

HARMONIC FREQUENCIES AND ANHARMONICITY CONSTANTS FOR THE ANTISYMMETRIC SO_4 STRETCHING VIBRATIONS OF ISOMORPHOUSLY ISOLATED SO_4 IONS IN K_2CrO_4

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SUMMARY

In order to get some idea for the magnitude of the anharmonicity constants for the stretching SO_4 vibrations in K_2SO_4 , the FT IR spectra of K_2CrO_4 containing small amount of K_2SO_4 were recorded at LNT, in the 2350-500 cm^{-1} region. All stretching fundamentals were precisely measured, as well as nine of ten possible second-order transitions. Combination bands between stretching and bending vibrations could not be identified in the spectra of the mixed crystals. The analogous bands in pure K_2SO_4 are probably of very low intensity, thus indicating that the corresponding anharmonicity constants could be neglected. Using suitable equations [1], the values for the harmonic (zero-order) frequencies of the antisymmetric stretching fundamentals and anharmonicity constants were calculated.

INTRODUCTION

The vibrational spectra of sulfate compounds were extensively studied. Despite that, there is a lack of literature data on the anharmonicity constants of the SO_4 ions in these compounds. The reasons for this seem to be clear : as a consequence of correlation field splitting, dispersion of the phonon curves, LO-TO splitting and relaxation of the selection rules for multiphonon transitions (the wavevector of the individual phonons may be anywhere in the first Brillouin zone), it is impossible to measure the frequencies of the fundamental and second-order transitions precisely.

The spectra of SO_4 ions trapped in different alkali-halides were also studied (see [2] and the references therein). Valuable informations could be obtained from this spectra. However, due to

the specific environment of the SO_4 ions it is not possible to extend these informations to pure sulfate compounds (e. g. if Ca and SO_4 ions are trapped in KBr, the spectroscopic results could say nothing about the sulfate ions in CaSO_4).

The vibrational spectra of isomorphously isolated SO_4 ions were also investigated [3-5], but only the frequencies of some of the fundametal transitions of the isolated ions were published. Therefore, a carefull reinvestigation of the IR spectra of such compounds is needed in order to get some informations on the anharmonicity constants in pure sulfate compounds (the environment of the isomorphously isolated ions is almost the same as in the parent compound [6, 7]). In the present paper, the results of the investigation of the IR spectra of SO_4 doped K_2CrO_4 are reported. Special attention was paid to the $2350\text{-}2000\text{ cm}^{-1}$ region of the spectra where bands due to second-order transitions are expected.

EXPERIMENTAL

K_2CrO_4 doped with 2% and 5% of K_2SO_4 was prepared by dissolving appropriate amounts of the two salts in water, followed by slow evaporation until crystals are obtained. The IR spectra were recorded on Perkin Elmer 1720 FT IR spectrophotometer. The spectra (KBr pellets) were recorded at 75 K using continuous flow cryostat cooled with liquid nitrogen. Resolutions of 1 cm^{-1} (for the fundamentals) and 2 cm^{-1} (for second-order transitions) were used. Twenty scans appear to be enough in the $1300\text{-}500\text{ cm}^{-1}$ region, while in the $2320\text{-}2000\text{ cm}^{-1}$ region the noise was still appreciable, even with 100 scans.

RESULTS AND DISCUSSION

The low-temperature IR spectra of pure K_2SO_4 are presented on Figs. 1a and 1b. As mentioned above, the informations obtainable from these spectra are far from being enough to calculate the anharmonicity constants and zero-order frequencies for the SO_4 ions. The major problem is the determination of the frequencies of the second-order transitions (cf. Fig. 1b). These informations are completely obscured; the spectrum, namely, maps the two-phonon

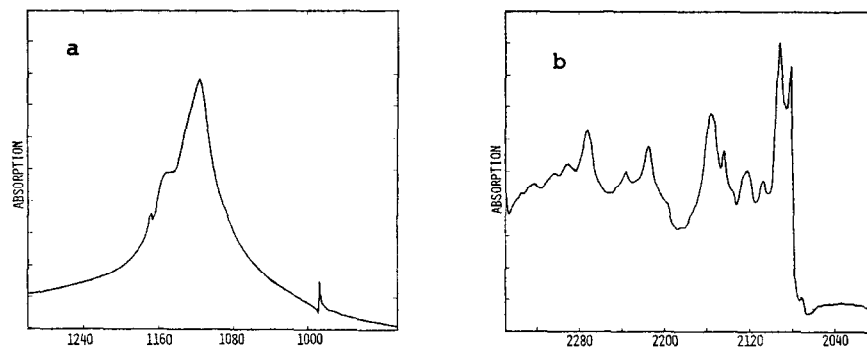


Fig. 1 : LNT IR spectra of K_2SO_4

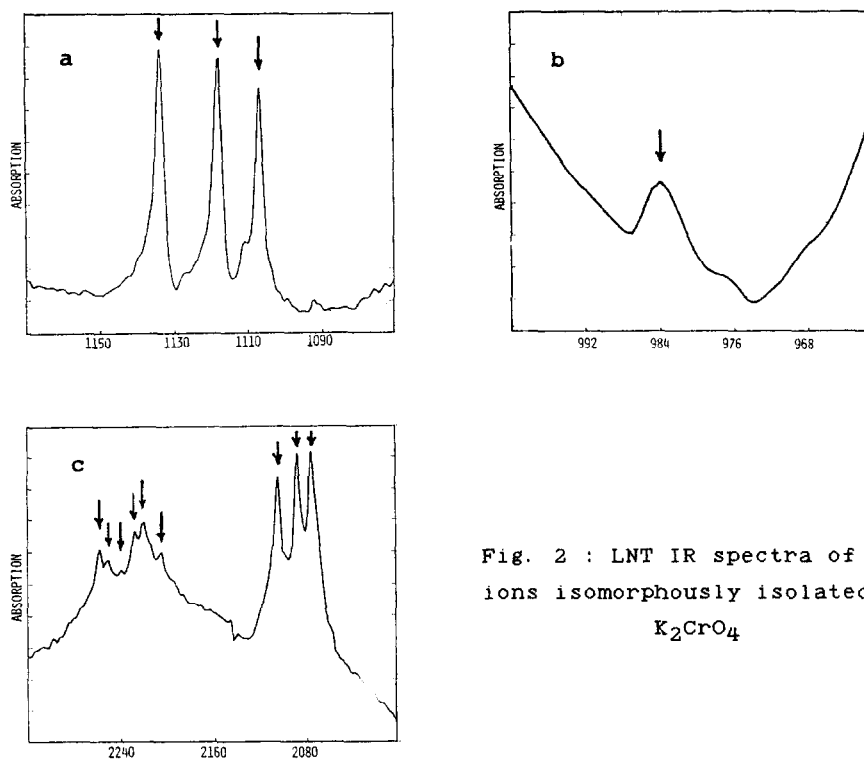


Fig. 2 : LNT IR spectra of SO_4 ions isomorphously isolated in K_2CrO_4

density of states of the form $\nu_1 + \nu_3$ and $\nu_3 + \nu_3$, hence the bands could not be assigned to any particular transition.

The isomorphous isolation eliminates the correlation field splitting and similar crystal effects. As a consequence, the IR spectra (cf. Figs. 2a-c) are much simpler to analyse. On the other hand, due to the fact the the two compounds (K_2CrO_4 and K_2SO_4) are strictly isomorphous, the basic informations on the effect of the condensed phase (K_2SO_4) on the sulfate frequencies are retained even when the SO_4 ions are isolated in a K_2CrO_4 matrix. Thus, it is expected that the present results on the anharmonicity constants of the isolated sulfate ions are transferable to K_2SO_4 .

No bands assignable to two-phonon processes between stretching and bending modes of the SO_4 ions could be identified in the IR spectra of the isolated ions as well as in pure K_2SO_4 . This indicates that the corresponding anharmonicity constants are negligibly small. The band corresponding to $2\nu_1$ was not present in the IR spectra, most probably as a result of its extremely low IR intensity (the symmetry of the SO_4 ions only slightly deviates from T_d in K_2SO_4 [6, 8] and under the selection rules of the T_d point group both the fundamental ν_1 and its overtone are IR forbidden). Since the site symmetry of the tetrahedral ions is C_3 , one can use the equation [1] for non-degenerate case in the calculation. Therefore, we were able to calculate nine of the ten existing stretch-stretch anharmonicity constants, as well as the harmonic frequencies for the components of the antisymmetric stretching vibrations (cf. Table 1).

Table 1 shows that the anharmonicity constants of the form x_{131} have much larger values than x_{313j} . This may indicate that the anharmonicity of the symmetric stretching mode ν_1 , is larger compared with the anharmonicity of ν_3 . This is to be expected because, as mentioned earlier, the symmetry of the SO_4 ions in K_2SO_4 deviates only slightly from T_d and all the odd terms in the potential energy expansion of the ν_3 mode could be neglected to a first approximation (in fact, these terms are zero for a tetrahedral ion with T_d symmetry). Thus it seems interesting to study in an analogous way other SO_4 doped compounds in which the sulfate ions are more distorted. SO_4 doped $SnSeO_4$ is probably a good example, as it is known [9] that the sulfate ions in the related $SnSO_4$ are appre-

ν/cm^{-1}	Mode	ω/cm^{-1}	x_{1j}/cm^{-1}
984.0	ν_1	?	
1106.5	ν_{3a}	1124	
1117.5	ν_{3b}	1135	
1133.5	ν_{3c}	1150	
2075.0	$\nu_1 + \nu_{3a}$?	-15.5
2087.0	$\nu_1 + \nu_{3b}$?	-14.5
2104.0	$\nu_1 + \nu_{3c}$?	-13.5
2205.0	$2\nu_{3a}$	2248	-4.0
2220.0	$\nu_{3a} + \nu_{3b}$	2259	-4.0
2227.0	$2\nu_{3b}$	2270	-4.0
2239.0	$\nu_{3a} + \nu_{3c}$	2274	-1.0
2250.0	$\nu_{3b} + \nu_{3c}$	2285	-1.0
2258.0	$2\nu_{3c}$	2300	-4.5

TABLE 1 : The calculated harmonic frequencies and anharmonicity constants of the sulfate ions in SO_4 doped K_2CrO_4

ciably distorted. In the latter case, the ratio x_{131}/x_{313j} is expected to be smaller.

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