

VIBRATIONAL ANHARMONICITY AND VIBRATIONAL STARK EFFECT OF SULPHATE IONS TRAPPED IN POTASSIUM, RUBIDIUM AND CESIUM CHROMATE

Ljupco Pejov, Vladimir M. Petrusovski

Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Sts. Cyril and Methodius University, POB 162, Arhimedova 5, 91000 Skopje, Republic of Macedonia, e-mail: ljupcop@iunona.pmf.ukim.edu.mk

Abstract. Room and low temperature (~ 100 K) FT-IR and Raman spectra of the sulphate doped K_2CrO_4 , Rb_2CrO_4 and Cs_2CrO_4 were recorded. Nine (out of a possible ten) second-order stretch-stretch vibrational transitions of the dopant anions were detected. On the basis of these data, the anharmonicity constants and the corresponding harmonic eigenvalues were calculated for several vibrational transitions using the second-order perturbation theoretical expressions. In all cases, the splitting of the ν_3 mode is higher than for the ν_4 one, indicating a smaller angular distortion than the bond length one. The theory of vibrational Stark effect suggests that the observed frequency shifts of the ν_1 , ν_3 and ν_4 mode components may be attributed to the increase of the field strength at the doped anion site going from K_2CrO_4 to Cs_2CrO_4 . The Stark splitting of these modes, on the other hand, implies that the internal crystalline field vector is almost parallel to the (hypothetical) C_2 axis of the dopant (slightly distorted) tetrahedral anions.

Key words: isomorphously isolated ions, IR and Raman spectra of; sulfate ion distortion; harmonic frequencies; anharmonicity constants; Vibrational Stark effect.

1. Introduction

The matrix isolation techniques have been long recognized as powerful tools in studying various phenomena in many areas of chemical physics [1, 2]. Although nowadays the term "matrix isolation" usually refers to the isolation of molecular species in inert gas matrices [2], the methodology of *isomorphous isolation* (isolation of molecular/ionic species in an *isomorphous* solid matrix) is still referred under the same wider topic. Such studies of isomorphously isolated species allow significant conclusions to be derived regarding the anharmonicity of molecular vibrations, the effect of internal fields on vibrational transitions (known as the Vibrational Stark Effect – VSE), as well as for the influence of molecular environment on the vibrational relaxation processes.

Vibrational spectra of polyatomic species trapped in various hosts (mainly alkali halides) were extensively studied by a number of authors [3-8]. However, only a few studies were devoted to the study of anharmonicity of the dopant species internal vibrations [3-5]. Continuing our studies of the vibrational anharmonicity and vibrational Stark effect of sulphate anions isomorphously isolated in various solid matrices [3-5], in this paper we report the IR and Raman spectra of SO_4^{2-} species trapped in K_2CrO_4 , Rb_2CrO_4 and Cs_2CrO_4 hosts.

2. Experimental

The sulphate doped K_2CrO_4 , Rb_2CrO_4 and Cs_2CrO_4 (with molar fractions of sulfate ions of 2 % and 5 %) were prepared by dissolving appropriate amounts of sulphate and

chromate salts in water, followed by slow evaporation. The chromate compounds (except the K_2CrO_4 , which was commercially available) were prepared by adding the corresponding carbonates to aqueous solution of CrO_3 , and adjusting the final pH value. IR spectra of the sulfate doped chromates were recorded in Nujol mulls at room temperature (RT) and at low temperature (LT, ~ 100 K), on a Perkin Elmer FT-IR system 2000 interferometer. A variable-temperature cell (Graseby Specac) was used for the low-temperature measurements. Resolution of 2 cm^{-1} was used, taking 256 scans in order to obtain a good signal to noise ratio. RT and LT Raman spectra of the mixed crystals were recorded on a Perkin Elmer NIR FT-Raman spectrometer, model 1700-x using the Nd-YAG laser operating at 1064 nm. Curve-fitting procedures and other numerical analyses of the spectra were performed using the GRAMS32 program package.

3. Results and Discussion

As can be seen from the regions of appearance of bands due to the ν_3 and ν_4 modes in the IR spectra of the sulfate impurities in K_2CrO_4 , Rb_2CrO_4 and Cs_2CrO_4 matrices, the degeneracy of the triply degenerate ν_3 and ν_4 modes of the sulfate anions is completely removed upon the isomorphous replacement at a particular site of the host crystal lattice. (The ν_3 and ν_4 mode components are denoted as ν_{ia} , ν_{ib} and ν_{ic} , $i \in \{3,4\}$ further in the text.) Such findings may be fully explained within the C_s site symmetry. Evidently, as in the case of sulphate doped potassium chromate, the latent site symmetry effects are of little importance for the sulphate species, owing to the relatively high intrinsic intensities of their IR-active modes. The situation is opposite in the case of chromate doped alkaline sulfates. The low SO_4^{2-} site symmetry in the studied matrices, implies an "activation" of the ν_1 and ν_2 modes, which are forbidden under the selection rules of the T_d point group. The appearance of a weak band due to the ν_1 mode of the dopant anions in the IR and Raman spectra of the SO_4 doped K_2CrO_4 , Rb_2CrO_4 and Cs_2CrO_4 is in line with the previous site-group analysis.

The regions of the second order transitions of the sulfate anion internal modes in the IR spectra of pure K_2SO_4 , Rb_2SO_4 and Cs_2SO_4 compounds have been previously published [3-5]. As discussed, these regions map the two-phonon density of states of the form $\nu_1 + \nu_3$ and $\nu_3 + \nu_3$ thus obscuring the possibility to extract information regarding the anharmonicity of any particular second-order transition. On the other hand, in the case of isomorphously isolated sulfate anions, the situation is much clearer, the appearance of spectra being fully in line with the predictions of the site-group analysis. As can be seen from the region of the second order transitions of the forms $\nu_1 + \nu_{3i}$ and $\nu_{3i} + \nu_{3j}$ of the dopant SO_4^{2-} anions in the studied chromate matrices, nine (out of possible ten) second-order stretch-stretch transitions were detected, thus allowing calculation of the corresponding anharmonicity constants and the harmonic eigenvalues, using the results of second-order non-degenerate stationary perturbation theory. Since the geometry of the SO_4^{2-} ions in these compounds deviates only slightly from the ideal T_d one, the absence of the $2\nu_1$ band and the extremely low intensity of the ν_1 mode are self-understood. The results from the calculations, together with the experimental data are summarized in Table 1.

Bands due to the second-order transitions of the form $\nu_1 + \nu_{4i}$ and $\nu_{3i} + \nu_{4j}$ were not detected in this study, implying very low values of the corresponding anharmonic coupling constants in the potential energy expression.

Table 1. Band frequencies and anharmonicity constants for SO_4^{2-} ions doped in K_2CrO_4 , Rb_2CrO_4 and Cs_2CrO_4

Mode	K_2CrO_4		Rb_2CrO_4		Cs_2CrO_4	
	ν/cm^{-1}	$X_{ii}(\omega)/\text{cm}^{-1}$	ν/cm^{-1}	$X_{ii}(\omega)/\text{cm}^{-1}$	ν/cm^{-1}	$X_{ii}(\omega)/\text{cm}^{-1}$
ν_{4a}	612.1		610.2		607.7	
ν_{4b}	616.5		615.0		612.1	
ν_{4c}	622.3		618.8		614.5	
ν_1	974.8		969.4		965.0	
ν_{3a}	1106.3	1117.2	1100.3	1110.8	1091.2	1106.9
ν_{3b}	1117.2	1127.8	1109.9	1119.3	1100.2	1113.5
ν_{3c}	1132.8	1141.7	1121.2	1129.1	1111.6	1125.5
$\nu_1 + \nu_{3a}$	2075.5	-5.60	2064.1	-5.60	2048.4	-7.80
$\nu_1 + \nu_{3b}$	2087.2	-4.80	2074.5	-4.80	2058.4	-6.80
$\nu_1 + \nu_{3c}$	2103.4	-4.20	2085.9	-4.70	2070.4	-6.20
$2\nu_{3a}$	2205.2	-3.70	2193.1	-3.75	2174.4	-4.00
$\nu_{3a} + \nu_{3b}$	2220.2	-3.30	2207.6	-2.60	2188.1	-3.30
$2\nu_{3b}$	2227.5	-3.45	2213.5	-3.15	2192.4	-4.00
$\nu_{3a} + \nu_{3c}$	2241.0	1.90	2223.7	2.20	2198.5	-4.30
$\nu_{3b} + \nu_{3c}$	2250.7	0.70	2232.4	1.30	2211.4	-0.40
$2\nu_{3c}$	2257.5	-4.05	2235.1	-3.65	2214.8	-4.20

According to the theory of vibrational Stark effect [6-19], within the *effective local homogeneous field approximation*, the frequency downshift of the sulphate internal modes on going from K_2CrO_4 to Cs_2CrO_4 matrix may be attributed to an increase in the field strength. The frequency shift is governed by the term:

$$\left[\frac{a_{iil}}{a_{11}} \left(\frac{\partial \alpha_{zz,0}}{\partial S_1} \right)_0 + \frac{3a_{iii}}{a_{ii}^2} \left(\frac{\partial \mu_z}{\partial S_i} \right)_0^2 + \frac{3}{2} \sum_{m \neq i} \frac{a_{iimm}}{a_{ii} a_{mm}} \left(\frac{\partial \mu_z}{\partial S_i} \right)_0 \cdot \left(\frac{\partial \mu_z}{\partial S_m} \right)_0 \right] \cdot E_z^2$$

where standard notation of the VSE theory is used.

According to the data for the anharmonicity constants presented in Table 1, the potential constants a_{iii} are negative for the ν_3 mode components. Such is also the case with practically all of the constants of the type a_{iimm} and a_{iil} as well. Also, the derivative $(\partial \alpha_{zz,0} / \partial S_1)_0 > 0$. The term in parentheses in the above equation is thus, negative. Two important conclusions follow from the presented model. First, the shift to lower frequencies may be explained as being due to the increase of the effective local electrostatic field in the studied series of matrices. Second, a quadratic field dependence of the frequency shift is implied. Since the Stark tuning rate $(d\tilde{\nu}_i / dE)$ should increase linearly with the field strength, the observed increase in the difference $\tilde{\nu}_{01}^{\text{Rb}}(E_z) - \tilde{\nu}_{01}^{\text{Cs}}(E_z)$ compared to the $\tilde{\nu}_{01}^{\text{K}}(E_z) - \tilde{\nu}_{01}^{\text{Rb}}(E_z)$ one is also expected.

The following expression may be straightforwardly obtained for the ratio of the distortions of ν_3 and ν_4 coordinates on the basis of the proposed model:

$$\frac{(S_{3k})_e}{(S_{4k})_e} = \frac{(\partial \mu_z / \partial S_{3k})_0 m_{4k} \omega_{04k}}{(\partial \mu_z / \partial S_{4k})_0 m_{3k} \omega_{03k}}$$

Since in the case of the studied systems, the ratio of the effective charges:

$$\frac{(\partial\mu/\partial S_{3k})_0}{(\partial\mu/\partial S_{4k})_0}$$

is practically equal to the square root of the ratio of measured band intensities, it is easily estimated from the experimental data. The band intensities were obtained with a standard curve-fitting procedure, using the GRAMS32 programming package. Since the ν_3 and ν_4 band components are well resolved, the curve-fitting procedures are easily implemented, without the usual problems of uniqueness of solution, arising from the band overlaps. The obtained ratio $(\partial\mu/\partial S_{3k})_0/(\partial\mu/\partial S_{4k})_0$ is $\sim 3-4$. On the other hand, the ratio of the harmonic wavenumbers for the ν_4 and ν_3 mode components is ~ 0.5 , while the ratio of the corresponding reduced masses is ~ 1 . Thus, the field-induced displacements are significantly larger for the ν_3 than for the ν_4 mode components, as is observed experimentally.

On the basis of the results presented in Ref. [20], the observed Stark splitting of the ν_3 and ν_4 modes of the dopant anions indicate that the effective local crystalline field vector is directed almost parallel to the pseudo- C_2 axis of the (slightly distorted) tetrahedral species.

4. References

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Апстракт. Снимени се Фуриетрансформни инфрацрвени и Рамански спектри на сулфатни јони изолирани во K_2CrO_4 , Rb_2CrO_4 и Cs_2CrO_4 . Забележани се девет (од можни десет) вибрациони премини од втор ред на гостинските јони. Користејќи ги изразите од теоријата на пертурбации, пресметани се константите на анхармоничност и хармониските сопствени вредности за неколку вибрациони премини. Теоријата на вибрациониот Штарков ефект имплицира дека набљудуваните помесувања на фреквенциите на компонентите на ν_1 , ν_3 и ν_4 модовите можат да бидат припишани на зголемување на јачината на локалното електростатско поле одејќи од K_2CrO_4 кон Cs_2CrO_4 . Расцепувањето на овие модови имплицира дека векторот на кристалното поле е насочен долж псевдо- C_2 оската на гостинските јони.