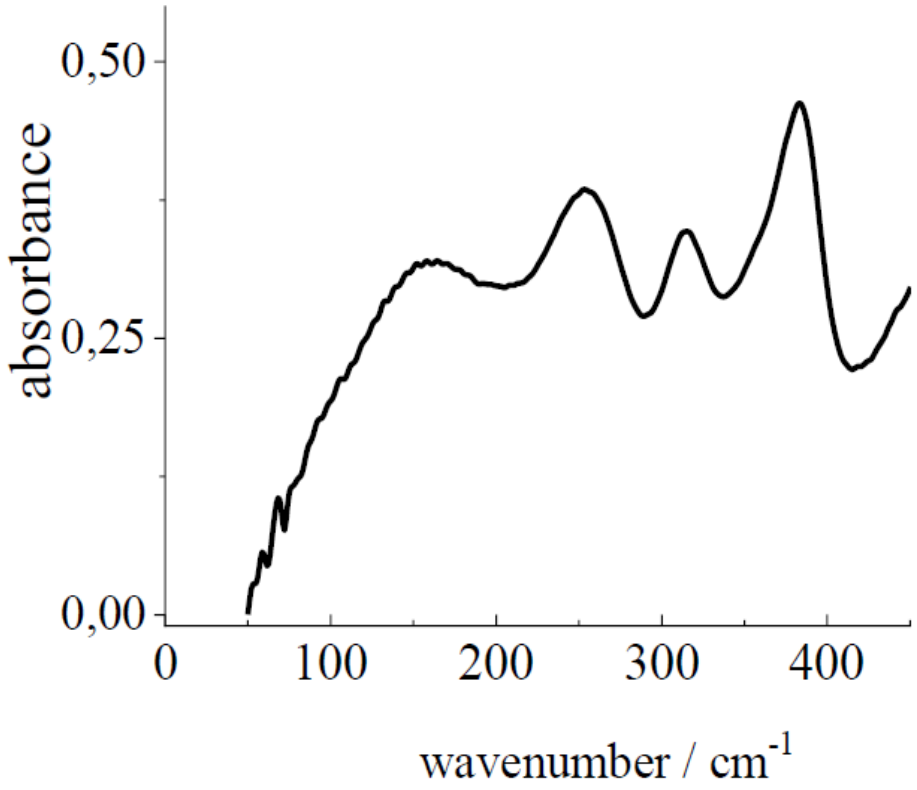


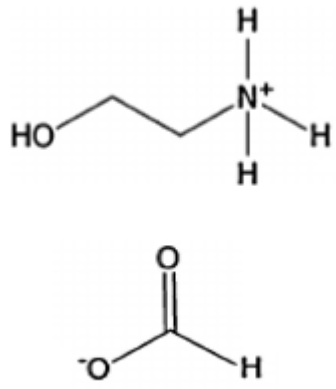
153 cm^{-1}



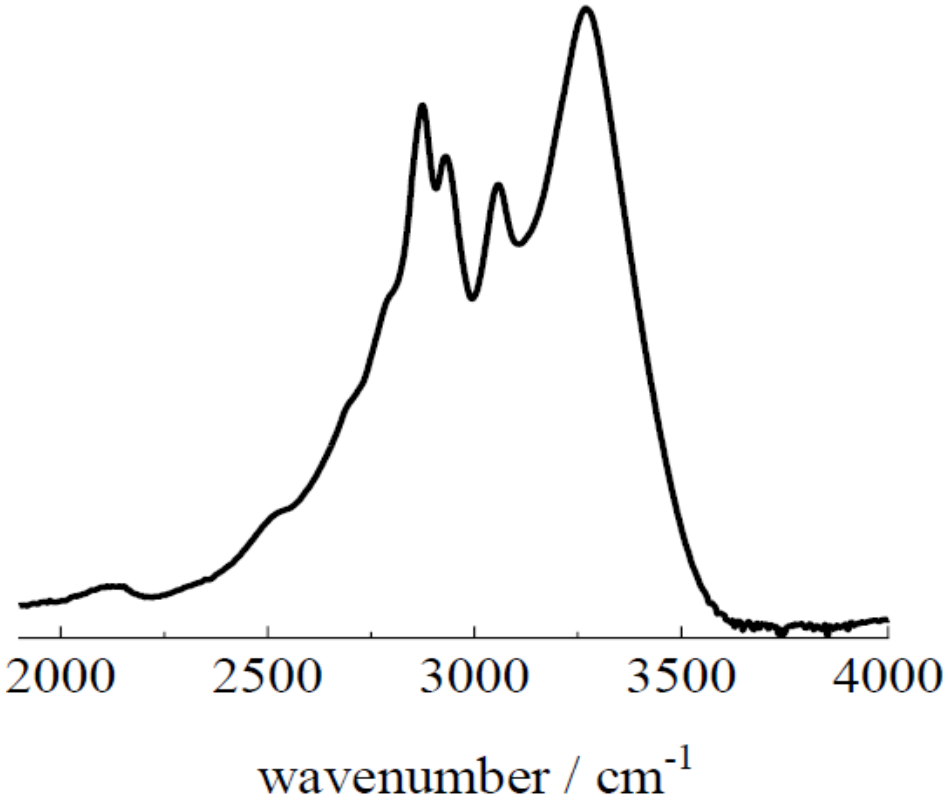
168 cm^{-1}

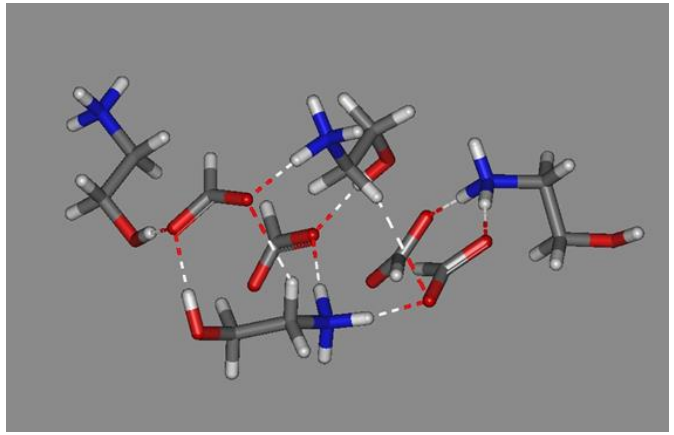
A case study...



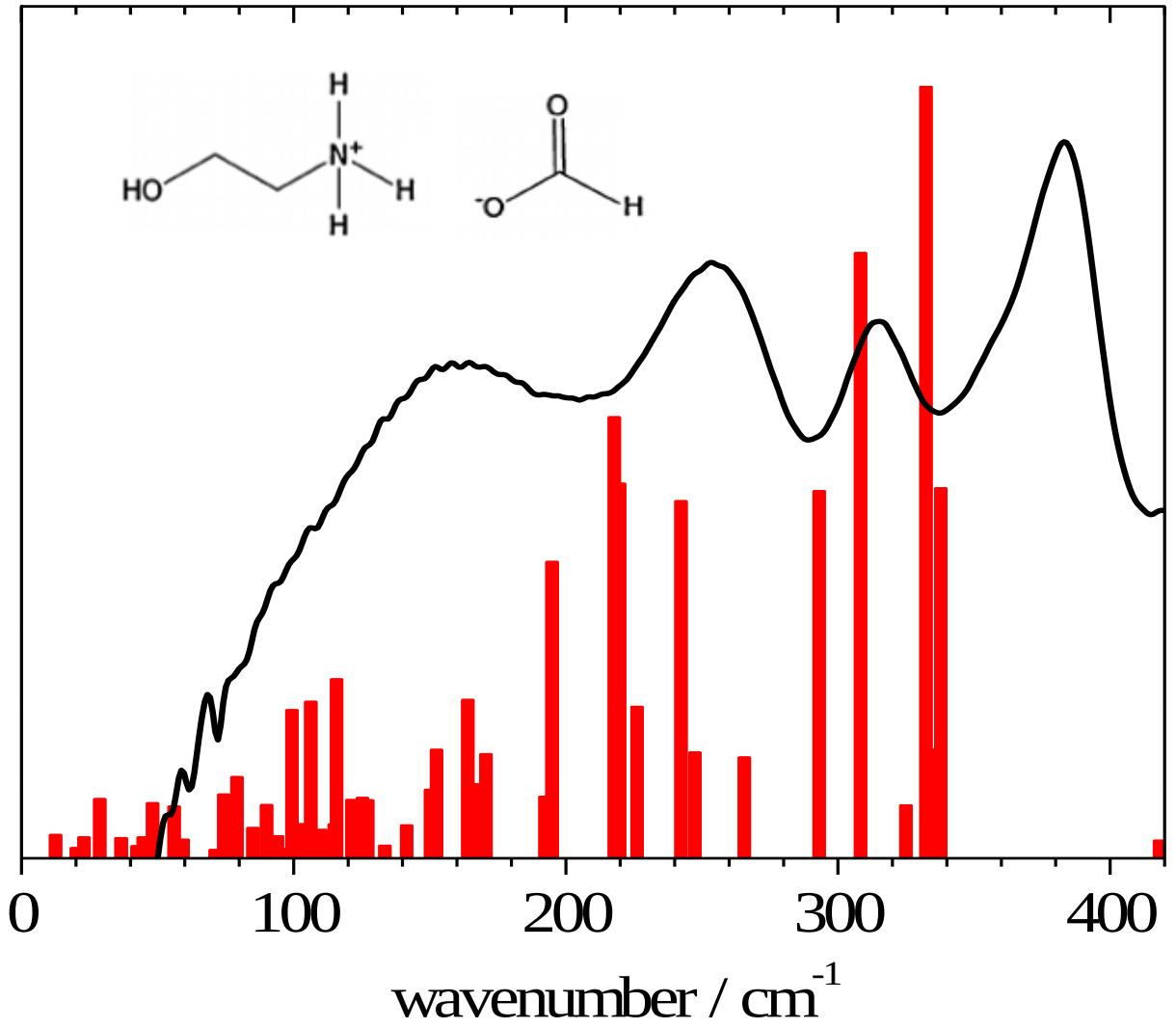


2-hydroxyethylammonium formate



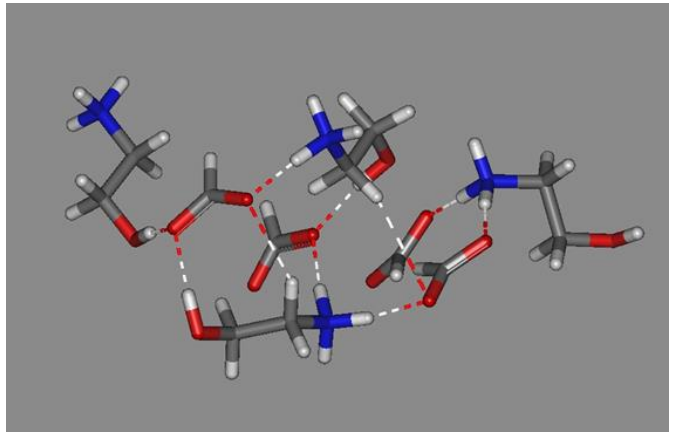


DFT/ B3LYP-D3/def2-TVZP
CPCM, $\varepsilon = 61.0$

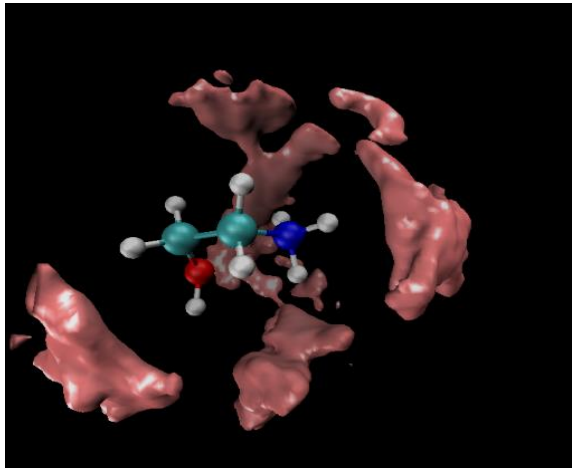


far-IR

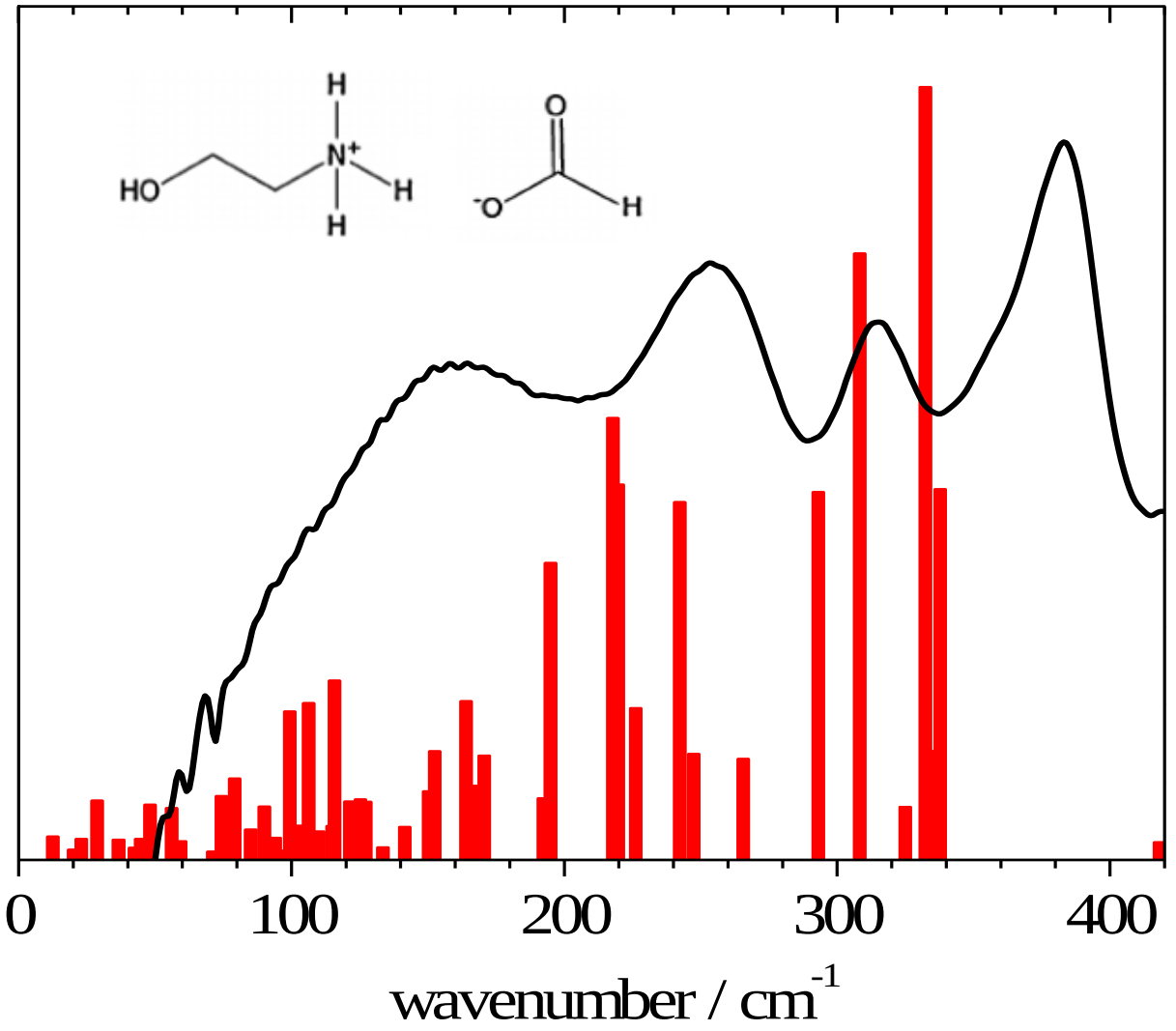
DFT



DFT/ B3LYP-D3/def2-TVZP
CPCM, $\varepsilon = 61.0$

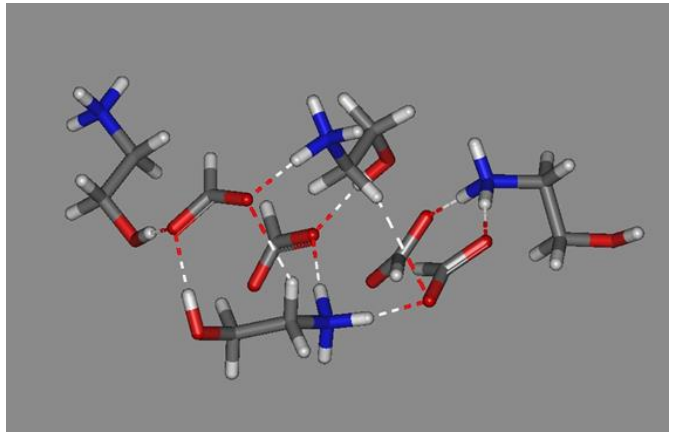


ab initio MD simulation (AIMD)

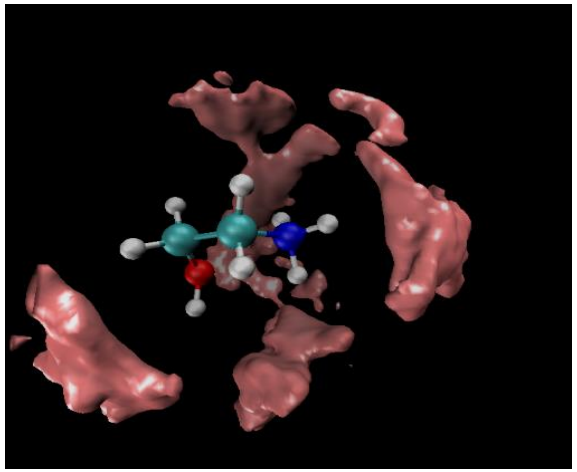


far-IR

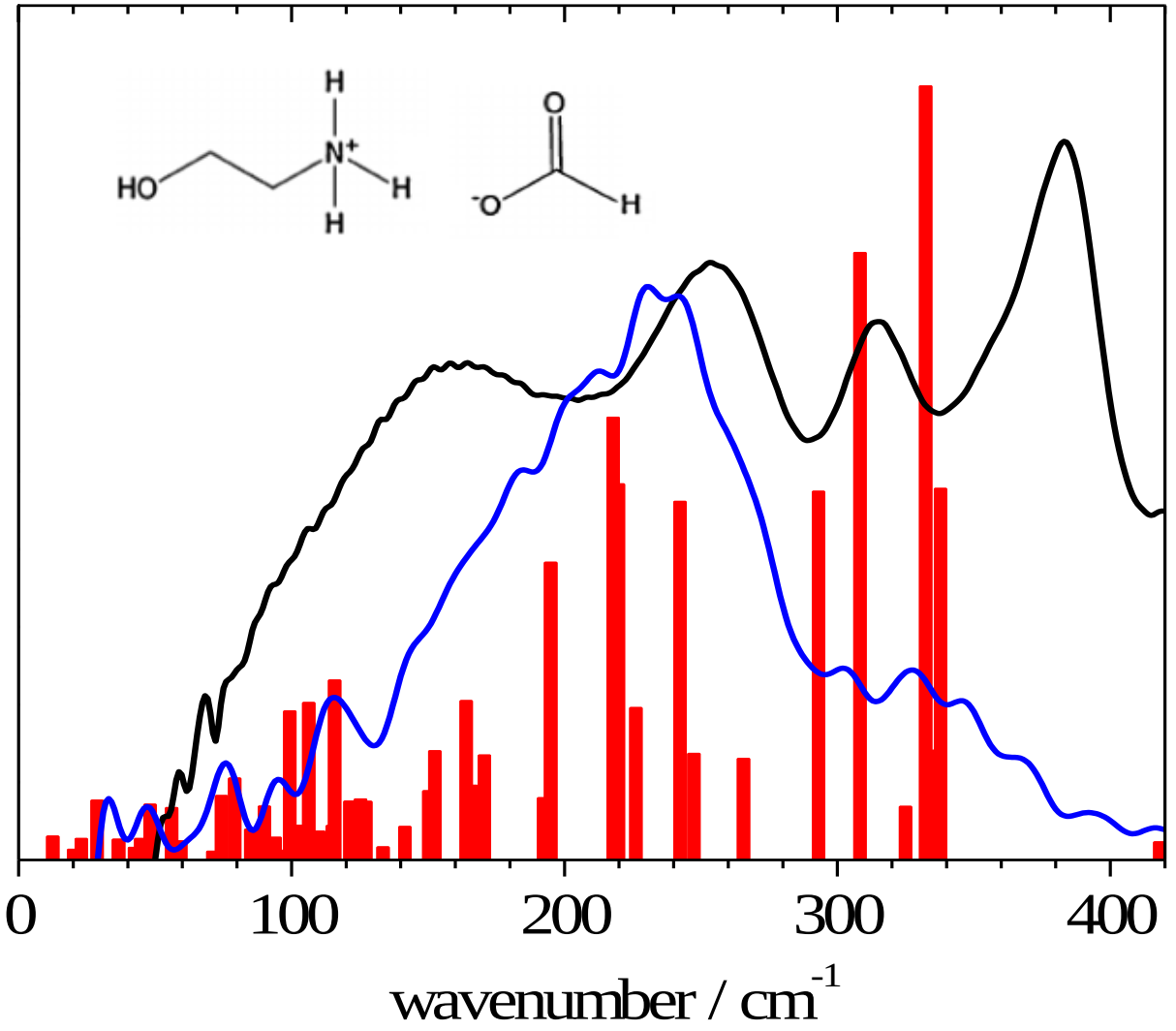
DFT



DFT/ B3LYP-D3/def2-TVZP
CPCM, $\varepsilon = 61.0$



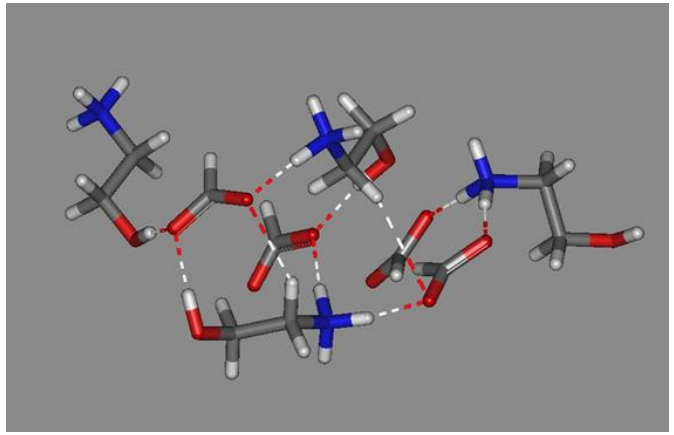
ab initio MD simulation (AIMD)



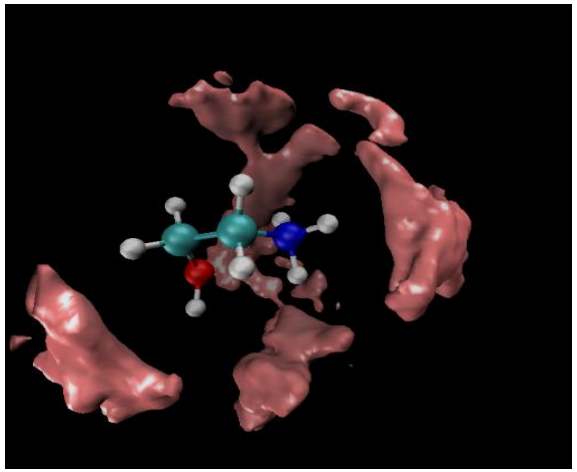
far-IR

DFT

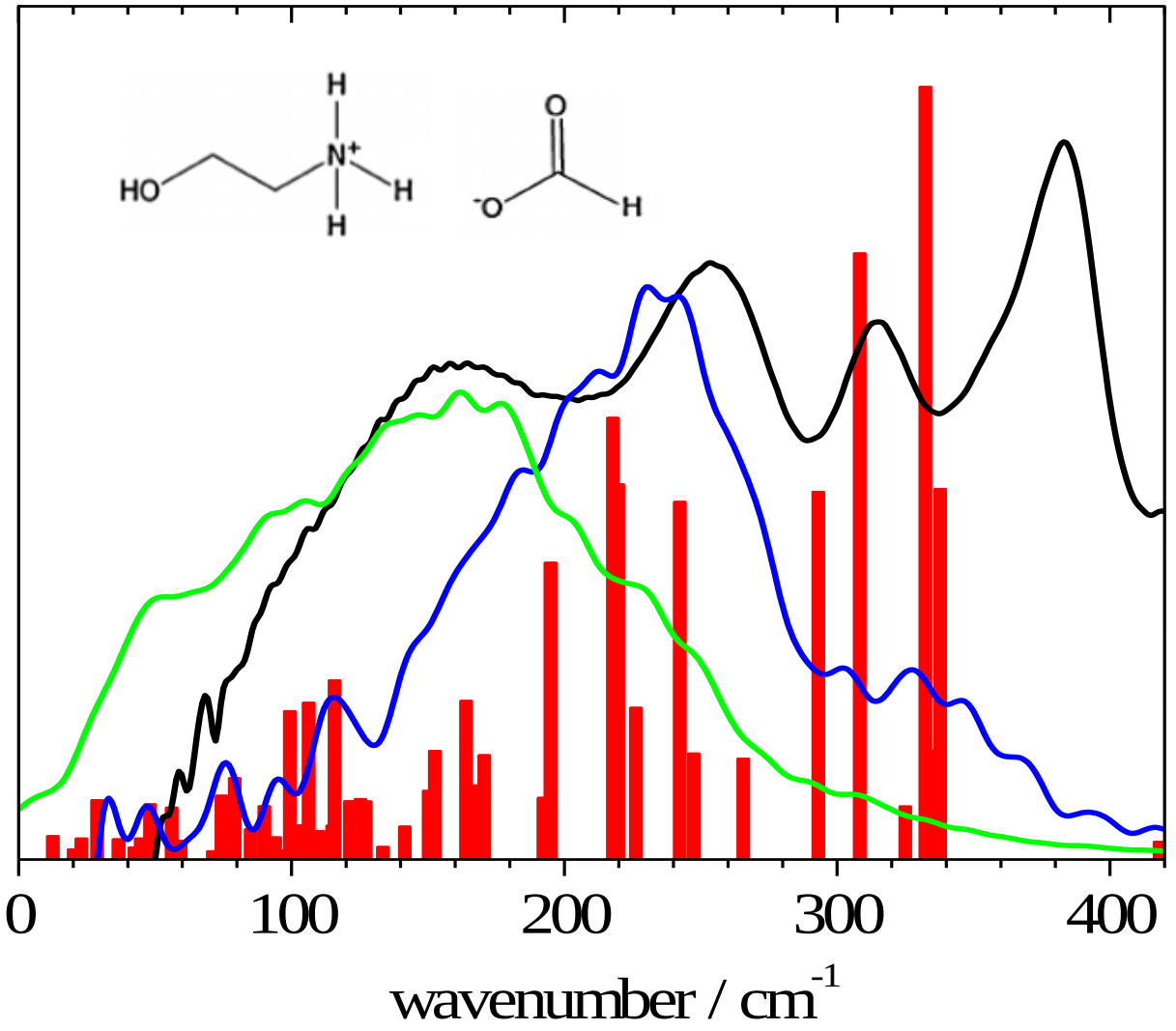
AIMD
$N_{cation} - O_{anion}$



DFT/ B3LYP-D3/def2-TVZP
CPCM, $\varepsilon = 61.0$



ab initio MD simulation (AIMD)

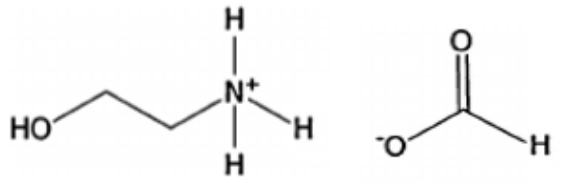


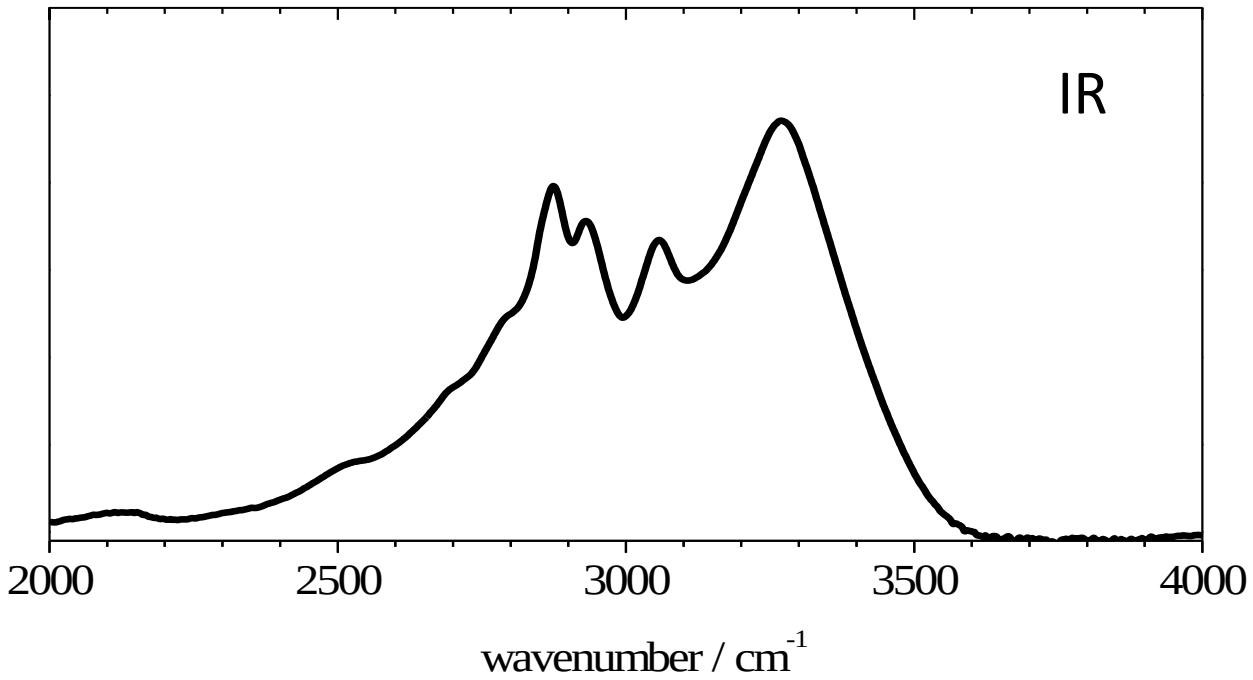
far-IR

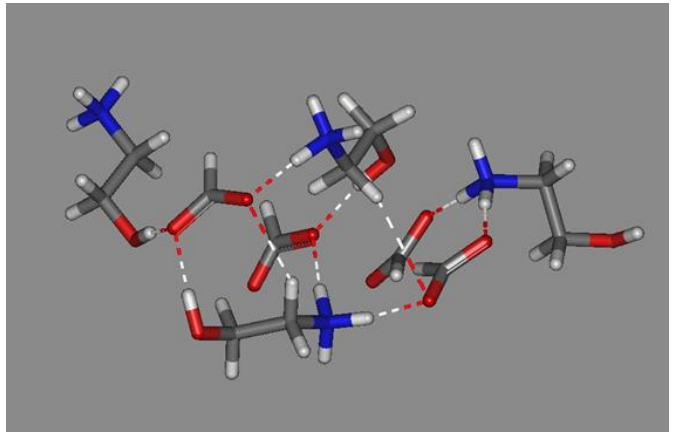
DFT

AIMD
$N_{cation} - O_{anion}$

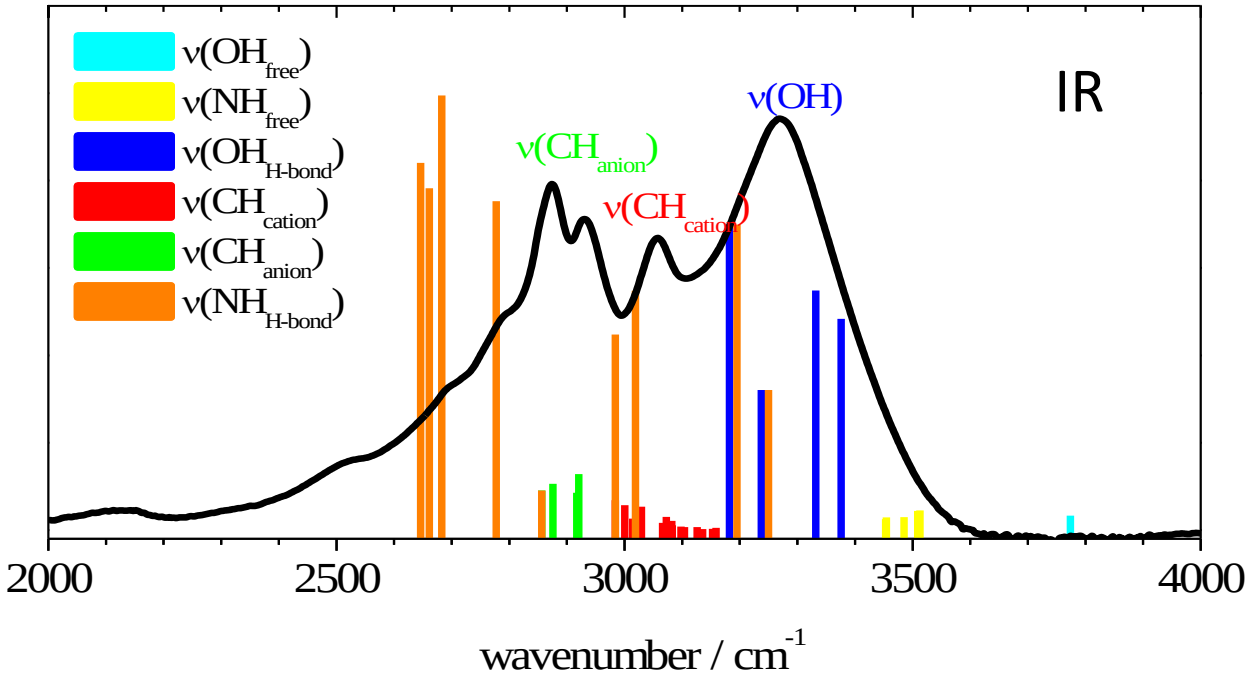
AIMD
$veloc._{anion}$

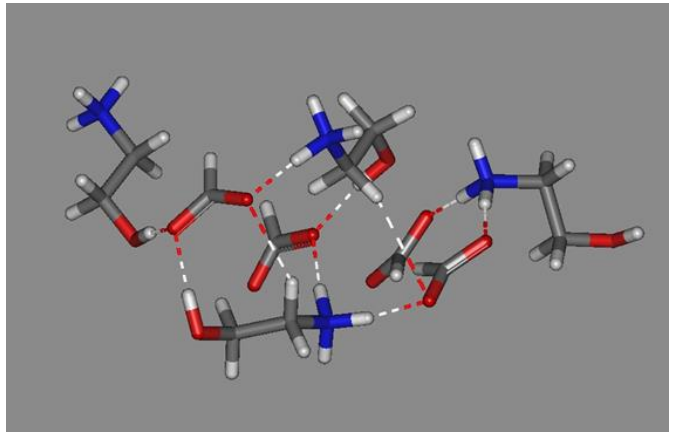

H
HO
N+
H
H
O
-O
H


IR
2000
2500
3000
3500
4000
wavenumber / cm-1

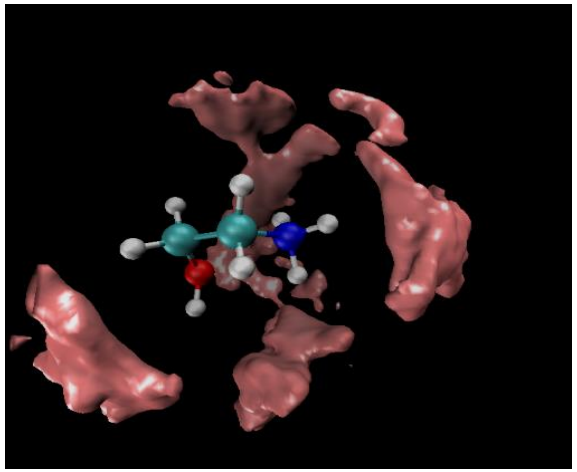


DFT/ B3LYP-D3/def2-TVZP
CPCM, $\varepsilon = 61.0$

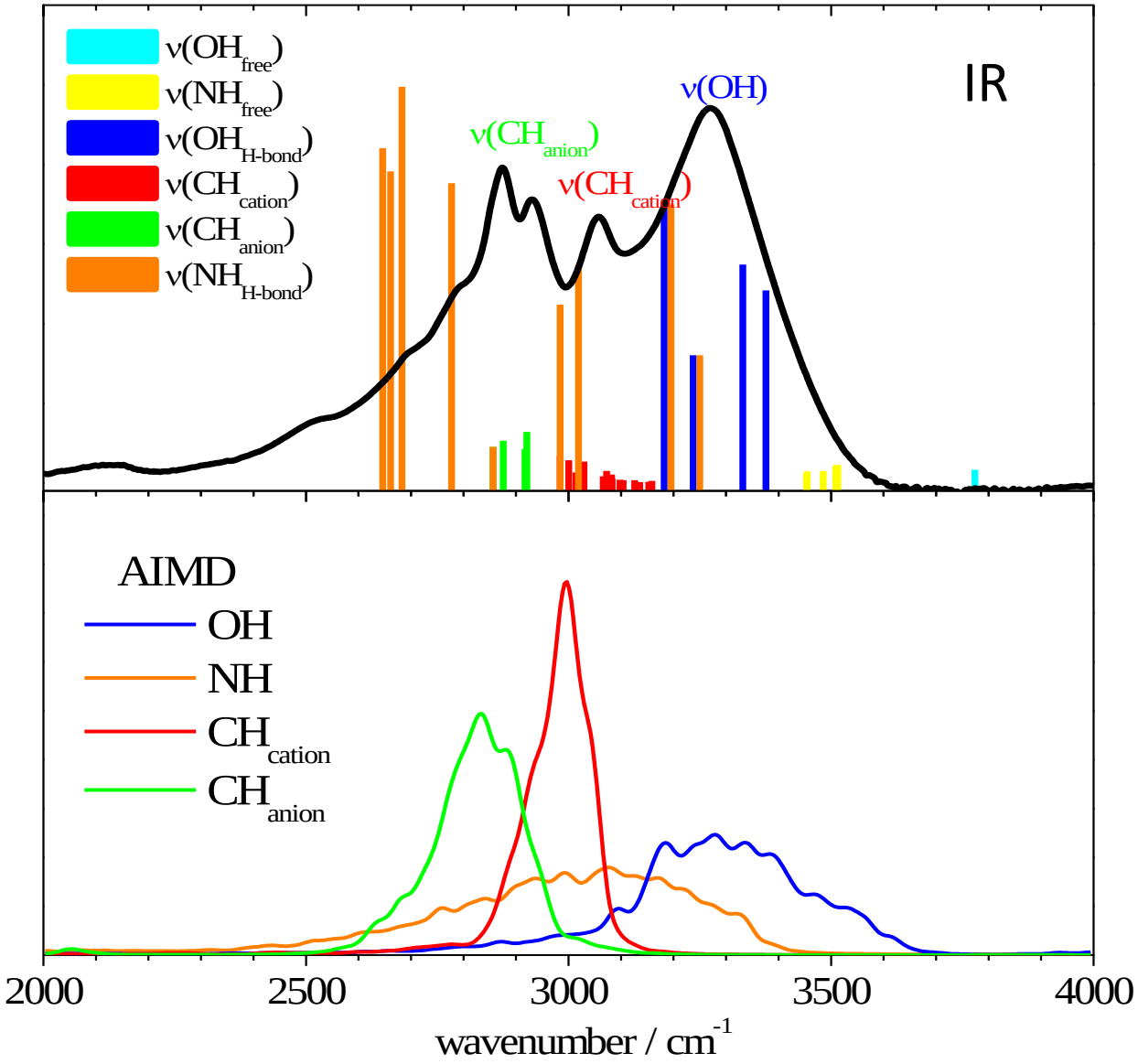




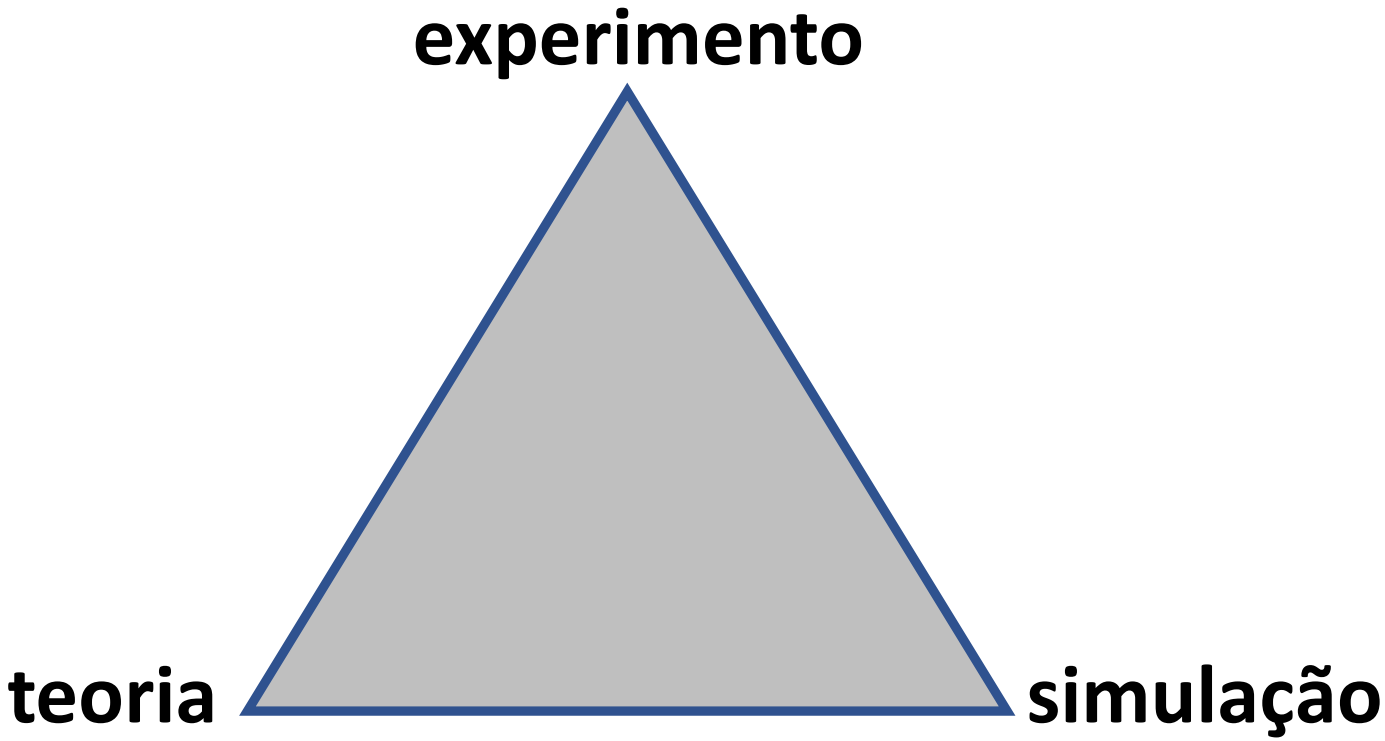
DFT/ B3LYP-D3/def2-TVZP
CPCM, $\varepsilon = 61.0$



ab initio MD simulation (AIMD)



Considerações Finais:




Universidade de São Paulo
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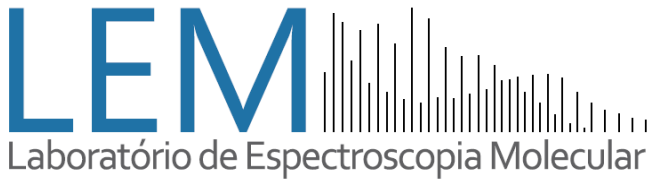
LEM
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FAPESP
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CAPES