Towards ab-initio Anharmonic Vibrational Circular Dichroism Spectra in Condensed Phase

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Anharmonic Transition Electric and Magnetic Dipoles for solvated systems described by means of the PCM with the inclusion of direct, indirect, local field and vibrational nonequilibrium solvent effects

By following Ref.[1], and extending the treatment to PCM solutes, the transition integral for a vibrational fundamental band ($\langle\, P^a \,\rangle^{sol}_{0,1_i}$) is given by:

$$
\begin{aligned}
\langle\, P^a \,\rangle^{sol}_{0,1_i} = {} & s_0 \times \mathrm{S} \times P^a_i + \tfrac{s_2}{2} \textstyle\sum_j \left\{ P^a_{jij} + P^a_{ijj} + \mathrm{S} P^a_{jji} \right\} - \tfrac{s_0}{8} \textstyle\sum_{jk} k_{ijkk} P^a_j \left[\frac{1}{\omega_i+\omega_j} - \frac{\mathrm{S}(1-\delta_{ij})}{\omega_i-\omega_j} \right] \\
& - \tfrac{s_1}{8} \textstyle\sum_{jk} \left\{ k_{ijk} \left(P^a_{jk} + P^a_{kj} \right) \left(\frac{1}{\omega_i+\omega_j+\omega_k} - \frac{\mathrm{S}}{\omega_i-\omega_j-\omega_k} \right) + \frac{k_{jkk}}{\omega_j} \left[2\mathrm{S} P^a_{ji} + (1+\mathrm{S}) P^a_{ij} \right] \right\} \\
& + \tfrac{s_0}{2} \textstyle\sum_{jk} \left(\sum_\tau B^\tau_e \zeta^\tau_{ik} \zeta^\tau_{jk} \right) P^a_j \left\{ \frac{\sqrt{\omega_i \omega_j}}{\omega_k} \left(\frac{1}{\omega_i+\omega_j} + \frac{\mathrm{S}(1-\delta_{ij})}{\omega_i-\omega_j} \right) - \frac{\omega_k}{\sqrt{\omega_i \omega_j}} \left(\frac{1}{\omega_i+\omega_j} - \frac{\mathrm{S}(1-\delta_{ij})}{\omega_i-\omega_j} \right) \right\} \\
& + \tfrac{s_0}{16} \textstyle\sum_{jkl} k_{ikl} k_{jkl} P^a_j \left\{ (1-\delta_{ij})(1-\delta_{ik})(1-\delta_{il}) \left[\frac{1}{(\omega_i+\omega_j)(\omega_j+\omega_k+\omega_l)} - \frac{\mathrm{S}}{(\omega_i-\omega_j)(\omega_j+\omega_k+\omega_l)} \right.\right. \\
& \qquad + \frac{\mathrm{S}}{(\omega_i+\omega_k+\omega_l)(\omega_j+\omega_k+\omega_l)} - \frac{1}{(\omega_i-\omega_k-\omega_l)(\omega_j+\omega_k+\omega_l)} + \frac{\mathrm{S}}{(\omega_i-\omega_j)(\omega_i-\omega_k-\omega_l)} \\
& \qquad \left. + \frac{1}{(\omega_i+\omega_j)(\omega_i+\omega_k+\omega_l)} \right] \\
& \quad + \delta_{ij}(1+\delta_{ik})(1-\delta_{il}) \left[\frac{1}{2\omega_i(\omega_i+\omega_k+\omega_l)} - \frac{1}{2\omega_i(\omega_i-\omega_k-\omega_l)} + \frac{\mathrm{S}}{2(\omega_i+\omega_k+\omega_l)^2} \right. \\
& \qquad \left. - \frac{\mathrm{S}}{2(\omega_i-\omega_k-\omega_l)^2} \right] \\
& \quad + (1-\delta_{ij})(1-\delta_{ik})\delta_{il} \left[\frac{1}{\omega_k(\omega_i+\omega_j)} + \frac{2}{(2\omega_i+\omega_k)(\omega_i+\omega_j)} + \frac{3}{(\omega_i+\omega_j)(\omega_i+\omega_j+\omega_k)} \right. \\
& \qquad + \frac{\mathrm{S}}{(\omega_i-\omega_j)(\omega_i-\omega_j-\omega_k)} - \frac{2\mathrm{S}}{(\omega_i-\omega_j)(\omega_i+\omega_j+\omega_k)} - \frac{3\mathrm{S}}{\omega_k(\omega_i-\omega_j)} \\
& \qquad \left.\left. - \frac{\mathrm{S}}{\omega_k(\omega_i-\omega_j-\omega_k)} + \frac{2\mathrm{S}}{(2\omega_i+\omega_k)(\omega_i+\omega_j+\omega_k)} + \frac{3}{\omega_k(\omega_i+\omega_j+\omega_k)} \right] \right\} \\
& + k_{ijk} k_{llk} P^a_j \left\{ \frac{\delta_{ij}}{\omega_i \omega_k} \left(1 + \frac{\delta_{ik}\delta_{il}(6-4\mathrm{S})}{9} \right) \right. \\
& \quad + (1-\delta_{ij})(1-\delta_{ik})(1-\delta_{il}) \left[\frac{1}{(\omega_i+\omega_j)(\omega_i+\omega_j+\omega_k)} + \frac{1}{\omega_k(\omega_i+\omega_j)} - \frac{\mathrm{S}}{\omega_k(\omega_i-\omega_j)} \right. \\
& \qquad \left. + \frac{\mathrm{S}}{(\omega_i-\omega_j)(\omega_i-\omega_j-\omega_k)} + \frac{1}{\omega_k(\omega_i+\omega_j+\omega_k)} - \frac{\mathrm{S}}{\omega_k(\omega_i-\omega_j-\omega_k)} \right] \\
& \quad + \delta_{ik}(1-\delta_{ij}) \left[(1+\delta_{il}) \left(\frac{1}{(2\omega_i+\omega_j)(\omega_i+\omega_j)} - \frac{\mathrm{S}}{\omega_i(\omega_i-\omega_j)} + \frac{1}{\omega_i(2\omega_i+\omega_j)} \right) \right. \\
& \qquad + \delta_{il} \left(\frac{1}{3\omega_i(\omega_i+\omega_j)} + \frac{\mathrm{S}}{3\omega_i(2\omega_i+\omega_j)} - \frac{\mathrm{S}}{(\omega_i-\omega_j)(2\omega_i+\omega_j)} \right) \\
& \qquad \left.\left. + \frac{1}{\omega_i(\omega_i+\omega_j)} - \frac{\mathrm{S}}{\omega_j(\omega_i-\omega_j)} + \frac{\mathrm{S}}{\omega_i \omega_j} \right] \right\}
\end{aligned}
$$

with δ_{ij} is the Kronecker delta. Similarly, the overtones ($\langle P^a \rangle_{0,2_i}$) and combination bands ($\langle P^a \rangle_{0,1_i 1_j}$)

are given by,

$$\langle P^a \rangle^{sol}_{0,(1+\delta_{ij})_i(1-\delta_{ij})_j} = \left(\sqrt{2}+(1-\sqrt{2})\delta_{ij}\right) \times \left[\frac{s_1 \times \mathrm{S}}{2}\left(P^a_{ij}+P^a_{ji}\right)+\frac{s_0}{4}\sum_k\left(\frac{\mathrm{S}}{\omega_i+\omega_j-\omega_k}-\frac{1}{\omega_i+\omega_j+\omega_k}\right)\right] \tag{1}$$

By following again the treatment reported in Ref.[1], the magnetic transition dipole for PCM solutes becomes:

$$\langle\, m^a \,\rangle^{sol}_{1_i,0} = -2\langle\, P^a \,\rangle^{sol}_{0,1_i} + 2s_2 \textstyle\sum_j \mathrm{P}^a_{ijj}$$

$$\langle\, m^a \,\rangle^{sol}_{(1+\delta_{ij})_i(1-\delta_{ij})_j,0} = -2\langle\, P^a \,\rangle^{sol}_{0,(1+\delta_{ij})_i(1-\delta_{ij})_j}$$

In the previous equations, where specified to the transition electric dipole moment, all the P^as quantities refer to derivatives of the so-called "effective" electric dipole moment,[2] which introduces local field effects. Such derivatives are calculated with respect to non-equilibrium normal modes and the vibrational nonequilibrium free energy is differentiated to yield the harmonic frequencies ω_js and the cubic and quartic force constants k_{ijk} and k_{ijkl}. B^τ_e is the diagonal inertia tensor of the molecule at equilibrium geometry and ζ^τ_{ij}, the Coriolis constant coupling modes i and j along the rotation axis I_τ. s_0, s_1 and s_2 are constant factors and S represents the sign and is +1 in case of the electric transition dipole moment and -1 in the case of the magnetic transition dipole moment. s_0, s_1 and s_2 are $1/\sqrt{2}$, $1/2\sqrt{2}$ and $1/6\sqrt{2}$ respectively for the electric transition dipole moment and $\imath\hbar/\sqrt{2}$, $\imath\hbar/\sqrt{2}$ and $\imath\hbar/2\sqrt{2}$ for the magnetic transition dipole moment. More details can be found in the cited reference.[1] Notice that, as an additional non-equilibrium effect, the PCM cavity is assumed to remain fixed during molecular vibrations, therefore when computing all the numerical and analytical derivatives involved in the previous equations, the program only moves the atoms, while the cavity remains immobile.

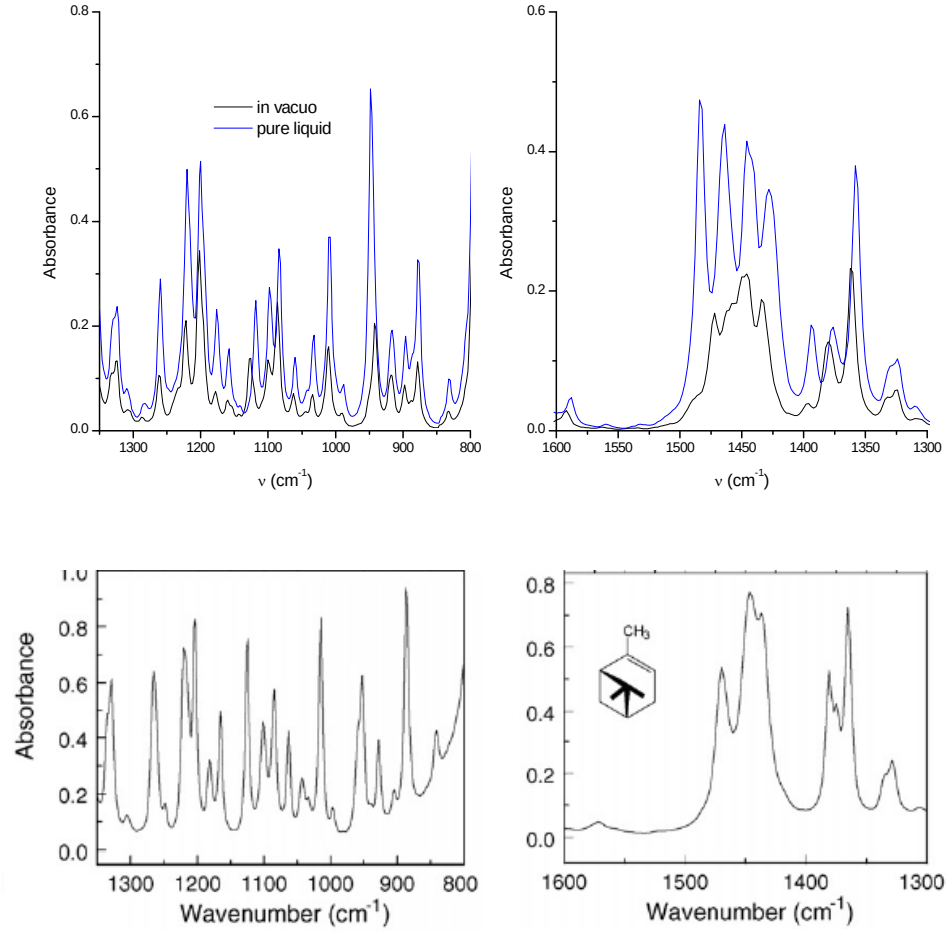

FIG. 1. Calculated Anharmonic IR Absorption Spectra of α-pinene in gas phase and pure liquid phase. Experimental spectra in the same range taken from Ref.[3] are also reported for the sake of a direct comparison.

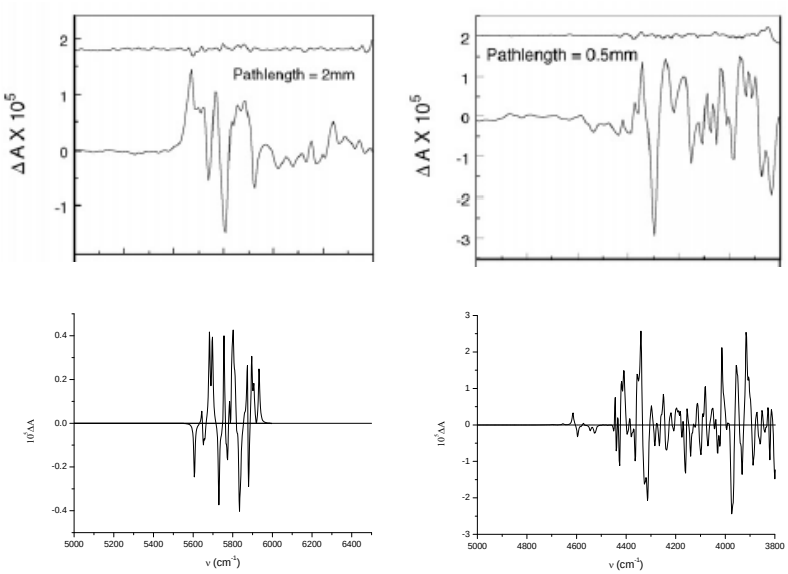

FIG. 2. Calculated Anharmonic VCD Spectra of pure liquid α-pinene. Experimental spectra in the same ranges taken from Ref.[3] are also reported for the sake of a direct comparison.

[1] Bloino, J.; Barone, V. A VPT2 route to vibrational averages and transition properties of molecules: General formulation and application to IR and VCD spectroscopies. *J. Chem. Phys.* **2012**, *136*, 124108.

[2] Cammi, R.; Cappelli, C.; Corni, S.; Tomasi, J. On the Calculation of Infrared Intensities in Solution within the Polarizable Continuum Model. *J. Phys. Chem. A* **2000**, *104*, 9874–9879.

[3] Guo, C.; Shah, R. D.; Dukor, R. K.; Freedman, T. B.; Cao, X.; Nafie, L. A. Fourier transform vibrational circular dichroism from 800 to 10,000 cm^{-}1: Near-IR-VCD spectral standards for terpenes and related molecules. *Vibr. Spectrosc.* **2006**, *42*, 254.