VIBRATIONAL ANHARMONICITY AND ORIENTATIONAL DYNAMICS OF SO_4^{2-} ANIONS ISOLATED IN Ag_2SeO_4 MATRIX

Ljupco Pejov, Vladimir M. Petrusevski

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 spectra of sulphate anions isomorphously isolated in Ag_2SeO_4 were recorded. The anharmonicity constants and harmonic vibrational frequencies for the ν_3 and ν_4 internal modes of the dopant anions were calculated, on the basis of the measured fundamental and second order transitions. The appearance of the IR spectrum of the studied species may be explained in terms of D_{2d} effective symmetry. According to the magnitude of the splitting of ν_3 and ν_4 modes of the dopant anions, the bond length distortion of the sulphate impurities is lower, and the angular distortion is significantly higher in Ag_2SeO_4 than in all other matrices studied so far. The OSO angle calculated from the ratio of the intensities of B_2 and E ν_3 mode components is 111.6 °. Using the transition dipole moment time correlation function approach, the period of "undisturbed" rotational motion for the dopant anions about the pseudo-C_2 axes is estimated to be approximately 0.035 ps.

Key words: Vibrational anharmonicity, anharmonicity constants, orientational dynamics, correlation function, sulfate impurities, isomorphous isolation, sulfate ion distortion.

1. Introduction

The general advantages of the matrix isolation technique for studying polyatomic molecular/ionic systems in solid state have been well recognized [1-5]. When polyatomic species are doped at low concentration in an isomorphous matrix, the interactions between identical oscillators (leading to correlation field splitting, and the dispersion of phonon curves), as well as the long-range forces of electrostatic origin (leading to LO-TO splitting) can be neglected. Thus, the vibrational spectrum of a particular molecular/ionic system isolated in a solid matrix may be interpreted using only the site group analysis. This is particularly useful for a study of the vibrational anharmonicity of the dopant species [6-17]. While for a pure substance the region of appearance of the second-order transitions of a given mode maps the two-phonon density of states of a given type and practically no band can be assigned to any particular transition, the analysis of the second order spectra in the case of matrix isolated species is often straightforward. It is thus possible to obtain information regarding the anharmonic terms in the molecular potential energy hypersurface, and at least partially solve the inverse spectroscopic problem. On the other hand, study of a single system isolated in various matrices, leads to important information regarding the lattice dynamics and crystal fields and forces. We have recently reported the anharmonicity constants and harmonic vibrational frequencies for sulfate anions isomorphously isolated in several matrices [3-5]. An attempt was also made to derive an exact quantum theoretical basis for the observed Stark shifts of the SO_4 internal modes in the studied matrices. In this work, we report the FT-IR spectra of the SO_4^{2-} anions isomorphously isolated in Ag_2SeO_4.

2. Experimental

The solid solutions of Ag_2SO_4 in Ag_2SeO_4 were obtained by mixing a solution of $AgNO_3$ with one containing appropriate molar ratios of K_2SO_4 and K_2SeO_4. A white precipitate immediately formed, which was afterwards washed with deionized water and dried in a dark place (to preserve the photochemical reduction of Ag^+ ions). The content of Ag_2SO_4 in Ag_2SeO_4 was varied from 2 % to 5 %. Fourier transform infrared spectra at room (RT) and low temperature (LT, ~100 K) were recorded on a Perkin-Elmer System 2000 FT IR in both Nujol mulls and AgCl pellets. LT measurements were performed in a Graseby-Specac variable-temperature cell. In order to obtain a satisfactory signal-to-noise ratio, 256 scans were collected at low temperature, especially for a study of the second-order transitions. 64 to 128 scans appeared to be enough for the RT studies. Both RT and LT spectra were recorded at a resolution of 2 cm^{-1}. Further analysis of the spectra was performed with the GRAMS32 programming package [18]. Mathematical analyses were performed with Mathematica 2.2 [19] and MathCad 7.0 [20] programming packages.

3. Results and Discussion

As can be seen from the regions of appearance of the ν_3 and ν_4 modes in the RT and LT FT-IR spectra of the SO_4^{2-} ions isomorphously isolated in Ag_2SeO_4 matrix, the ν_3 mode exerts a visible splitting only at LT. The ν_3 mode components will be further referred to as ν_{3a} and ν_{3b} (the index "a" referring to the higher-frequency component, and "b" to the lower). On the other hand, the ν_4 mode is split even at RT, while the splitting increases with the lowering of the temperature. The ν_4 mode components will be also referred to as ν_{4a} and ν_{4b} (using the same convention as for the ν_3 mode components). It can be concluded from the spectral data that the effective site symmetry of the SO_4^{2-} anions in the Ag_2SeO_4 matrix is substantially different from the one in the previously studied series of chromate and selenate matrices [3-5]. In the case of the sulfate ions isomorphously isolated in potassium, rubidium and cesium chromate and selenate matrices the ν_3 and ν_4 modes split into three components, implying a lower effective symmetry than in the present case. The observed splitting of the ν_3 mode $[\tilde{\nu}(\nu_{3a})-\tilde{\nu}(\nu_{3b})]$ in the case of SO_4^{2-} ions isolated in Ag_2SeO_4 matrix is 6.3 cm^{-1}, which is approximately half of the $\tilde{\nu}(\nu_{3a})-\tilde{\nu}(\nu_{3c})$ values previously measured in the other solid matrices (chromates and selenates). On the other hand, the splitting of the ν_4 mode $[\tilde{\nu}(\nu_{4a})-\tilde{\nu}(\nu_{4b})]$ in the present case is about twice the value $\tilde{\nu}(\nu_{4a})-\tilde{\nu}(\nu_{4c})$ measured in other matrices. The last finding implies that the angular distortion of the dopant anions in Ag_2SeO_4 is considerably larger than in other cases. The observed spectral features for the present matrix may be consistently explained assuming D_{2d} effective (site) symmetry of the dopant anions. However, since the overall distortion of the dopant anions is rather small on an absolute scale, the crystalline field effects may be treated as a perturbation, and not only the positions, but also the forms of the normal modes may be regarded as slightly affected upon the isomorphous isolation. Therefore, in the following text the usual notation for the normal modes of the (ideal) T_d sulfate anion will be used.

Because of the symmetry lowering of the guest SO_4^{2-} anions due to the internal crystalline fields, the otherwise inactive ν_1 mode is often activated. The region of appearance of this mode in the LT IR spectrum of the SO_4^{2-} anion isolated in Ag_2SeO_4 is in line with the previous statement. However, within the proposed effective symmetry, in the present case it

should still be IR inactive, so its appearance may be explained as being due to a further relaxation of the vibrational selection rules slightly different for the totally symmetric stretching S-O vibration than for the other internal modes. Since the intensity of the ν_1 band is rather low, in order to check whether it really corresponds to the SO_4 ν_1 mode, IR spectra from samples with higher sulphate contents were recorded. The activated ν_1 mode (due to the increase of the dopant ions concentration) appears at practically the same position as in the case of the specimen containing matrix isolated species (the shift is only about 2 cm^{-1} to higher wavenumbers), thus confirming the origin of the band in question.

As obvious from the region of the second order transitions involving the ν_3 mode components in the spectra of the Ag_2SO_4/ Ag_2SeO_4 solid solutions, the two most intensive bands are due to $\nu_{3i} + \nu_1$ combination modes. On the other hand, only two bands appear in the region where $\nu_{3i} + \nu_{3j}$ combinations and the $2\nu_{3i}$ overtones are expected. Regarding the ν_4 modes of the dopant anion in case of the SO_4/Ag_2SeO_4 system, only one second order transition involving the ν_4 modes was detected. On the basis of the measured X_{ik} values, the harmonic vibrational frequencies for several vibrational transitions were calculated (Table 1).

Table I. RT and LT spectroscopic data for fundamental and second order vibrational transitions of the dopant SO_4^{2-} anions in Ag_2SeO_4

Mode	Sym.[a]	$\tilde{\nu}$ / cm^{-1} [b]	$\tilde{\nu}$ / cm^{-1} [c]	I / a. u. [c]	X_{ii} / cm^{-1} [c]	ω / cm^{-1} [c]
ν_4	B_2	591.2	590.1	3.4698		
	E	610.2	610.2	9.3476		
ν_1	A_1		960.7	0.3020		
ν_3	E	1067.1	1065.4	16.904		1089.9
	B_2		1071.7	9.9498		1081.4
$\nu_{4a} + \nu_{4b}$	E		1200.3	0.0091	-0.1	
$\nu_1 + \nu_3$	E		2019.7	0.5261	-7.7	
	B_2		2024.6	0.1673	-7.6	
$2\nu_{3b}$	B_2		2125.7	0.1180	-5.9	
$\nu_{3a} + \nu_{3b}$	E		2130.9	0.0871	-5.9	

[a]Symmetry; [b]RT values; [c]LT values

Using the spectroscopic data given in Table I, within the bond moment additivity approximation, the value of 111.6 ° was obtained for the OSO angle, indicating a rather small absolute angular distortion of the dopant anionic species.

On the basis of the dipole time correlation function formalism, the value of 0.035 ps was obtained for the period of essentially free rotation along the pseudo-C_2 axis of the dopant sulfate anion. The dipole moment correlation function of a given transition is defined as:

$$\left\langle \hat{\tilde{\mu}}(0)\cdot\hat{\tilde{\mu}}(t)\right\rangle = \mathrm{Re}\left(\int_{\mathrm{band}} \hat{I}(\tilde{\nu})\exp(-\mathrm{i}\cdot 2\pi c\Delta\tilde{\nu}t)\mathrm{d}\tilde{\nu}\right)$$

where $\Delta\tilde{\nu} = \tilde{\nu} - \tilde{\nu}_0$ ($\tilde{\nu}_0$ being the band center), the integration is performed over the whole band, while $\langle\ \rangle$ denotes ensemble average. The symbol $\hat{I}(\tilde{\nu})$ denotes normalized (over the whole band) intensity data:

$$\hat{I}(\tilde{\nu}) = \frac{I(\tilde{\nu})}{\int_{\text{band}} I(\tilde{\nu})\,\mathrm{d}\tilde{\nu}}$$

The time evolution of the transition dipole moment operator, determined essentially by molecular orientational motion around the pseudo-C_2 axes, may be divided into two distinct time regimes. During the brief initial period, it is the "free" rotation of the doped species that determines the kinetics of the dipole rotation. The short time dynamics of species in condensed phases, generates a Gaussian decay rate of the transition dipole moment time correlation function. At longer times, on the other hand, the reorientation becomes random, as a result of the influence of the neighboring molecules/ions in the condensed phase, resulting in exponential decay of the dipole time correlation function and a Lorentzian frequency spectrum.

4. References

[1] J. C. Decius, R. M. Hexter, Molecular Vibrations in Crystals, McGraw-Hill, New York, 1977.
[2] G. Turell, Infrared and Raman Spectra of Crystals, Academic Press, London and New York, 1972.
[3] V. Petruševski, W.F. Sherman, J. Mol. Struct., 219 (1990) 171.
[4] V. Petruševski, W.F. Sherman, Bull. Chem. Technol. Macedonia, 13 (1994) 69.
[5] Lj. Pejov, V. M. Petruševski, J. Mol. Struct., (in press).
[6] C. J. Chunnilall, W. F. Sherman, G. R. Wilkinson, J. Mol. Struct., 115 (1984) 205.
[7] M. R. Mohammad, W. F. Sherman, J. Mol. Struct., 80 (1982) 117.
[8] A. D. Buckingham, Proc. Roy. Soc. (London), A248 (1958) 169.
[9] A. M. Benson, H. G. Drickamer, J. Chem. Phys., 27 (1957) 1164.
[10] A. D. E. Pullin, Spectrochim. Acta, 13 (1958) 125.
[11] J. I. Bryant, G. C. Turell, J. Chem. Phys., 37 (1962) 1069.
[12] Lj. Pejov, L. Andreeva, B. Minceva-Sukarova, V. M. Petruševski, J. Mol. Struct., (in press).
[13] M. R. Mohammad, W. F. Sherman, J. Phys. C: Solid State Phys., 18 (1985) 1079.
[14] Y. S. Jain, R. Bhattacharjee, J. Phys. C: Solid State Phys., 18 (1985) 5299.
[15] E. Bauer, M. Magat, J. Phys. Radium, 9 (1938) 319.
[16] S. Califano, Vibrational States, John Wiley&Sons, London, 1976.
[17] R. Kahn, E. C. de Lara, K. D. Möller, J. Chem. Phys., 83 (1985) 2653.
[18] GRAMS32/Spectral notebase, Galactic Industries Co.,version 4.10, 1996.
[19] Mathematica for Windows, version 2.2., Wolfram Research, 1993.
[20] Mathcad 7.0, MathSoft Inc, 1997.

Апстракт. Снимени се Фуриетрансформи инфрацрвени спектри на сулфати јони изоморфно изолирани во Ag_2SeO_4. Врз основа на измерените положби на фундаменталните премини и преминитe од втор ред, пресметани се константите на анхармоничност и хармониските вибрациони фреквенции за компонентите на ν_3 модот на гостинските анјони. Инфрацрвените спектри можат да бидат потполно објаснети во рамките на ефективна D_{2d} симетрија. Според големината на расцепувањата на ν_3 и ν_4 модовите на гостинските анјони, нивната дисторзија во Ag_2SeO_4 матрица е значително помала одошто во сите матрици испитувани досега. Претпоставувајќи валидност на апроксимацијата за адитивност на моментите на врски, користејќи ги соодветните изводи во однос на симетриските координати, OCO аголот пресметан од односот на интензитетите на B_2 и E компонентите на ν_3 модот изнесува 111.6 °.