

## The Vibrational Stark Shifts of Sulfate Internal Modes in $\text{SO}_4^{2-}$ Doped Potassium, Rubidium and Cesium Selenates. A Quantum Model for Measurement of Crystalline Fields

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A quantum theoretical basis for the experimentally observed vibrational Stark shifts of the sulfate internal modes in  $\text{SO}_4^{2-}$  doped  $\text{K}_2\text{SeO}_4$ ,  $\text{Rb}_2\text{SeO}_4$  and  $\text{Cs}_2\text{SeO}_4$  is presented. Analytical first order perturbation theoretical expressions are derived for the field-dependent wavenumbers of the  $1\leftarrow 0$  and  $2\leftarrow 0$  transitions, harmonic wavenumbers, as well as for the Stark tuning rate and the electrostatic field strength at the  $C_s$  sites of the host lattices. It is shown that the local field differences are the factor dominating over the differences in the anharmonicities of the guest anions in various host lattices, and are thus responsible for the experimentally observed trends. The proposed method allows calculation of the local crystalline field strength if the anharmonic potential energy parameters of the dopant anions are known. The calculated values for the studied series of matrices range from 229 to 259  $\text{V nm}^{-1}$ , which are approximately 3 times larger than those reported for water molecule sites in several clathrate hydrates and for the  $\text{N}_2\text{O}$  adsorbed in the NaA zeolite cavities. The model also successfully explains the greater bond length distortions than the angular ones of the dopant anions observed in all studied cases.

*Key words:* vibrational Stark effect, perturbation theory, sulfate impurities, internal crystalline fields, solid solutions, isomorphous isolation, mixed crystals.

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## INTRODUCTION

The vibrational Stark effect is, in some way, a generic name for the effects of electrostatic fields on molecular vibrational transitions.<sup>1-4</sup> The fields in question may be of different origin. Thus, they may be externally applied,<sup>5-7</sup> but they may also be due to a particular surface charge distribution in cases of adsorbed particles,<sup>8-15</sup> or, as it is the case in this paper, due to host crystal lattices. It is well-known<sup>2</sup> that the homogeneous electrostatic field does not affect the frequencies of vibrational transitions in the case of a *harmonic* quantum oscillator (as a matter of fact, the true energy spectrum is shifted as a whole, keeping the level spacing unchanged). However, when coupled to the anharmonic terms in the molecular potential energy, it can cause a variety of effects, depending on the nature of the system under consideration. The *vibrational Stark effect* (VSE) and the *vibrational intensity effect* (VIE)<sup>16</sup> have been thoroughly studied, both theoretically and experimentally. However, such studies have been practically limited to molecular species adsorbed on surfaces as well as to species placed in external electric fields. There are significantly less data regarding the species trapped at a particular site in a crystal lattice, which especially refers to isomorphously isolated molecules and molecular ions. It has been already pointed out<sup>1</sup> that theoretical studies of the VSE and VIE phenomena are not important only in their own right, but also because, when combined with experimental findings, they allow conclusions regarding the electric fields of the molecular environment.

The methods for analysis of the electric-field-induced perturbations to molecular vibrations may be generally divided into two groups: (a) perturbation-theoretic and (b) finite-field based. Their extensive comparative analysis is given in Ref. 17. Compact formulae for vibrational dynamic dipole polarizabilities and hyperpolarizabilities as well as for the vibrational corrections for some electric and magnetic properties of several molecular species were derived using the perturbation approach.<sup>18-21</sup> Both methodologies have been applied to the analysis of the VSE of the CO molecule in electrostatic fields of different origins.<sup>1,8,9,11,12</sup> Closely related to the approach described in this paper is the semiclassical study of the VSE on the  $\nu_3$  modes of methane molecule in an electrostatic field.<sup>13,14</sup> Several *ab initio* studies of the effect of external fields on vibrational frequencies for several molecular species were performed as well.<sup>22-25</sup>

In the present work, the Stark shifts of the  $1\leftarrow 0$  and  $2\leftarrow 0$  vibrational transitions of the internal modes of sulfate ions isomorphously isolated in  $\text{K}_2\text{SeO}_4$ ,  $\text{Rb}_2\text{SeO}_4$  and  $\text{Cs}_2\text{SeO}_4$  matrices are studied. Starting from the stationary perturbation theory, including the anharmonicity corrections to the energy spectrum within a field-dependent basis, we derive approximate an-

alytical formulae for the wavenumbers of the  $\text{SO}_4^{2-}$   $1 \leftarrow 0$  and  $2 \leftarrow 0$  vibrational transitions in some effective local field at the  $C_s$  sites of the host lattices. The derived expressions allow evaluation of the relative importance of the local field strengths *versus* the anharmonicities of the  $\text{SO}_4^{2-}$  internal modes in determining the shift trends. Also, calculation of the local field strength is possible if the anharmonic force constant data are available, and *vice versa*. A theoretical model dealing with the splitting of the triply degenerate  $\nu_3$  and  $\nu_4$  as well as doubly degenerate  $\nu_2$  modes will be the subject of a subsequent report.<sup>26</sup>

### THEORETICAL MODEL

The potential of a polyatomic molecule/ion in some effective local homogeneous electrostatic field due to the host lattice can be written in the form:

$$V = V_0 + \frac{1}{2} \sum_i m_i \omega_{0i}^2 q_i^2 + \sum_{i \leq j \leq k} k_{ijk} q_i q_j q_k + \sum_{i \leq j \leq k \leq l} k_{ijkl} q_i q_j q_k q_l - \vec{\mu} \cdot \vec{E} \quad (1)$$

where  $m_i$  is the reduced mass of the  $i$ -th normal mode  $q_i$ ,  $\omega_{0i}$  is the corresponding harmonic frequency,  $\vec{\mu}$  the dipole moment vector,  $k_{ijk}$  and  $k_{ijkl}$  are the cubic and quartic force constants, respectively, while  $\vec{E}$  is the effective field vector at the center of gravity of the molecule. Expanding the dipole moment in power series:

$$\vec{\mu} = \vec{\mu}_0 + \sum_i \left( \frac{\partial \vec{\mu}}{\partial q_i} \right) \cdot q_i + \dots \quad (2)$$

the scalar product  $\vec{\mu} \cdot \vec{E}$  takes the form:

$$\begin{aligned} [\mu_x \ \mu_y \ \mu_z] \cdot \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} &= [\mu_{x0} \ \mu_{y0} \ \mu_{z0}] \cdot \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} + \\ &+ \sum_i \left[ \frac{\partial \mu_x}{\partial q_i} \ \frac{\partial \mu_y}{\partial q_i} \ \frac{\partial \mu_z}{\partial q_i} \right]_0 \cdot q_i \cdot \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \quad (3) \end{aligned}$$

Since the dipole moment of the unperturbed (free) tetrahedral species  $\text{SO}_4^{2-}$  is zero, where the direction of the field is chosen along the  $z$ -axis of a laboratory coordinate system, the previous expression simplifies to:

$$\vec{\mu} \cdot \vec{E} = \sum_i \left( \frac{\partial \mu_z}{\partial q_i} \right) \cdot q_i E_z. \quad (4)$$

After reordering some terms, Eq. (1) takes the form:

$$V = V_0 + \sum_i \left[ \frac{1}{2} m_i \omega_{0i}^2 q_i^2 + k_{iii} q_i^3 + k_{iiii} q_i^4 - \left( \frac{\partial \mu_z}{\partial q_i} \right) \cdot q_i E_z \right] + \\ + \sum_{i \leq j < k} k_{ijk} q_i q_j q_k + \sum_{i \leq j \leq k < l} k_{ijkl} q_i q_j q_k q_l + \dots \quad (5)$$

If the last two sums are omitted from this expression, the total Hamiltonian is diagonal within the electrical harmonic approximation. In the case of isomorphously isolated  $\text{SO}_4^{2-}$  anions, the cubic and quartic anharmonic force constants are significantly smaller than the (diagonal) harmonic ones, as it has been shown<sup>27-29</sup> by our previous experimental investigations of these systems, where it was found that the anharmonic coupling constants are about 0.5% of the  $1 \leftarrow 0$  transition wavenumber. Since the sulfate anions occupy the  $C_s$  sites in the host lattices,<sup>30-32</sup> the degeneracy of the  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  modes is completely removed. Each  $i$ -th term appearing in the first sum of Eq. (5) may thus be considered as an independent anharmonic oscillator of an effective dipole moment  $(\partial \mu_z / \partial q_i)_0 \cdot q_i$  in the effective local field  $E_z$ . The total vibrational wavefunction of the dopant anion may be accordingly factorized:

$$|\Psi_{\{n\}}(\{q\}, E_z)\rangle = \prod_i |\Psi_{n_i}(q_i, E_z)\rangle \quad (6)$$

where:  $\{q\} = \{q_1, q_2, \dots, q_N\}$ , and  $\{n\} = \{n_1, n_2, \dots, n_N\}$ .

The wavefunctions  $|\Psi_{n_i}(q_i, E_z)\rangle$  are eigenfunctions of the cubic-quartic anharmonic oscillator placed in a homogeneous effective field  $E_z$ . By treating the anharmonic terms in the potential as a perturbation, the wavefunction  $|\Psi_{n_i}(q_i, E_z)\rangle$  and the energy of the corresponding  $n$ -th level may be represented by the perturbation series:

$$|\Psi_{n_i}(q_i, E_z)\rangle = |\Psi_{n_i}^{(0)}(q_i, E_z)\rangle + |\Psi_{n_i}^{(1)}(q_i, E_z)\rangle + |\Psi_{n_i}^{(2)}(q_i, E_z)\rangle + \dots \quad (7)$$

$$E_{ni} = E_{ni}^{(0)} + E_{ni}^{(1)} + E_{ni}^{(2)} + \dots \tag{8}$$

where  $|\Psi_{ni}^{(0)}(q_i, E_z)\rangle$  and  $E_{ni}^{(0)}$  are the unperturbed wavefunction and energy, respectively, of a harmonic oscillator in a homogeneous field  $E_z$ , while  $|\Psi_{ni}^{(k)}(q_i, E_z)\rangle$  and  $E_{ni}^{(k)}$  are perturbation corrections of the  $k$ -th order. The unperturbed eigenvalue problem is analytically solvable in this case, with the corresponding eigenfunctions and eigenvalues being:

$$|\Psi_{ni}^{(0)}(q_i, E_z)\rangle = \left(\frac{m_i \omega_{0i}}{\pi \hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} \exp\left[-\frac{m_i \omega_{0i}}{2\hbar} \left(q_i - \left(\frac{\partial \mu_z}{\partial q_i}\right)_0 \frac{E_z}{m_i \omega_{0i}^2}\right)^2\right] \cdot H_n \left[\sqrt{\frac{m_i \omega_{0i}}{\hbar}} \left(q_i - \left(\frac{\partial \mu_z}{\partial q_i}\right)_0 \frac{E_z}{m_i \omega_{0i}^2}\right)\right] \tag{9}$$

$$E_{ni}^{(0)} = \hbar \omega_0 \left(n + \frac{1}{2}\right) - \frac{1}{2} \left(\frac{\partial \mu_z}{\partial q_i}\right)_0^2 \frac{E_z^2}{m_i \omega_{0i}^2} \tag{10}$$

where  $H_n$  is the Hermite polynomial of the  $n$ -th degree. The first-order energy corrections are equal to the diagonal matrix elements of the anharmonicity perturbation operator calculated in the basis of non-perturbed field-dependent wavefunctions:

$$E_{ni}^{(1)} = \langle \Psi_{ni}^{(0)}(q_i, E_z) | \hat{H}_i^{(1)} | \Psi_{ni}^{(0)}(q_i, E_z) \rangle \tag{11}$$

where the anharmonicity perturbation operator for a particular  $i$ -th mode is given by:

$$\hat{H}_{ni}^{(1)} = k_{iii} \hat{q}_i^3 + k_{iiii} \hat{q}_i^4 \tag{12}$$

Introducing a new variable  $z_i$ :

$$z_i = \sqrt{\frac{m_i \omega_{0i}}{\hbar}} \left[ q_i - \left(\frac{\partial \mu_z}{\partial q_i}\right)_0 \frac{E_z}{m_i \omega_{0i}^2} \right] \tag{13}$$

$E_{ni}^{(1)}$  becomes:

$$E_{ni}^{(1)} = k_{iii} \langle \Psi_{ni}^{(0)}(q_i, E_z) | \hat{q}^3 | \Psi_{ni}^{(0)}(q_i, E_z) \rangle + k_{iii} \langle \Psi_{ni}^{(0)}(q_i, E_z) | \hat{q}^4 | \Psi_{ni}^{(0)}(q_i, E_z) \rangle. \quad (14)$$

$$E_{ni}^{(1)} = \frac{1}{2^n n! \sqrt{\pi}} \left\{ k_{iii} \int_{-\infty}^{+\infty} \left[ \sqrt{\frac{\hbar}{m_i \omega_{0i}}} \cdot z_i + \left( \frac{\partial \mu_z}{\partial q_i} \right)_0 \cdot \frac{E_z}{m_i \omega_{0i}^2} \right]^3 \cdot \exp(-z_i^2) \cdot H_n^2(z_i) dz_i + \right. \\ \left. + k_{iii} \int_{-\infty}^{+\infty} \left[ \sqrt{\frac{\hbar}{m_i \omega_{0i}}} \cdot z_i + \left( \frac{\partial \mu_z}{\partial q_i} \right)_0 \cdot \frac{E_z}{m_i \omega_{0i}^2} \right]^4 \cdot \exp(-z_i^2) \cdot H_n^2(z_i) dz_i \right\}. \quad (15)$$

By calculating Eq. (14) and combining it with Eq. (10), the wavenumbers corresponding to the  $1 \leftarrow 0$  and  $2 \leftarrow 0$  transitions within up to the first order perturbation are given by:

$$\tilde{\nu}_{01,i}(E_z) = \tilde{\nu}_{01,i}^{(h)} + \frac{3 \cdot (\partial \mu_z / \partial q_i)_0 E_z \cdot k_{iii}}{16\pi^4 c^4 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^3} + \\ + \frac{3 \cdot h \cdot k_{iii}}{16\pi^4 c^3 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^2} + \frac{3 \cdot (\partial \mu_z / \partial q_i)_0^2 E_z^2 \cdot k_{iii}}{32\pi^6 c^6 m_i^3 (\tilde{\nu}_{01,i}^{(h)})^5}. \quad (16)$$

$$\tilde{\nu}_{02,i}(E_z) = 2\tilde{\nu}_{01,i}^{(h)} + \frac{3 \cdot (\partial \mu_z / \partial q_i)_0 E_z \cdot k_{iii}}{8\pi^4 c^4 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^3} + \\ + \frac{9 \cdot h \cdot k_{iii}}{16\pi^4 c^3 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^2} + \frac{6 \cdot (\partial \mu_z / \partial q_i)_0^2 E_z^2 \cdot k_{iii}}{32\pi^6 c^6 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^5}. \quad (17)$$

where  $\tilde{\nu}_{01,i}^{(h)}$  are the harmonic wavenumbers, while  $\tilde{\nu}_{01,i}(E_z)$  and  $\tilde{\nu}_{02,i}(E_z)$  values are, in fact, the experimentally measured ones. The anharmonicity constant  $X_{ii}$  is defined as:

$$X_{ii} = \tilde{\nu}_{01,i}(E_z) - \frac{1}{2} \tilde{\nu}_{02,i}(E_z) \quad (18)$$

and according to Eqs. (16) and (17), it equals:

$$X_{ii} = -\frac{3 \cdot h \cdot k_{iiii}}{32\pi^4 c^3 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^2}. \quad (19)$$

Now  $\tilde{\nu}_{01,i}(\mathbf{E}_z)$  may be represented as:

$$\tilde{\nu}_{01,i}(\mathbf{E}) = \tilde{\nu}_{01,i}^{(h)}(\mathbf{E}_z) - 2X_{ii} \quad (20)$$

where:

$$\tilde{\nu}_{01,i}^{(h)}(\mathbf{E}_z) = \tilde{\nu}_{01,i}^{(h)} + \frac{3 \cdot (\partial \mu_z / \partial q_i)_0 \mathbf{E}_z \cdot k_{iiii}}{16\pi^4 c^4 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^3} + \frac{3 \cdot (\partial \mu_z / \partial q_i)_0^2 \mathbf{E}_z^2 \cdot k_{iiii}}{32\pi^6 c^6 m_i^3 (\tilde{\nu}_{01,i}^{(h)})^5}. \quad (21)$$

Both the measured  $1 \leftarrow 0$  wavenumber and the harmonic one are field dependent quantities. The Stark tuning rate, within the presented approach, is given by:

$$\frac{d\tilde{\nu}_{01,i}(\mathbf{E}_z)}{d\mathbf{E}_z} = \frac{3 \cdot (\partial \mu_z / \partial q_i)_0 \cdot k_{iiii}}{16\pi^4 c^4 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^3} + \frac{3 \cdot (\partial \mu_z / \partial q_i)_0^2 \mathbf{E}_z \cdot k_{iiii}}{16\pi^6 c^6 m_i^3 (\tilde{\nu}_{01,i}^{(h)})^5}. \quad (22)$$

It is important to note that this quantity is also equal to the derivative  $d\tilde{\nu}_{01,i}^{(h)}(\mathbf{E}_z)/d\mathbf{E}_z$ .

All of the derived equations are valid for cubic-quartic anharmonic oscillators in a homogeneous electrostatic field. However, since the symmetry of the trapped sulfate anions at the lattice sites deviates only slightly from the ideal  $T_d$  one, the terms due to the cubic anharmonicity are significantly smaller than those generated by the quartic ones. Such is the case, for instance, of the  $\nu_3$  and  $\nu_4$  mode components in sulfate doped potassium, rubidium and cesium selenates. For such modes, the previously obtained expressions take simpler forms:

$$\tilde{\nu}_{01,i}(\mathbf{E}_z) = \tilde{\nu}_{01,i}^{(h)} + \frac{3 \cdot h \cdot k_{iiii}}{16\pi^4 c^3 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^2} + \frac{3 \cdot (\partial \mu_z / \partial q_i)_0^2 \mathbf{E}_z^2 \cdot k_{iiii}}{32\pi^6 c^6 m_i^3 (\tilde{\nu}_{01,i}^{(h)})^5}. \quad (23)$$

$$\tilde{\nu}_{02,i}(\mathbf{E}_z) = 2\tilde{\nu}_{01,i}^{(h)} + \frac{9 \cdot h \cdot k_{iiii}}{16\pi^4 c^3 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^2} + \frac{6 \cdot (\partial \mu_z / \partial q_i)_0^2 \mathbf{E}_z^2 \cdot k_{iiii}}{32\pi^6 c^6 m_i^3 (\tilde{\nu}_{01,i}^{(h)})^5}. \quad (24)$$

$$\tilde{\nu}_{01,i}^{(h)}(\mathbf{E}_z) = \tilde{\nu}_{01,i}^{(h)} + \frac{3 \cdot (\partial \mu_z / \partial q_i)_0^2 \mathbf{E}_z^2 \cdot k_{iiii}}{32\pi^6 c^6 m_i^3 (\tilde{\nu}_{01,i}^{(h)})^5}. \quad (25)$$

$$\frac{d\tilde{\nu}_{01,i}^{(h)}(\mathbf{E}_z)}{d\mathbf{E}_z} = \frac{d\tilde{\nu}_{01,i}^{(h)}(\mathbf{E}_z)}{d\mathbf{E}_z} = \frac{3 \cdot (\partial \mu_z / \partial q_i)_0^2 \mathbf{E}_z \cdot k_{iiii}}{16\pi^6 c^6 m_i^3 (\tilde{\nu}_{01,i}^{(h)})^5}. \quad (26)$$

It should be noted at this point that the model outlined here, which relates the measured wavenumbers of the fundamental and second-order vibrational transitions with the field strength, was derived within the effective local homogeneous field approximation. In other words, only the long-range (electrostatic) crystal forces have been accounted for, neglecting the short-range repulsive ones. Although the latter may be significant in particular systems, their neglect may be verified for the present case of interest (sulfate anions in selenate matrices). Namely, since the dopant (guest) anions replace the (larger) host ones, the size of the dopant site is larger than the dopant anion itself. On the other hand, since the short-range forces decrease almost exponentially, they are mostly of a second-order importance for the present case.

## RESULTS AND DISCUSSION

The results from experimental studies of the fundamental vibrational transitions of sulfate ions isomorphously isolated in several selenate matrices, which are of key importance to this study, are presented in Table I. Brief reports containing the data regarding the second-order transitions as well are given in Refs. 28 and 29 where it has been shown that the anharmonicity of practically all of the studied second-order transitions decreases in the order  $(\text{SO}_4/\text{K}_2\text{SeO}_4) > (\text{SO}_4/\text{Rb}_2\text{SeO}_4) > (\text{SO}_4/\text{Cs}_2\text{SeO}_4)$ . Also, according to the measured relative splitting of the  $\nu_3$  and  $\nu_4$  mode components, both angular and bond-length distortions of the dopant  $\text{SO}_4^{2-}$  anions decrease in the same order. In all cases, the angular distortion is smaller than the bond length one.

How can these experimental observations be explained in terms of the presented model? First, since the anharmonicity constants decrease on going from sulfate doped  $\text{K}_2\text{SeO}_4$  to  $\text{Cs}_2\text{SeO}_4$ , the force constant  $k_{iiii}$  should also decrease (in absolute value) in the same order. Therefore, for equal local fields, this order of anharmonicities would imply an opposite trend in the  $\tilde{\nu}_{01,i}(\mathbf{E}_z)$  values from the observed one. Thus, the observed trend may be attributed to the increase of the effective local homogeneous fields at the  $C_s$



TABLE I

Band frequencies for the  $\text{SO}_4^{2-}$  ions doped in  $\text{K}_2\text{SeO}_4$ ,  $\text{Rb}_2\text{SeO}_4$  and  $\text{Cs}_2\text{SeO}_4$  at low temperatures (primes refer to  $^{34}\text{SO}_4^{2-}$  species)

Mode	$\text{K}_2\text{SeO}_4$	$\Delta/\text{cm}^{-1}$	$\text{Rb}_2\text{SeO}_4$	$\Delta/\text{cm}^{-1}$	$\text{Cs}_2\text{SeO}_4$
	$\nu/\text{cm}^{-1}$		$\nu/\text{cm}^{-1}$		$\nu/\text{cm}^{-1}$
$\nu_{4a}'$	610.0		607.4		
$\nu_{4a}$	613.5	2.4	611.1	3.1	608.0
$\nu_{4b}$	617.0	1.8	615.2	3.3	611.9
$\nu_{4c}$	623.0	3.7	619.3	5.1	614.2
$\nu_1$	980.5	8.8	971.7	6.5	965.2
$\nu_{3a}'$	1089.5	4.6	1084.9	9.5	1075.4
$\nu_{3b}'$	1096.5	3.1	1093.4	8.3	1085.1
$\nu_{3a}$	1103.5	4.3	1099.2	9.3	1089.9
$\nu_{3b}$	1115.5	7.4	1108.1	11.8	1096.3
$\nu_{3c}$	1142.0	14.2	1127.8	12.6	1115.2
$2\nu_{3a}$	2199.0	8.9	2190.1	18.8	2171.3
$2\nu_{3b}$	2224.3	14.9	2209.4	22.8	2186.6
$2\nu_{3c}$	2274.0	27.3	2246.7	24.6	2222.1

sites in the order  $(\text{SO}_4/\text{K}_2\text{SeO}_4) < (\text{SO}_4/\text{Rb}_2\text{SeO}_4) < (\text{SO}_4/\text{Cs}_2\text{SeO}_4)$ . Note that the  $\tilde{\nu}_{01,i}(\mathbf{E}_z)$  varies as  $E_z^2$  for the quartic oscillators, and the vibrational frequencies are thus invariant with respect to the direction of the field vector. Since the Stark tuning rate depends linearly on the electric field strength, the observed increase of the difference  $\tilde{\nu}_{01,i}^{\text{K}}(\mathbf{E}_z) - \tilde{\nu}_{01,i}^{\text{Rb}}(\mathbf{E}_z)$  compared to  $\tilde{\nu}_{01,i}^{\text{Rb}}(\mathbf{E}_z) - \tilde{\nu}_{01,i}^{\text{Cs}}(\mathbf{E}_z)$  is also expected. Further, as mentioned above,  $d\tilde{\nu}_{01,i}(\mathbf{E}_z)/d\mathbf{E}_z = d\tilde{\nu}_{01,i}^{(h)}(\mathbf{E}_z)/d\mathbf{E}_z$  holds within the present model. Thus, one would expect that

$$\tilde{\nu}_{01,i}^{\text{K}}(\mathbf{E}_z) - \tilde{\nu}_{01,i}^{\text{Rb}}(\mathbf{E}_z) \approx \tilde{\nu}_{01,i}^{(h)\text{K}}(\mathbf{E}_z) - \tilde{\nu}_{01,i}^{(h)\text{Rb}}(\mathbf{E}_z) \quad \text{and} \quad (27)$$

$$\tilde{\nu}_{01,i}^{\text{Rb}}(\mathbf{E}_z) - \tilde{\nu}_{01,i}^{\text{Cs}}(\mathbf{E}_z) \approx \tilde{\nu}_{01,i}^{(h)\text{Rb}}(\mathbf{E}_z) - \tilde{\nu}_{01,i}^{(h)\text{Cs}}(\mathbf{E}_z). \quad (28)$$

This is indeed the case (Table II). By careful comparison one finds that the  $\Delta\tilde{\nu}_{01,i}$  values are systematically slightly smaller than the  $\Delta\tilde{\nu}_{01,i}^{(h)}$  ones. In fact, this is expected, since the latter values should be calculated by including the contributions of combinations as well (*i.e.* the non-diagonal terms in the potential), which have been neglected in the present model. On the

TABLE II

Harmonic eigenvalues (at low temperatures) for the stretching vibrations of the  $\text{SO}_4^{2-}$  ions doped in  $\text{K}_2\text{SeO}_4$ ,  $\text{Rb}_2\text{SeO}_4$  and  $\text{Cs}_2\text{SeO}_4$ , calculated on the basis of anharmonicity data

Mode	$\omega_0/\text{cm}^{-1}$	$\Delta/\text{cm}^{-1}$	$\omega_0/\text{cm}^{-1}$	$\Delta/\text{cm}^{-1}$	$\omega_0/\text{cm}^{-1}$
	$\text{K}_2\text{SeO}_4$		$\text{Rb}_2\text{SeO}_4$		$\text{Cs}_2\text{SeO}_4$
$\nu_{3a}$	1118.75	6.00	1112.75	9.85	1102.90
$\nu_{3b}$	1129.30	9.25	1120.05	13.60	1106.45
$\nu_{3c}$	1157.50	18.00	1139.50	14.20	1125.30

other hand, if the diagonal quartic force constants are known, the model allows estimation of the field strength at a particular lattice site. Because of the approximations employed, the values might not be highly accurate, but would allow an insight into their relative magnitude in the series of sulfate doped selenates. In Table III, the field strengths calculated on the basis of our previously obtained  $k_{iiii}$  values (employing a self-consistent iterative methodology)<sup>30</sup> are presented. These values are 2–3 times higher than those reported for the water molecule sites in several clathrate hydrates, as well as for the  $\text{N}_2\text{O}$  adsorbed in the cavities of NaA zeolite.<sup>31,32</sup> Somewhat higher values are actually expected for a site within selenate matrices, in comparison to the matrices in which the host-guest interactions are noticeably weaker. However, the order of magnitude of the internal fields is basically the same. The dependence of  $\tilde{\nu}_{01,i}$  on the local field strength and on the anharmonic force constant  $k_{iiii}$  is presented in Figure 1.

TABLE III

The estimated absolute and relative effective field strengths at the  $C_s$  sites of the host lattices using equation (21) on the basis of the experimental data for the  $\nu_{3a}$  mode component, and for  $k_{iiii} = -2.5 \times 10^{23} \text{ kg m}^{-2} \text{ s}^{-2}$  and  $\tilde{\nu}_{01}^{(h)} = 1160 \text{ cm}^{-1}$

Matrix	$\text{K}_2\text{SeO}_4$	$\text{Rb}_2\text{SeO}_4$	$\text{Cs}_2\text{SeO}_4$
$E_i/V \text{ nm}^{-1}$	229	239	259
$E_i/E (\text{K}_2\text{SeO}_4)$	1.000	1.039	1.131

The dipole polarizability has not been explicitly included in the present model. Inclusion of this quantity within the electrical harmonic approximation would result in an additional term in the potential (6), of the form:

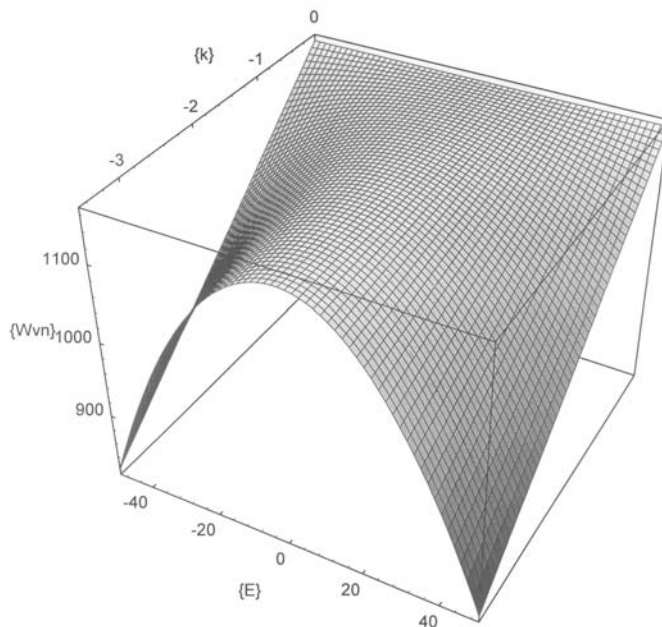


Figure 1. The wavenumber of the  $1 \leftarrow 0$  vibrational transition (for a quartic anharmonic oscillator) as a function of the local electrostatic field strength and of the potential constant;  $\{Wv_n\}$  = Wavenumber/cm<sup>-1</sup>;  $\{E\}$  =  $E \times 0.1/V \text{ nm}^{-1}$ ;  $\{k\}$  =  $k_{iiii} \times 10^{-23} / \text{kg m}^{-2} \text{ s}^{-2}$ .

$$-\alpha_{zz,0}E_z^2 - \sum_i \left( \frac{\partial \alpha_{zz}}{\partial q_i} \right) \hat{q}_i E_z^2$$

where  $\alpha_{zz}$  denotes the polarizability tensor component. Thus, it will contribute to the linear in  $q_i$  term in the single mode field dependent Hamiltonian and the effective charge of the oscillator placed in electric field will be  $(\partial \mu_z / \partial q_i)_0 + (\partial \alpha_{zz} / \partial q_i)_0 E_z$  instead of  $(\partial \mu_z / \partial q_i)_0$ .

Thus, the same equations as the previously obtained ones will hold, except for the modified expression for the effective charge (instead of the field-independent one).

The greater bond length distortions than the angular ones in the dopant sulfate anions may also be understood within the present model. Namely, the equilibrium geometry of the trapped ion/molecule in the presence of the local electrostatic field corresponds to a stationary point on the potential energy hypersurface, which is different from the one corresponding to the free species. Considering the  $i$ -th normal mode, the condition:

$$\left( \frac{\partial V}{\partial q_i} \right)_E = 0 \quad (29)$$

holds and it leads to the following algebraic equation:

$$m_i \omega_{0i}^2 q_i^{(E)} + 4k_{iiii} q_i^{3(E)} + \sum_{j \leq k < l} k_{ijkl} q_j q_k q_l - \left( \frac{\partial \mu_z}{\partial q_i} \right) E_z + \dots = 0 \quad (30)$$

where  $q_i^{(E)}$  is the equilibrium value of the  $i$ -th normal coordinate in the presence of the field. Omitting all higher order terms, it reduces to:

$$m_i \omega_{0i}^2 q_i^{(E)} - \left( \frac{\partial \mu_z}{\partial q_i} \right)_0 E_z = 0 \quad (31)$$

leading to the following expression for the ratio of the values corresponding to the  $\nu_3$  and  $\nu_4$  mode components:

$$\frac{q_{3k}^{(E)}}{q_{4k}^{(E)}} = \frac{(\partial \mu_z / \partial q_{3k})_0 m_{4k} \omega_{04k}}{(\partial \mu_z / \partial q_{4k})_0 m_{3k} \omega_{03k}}. \quad (32)$$

Since in the case of the studied systems the ratio of the effective charges  $(\partial \mu / \partial q_{3k})_0 / (\partial \mu / \partial q_{4k})_0$  is practically equal to the square root of the ratio of the measured band intensities, it is easily estimated from the reported experimental data.<sup>27–29</sup> This ratio is  $\sim 6$ – $7$ . On the other hand, the ratio of the harmonic wavenumbers for the  $\nu_4$  and  $\nu_3$  mode components is  $\sim 0.5$ , while the ratio of the corresponding reduced masses is  $\sim 1$ . Thus, the field-induced displacements are significantly larger for the  $\nu_3$  than for the  $\nu_4$  mode components, in line with experimental results. Namely, larger field-induced displacements of particular mode components imply a larger overall distortion of a given type.

## CONCLUSIONS

A quantum-theoretical model is proposed, based on the stationary perturbation theory, which successfully explains the observed vibrational Stark shifts of the (dopant) sulfate anion internal modes in  $\text{K}_2\text{SeO}_4$ ,  $\text{Rb}_2\text{SeO}_4$  and  $\text{Cs}_2\text{SeO}_4$  host lattices. Within the effective local homogeneous field approximation, it is shown that the local electrostatic field differences at the  $C_s$  lat-

tice sites in the mentioned matrices are responsible for the observed trends of the wavenumbers corresponding to the  $1\leftarrow 0$  and  $2\leftarrow 0$  vibrational transitions. Effects due to the vibrational anharmonicities would lead to opposite trends from the observed ones. Analytical expressions are derived for the field-dependent wavenumbers of the  $1\leftarrow 0$  and  $2\leftarrow 0$  vibrational transitions, as well as for the field-dependent harmonic wavenumbers. All these wavenumbers are second-order polynomial functions of the local electrostatic field strength. The method allows calculation of the local crystalline field strength if the anharmonic potential energy parameters of the dopant anions are known. The calculated values for the studied series of matrices range from 229 to 259 V nm<sup>-1</sup>, which are approximately 3 times larger than those reported for water molecule sites in several clathrate hydrates and for the N<sub>2</sub>O adsorbed in the NaA zeolite cavities. The derived analytical expressions for the Stark tuning rates are consistent with the experimental observations as well. The presented model also explains the larger bond length distortions than the angular ones of the dopant sulfate anions in all of the studied selenate matrices.

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## SAŽETAK

### Vibracijski Starkovi pomaci sulfatnih internih modova u selenatima kalija, rubidija i cezija dopiranim sa $\text{SO}_4^{2-}$ . Kvantni model za određivanje kristalnih polja

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Opaženi vibracijski Starkovi pomaci sulfatnih internih modova u  $\text{K}_2\text{SeO}_4$ ,  $\text{Rb}_2\text{SeO}_4$  i  $\text{CsSeO}_4$  dopiranim sa  $\text{SO}_4^{2-}$  objašnjeni su kvantno-teorijskim modelom. Na temelju teorije smetnje prvoga reda izvedeni su analitički izrazi za valne brojeve prijelaza  $1\leftarrow 0$  i  $2\leftarrow 0$  koji ovise o polju, za harmoničke valne brojeve kao i za Starkove brzine podešavanja i jačinu elektrostatskog polja na  $C_s$  mjestima kristalne rešetke domaćina. Eksperimentalno opaženi trendovi teorijski su objašnjeni razlikama u lokalnim poljima koje su dominantniji faktor od razlika u anharmoničnosti aniona-gosta uklopljenog u različite kristalne rešetke domaćina. Predložena metoda omogućuje računanje jačine lokalnih kristalnih polja ako su poznati parametri anharmoničke potencijalne energije za anion koji je dopiran. Proračunane vrijednosti u istraživanim matricama u rasponu su od 229 do 259  $\text{V nm}^{-1}$ , što je približno tri puta veća vrijednost od one za molekule vode u nekim hidratima klatrata kao i od one za molekule  $\text{N}_2\text{O}$  adsorbirane u šupljinama NaA zeolita. Za sve istražene molekule model uspješno predviđa veće promjene duljine veze od promjena veznog kuta u anionu koji je dopiran.