

SHORT COMMUNICATION

FT-IR reflection spectra of single crystals: resolving phonons of different symmetry without using polarised radiation

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Fourier-transform infrared (FT-IR) reflection spectra, asquired at nearnormal incidence, were recorded from single crystals belonging to six crystal systems: $\text{CsCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (alum, cubic), $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ (Mitscherlichite, tetragonal), CaCO_3 (calcite, hexagonal), KHSO_4 (mercallite, orthorhombic), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum, monoclinic) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (chalcantite, triclinic). The acquired IR reflection spectra were further transformed into absorption spectra, employing the Kramers-Kronig transformation.¹ Except for the cubic alums, the spectra strongly depend on the crystal face from which they were recorded; this is a consequence of anisotropy. Phonons of a given symmetry (E-species, in tetragonal/hexagonal and B-species, in monoclinic crystals) may be resolved *without using a polariser*. The spectrum may be simplified in the case of an orthorhombic crystal, as well. The longitudinal-optical (LO) and transversal-optical (TO) mode frequencies were calculated² in the case of optically isotropic and the simplified spectra of optically uniaxial crystals.

Keywords: reflection spectra, anisotropy, Kramers-Kronig transformation, phonons, symmetry resolving, LO phonons, TO phonons.

INTRODUCTION

Infrared spectroscopy is a well-known tool in the study of crystals. It is particularly useful in conjunction with diffraction (X-ray or neutron) studies, often giving valuable complementary results. On some occasions,³⁻⁵ IR spectroscopy even appears to be more sensitive to the details of the crystal structure, than the diffraction methods.⁶⁻⁸

Studies of single crystals in polarised light give much more relevant information (*e.g.*, the direction of the transition dipole moment^{9,10}) resulting very often in unequivocal assignment of the bands. Polarised IR reflection studies, on the other hand, give the above but also additional information about the optical and dielectric properties, as well as the magnitude of the LO-TO splitting.¹¹⁻¹³ Obviously, reflection studies are advantageous since the information thus obtainable is beyond the simple $k = 0$ approximation.

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When a polariser is not available, it may seem that the use of reflection spectroscopy is severely limited. The purpose of the present paper is to show that, even then, lots of useful information may be gained from reflection spectra. Providing a correct indexing of the crystal faces is possible, phonons of a certain symmetry may be switched off or even, in favourable cases, only phonons of a definite symmetry may be resolved.

THEORETICAL CONSIDERATIONS

For the purpose of the present paper, the optical properties of crystals may be best described using the Fresnel equation.^{14,15} In the approximation of a non-magnetic and non-absorbing medium, this equation takes the form:

$$n^2(\epsilon_x n_x^2 + \epsilon_y n_y^2 + \epsilon_z n_z^2) - [\epsilon_x n_x^2 (\epsilon_y + \epsilon_z) + \epsilon_y n_y^2 (\epsilon_x + \epsilon_z) + \epsilon_z n_z^2 (\epsilon_x + \epsilon_y)] + \epsilon_x \epsilon_y \epsilon_z = 0 \quad (1)$$

where n is the refractive index in the direction of propagation of the wave, n_x , n_y and n_z are its projections on the coordinate axes and ϵ_x , ϵ_y and ϵ_z are the principal values of the permittivity tensor and are known as *principal dielectric axes*. Two special cases will be considered.

For cubic crystals, ($\epsilon_x = \epsilon_y = \epsilon_z$), the Fresnel equation reduces to

$$n^2 = \epsilon \quad (2)$$

In optically *uniaxial crystals*, (tetragonal and hexagonal crystallographic systems), one of the primary dielectric axis is symmetry fixed ($\epsilon_z = \epsilon_{||}$), the other two lie in the plane normal to this axis ($\epsilon_x = \epsilon_y = \epsilon_{\perp}$). When light propagates in an arbitrary direction, *ordinary*,

$$n^2 = \epsilon_{\perp} \quad (3)$$

and *extraordinary*

$$1/n^2 = \cos^2 \theta / \epsilon_{\perp} + \sin^2 \theta / \epsilon_0 \quad (4)$$

waves appear (θ is the angle between the wave vector of the incident radiation and the symmetry axis).

When the light beam propagates parallel to the direction of high symmetry, *i.e.*, $n_x = n_y = 0$, only ordinary rays appear with the polarisation of the electric vector perpendicular to the high symmetry axis (*i.e.*, in the xy plane).

For optically *biaxial crystals*, ($\epsilon_x \neq \epsilon_y \neq \epsilon_z$; orthorhombic, monoclinic and triclinic), the Fresnel equation (1) holds in its original form. Some simplifications can be applied according to the propagation direction of the incident wave.

In a real situation, the crystal is an absorbing medium, leading to complex values for the permittivity and refractive index (N). For cubic crystals (and also for uniaxial crystals, providing the light beam propagates along a direction of high

symmetry), valuable information may be gained *even with unpolarised light*. The important quantities are n and k , defined as:

$$N = n - ik \quad (5)$$

that is, the real and imaginary part of the complex refraction index. These quantities are further used to introduce the real and imaginary part of the complex permittivity, ϵ' and ϵ'' ($\epsilon = \epsilon' - i\epsilon''$), in the following way:

$$\epsilon_r' = n^2 - k^2; \quad \epsilon_r'' = 2nk \quad (6)$$

The last two quantities are used to define the conductivity (σ) and resistivity (ρ) functions

$$\sigma = \omega \epsilon_0 \epsilon_r''; \quad \rho = \frac{\epsilon_r''}{\omega \epsilon_0 [(\epsilon_r')^2 + (\epsilon_r'')^2]} \quad (7)$$

whose maxima give the frequencies of the TO and LO phonons, respectively ($\omega = 2\pi\nu$). Note that these two quantities are not simply interrelated. Since it is only the maxima of these functions that yield important information, they are as a rule given in arbitrary units.

In practice, n and k are calculated from the reflection spectrum, using the Kramers-Kronig transformation. All other quantities are then easily calculated.

EXPERIMENTAL

Single crystals of the cubic $\text{CsCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ alum, were grown from aqueous solutions of the corresponding salts, taken in stoichiometric amounts. Commercially available Cs_2SO_4 and $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ of reagent grade purity were used. Large $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ crystals were grown from aqueous solutions of KCl and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Pieces of calcite (CaCO_3), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) were cut from naturally grown minerals. Large KHSO_4 single crystals of excellent quality were accidentally obtained from used 'chromosulfuric acid' (originally, concentrated H_2SO_4 containing dissolved $\text{K}_2\text{Cr}_2\text{O}_7$). $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was simply recrystallized from water with a few drops of H_2SO_4 . The (210) faces were developed in $\text{CsCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, (111) in $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$, rhombohedral faces (10 14) were found in calcite, both (113) and (001) in KHSO_4 , (010) in gypsum and several different faces in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, which were left unindexed. Crystal polishing was inevitable for calcite, $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ and KHSO_4 , thus revealing smooth and shiny (0001), *i.e.*, (001) faces.

The IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR interferometer using a specular reflectance accessory, enabling spectra acquisition at near-normal incidence. All spectra were recorded with a 4 cm^{-1} resolution, taking 16 background and 32 (64) sample scans, depending on the crystal size. The OPD velocity was 0.2 cm/s . The wavenumber accuracy was better than $\pm 1 \text{ cm}^{-1}$.

GRAMS2000¹⁶ and GRAMS386¹⁷ software packages were used for spectra acquisition and manipulations, including Kramers-Kronig transformation. The LO and TO frequencies were calculated using a computer program written in Array Basic.¹⁸

RESULTS AND DISCUSSION

Optically isotropic crystals

The studied $\text{CsCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ alum (of β type) belongs to the cubic crystal system, $Pa3$ space group.¹⁹ The symmetry of the metal cations is S_6 , that of the

sulfate tetrahedra is C_3 and water molecules lie on positions of general symmetry. Only modes of F_u symmetry are IR active. Being optically isotropic, (Eq. (2)), it is irrelevant from which crystal face is the spectrum acquired. Reflection at near-to-normal incidence with unpolarised light, renders all relevant IR spectroscopic information (Fig. 1a, b). As demonstrated by Ivanovski *et al.*,²⁰ the LO-TO splitting (Fig. 1c, d), varies between 0 and $\approx 60 \text{ cm}^{-1}$, depending mainly on the transition strength of the oscillator. For some modes (*i.e.*, the antisymmetric SO_4 stretchings), this LO-TO splitting dominates over site-group and correlation field splitting,^{20,21} while for other (*i.e.*, the librational modes of the water molecules) the correlation field splitting is dominant.^{21,22}

Thus for cubic crystals, complete information beyond the unit cell group approximation may be obtained with unpolarised light.

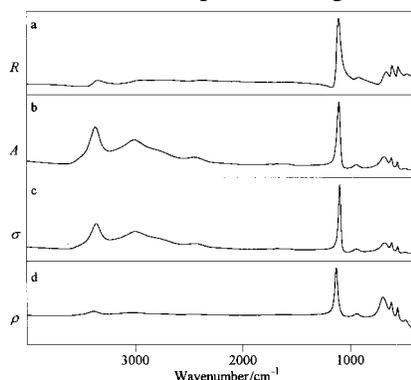


Fig. 1. Spectra of $\text{CsCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$: reflection a), absorption b), conductivity- σ c) and resistivity- ρ d). All quantities are given in arbitrary units. The maxima in the last two curves give the frequencies of the TO and LO phonons, respectively.

Uniaxial crystals

Of the studied crystals, the hexagonal calcite (space group $R\bar{3}c^{23}$) and the tetragonal $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ (space group $P4_2/mnm^{24}$) are uniaxial crystals. The carbonate anions in the structure of calcite occupy positions of D_{3d} symmetry, the z -axis being perpendicular to the CO_3^{2-} plane. The local symmetry of the complex anion $[\text{CuCl}_4(\text{H}_2\text{O})_2]^{2-}$ is D_{2h} , the z -axis passing through the copper and two oxygen atoms. The IR active modes in both cases belong to the A_{2u} and E_u symmetry species, the former being z -polarised and the latter (doubly degenerate) is polarised in the xy plane.

Only E modes are excited when the beam enters the crystal in a direction parallel to the z (c) crystal axis, Eq. (3), since the polarisation is necessarily in the xy plane and only transition dipoles in the same plane may be excited. Consequently, it is possible to 'switch-off' the symmetric bending CO_3^{2-} vibration in calcite, or the symmetric stretching and bending vibrations of the H_2O molecules in Mitscherlichite, since the transition dipole moment in all these cases is parallel to the c -crystal

axis. This condition is met upon reflection from (0001), *i.e.*, (001) planes (*cf.* Figs. 2a, b and 3a, b, respectively). It is thus possible to *resolve the E phonons in uniaxial crystal without using polarised radiation*. For these 'pure' E-spectra it is then easy to calculate the σ and ρ functions, the maxima of which give the frequencies of the TO and LO phonons (Figs. 2c, d and 3c, d).

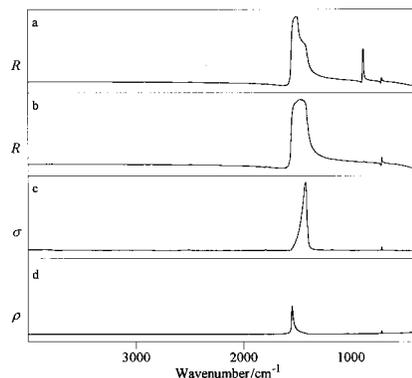


Fig. 2. Spectra of calcite, CaCO_3 : reflection from the (10T4) and (0001) faces (a and b, respectively), as well as the conductivity and resistivity curves, for the (0001) reflection geometry (c and d).

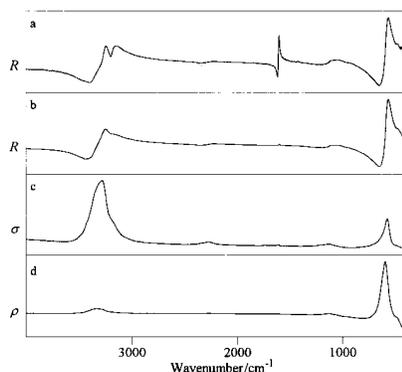


Fig. 3. Spectra of $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$: reflection from the (111) and (001) faces (a and b), and the σ and ρ curves, for the (001) reflection geometry (c and d).

Biaxial crystal

Case i) Orthorhombic crystals. KHSO_4 (mercallite) crystallises in the $Pbca$ group (one of the D_{2h} groups²⁵). There are two crystallographically different K^+ and HSO_4^- ions on positions of general symmetry.

If acquired from the (113) face, the spectrum contains phonons of B_{1u} , B_{2u} and B_{3u} symmetry (Fig. 4a). The spectrum is somewhat simplified, when acquired from the (001) face, as in this case, according to equation (6), the z -polarised modes are 'switched-off' (*cf.* Fig. 4b). These 'missing bands' are due to the B_{3u} modes ($E \parallel c$).

Case ii) Monoclinic crystals. Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, crystallises in the $I2/a$ space group (non-standard setting of the $C2/c$ group²⁶). The metal cations are on

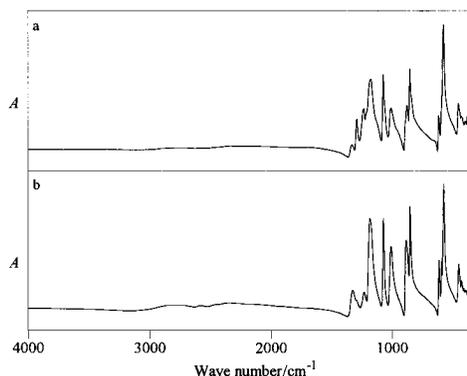


Fig. 4. Absorption (transformed reflection) spectra of KHSO_4 , acquired from the (113) and (001) faces (a and b, respectively).

inversion centres, the sulfate groups lie on the C_2 axes and the water molecules lie on positions of general symmetry. The vibrational spectra of gypsum have been studied extensively in the past,^{2,12,27-31} revealing unusually strong resonance splitting of the HOH bending modes.

The IR spectrum of a powdered sample of gypsum is shown in Fig. 5a. Note the strong resonant splitting of the HOH bending modes. However, when the spectrum is acquired from the (010) face, the IR beam is parallel to the b crystal axis, which is in the same time a symmetry axis (C_2). Only vibrations with transition dipoles perpendicular to the axis may be excited. Therefore, *even with unpolarised light, only B_u phonons are excited in this geometry*. The spectrum is correspondingly simplified (*cf.* Fig. 5b).

Case iii) Triclinic crystals. Chalcantite, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, crystallises in the $P\bar{1}$ space group.³² The copper cations are on inversion centres, all other groups being at positions of general symmetry. Since none of the dielectric axes is fixed by symmetry and all IR active vibrations are of the same (A_u) symmetry type, it is virtually impossible to make any presumptions about the spectral appearance upon reflection from a certain face.

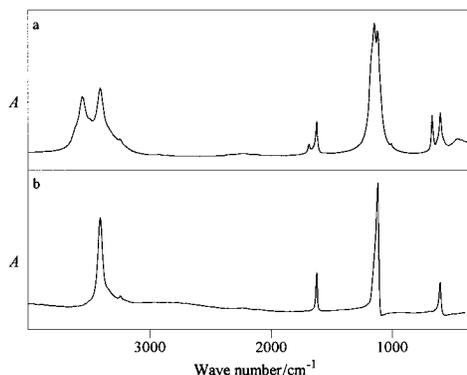


Fig. 5. Absorption spectra of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$: from KBr pellet a) and transformed from reflection, from the (010) face b).

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ИЗВОД

ФУРИЈЕ-ТРАНСФОРМНИ ИНФРАЦРВЕНИ РЕФЛЕКСИОНИ СПЕКТРИ
МОНОКРИСТАЛА: РАЗДВАЈАЊЕ ФОНОНА РАЗЛИЧИТОГ СИМЕТРИЈСКОГ ТИПА,
БЕЗ УПОТРЕБЕ ПОЛАРИЗАТОРА

ВЛАДИМИР М. ПЕТРУШЕВСКИ, ВЛАДИМИР ИВАНОВСКИ и МЕТОДИЈА НАЈДОСКИ

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Снимљени су Фурије-трансформни инфрацрвени рефлексиони спектри (при скоро нормалном упаду светлосног снопа) различитих кристалних примерака: $\text{CsCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (цезијум-хромна стипса, кубична), $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ (мичерлихит, тетрагоналан), CaCO_3 (калцит, хексагоналан) KHSO_4 (меркалит, орторомбичан), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (гипс, моноклиничан) и $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (халкантит, трикличан). Добивени спектри су даље трансформисани помоћу Крамерс-Кронигове трансформације, чиме се добијају апсорпциони спектри. Осим код кубичних стипси, резултатни спектар јако зависи од пласни од које се врши рефлексија (резултат анизотропије). Фонони одређеног симетријског типа (Е-симетрије, код оптички једноосних и В-симетрије, код моноклиничних кристала) могу да се одвоје без употребе поларизатора. Спектар се може упростити и у случају орторомбичних кристала. Фреквенције лонгитудиналних и трансверзалних оптичких фонона могу да се израчунају код кубичних кристала и код "упрошћених" спектра оптички једноосних кристала.

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REFERENCES

1. R. Kronig, *J. Opt. Soc. Am. Rev. Sci. Instrum.* **12** (1926) 547
2. M. Hass, G. B. V. M. Sutherland, *Proc. Roy. Soc.* **236** (1956) 427
3. V. Stefov, B. Šoptrajanov, V. Petruševski, *Bull. Chem. Technol. Macedonia* **7** (1989) 151
4. B. Šoptrajanov, V. Stefov, V. M. Petruševski, *Spectrosc. Lett.* **26** (1993) 1839
5. S. C. Nyburg, B. Šoptrajanov, V. Stefov, V. M. Petruševski, *Inorg. Chem.* **36** (1997) 2248
6. D. Michalska-Fong, P. J. McCarthy, K. Nakamoto, *Spectrochim. Acta* **39A** (1983) 835
7. A. Hergold-Brundić, V. Stefov, *Symposium Ecologically Rational Development of Chemical Technologies*, Zagreb, 1991, 33
8. R. G. Delaplane, J. Ibers, J. R. Ferraro, J. J. Rush, *J. Chem. Phys.* **50** (1969) 1920
9. J. C. Ward, *Proc. Roy. Soc.* **228A** (1955) 205
10. H. Susi, *Spectrochim. Acta* **17** (1961) 1257
11. J. C. Decius, R. Frech, P. Brüesch, *J. Chem. Phys.* **58** (1973) 4056
12. H. Takahashi, I. Machara, N. Kaneko, *Spectrochim. Acta* **39A** (1983) 449
13. D. Hadži, B. Orel, *Ind. J. Pure Appl. Phys.* **16** (1978) 376
14. M. Born, E. Wolf, *Principles of Optics*, Pergamon Press, London, 1970
15. L. D. Landau, *Electrodynamics of Continuous Media*, Pergamon Press, London 1960
16. GRAMS AnalystTM for PE-2000 FT-IR, Version 3.01B, Level II, Galactic Industries Corp., 1991-1994
17. GRAMS/386 for Microsoft Windows, Version 2.02, Galactic Industries Corp., 1991-1993
18. V. M. Petruševski, V. G. Ivanovski, *Bull. Chem. Technol. Macedonia* **15** (1996) 131
19. J. K. Beattie, S. P. Best, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton* (1981) 2105

20. V. Ivanovski, V. M. Petruševski, B. Šoptrajanov, *Vibrat. Spectrosc.* **19** (1999) 425
21. V. Ivanovski, V. M. Petruševski, B. Šoptrajanov, *J. Mol. Struct.*, **480-481** (1999) 480
22. V. Petruševski, B. Šoptrajanov, *J. Mol. Struct.* **219** (1990) 67
23. M. Ishigame, T. Sato, T. Sakurai, *Phys. Rev.* **B3** (1971) 4388
24. R. Chidambaram, Q. O. Navarro, A. Garcia, K. Linggoatmodjo, L. Shi-Chien, I. -H. Suh, *Acta Crystallogr.* **B26** (1970) 827
25. F. Payan, R. Haser, *Acta Crystallogr.* **B32** (1976) 1875
26. B. F. Pedersen, D. Semmingsen, *Acta Crystallogr.* **B38** (1982) 1074
27. V. Seidl, O. Knop, M. Falk, *Can. J. Chem.* **47** (1969) 1361
28. B. J. Berenblut, P. Dawson, G. R. Wilkinson, *Spectrochim. Acta* **29A** (1973) 29
29. A. Eriksson, J. Lindgren, *J. Mol. Struct.* **53** (1979) 97
30. V. Petruševski, B. Šoptrajanov, *J. Mol. Struct.* **115** (1984) 343
31. J. Cvetković, V. M. Petruševski, B. Šoptrajanov, *J. Mol. Struct.* **408/409** (1997) 463
32. J. N. Varghese, E. N. Maslen, *Acta Crystallogr.* **B41** (1985) 184.