Raman spectroscopy as an additional tool in HP (and LT) research

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Lecture plan

1) Basics of spectroscopy
2) Several aspects of Raman and IR-spectroscopy. Why use Raman but not IR for non-ambient conditions studies?
3) Information which can be extracted from Raman spectra
4) How do we perform HP (or LT) joint Raman and X-ray diffraction experiments
5) Examples of Raman & X-ray diffraction studies of molecular compounds
6) Questions and Discussion
Basics of spectroscopy

Vibrational spectrum is the most easy way to obtain information about pairwise atom interactions. This information is reflected in frequencies of vibrations of the system.

Methods of obtaining vibrational spectra

- IR-spectroscopy
- Raman spectroscopy

IR absorption and Raman scattering characterized by different selection rules that is why they complement each other. These methods are very qualitative analytic techniques for studying different chemical compounds.
Basics of spectroscopy

Processes leading to IR absorption and Raman scattering for two-atom molecules

The electric field of the incident beam interact with charged atoms in molecules. If the radiation frequency is comparable with frequency of molecule vibration, light quantum can be absorbed leading to appearance of vibrational quantum. If one have more complicated molecule, a set of vibrations can appear and one can see IR absorption spectrum in this case.

Appearance of vibrational (a) and electron (b) spectra.
It is generally accepted that the lifetime of an electron in a virtual state is very small that is why the electron is forced to live these state giving the light quantum with the same wavelength as for incident light. This process is elastic (Rayleigh) scattering (a). But appearance of a quantum of vibration in the system is also possible. In this case the electron live the excited state to give the light quantum with energy less than that of the incident photon that is Stokes Raman scattering (b). The scattering process can also be characterized by absorption and already existed vibrational quantum. In this case the Anti-Stokes Raman scattering is observed (c).
Several aspects of Raman and IR-spectroscopy. Why use Raman but not IR especially at HP and LT?

* Raman experiment is performed for visible region of the spectrum. That is why the whole optical system of the experiment (lenses, microscope, high-pressures cell, thermostats) can be configured for the visible region that makes Raman experiment more flexible than IR.
* Fully symmetric vibrations which are usually more intensive in the spectrum and easy for assignment are always visible in Raman but often not active in IR.
* Multiple tones and overtones are quite intensive in infrared spectra but are almost invisible in Raman spectrum.
* For the recording of Raman spectrum the oriented single crystals can be used that allows one to correlate spectrum with crystallographic directions (crystallographic axes).
Information which can be extracted from Raman spectra

* Information about composition and structure of a compound
* Information about functional groups and their configuration
* Information about inter- and intramolecular vibrations
* Information about physical state of a compound
How we perform HP (or LT) Raman experiment

- Single-crystal X-ray diffraction (evaluation of atomic coordinates, geometrical H-bonds parameters, information about phase transitions and conformational changes)

- Polarized Raman spectroscopy (evaluation of parameters of vibrational frequencies for selected bonds)

XRD:
HP: Oxford Diffraction Gemini R Ultra
LT: STOE IPDS II

Raman
HP + LT: HORIBA Jobin Yvon LabRAM HR 800
How we perform HP (or LT) Raman experiment

Things to be taken into account:

1) DAC dimensions; is it possible to put the sample (crystal) into the incident beam focus?
2) Beam and scattering area size
3) Laser power
4) Crystal orientation inside DAC
5) Only 2 dimensions are available for DAC
6) Diamond spectrum (some regions of the spectrum are overlapped)

DAC = diamond anvil cell
Asymmetric units structures of the objects of studies, types of H-bonds

Bis(DL-serinium) oxalate dihydrate

DL-alaninium semi-oxalate monohydrate

Co-crystal of glycine with glutaric acid
Geometrical parameters for selected H-bonds in bis(DL-serininium) oxalate dihydrate

Zakharov, Kolesov & Boldyreva, PCCP, 2011
Temperature dependencies of O-H stretching vibrations for selected H-bonds

Zakharov, Kolesov & Boldyreva, PCCP, 2011
Geometrical parameters for selected H-bonds in DL-alanininium semi-oxalate monohydrate

Zakharov, Kolesov & Boldyreva, PCCP, 2011
Temperature dependencies of O-H stretching vibrations for selected H-bonds

Zakharov, Kolesov & Boldyreva, PCCP, 2011
Dependence of O-H stretching vibrations from the (O…O) distance on cooling

Points a – bis(DL-serinium) oxalate dihydrate, b – DL-alaninium semi-oxalate monohydrate

Points 1-6 – salt hydrates, 7 – oxalic acid dihydrate, 8 and 9 – ices VI and I, 33-38 – strong hydrogen bonds in organic anions, containing hydrogen atoms [I].

Phase transition in glycine – glutaric acid co-crystals on cooling

Phase transition in glycine – glutaric acid co-crystals on cooling

High Pressure Raman Experiments in DACs

• Typical Spectrum

Diamonds + Sample + PTM

Common pressure transmitting media (PTM) types:
- pentane-isopentane mixture,
- methanol-ethanol mixture,
- isopropanol,
- paraffin,
- inert gases

Bis(DL-serininium) oxalate dihydrate
A compact device for loading diamond anvil cells with low-boiling pressure-transmitting media

Principal construction of the chamber for loading diamond anvil cells with a low-boiling liquid (e.g. pentane–isopentane mixture). (1) Body case, (2) cover for the chamber, (3) copper–zinc alloy base, (4) thermometer, (5) vessel for cooling agent (liquid nitrogen or solid CO2).

An example of DL-serine study

An example of DL-serine study

Polarized light

Methanol-
Ethanol (4:1)
mixture

New crystals after recrystallization at high pressures

Partially dissolved crystal

Pentane-isopentane (1:1) mixture

1.3 GPa
Zakharov & Boldyreva, J. Mol. Str., 2014

6.2 GPa, polarized light

0.7 GPa, on pressure release
Raman spectra of bis(DL-serinimum) oxalate dihydrate at pressures 0.7 – 5.3 GPa

Zakharov & Boldyreva, J. Mol. Str., 2014
Anisotropy of lattice strain for bis(DL-serininium) oxalate dihydrate at extreme conditions

$$\lambda = 0.69775 \text{ Å}$$
A single-crystal X-ray diffraction study of bis(DL-serinimum) oxalate dihydrate (at P > 4 GPa)

Reconstruction of layers containing vectors [010] and [001] (a), [010] and [100] (b) (point of origin [000]). Pressure transmitting medium – n-pentane and 2-methylbutane (1:1 mixture).
Phase transition in DL-alaninum semi-oxalate monohydrate

First-order single-crystal to single-crystal phase transition without change in space group ($P2_1/c$)

**Phase transition in DL-alaninium semi-oxalate monohydrate**

H-bonds which do not switch-over during the phase transition

- O3-H3···O6v
- O1-H1···O2iii
- O1-H1···O1W
- N1-H1B···O5

H-bonds which switch-over during the phase transition and become bifurcated

- N1-H1A···O2ii
- N1-H1C···O6i
- N1-H1A···O1Wii

<table>
<thead>
<tr>
<th>Pressure, GPa</th>
<th>O-O, Å</th>
<th>N-O, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.50</td>
<td>3.00</td>
</tr>
<tr>
<td>1</td>
<td>2.55</td>
<td>3.10</td>
</tr>
<tr>
<td>2</td>
<td>2.60</td>
<td>3.20</td>
</tr>
<tr>
<td>3</td>
<td>2.65</td>
<td>3.30</td>
</tr>
<tr>
<td>4</td>
<td>2.70</td>
<td>3.40</td>
</tr>
</tbody>
</table>

**Note:**
- H-bonds which do not switch-over during the phase transition remain linear.
- H-bonds which switch-over become bifurcated during the phase transition.
Raman spectrum of DL-alaninium semi-oxalate monohydrate at high pressures
Phase transition in glycine – glutaric acid co-crystals on increasing pressure

**Experiment 1**
liquid – pentane:isopentane, 1:1, 
\( P_0 = 1.75 \text{ GPa} \)
Cell parameters (a, b, c, \( \alpha \), \( \beta \), \( \gamma \)):
4.732(5), 19.92(3), 9.83(1), 84.9(2), 114.3(1), 86.9(2) (Å, °)

**Experiment 2**
liquid – glycerol, \( P_0 = 0.14 \text{ GPa} \)
Cell parameters (a, b, c, \( \alpha \), \( \beta \), \( \gamma \)):
4.9180(6), 20.285(8), 10.165(1), 85.66(2), 113.352(9), 88.334(22) (Å, °)

Cell parameters (a, b, c, \( \alpha \), \( \beta \), \( \gamma \)) for phase II at 200 K:
4.9155(7), 9.4116(14), 20.215(3), 84.322(13), 88.301(13), 84.429(12)

Zakharov et al., CrystEngComm, 2013
Polymorphism of chlorpropamide

4-chloro-N-(propylamino-carbonyl)benzenesulfonamide, $C_{10}H_{13}ClN_2O_3S$

Antidiabetic drug

One of the best model systems to study polymorphism ($\alpha$-, $\beta$-, $\gamma$-, $\delta$-, $\varepsilon$-polymorphs can be preserved indefinitely long under ambient conditions)
Polymorphism of chlorpropamide

<table>
<thead>
<tr>
<th>Chlorpropamide polymorph</th>
<th>$\alpha^{[1]}$ (295 K, 0 GPa)</th>
<th>$\beta^{[2]}$ (295 K, 0 GPa)</th>
<th>$\gamma^{[3]}$ (295 K, 0 GPa)</th>
<th>$\delta^{[4]}$ (295 K, 0 GPa)</th>
<th>$\varepsilon^{[4]}$ (250 K, 0 GPa)</th>
<th>$\varepsilon^{[11]}$ (100 K, 0 GPa)</th>
<th>$\alpha^{[5]}$ (293 K, 2.91 GPa)</th>
<th>$\beta^{[m]}$ (200 K, 0 GPa)</th>
<th>$\beta^{[m]}$ (100 K, 0 GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>$P2_12_12_1$</td>
<td>$Pbca$</td>
<td>$P2_1$</td>
<td>$P2_1$</td>
<td>$Pna2_1$</td>
<td>$Pna2_1$</td>
<td>$P2_111$</td>
<td>$P2/c$</td>
<td>$P2/n$</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>8</td>
<td>2</td>
<td>8</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>8</td>
<td>16</td>
</tr>
<tr>
<td>$Z'$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>b, Å</td>
<td>5.2296(19)</td>
<td>9.316(4)</td>
<td>8.941(6)</td>
<td>10.3218(3)</td>
<td>7.3459(4)</td>
<td>5.1398(4)</td>
<td>4.6340(2)</td>
<td>9.2584(2)</td>
<td>9.2322(3)</td>
</tr>
<tr>
<td>$\beta$, °</td>
<td>90</td>
<td>90</td>
<td>99.68(3)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>$\alpha = 99.109(4)$</td>
<td>93.260(3)</td>
<td>95.562(4)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>1267.6(6)</td>
<td>2646.4(14)</td>
<td>649.0(5)</td>
<td>2526.74(16)</td>
<td>1336.69(12)</td>
<td>1234.33(15)</td>
<td>1037.01(14)</td>
<td>2582.71(13)</td>
<td>5026.6(3)</td>
</tr>
<tr>
<td>$\rho$, g·cm$^{-3}$</td>
<td>1.450</td>
<td>1.389</td>
<td>1.416</td>
<td>1.455</td>
<td>1.375</td>
<td>1.489</td>
<td>1.773</td>
<td>1.423</td>
<td>1.463</td>
</tr>
<tr>
<td>Orientation of alkyl tail in the molecule</td>
<td><img src="image" alt="Orientation Diagram" /></td>
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</tr>
</tbody>
</table>

H-bonded ribbon type

- z
- π

H-bonded ribbon types: z – ![H-bonded Ribbon](image) and π – ![H-bonded Ribbon](image). Polymorphs studied at low temperature indicated by blue, at high pressure – by red.

Polymorphs discussed in the present contribution indicated by green.

Polymorphism of chlorpropamide

Pentane-isopentane mixture (1:1) was used as pressure transmitting media.

Raman spectra of α-, β-, δ-polymorphs of chlorpropamide and the new needle-shaped (γ) polymorph at 0.3 GPa.

Raman spectra of α- and δ-polymorphs of chlorpropamide. The most significant changes in Raman spectra and are mainly related to lattice vibrations (50-350 cm⁻¹), CC and SO stretching vibrations (750-1250 cm⁻¹) and rearrangements of H-bonds (3050-3360 cm⁻¹)

Polymorphism of chlorpropamide

The relative densities were calculated from unit cell parameters measured at 0.35 and 0.50 GPa. The densities at 0.35 and 0.50 GPa, respectively, were as follows:

α-polymorph – 1.528 and 1.546 g/cm³;
γ-polymorph – 1.522 and 1.549 g/cm³,
δ-polymorph – 1.534 and 1.554 g/cm³.
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