



Exploration of the Solvent Dependence of Raman optical activity



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Introduction

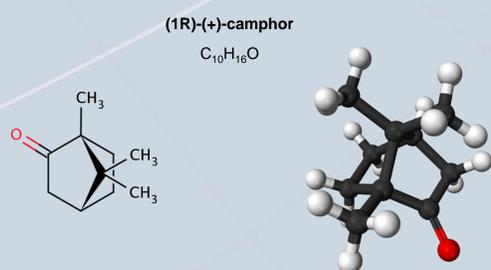
Raman optical activity (ROA) has proved to be very sensitive probe of molecular structure and conformational dynamics in solution. This method combines variability of scattering experiments with structural sensitivity of chiral spectroscopy (1). Spectral features of many systems including large proteins can be reasonably well interpreted with the help of *ab initio* simulations (2).

Simulations done in **vacuum** are often not realistic. **Implicit (dielectric) solvent** models represent important improvement. They are associated with a small increase of computational complexity only. Even such treatment is often not sufficient and the best results are obtained with **explicit inclusion** of solvent molecules in the calculations (3–5). Explicit modeling, however, is computationally demanding because of the size and averaging of involved solvent-solute clusters, and it may be superfluous for systems of medium polarity.

Aim

We have tested several solvent approaches on **camphor**, where the solvent effect is not obscured by molecular conformational freedom. Camphor is easily soluble in various solvents, including **methanol**, **cyclohexane** and **carbon tetrachloride**, in high concentrations. Experimental Raman and ROA spectra are compared with *ab initio* simulations using the implicit conductor-like screening model (COSMO) and clusters generated by molecular dynamics.

Comparison of experimental and calculated spectral intensities for various solvents enable better benchmark various computational approaches to solvent-solute interactions.



Methods

Computational methods

- Used version of Gaussian software: G09A02, G09D01
- Hybrid DFT functional: B3PW91/6-31G**
- MD calculations were performed within the TINKER software environment.
- Clusters with the first hydration sphere were created.

Experimental setup

- Back-scattering geometry
- Modulation scheme: SCP
- Excitation wavelength: 532 nm

Samples

- Concentration of camphor molecules in the solvent was 200 mg/ml for nonaqueous solvents and 1.00 mg/ml for water.
- Measured in rectangular 3x4 mm cell.

Results

Raman and ROA spectra of camphor in methanol

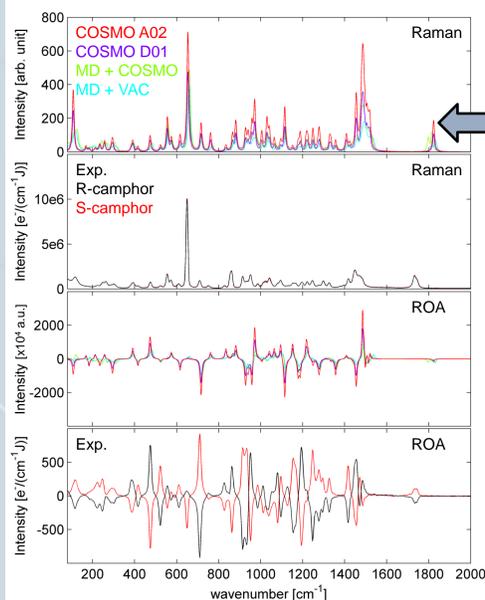


Figure 1. Experimental Raman and ROA spectra of (1R)-(+)- (black) and (1S)-(-) (red) camphor in methanol compared with simulations using the Gaussian A02 (red, a static cavity model) and D01 (purple, cavity adapted during vibrations) COSMO models, and with averaged spectra of five clusters in vacuum (blue) and D01/COSMO environment (green).

Raman and ROA spectra of camphor in cyclohexane

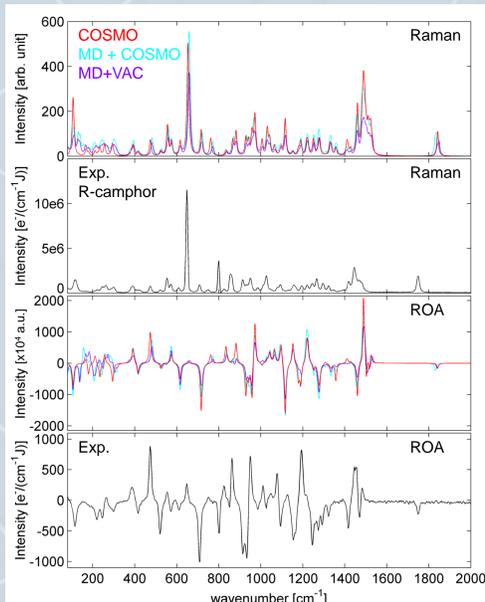


Figure 2. Experimental Raman and ROA spectra of (1R)-(+)-camphor (black) in cyclohexane compared with the simulation using the Gaussian D01/COSMO model (red), and with averaged spectra of five clusters in vacuum (purple) and D01/COSMO environment (blue).

Raman and ROA spectra of camphor in carbon tetrachloride

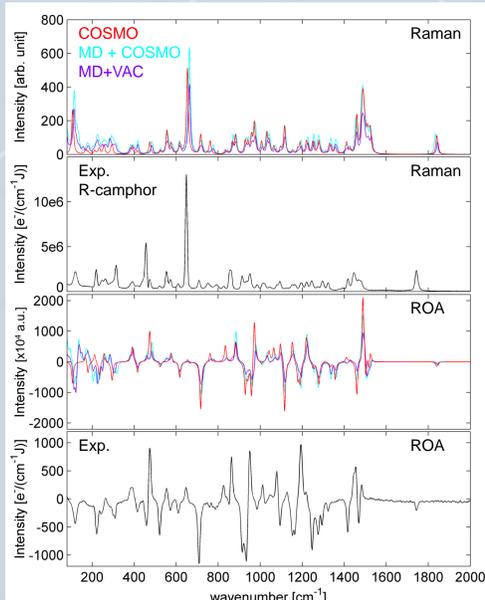


Figure 3. Simulated and experimental Raman and ROA spectra of (1R)-(+)-camphor (black) in carbon tetrachloride, see Figure 2 for the color code.

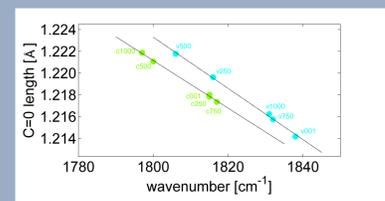


Figure 1.1. Frequency dependence of C=O bond length of R-(+)-camphor for each cluster including explicit methanol molecules in COSMO model (green) and vacuum (blue).

Raman and ROA spectra of camphor in water

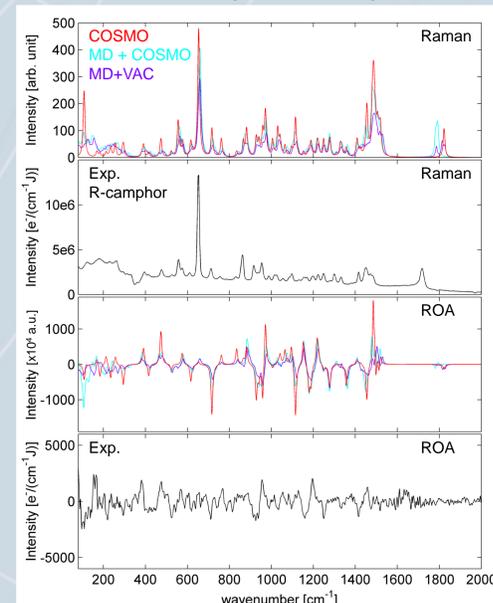


Figure 4. Simulated and experimental Raman and ROA spectra of (1R)-(+)-camphor (black) in water. Here ROA was difficult to measure due to the low solubility (concentration: 1mg/ml). Laser power at sample was 650 mW, accumulation time 50 h.

Raman scattering intensity should be enhanced by the **internal field factor** $L_n = [(n^2 + 2)/3]^4$ in comparison to vacuum and in case of used rectangular cuvette the signal is enhanced by internal field factor divided by n^2 (6).

Table 1. Internal field factor and relative coefficient for referred solvents

Solvent	n ($\lambda=532$ nm)	L_n	L_n/n^2 ^a	RAM/ROA ^b (simulation)	RAM/ROA ^c (experiment)
Methanol	1.3288	2.4826	1.0000	1.00/1.00	1.00/1.00
Cyclohexane	1.4279	3.2852	1.1460	1.18/1.23	1.20/1.20
Carbon tetrachloride	1.4629	3.6270	1.2054	1.34/1.12	1.35/1.30
Water	1.3337	2.5172	1.0065	0.89/0.85	1.55/2.20

^a relative to methanol

^b Simulated Raman/ROA spectra (clusters, D01/COSMO) of referred solvents to methanol relative coefficient.

^c Experimental Raman/ROA spectra of referred solvents to methanol relative coefficient.

Conclusions

We have performed “benchmark” computations with several solvent models to determine the most accurate and most economic one, and what is the impact on the spectra. Our experimental setup also enabled us to measure absolute Raman intensities, comparison of which with the calculations is planned for a near future.

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