

# THE STUDY OF LATTICE DYNAMICS IN LOW-DIMENSIONAL QUANTUM MAGNETS WITH CHAIN-LIKE CRYSTAL STRUCTURE

O. Vinnik<sup>1</sup>, L. Lederová<sup>1</sup>, R. Tarasenko<sup>1</sup>, L. Kotvytska<sup>1</sup>, K. Zakuťanská<sup>2</sup>, N. Tomašovičová<sup>2</sup> and A. Orendáčová<sup>1</sup>

<sup>1</sup> Institute of Physics, P. J. Šafárik University, Park Angelinum 9, 04001 Košice, Slovakia

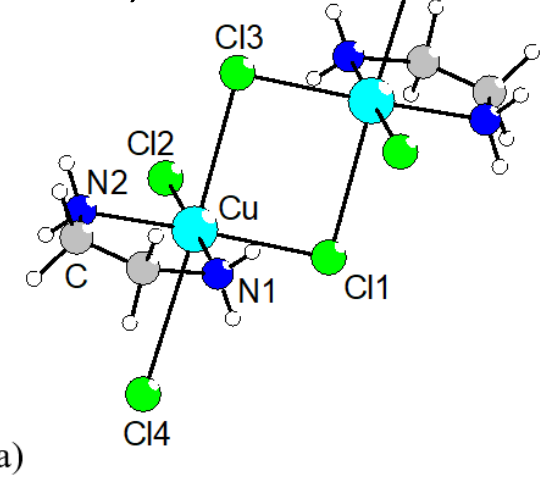
<sup>2</sup> Institute of Experimental Physics of SAS, Watsonova 47, 04001 Košice, Slovakia

**Motivation** Previous study of magneto-structural correlations of four Cu(II) based organo-metallic compounds with one-dimensional (1d) polymeric structure Cu(en)Cl<sub>2</sub>, Cu(tn)Cl<sub>2</sub>, Cu(en)<sub>2</sub>SO<sub>4</sub> and Cu(en)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub> (en = C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>, tn = C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>) revealed that their magnetic subsystem has pronounced 2d character with effective intralayer coupling  $J_{\text{eff}}/k_B \approx 3$  K. The intra-layer spatial anisotropy of exchange coupling indicated in all compounds was described within the S = 1/2 Heisenberg models on the rectangular and zig-zag lattice with nearest-neighbor intra-layer couplings  $J_1 > J_2$ . The purpose of this work is to study the lattice sub system of a low-dimensional magnet, which also has a low-dimensional structure (covalent chains/ladders connected by hydrogen bonds into a 3d structure).

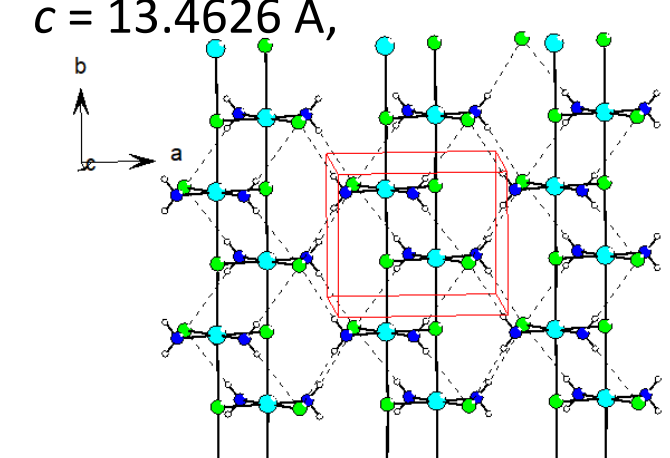
## Experimental details

### Cu(en)Cl<sub>2</sub>

Crystallizes at room temperature in a monoclinic space group  $P2_1/m$  with unit cell parameters  $a = 8.219 \text{ \AA}$ ,  $\beta = 93.72^\circ$ ,  $b = 5.747 \text{ \AA}$ ,  $z = 2$ ,  $c = 6.776 \text{ \AA}$ ,



The structural studies at 123 K determined a low-temperature structure characterized by a space-group  $P2_1/c$  with the unit cell parameters  $a = 8.1729 \text{ \AA}$ ,  $\beta = 95.076^\circ$ ,  $b = 5.7266 \text{ \AA}$ ,  $z = 4$ ,  $c = 13.4626 \text{ \AA}$ ,

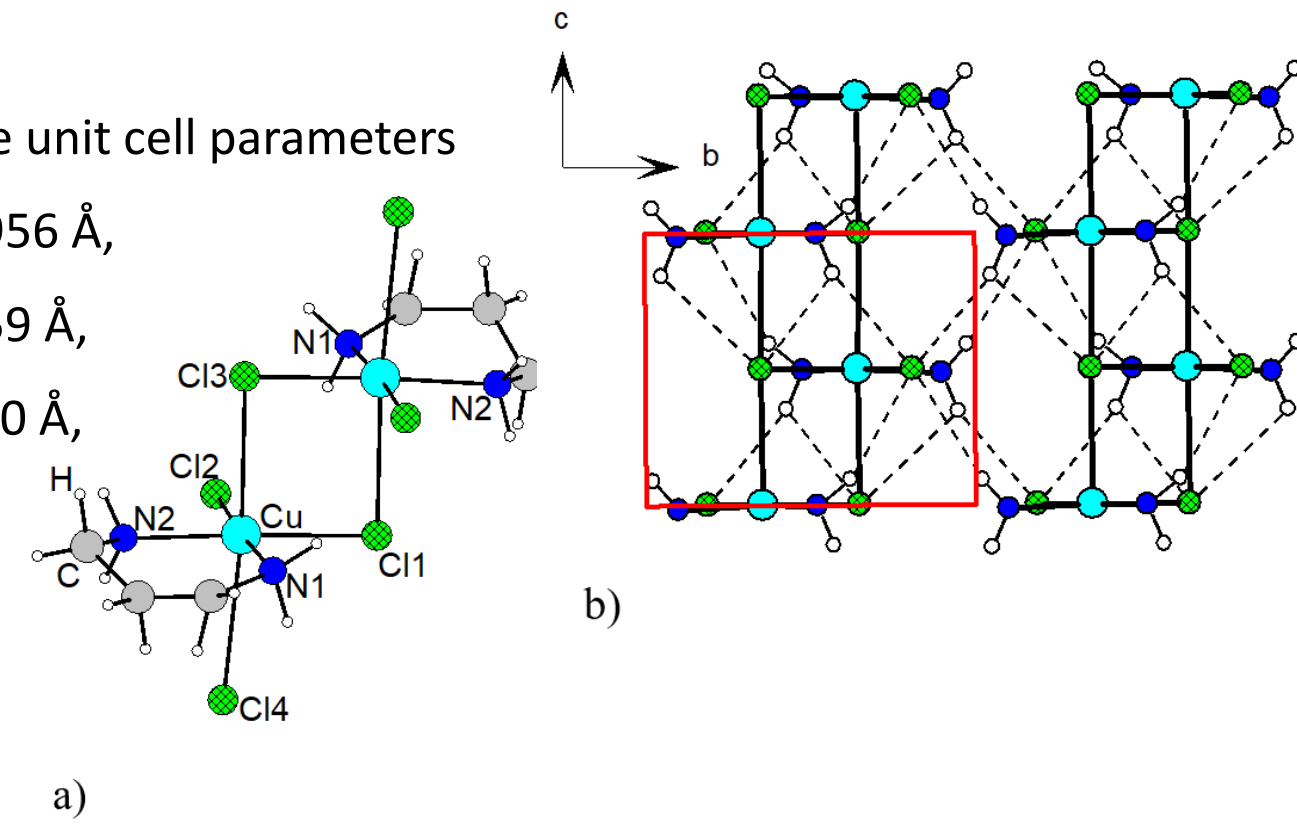


(a) Local octahedron of Cu(en)Cl<sub>2</sub> compound. (b) Crystal structure of Cu(en)Cl<sub>2</sub> with illustration of an elementary cell projected into the crystallographic plane ab [R. Tarasenko, PhD Thesis, P.J. Šafárik University, 2013].

### Cu(tn)Cl<sub>2</sub>

The orthorhombic crystal structure was determined at 150 K for the space group  $Pna2_1$

with the unit cell parameters  $a = 17.956 \text{ \AA}$ ,  $b = 6.859 \text{ \AA}$ ,  $c = 5.710 \text{ \AA}$ ,  $z = 4$ .

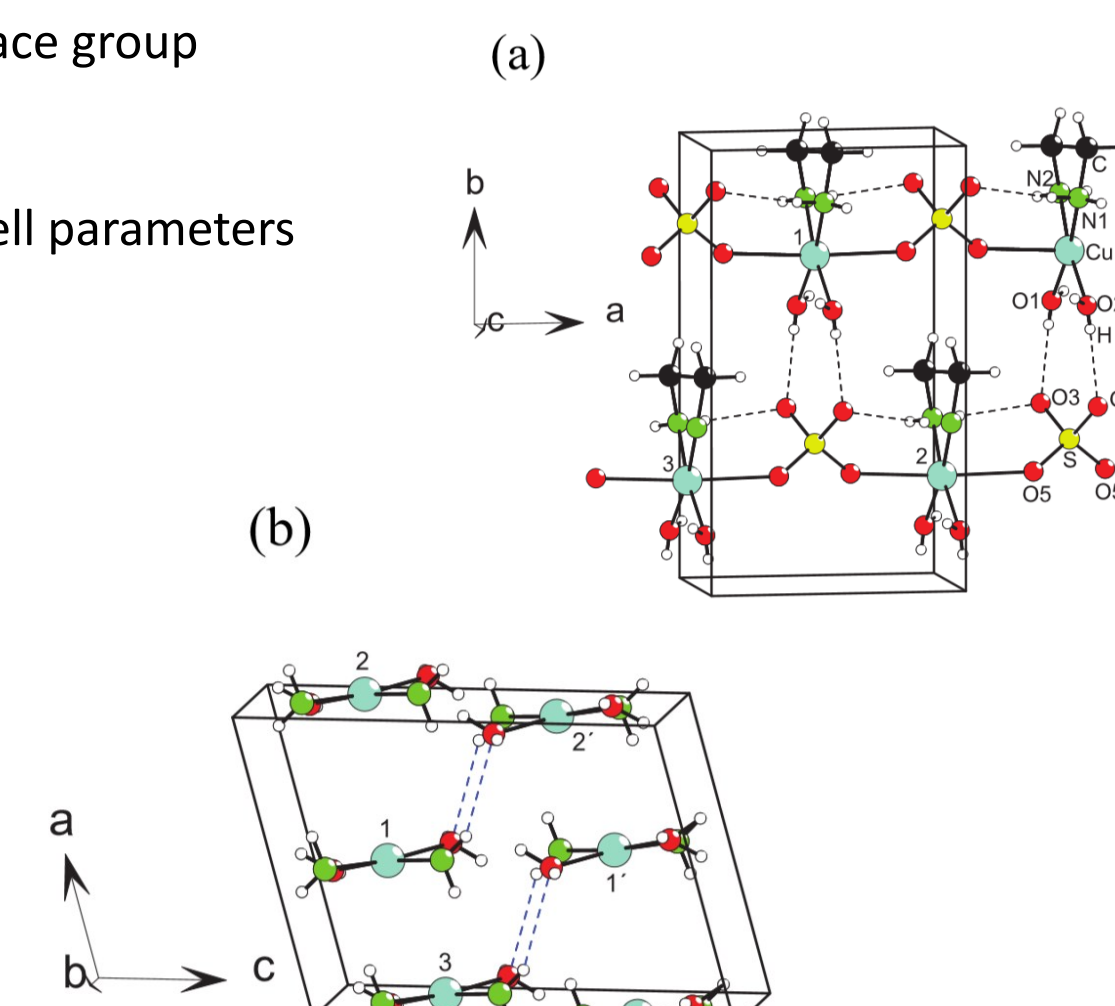


(a) Local octahedron of Cu(tn)Cl<sub>2</sub> compound. (b) Crystal structure of Cu(tn)Cl<sub>2</sub> with illustration of an elementary cell projected into the crystallographic plane bc [R. Tarasenko, PhD Thesis, P.J. Šafárik University, 2013].

### Cu(en)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub>

Monoclinic, space group  $C2/c$

with the unit cell parameters  $a = 7.232 \text{ \AA}$ ,  $b = 11.725 \text{ \AA}$ ,  $c = 9.768 \text{ \AA}$ ,  $\beta = 105.5^\circ$ ,  $z = 4$ .

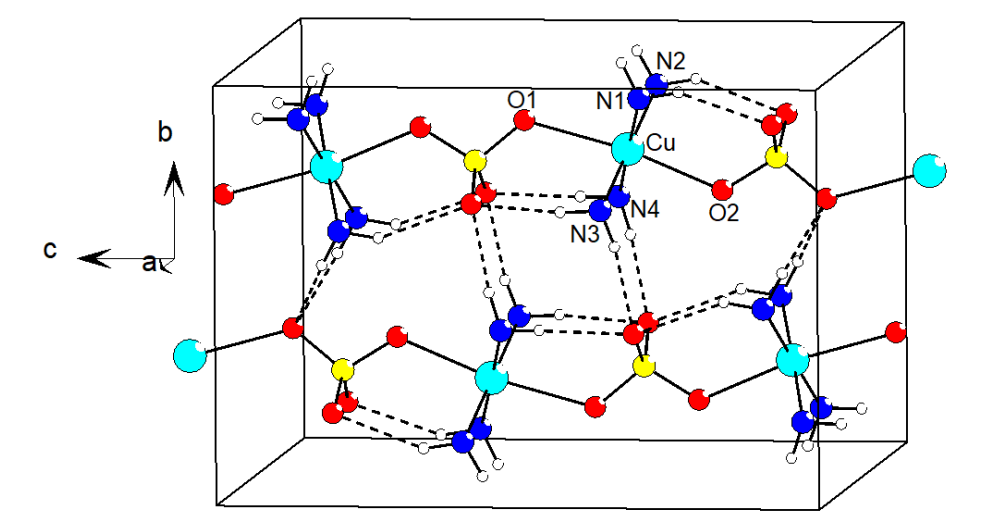


The crystal structure of Cu(en)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub> compound projected into the ab plane (a) and the ac plane (b). [R. Tarasenko *et al.*, Phys. Rev. B87, 174401 (2013)].

### Cu(en)<sub>2</sub>SO<sub>4</sub>

Orthorhombic,

$Cmca$  with the unit cell parameters  $a = 14.495 \text{ \AA}$ ,  $b = 9.637 \text{ \AA}$ ,  $c = 13.877 \text{ \AA}$ ,  $z = 8$ .



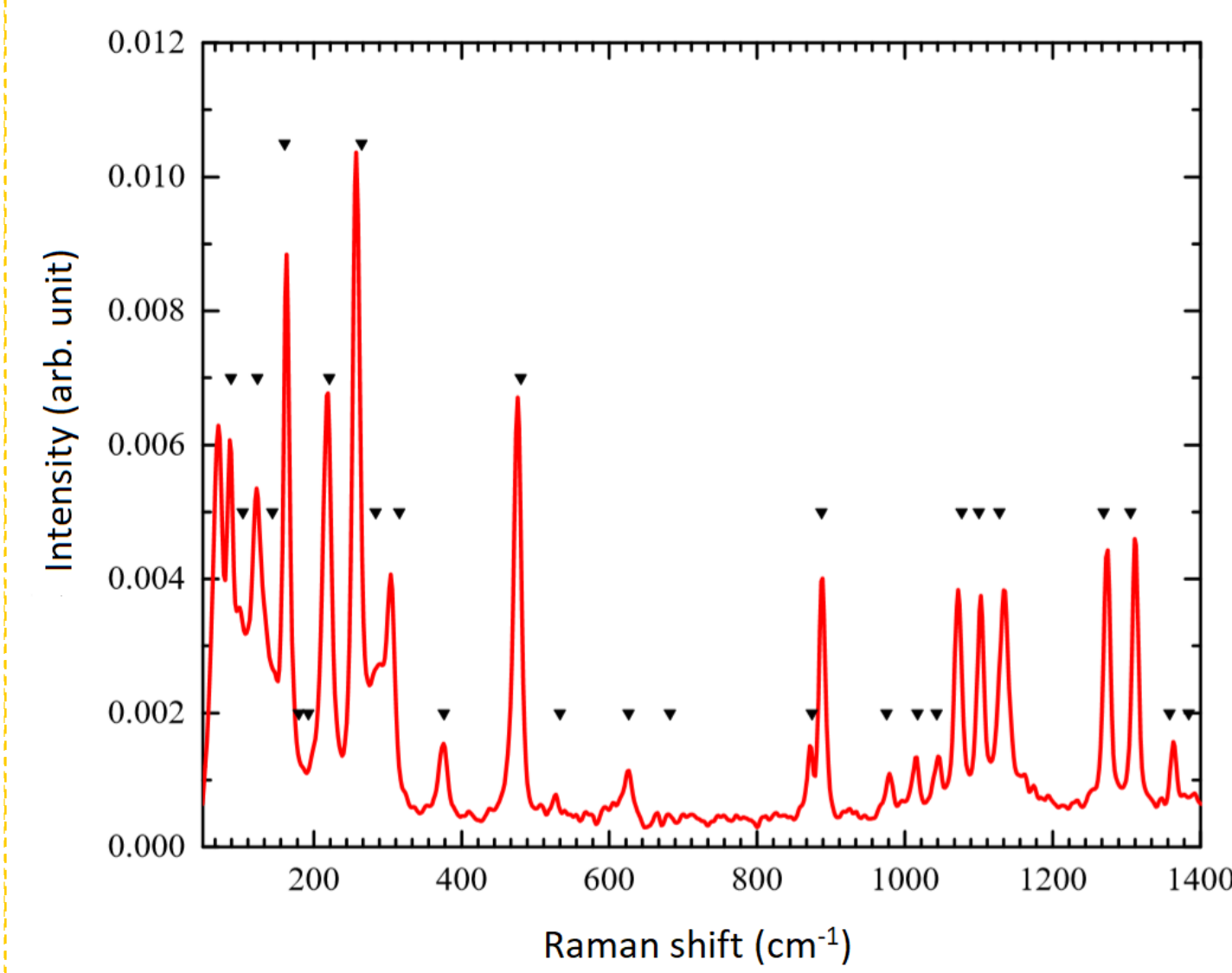
The crystal structure of the Cu(en)<sub>2</sub>SO<sub>4</sub> with the illustration of the unit cell projected into the crystallographic plane bc [R. Tarasenko, PhD Thesis, P.J. Šafárik University, 2013].

Measurements of the temperature dependence of the heat capacity were performed with the Quantum Design Physical Property Measurement System (PPMS) at the Institute of Physical Sciences, Faculty of Science, UPJŠ in Košice. The measurements were carried out in the temperature range from 1.8 to 300 K in a zero magnetic field for single-crystal samples.

The measurement of Raman spectra was performed using a Bruker vacuum FTIR spectrometer, model VERTEX 80 v with a RAM II module

for measuring Raman spectra at the Institute of Experimental Physics of the Slovak Academy of Sciences in Košice, which has a working range from 50 to 3500 cm<sup>-1</sup>. Experiments were performed at room temperature on powder samples placed in aluminum capsules. The power of the laser with a wavelength  $\lambda = 1064$  nm was 50 mW and reproducible vibrational spectra were obtained for the number of scans 2500.

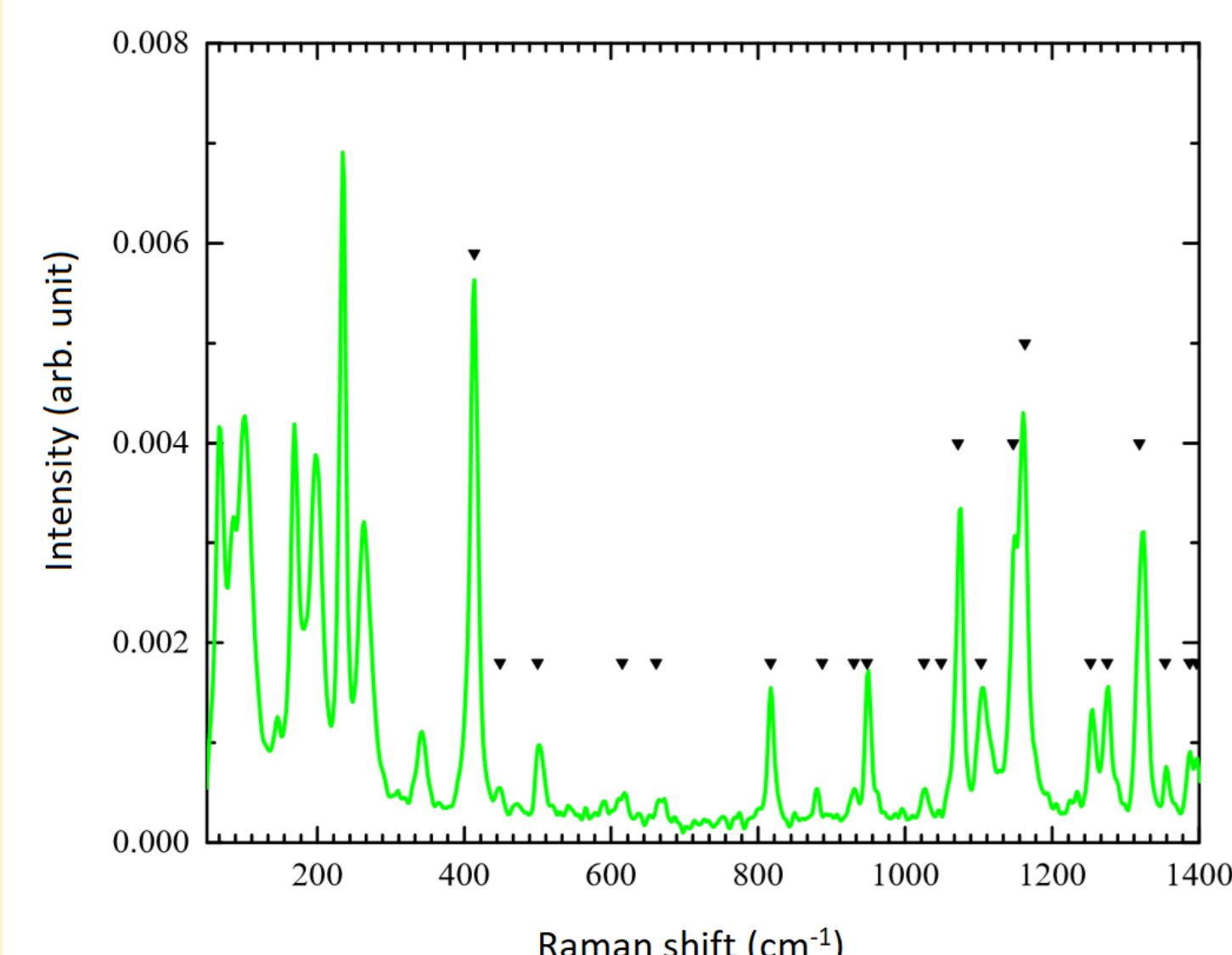
## Experimental Results



Raman spectrum of a polycrystalline Cu(en)Cl<sub>2</sub> sample measured at room temperature. Arrows indicate frequencies of IR active modes [G. Paliani *et al.*, Chem. Phys.4, 440 (1974)].

The energy of the IR [G. Paliani *et al.*, Chem. Phys.4, 440 (1974)] active modes in Cu(en)Cl<sub>2</sub> at room temperature (expressed in cm<sup>-1</sup>).

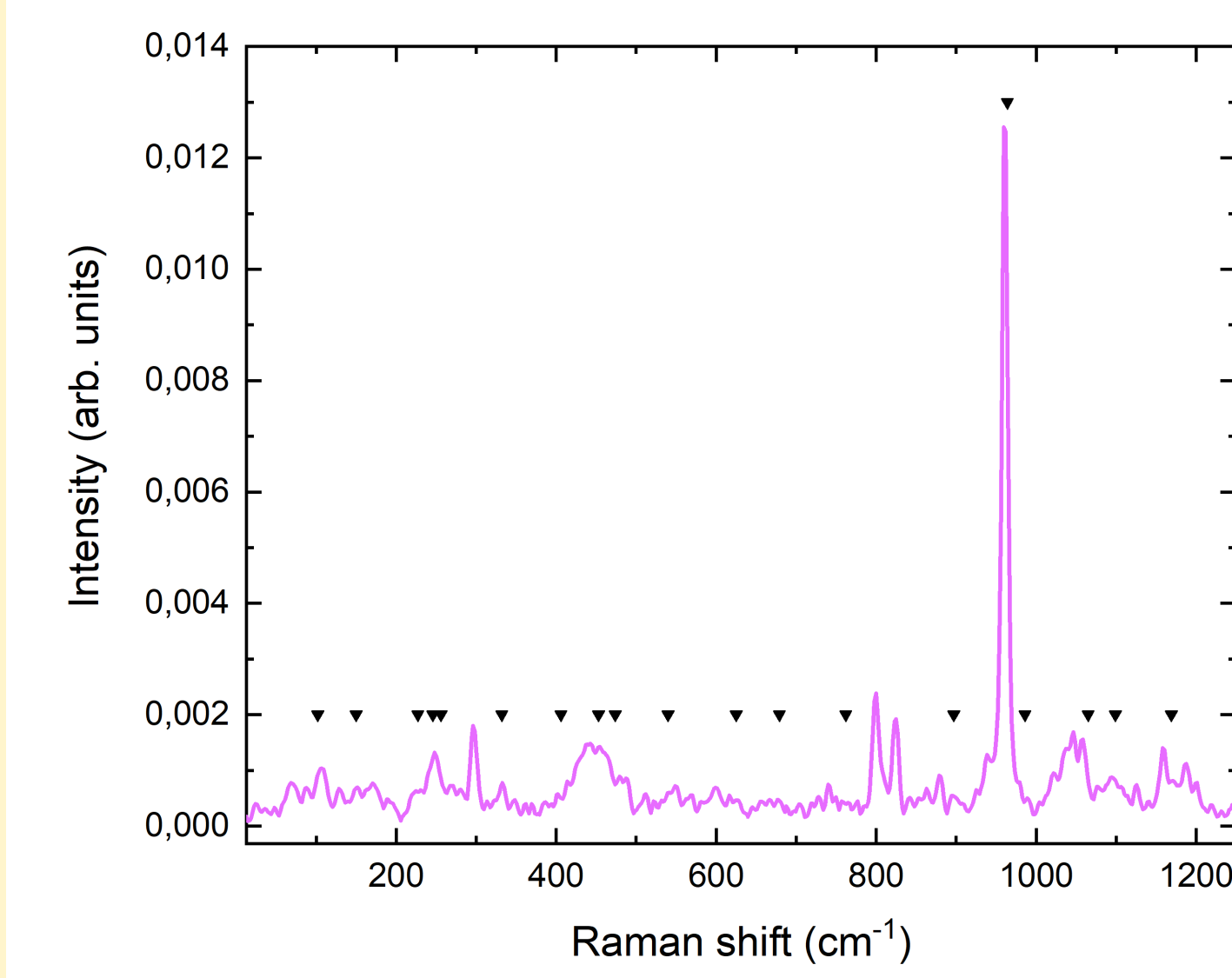
| Cu(en)Cl <sub>2</sub>  |
|--|
| 88, 104, 124, 144, 161, 180, 193, 221, 265, 284, 316, 376, 480, 533, 626, 682, 874, 887, 975, 1017, 1043, 1077, 1100, 1128, 1269, 1305, 1358, 1384 |



Raman spectrum of a polycrystalline sample of Cu(tn)Cl<sub>2</sub> measured at room temperature. Arrows indicate the peak positions of the infrared spectrum measured from 400 cm<sup>-1</sup> [R. Tarasenko, PhD Thesis, P.J. Šafárik University, 2013].

The energy of the Raman active modes in Cu(tn)Cl<sub>2</sub> at room temperature (expressed in cm<sup>-1</sup>).

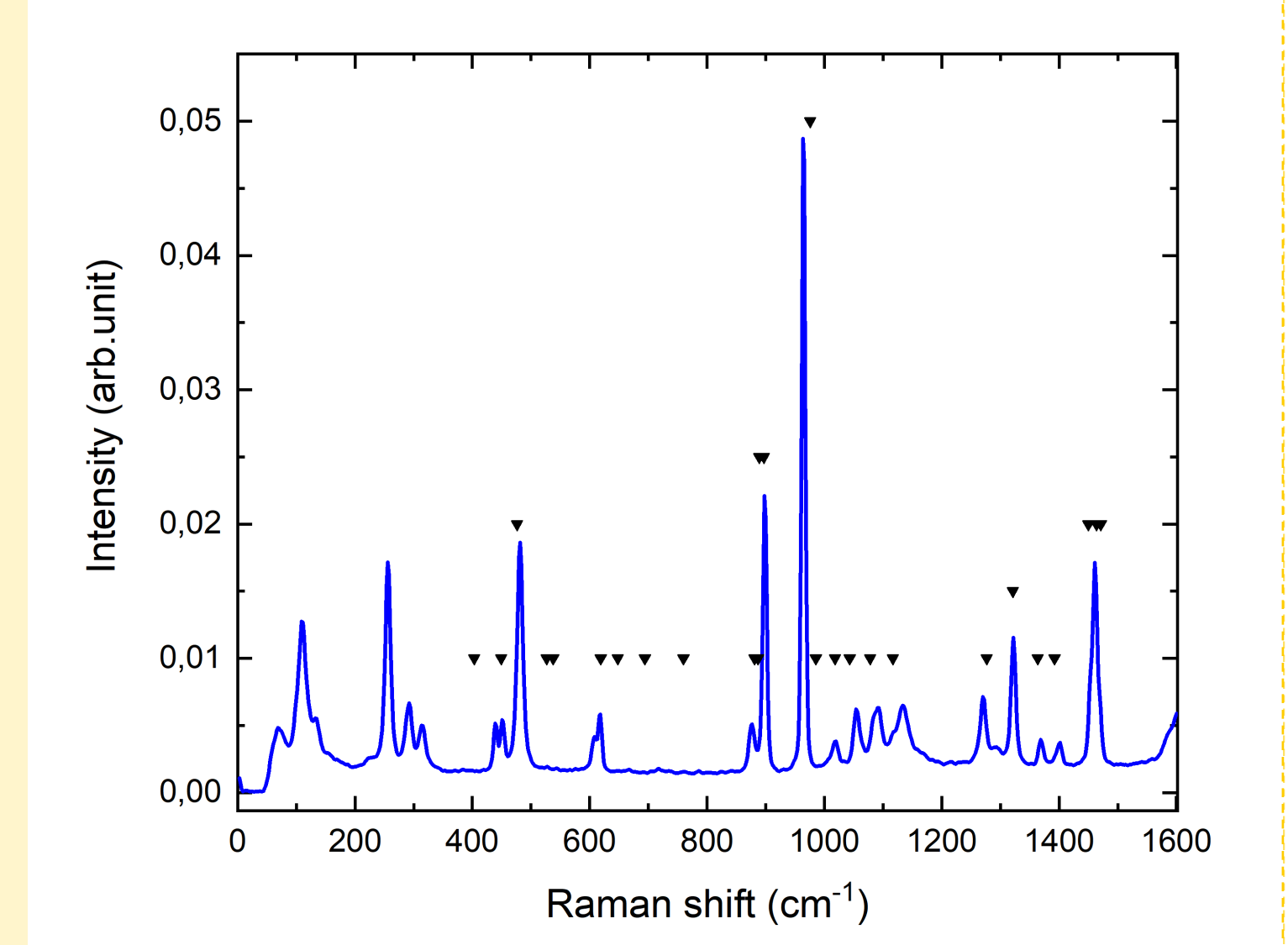
| Cu(tn)Cl <sub>2</sub>  |
|--|
| 68, 86, 100, 146, 169, 198, 235, 263, 309, 343, 414, 448, 502, 618, 665, 817, 880, 931, 950, 996, 1025, 1073, 1104, 1148, 1160, 1233, 1254, 1276, 1322, 1355, 1387, 1397, 1453, 1465, 1577 |



Raman spectrum of a polycrystalline Cu(en)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub> sample measured at room temperature. Arrows indicate frequencies of IR active modes [J. Chem. Crystall., 26(1), 15. (1996)].

The energy of the IR [J. Chem. Crystall., 26(1), 15. (1996)] and Raman active modes in Cu(en)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub> at room temperature (expressed in cm<sup>-1</sup>).

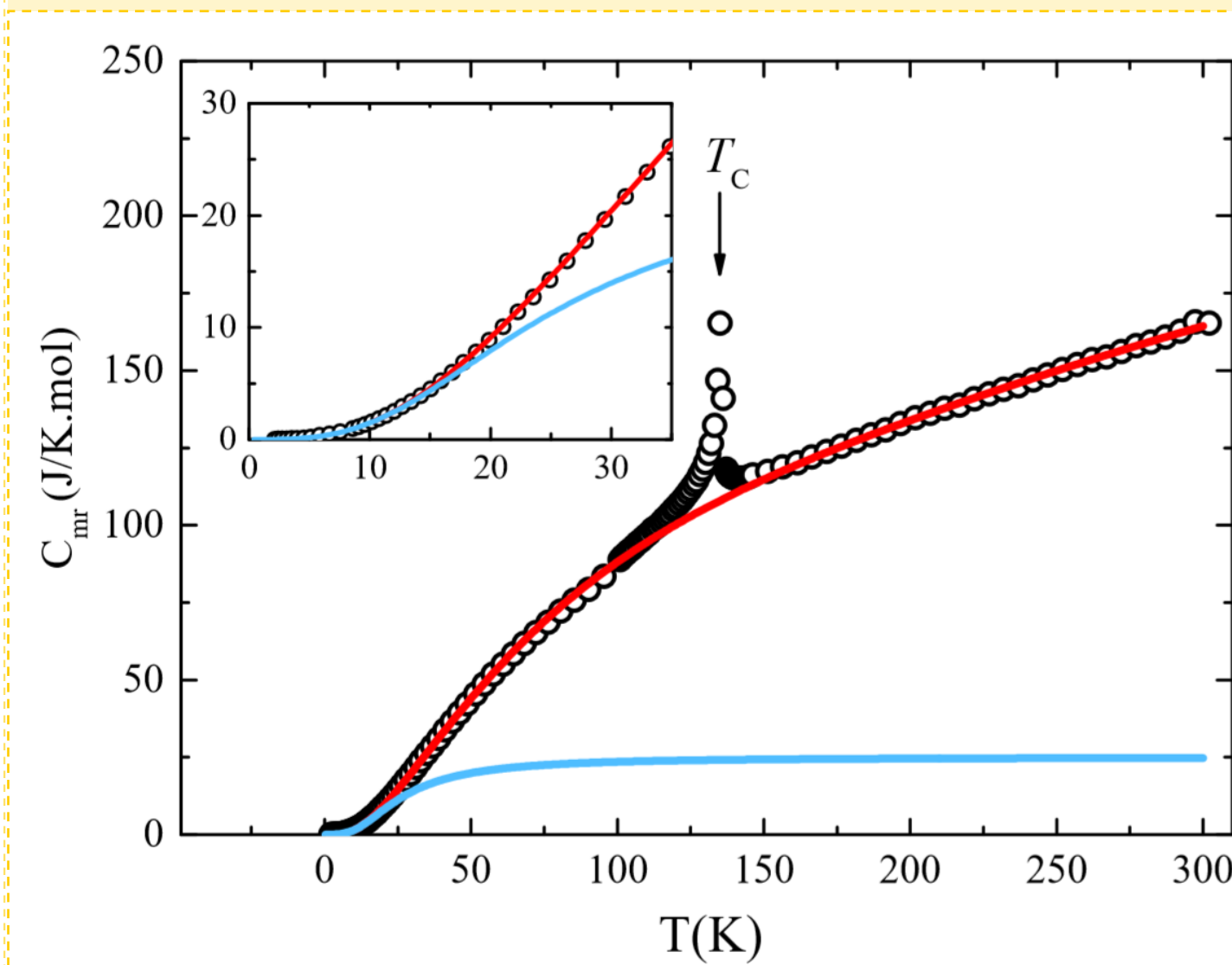
| Cu(en)(H <sub>2</sub> O) <sub>2</sub> SO <sub>4</sub>  |
|--|
| IR 102, 150, 227, 246, 256, 332, 406, 453, 474, 540, 625, 679, 762, 897, 964, 986, 1065  |
| Raman 68, 88, 107, 128, 151, 163, 170, 248, 296, 332, 413, 442, 454, 479, 487, 548, 599, 739, 799, 824, 863, 878, 925, 938, 959, 979, 1021, 1036, 1046 |



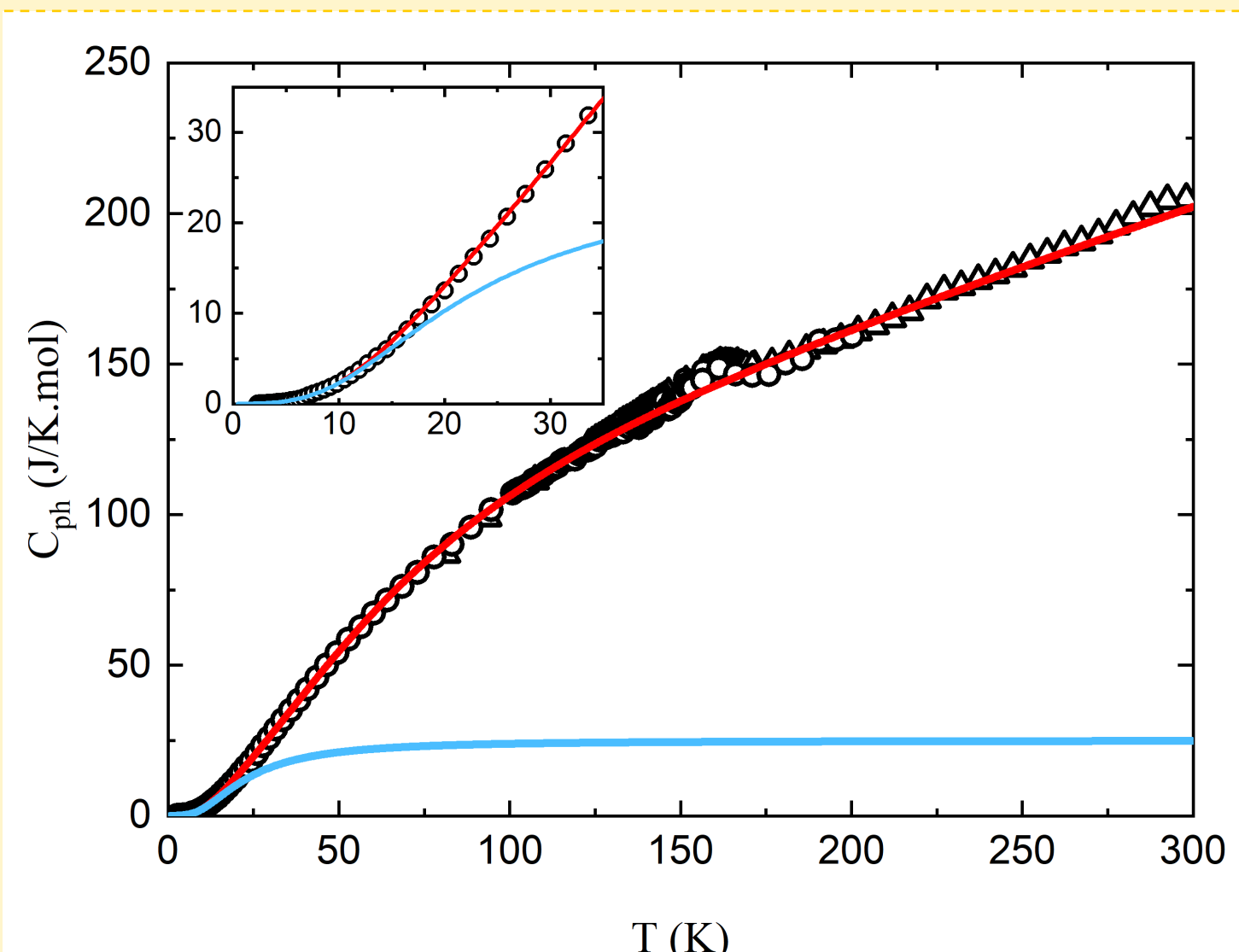
Raman spectrum of a polycrystalline sample of Cu(en)<sub>2</sub>SO<sub>4</sub> measured at room temperature. Arrows indicate the peak positions of the infrared spectrum measured from 400 cm<sup>-1</sup> [R. Tarasenko, PhD Thesis, P.J. Šafárik University, 2013].

The energy of the IR [R. Tarasenko, PhD Thesis, P.J. Šafárik University, 2013] and Raman active modes in Cu(en)<sub>2</sub>SO<sub>4</sub> at room temperature (expressed in cm<sup>-1</sup>).

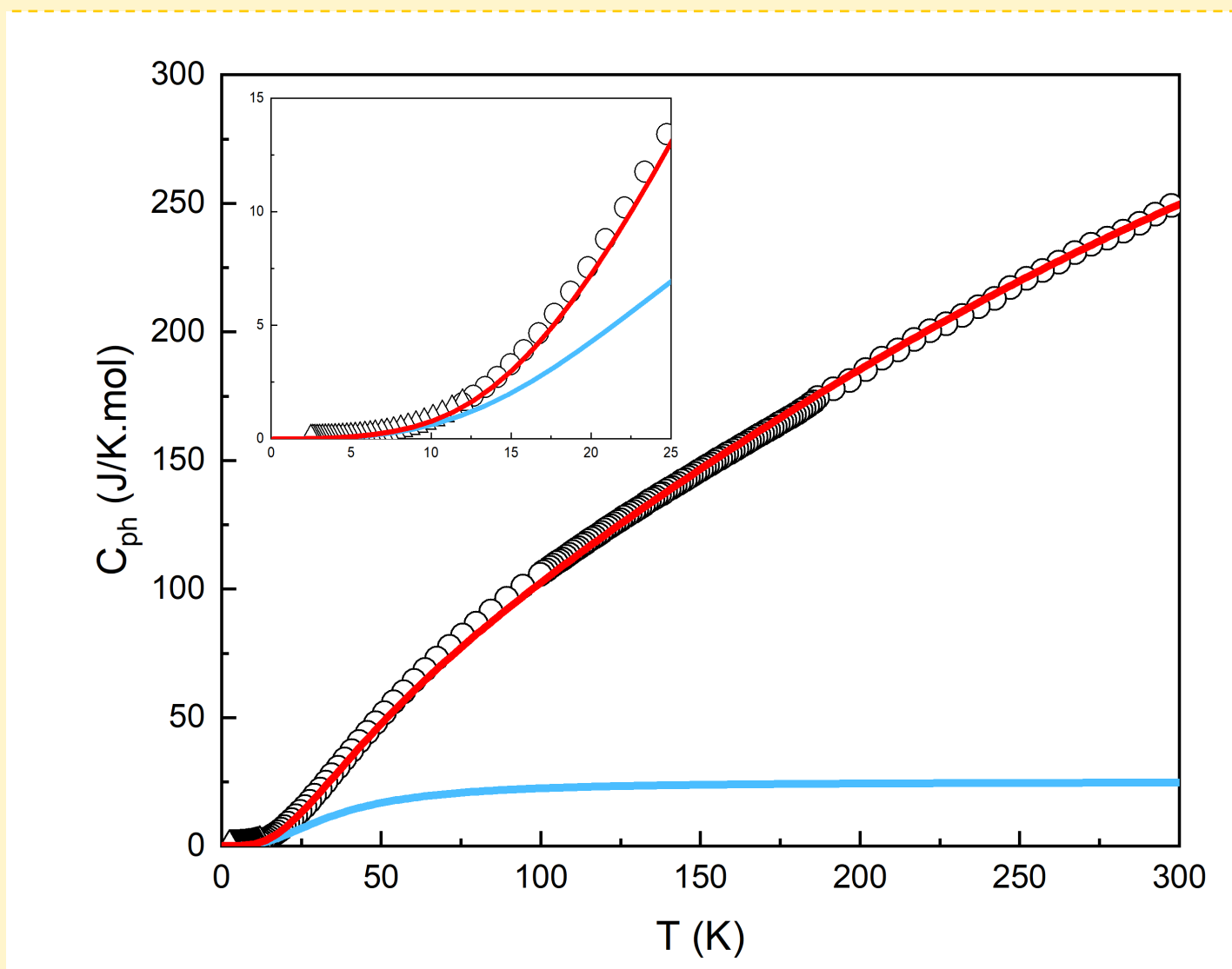
| Cu(en) <sub>2</sub> SO <sub>4</sub>  |
|--|
| IR 403, 449, 476, 526, 538, 619, 647, 694, 759, 881, 887, 889, 896, 975, 985, 1018, 1043, 1078, 1116, 1276   |
| Raman 68, 74, 109(2), 132(2), 153(3), 169(2), 178, 188, 209, 223, 230, 255, 292, 313, 439, 450, 481, 608, 618, 876, 898, 963, 1017, 1054, 1092, 1133, 1270 |



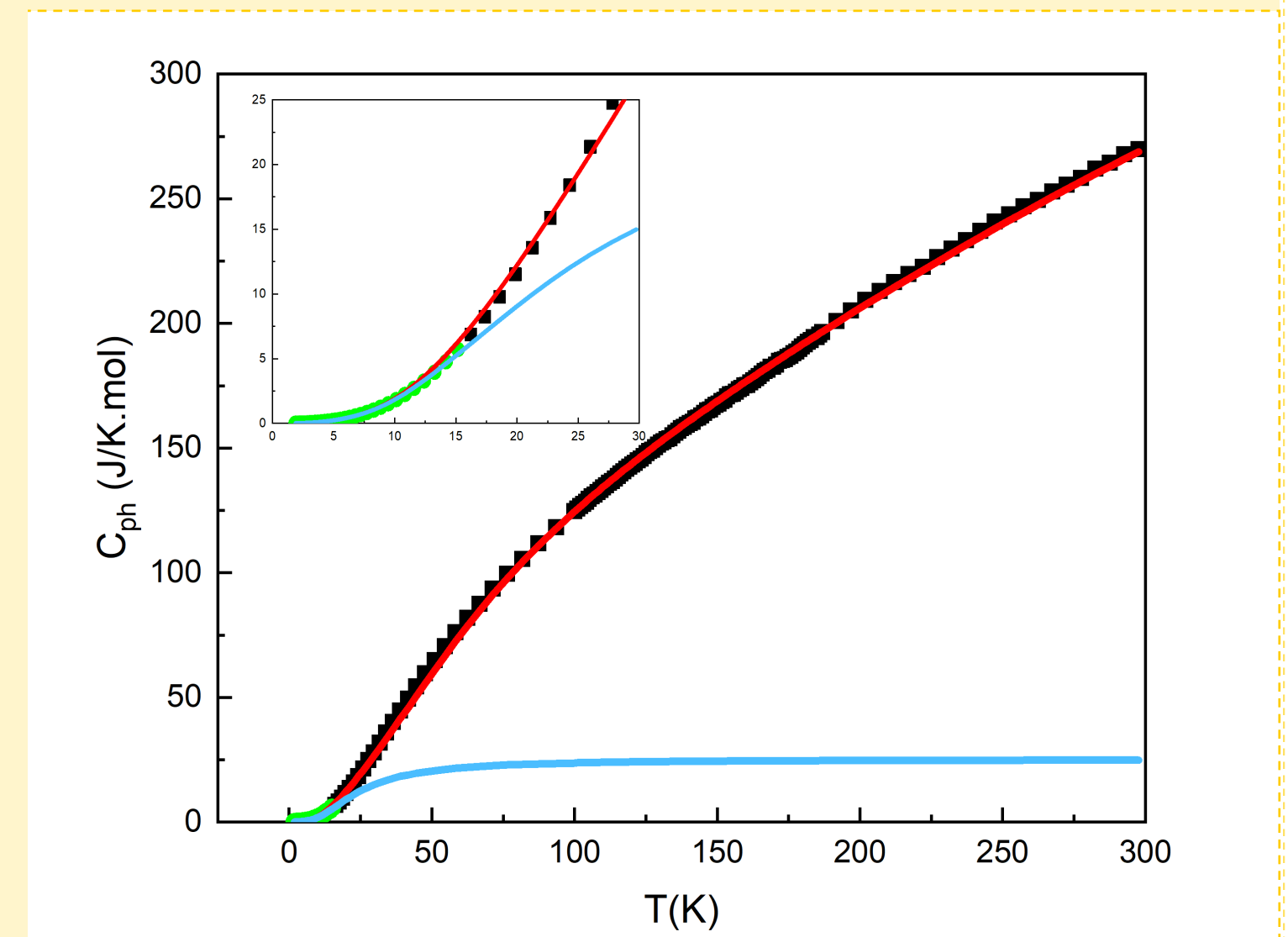
The temperature dependence of phonon specific heat in Cu(en)Cl<sub>2</sub> (open symbols). The blue line represents Debye model with  $\theta_D = 109$  K. The red line represents total phonon specific heat.



The temperature dependence of phonon specific heat in Cu(tn)Cl<sub>2</sub> (o monocrystal,  $\Delta$  powder sample). The blue line represents Debye model with  $\theta_D = 93$  K. The red line represents total phonon specific heat.



The temperature dependence of phonon specific heat in Cu(en)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub>. The blue line represents Debye model with  $\theta_D = 146$  K. The red line represents total phonon specific heat.



The temperature dependence of phonon specific heat in Cu(en)<sub>2</sub>SO<sub>4</sub>. The blue line represents Debye model with  $\theta_D = 100$  K. The red line represents total phonon specific heat.

**Debye model:**  
Oscillators have not the same frequency. In this model, the real oscillation spectrum is replaced by a simplified linear one,  $\omega = vk$   
If we assume that the speed of sound is isotropic then  
$$C_{Deb} = 9Nk_B(T/\theta_D)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$
  
$$x = \hbar\omega/k_B T$$
  
At low-temperatures phonon heat capacity behaves as  $C_{Deb} \approx 9Nk_B(T/\theta_D)^3 \frac{4\pi^4}{15} \equiv bT^3$  from which the Debye temperature  $\theta$  can be determined:  
$$\theta_D = \sqrt[3]{\frac{12\pi^4 R}{5b}}$$

**Einstein's model:**  
All oscillators have the same frequency. The frequency is not function of wave vector  $k$ . It describes the contribution of optical modes to specific heat.  
$$C_{Ein} = \frac{dE}{dT} = Nk_B \left( \frac{\hbar\omega_0}{k_B T} \right)^2 \frac{e^{\hbar\omega_0/(k_B T)}}{(e^{\hbar\omega_0/(k_B T)} - 1)^2}$$
  
The high-temperature limit of this dependence is  $Nk_B$  and corresponds to the theorem on equipartition. The energies calculated from the IR and Raman data from the table, were used to calculate the contribution of the optical modes in the Einstein approximation.

Whereas, the acoustic modes contribution can be well described within Debye approximation  $C_{Deb}$ , the specific heat of optical modes can be evaluated using Einstein modes,  $C_{Ein}$ . Then, the total phonon specific heat can be expressed as

$$C_{tot} = C_{Deb} + \sum_{i=1}^n C_{Ein}^i$$

## Conclusions

- The temperature dependence of specific heat in Cu(en)Cl<sub>2</sub>, Cu(tn)Cl<sub>2</sub>, Cu(en)<sub>2</sub>SO<sub>4</sub> and Cu(en)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub> was studied up to 300 K in zero magnetic field.
- The analysis of the contribution of acoustic modes performed within Debye approximation yielded Debye temperature  $\theta_D = 147$  K, 109 K, 100 K and 93 K for Cu(en)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub>, Cu(en)Cl<sub>2</sub>, Cu(en)<sub>2</sub>SO<sub>4</sub> and Cu(tn)Cl<sub>2</sub>, respectively.
- Considering available IR and Raman spectra optical modes energies described the data behaviour over the entire temperature range.