

## **An Iterative Perturbation Theory-Based Algorithm for Calculation of Diagonal Force Constants of the $\nu_3$ Modes in Quasi-Tetrahedral Systems with Low Anharmonicity**

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Received December 7, 1998; revised July 1, 1999; accepted July 22, 1999

A novel, stationary perturbation theory – based iterative algorithm for calculation of the diagonal force constants of the  $\nu_3$  modes in tetrahedral and quasi-tetrahedral systems with low anharmonicity is developed. The diagonal elements in the potential energy expression are calculated on the basis of experimentally measured fundamental and second-order transition wavenumbers, in a self-consistent manner. Perturbation corrections up to the second order are included in the model. The procedure is rapidly convergent, simple, and may be easily implemented within computer programs. The calculated diagonal force constants are consistent with the measured fundamental and second-order transition wavenumbers. The proposed model is applied to several isomorphously isolated (distorted-tetrahedral) sulfate impurities in selenate and chromate matrices. Experimental data for these systems were obtained by FT-IR spectroscopy.

*Key words:* Quasi-tetrahedral molecules, diagonal force constants – calculation of, Perturbation theory, anharmonic oscillator, sulfate impurities, isomorphous isolation

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## INTRODUCTION

The problem relating to the vibrational anharmonicity of molecular species has been widely studied, both experimentally and theoretically [Refs. 1–12 and references therein]. Starting with experimental data obtained by various spectroscopic techniques, it is possible to extract a complete set of information about molecular potential energy hypersurfaces only for the simplest cases. Since the number of terms in the potential energy expansion for polyatomic systems is rather large, especially for those characterized by low symmetry, a complete solution of the inverse spectroscopic problem is often impossible. Therefore, various algorithms allowing estimation of the anharmonic terms in the potential have been proposed.<sup>13–29</sup> With the enormous progress of *ab initio* and density functional methods, even first-principle calculations including the vibrational anharmonicity have become possible [Refs. 30–32 and references therein].

On the other hand, the problem of the anharmonic oscillator itself is interesting both from physical and purely mathematical viewpoints, so it has been studied many times as well.<sup>33–41</sup> Various methodologies have been employed for an effective inclusion of anharmonicity corrections into the harmonic energy spectrum.<sup>16–29, 36–41</sup>

However, when dealing with molecular species in solid state, in order to eliminate cooperative effects and to obtain a pure higher-order vibrational spectrum of the considered species, the technique of isomorphous isolation has been employed.<sup>42</sup> It is well known that in the case, for instance, of a pure  $\text{K}_2\text{SO}_4$ , the region of appearance of the second-order vibrational transitions due to the  $\text{SO}_4^{2-}$  internal modes maps the two-phonon density of states of the form  $\nu_1 + \nu_{3i}$  and  $\nu_{3i} + \nu_{3j}$ , so no band can be assigned to any particular transition. On the other hand, in the case of  $\text{SO}_4^{2-}$  ions isomorphously isolated in a matrix such as  $\text{K}_2\text{SeO}_4$  or  $\text{K}_2\text{CrO}_4$ , the interactions between identical oscillators (leading to dispersion of phonon curves and Davydov splittings), and the long-range electrostatic forces (leading to LO-TO splitting) for the dopant ions, may be switched off. This allows assignment of the  $\text{SO}_4^{2-}$  overtone spectrum employing only site-group analysis. The spectroscopically obtained parameters thus refer to the  $\text{SO}_4^{2-}$  anion in a particular crystalline field. These values may be legitimately used for solving the inverse spectroscopic problem.

In this work, a simple, perturbation theory based iterative algorithm is proposed, which allows calculation of the diagonal quartic force constants for the  $\nu_3$  mode components in the case of slightly distorted isomorphously isolated sulfate anions characterized by low vibrational anharmonicity, on the basis of experimental spectroscopic data. A partial solution of the inverse spectroscopic problem for the studied species is thus possible, with little computational effort.

## THEORETICAL MODEL

Within the normal-mode approach, including both cubic and quartic anharmonicities, the vibrational Hamiltonian of a polyatomic molecular/ionic system can be written in the form:<sup>43</sup>

$$\hat{H} = \sum_i \frac{\hat{p}_i^2}{2m_i} + \frac{1}{2} \sum_i m_i \omega_{0i}^2 \hat{q}_i^2 + \sum_{i \leq j \leq k} k_{ijk} \hat{q}_i \hat{q}_j \hat{q}_k + \sum_{i \leq j \leq k \leq l} k_{ijkl} \hat{q}_i \hat{q}_j \hat{q}_k \hat{q}_l \quad (1)$$

or, reordering some terms in Eq. (1):

$$\hat{H} = \sum_i \left[ \frac{\hat{p}_i^2}{2m_i} + \frac{1}{2} m_i \omega_{0i}^2 \hat{q}_i^2 + k_{iii} \hat{q}_i^3 + k_{iiii} \hat{q}_i^4 \right] + \sum_{i \leq j < k} k_{ijk} \hat{q}_i \hat{q}_j \hat{q}_k + \sum_{i \leq j \leq k < l} k_{ijkl} \hat{q}_i \hat{q}_j \hat{q}_k \hat{q}_l \quad (2)$$

where  $m_i$  is the reduced mass of a particular normal mode,  $\omega_{0i}$  is the corresponding harmonic frequency, while  $k_{ijk}$  and  $k_{ijkl}$  are cubic and quartic anharmonic force constants, respectively.

If no coupling exists between the normal modes (the case when constants  $k_{ijk}$  and  $k_{ijkl}$  have zero values), the total Hamiltonian will be diagonal, leading to a factorability of the total molecular vibrational wavefunction:

$$|\Psi_{\{n\}}(\{q\})\rangle = \prod_i |\Psi_{n_i}(q_i)\rangle \quad (3)$$

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

In some cases, the previous condition is almost fulfilled. Thus, our recent studies<sup>44-46</sup> of isomorphously isolated sulfate anions in selenate and chromate matrices have shown that both (diagonal) anharmonicity constants and the (non-diagonal) anharmonic coupling constants have very low values (about 0.1% of the value for the corresponding  $1 \leftarrow 0$  wavenumbers). In such cases, the normal mode concept is fully justified and the normal modes may also be treated as nearly independent (uncoupled) anharmonic oscillators. An individual vibrational Hamiltonian for such an independent (uncoupled) oscillator has the form:

$$\hat{H}_i = \frac{\hat{p}_i^2}{2m_i} + \frac{1}{2} m_i \omega_{0i}^2 \hat{q}_i^2 + k_{iii} \hat{q}_i^3 + k_{iiii} \hat{q}_i^4 \quad (4)$$

Existence of the anharmonic terms in Eq. (1) is dictated by the symmetry of the system under consideration. Since our studies<sup>44-46</sup> have shown that the symmetry of doped  $\text{SO}_4^{2-}$  species often deviates only slightly from the ideal  $T_d$  one (very small vibrational Stark splitting of the  $\nu_3$  and  $\nu_4$  modes observed by IR spectroscopy, as well as an extremely low intensity of the  $\nu_1$  mode), several restrictions are imposed on the form of the potential en-

ergy in Eq. (1). Thus, as it has already been discussed,<sup>45</sup> the cubic terms in the Hamiltonian referring to the  $v_3$  mode components practically vanish and the operator takes the form:

$$\hat{H}_i = \frac{\hat{p}_i^2}{2m_i} + \frac{1}{2}m_i\omega_{0i}^2\hat{q}_i^2 + k_{iii}\hat{q}_i^4. \quad (5)$$

In other words, this is a *quartic anharmonic oscillator*. If the anharmonicity constants are small, as in the case of the studied systems, the corrections to the energy spectrum of the individual harmonic oscillators may be treated within the stationary perturbation theoretical approach.<sup>47</sup> For that purpose, the individual Hamiltonians of the mentioned modes may be represented in the form:

$$\hat{H}_i = \hat{H}_{i0} + \hat{V}_i \quad (6)$$

where:

$$\hat{H}_{i0} = \frac{\hat{p}_i^2}{2m_i} + \frac{1}{2}m_i\omega_{0i}^2\hat{q}_i^2 \quad (7)$$

and

$$\hat{V}_i = k_{iii}\hat{q}_i^4. \quad (8)$$

The first and second order energy corrections to the unperturbed energy spectra are given by (Appendix 1):

$$E_{ni}^{(1)} = k_{iii} \frac{\hbar}{m_i^2 \omega_{0i}^2} \cdot \frac{3}{2} \cdot \left[ \left( n_i + \frac{1}{2} \right)^2 + \frac{1}{4} \right] \quad (9)$$

$$E_{ni}^{(2)} = k_{iii}^2 \frac{\hbar}{m_i^4 \omega_{0i}^5} \cdot \left\{ \frac{1}{64} [(n_i - 3)(n_i - 2)(n_i - 1)n_i - (n_i + 4)(n_i + 3)(n_i + 2)(n_i + 1)] + \right. \quad (10)$$

$$\left. + \frac{1}{8} [(2n_i - 1)^2(n_i - 1)n_i - (2n_i + 3)^2(n_i + 2)(n_i + 1)] \right\}.$$

The energy differences  $E_1 - E_0$  and  $E_2 - E_0$ , expressed through the wave-numbers of the corresponding vibrational transitions, take the form:

$$\tilde{\nu}_{01,i} = \tilde{\nu}_{01,i}^{(h)} + \frac{3}{16} \frac{hk_{iii}}{\pi^4 c^3 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^2} - \frac{144}{2048} \frac{h^2 k_{iii}^2}{\pi^8 c^6 m_i^4 (\tilde{\nu}_{01,i}^{(h)})^5} \quad (11)$$

$$\tilde{\nu}_{02,i} = 2\tilde{\nu}_{01,i}^{(h)} + \frac{9}{16} \frac{hk_{iii}}{\pi^4 c^3 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^2} - \frac{596}{2048} \frac{h^2 k_{iii}^2}{\pi^8 c^6 m_i^4 (\tilde{\nu}_{01,i}^{(h)})^5} \quad (12)$$

where  $\tilde{\nu}_{01,i}^{(h)}$  are the harmonic wavenumbers. Quantities  $\frac{1}{2}\tilde{\nu}_{02,i} - \tilde{\nu}_{01,i}$ , equal to the spectroscopically measured anharmonicity constants  $X_{ii}$ , according to previous expressions, take the form:

$$\frac{1}{2}\tilde{\nu}_{02,i} - \tilde{\nu}_{01,i} = \frac{3}{32} \frac{hk_{iii}}{\pi^4 c^3 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^2} - \frac{153}{2048} \frac{h^2 k_{iii}^2}{\pi^8 c^6 m_i^4 (\tilde{\nu}_{01,i}^{(h)})^5}. \quad (13)$$

Equations (11) and (13) form the base of the proposed algorithm. On the basis of these equations, including the experimentally measured wavenumbers of the  $1\leftarrow 0$  and  $2\leftarrow 0$  vibrational transitions, as well as the anharmonicity constants, it is possible to calculate the diagonal anharmonic force constants in the following manner.

Consider equations (13) and (11). We denote them as (A) and (B) in this context:

$$\frac{1}{2}\tilde{\nu}_{02,i} - \tilde{\nu}_{01,i} = \frac{3}{32} \frac{hk_{iii}}{\pi^4 c^3 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^2} - \frac{153}{2048} \frac{h^2 k_{iii}^2}{\pi^8 c^6 m_i^4 (\tilde{\nu}_{01,i}^{(h)})^5} \quad (A)$$

$$\tilde{\nu}_{01,i} = \tilde{\nu}_{01,i}^{(h)} + \frac{3}{16} \frac{hk_{iii}}{\pi^4 c^3 m_i^2 (\tilde{\nu}_{01,i}^{(h)})^2} - \frac{144}{2048} \frac{h^2 k_{iii}^2}{\pi^8 c^6 m_i^4 (\tilde{\nu}_{01,i}^{(h)})^5}. \quad (B)$$

Since the anharmonicity of the vibrational modes in nearly tetrahedral doped sulfate anions is small, as a first approximation to the *harmonic* wavenumbers  $\tilde{\nu}_{01,i}^{(h)}$ , one may substitute the *measured* wavenumbers of the  $1\leftarrow 0$  vibrational transitions in (A). A starting (first approximation) value for the quartic force constant  $k_{iii}$  is obtained from (A) in this way. Then, this value for  $k_{iii}$  is substituted in (B) and an improved value for  $\tilde{\nu}_{01,i}^{(h)}$  is obtained. Substituting this improved value in (A), an improved value for  $k_{iii}$  is obtained and the whole procedure is repeated until self-consistency of  $k_{iii}$  and  $\tilde{\nu}_{01,i}^{(h)}$  is achieved. It is important to note that by fixing the  $\tilde{\nu}_{01,i}^{(h)}$  value in (A), a quadratic equation with respect to  $k_{iii}$  is obtained. However, in all iteration steps, for all of the studied systems, only one solution was physically acceptable. This is the case as well when the value of  $k_{iii}$  is fixed in (B).

The proposed method is rapidly convergent (often less than 10 iterations are required to achieve self-consistency of  $\tilde{\nu}_{01,i}^{(h)}$  and  $k_{iii}$ ). As already mentioned, in all of the studied cases, only one physically reasonable parameter was obtained in all steps, thus confirming the physical basis of its applicability. It was tested with the experimentally obtained data for sulfate ions

isomorphously isolated in potassium, rubidium and cesium selenates, as well as in potassium chromate.<sup>44–46</sup> The obtained values for the quartic anharmonic force constants  $k_{iii}$  for the  $\nu_3$  mode components of the dopant anions in these cases are summarized in Table I, together with the spectroscopic data including the measured  $\tilde{\nu}_{01,i}$  and  $X_{ii}$  values.

The values obtained for the harmonic wavenumbers, consistent with the calculated values of the quartic force constants  $k_{iii}$ , are presented in Table II. These values are systematically lower than those calculated including the anharmonicity coupling constants (arising from the non-diagonal terms in the potential) in our previous works. However, since according to Ref. 48, the anharmonicity coupling constants contribute to the harmonic wavenumber by approximately  $-0.5 \cdot X_{ij}$ , including all of the spectroscopically measurable contributions to the harmonic wavenumbers calculated by this algorithm, an excellent agreement between the previous and the current results is obtained. The values of the harmonic wavenumbers corrected for anharmonic coupling are also presented in Table II.

It is obvious from the presented results that the calculated quartic anharmonic force constants seem to be a very good approximation to the real terms in the potential for these systems. The key reason why this model

TABLE I

The spectroscopically measured  $\tilde{\nu}_{01,i}$  and  $X_{ii}$  values for the  $\nu_3$  mode components of  $\text{SO}_4^{2-}$  ions isomorphously isolated in several matrices, together with the calculated  $k_{iii}$  values

System	Normal mode	$\tilde{\nu}_{01,i} / \text{cm}^{-1}$	$X_{ii} / \text{cm}^{-1}$	$k_{iii} \cdot 10^{-23} / \text{kg m}^{-2} \text{s}^{-2}$
$\text{SO}_4 / \text{K}_2\text{SeO}_4$	$\nu_{3a}$	1103.5	-4.00	-2.4651
	$\nu_{3b}$	1115.5	-3.35	-2.1147
	$\nu_{3c}$	1142.0	-5.00	-3.2908
$\text{SO}_4 / \text{Rb}_2\text{SeO}_4$	$\nu_{3a}$	1099.2	-4.15	-2.5362
	$\nu_{3b}$	1108.1	-3.40	-2.1174
	$\nu_{3c}$	1127.8	-4.45	-2.8610
$\text{SO}_4 / \text{Cs}_2\text{SeO}_4$	$\nu_{3a}$	1089.9	-4.25	-2.5523
	$\nu_{3b}$	1096.3	-3.00	-1.8311
	$\nu_{3c}$	1115.2	-4.15	-2.6111
$\text{SO}_4 / \text{K}_2\text{CrO}_4$	$\nu_{3a}$	1106.5	-4.00	-2.4786
	$\nu_{3b}$	1117.5	-4.00	-2.5285

TABLE II

The harmonic wavenumbers  $\tilde{\nu}_{01,i}^{(h)}$  of the  $\nu_3$  mode components of  $\text{SO}_4^{2-}$  ions isomorphously isolated in  $\text{K}_2\text{SeO}_4$  calculated by this algorithm, values from our previous works, and values corrected for the anharmonic coupling (all in  $\text{cm}^{-1}$ )

System	Normal mode	this work	Refs. 44–46	corrected
$\text{SO}_4 / \text{K}_2\text{SeO}_4$	$\nu_{3a}$	1111.38	1118.75	1118.63
	$\nu_{3b}$	1122.11	1129.30	1129.11
	$\nu_{3c}$	1151.82	1157.50	1156.82
$\text{SO}_4 / \text{Rb}_2\text{SeO}_4$	$\nu_{3a}$	1107.37	1112.75	1112.62
	$\nu_{3b}$	1114.81	1120.05	1119.96
	$\nu_{3c}$	1136.55	1139.50	1139.35
$\text{SO}_4 / \text{Cs}_2\text{SeO}_4$	$\nu_{3a}$	1098.26	1102.90	1102.76
	$\nu_{3b}$	1102.23	1106.45	1106.38
	$\nu_{3c}$	1123.37	1125.30	1125.17
$\text{SO}_4 / \text{K}_2\text{CrO}_4$	$\nu_{3a}$	1116.38	1124.0	1126.63
	$\nu_{3b}$	1127.16	1135.0	1136.91

yields such good approximations is the exact applicability of the normal-mode concept in the considered cases, *i.e.* independency of the (practically uncoupled) oscillators.

In principle, the proposed methodology may be applied to all systems for which the basic approximations of the model are applicable. These include: small quartic anharmonicity of the mode in question, negligible anharmonic coupling constants, available anharmonicity constants (*e.g.* from spectroscopic measurements).

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Appendix 1

The first and second order corrections to the energies of the harmonic vibrational eigenstates of the quartic anharmonic oscillators are straightforwardly obtained using the stationary perturbation theory.

Thus, the first order corrections are equal to the diagonal matrix elements calculated in the basis of the unperturbed (harmonic oscillator) wavefunctions:

$$|\Psi_{ni}^{(0)}(q_i)\rangle = \frac{1}{(2^{ni} n_i! \sqrt{\pi})^{1/2}} \left(\frac{m_i \omega_{01}}{\hbar}\right)^{1/4} \exp\left(-\frac{1}{2} \frac{m_i \omega_{01}}{\hbar} q_i\right) \cdot H_{ni} \left(\sqrt{\frac{m_i \omega_{01}}{\hbar}} q_i\right) \quad (14)$$

of the form:

$$E_{ni}^{(1)} = \langle \Psi_{ni}^{(0)}(q_i) | \hat{V}_i | \Psi_{ni}^{(0)}(q_i) \rangle = k_{iiii} \langle \Psi_{ni}^{(0)}(q_i) | q_i^4 | \Psi_{ni}^{(0)}(q_i) \rangle. \quad (15)$$

Since (see, for example Ref. 43):

$$\langle \Psi_{ni}^{(0)}(q_i) | q_i | \Psi_{ni}^{(0)}(q_i) \rangle = \frac{3}{2} \frac{\hbar}{m_i^2 \omega_{0i}^2} \left[ \left(n_i + \frac{1}{2}\right)^2 + \frac{1}{4} \right] \quad (16)$$

equation (9) is obtained.

The second order perturbational corrections to the energies are given by:

$$E_{ni}^{(2)} = \sum_{mi \neq ni} \frac{|V_{mi,ni}|^2}{\hbar \omega_{ni,mi}} \quad (17)$$

where:

$$V_{mi,ni} = \langle \Psi_{mi}^{(0)}(q_i) | \hat{V}_i | \Psi_{ni}^{(0)}(q_i) \rangle. \quad (18)$$

and

$$\omega_{mi,ni} = \frac{E_{mi}^{(0)} - E_{ni}^{(0)}}{\hbar}. \quad (19)$$

$E_{mi}^{(0)}$  and  $E_{ni}^{(0)}$  being the unperturbed eigenvalues. Since only four terms in sum (17) are different from zero,<sup>43</sup> the expression for  $E_{ni}^{(2)}$  reduces to the form:

$$E_{ni}^{(2)} = \frac{\hbar^4}{m_i^4 \omega_{0i}^4} \left( \frac{\left| \langle \Psi_{ni-4}^{(0)} | \hat{q}_i^4 | \Psi_{ni}^{(0)} \rangle \right|}{\hbar \omega_{ni,ni-4}} + \frac{\left| \langle \Psi_{ni-2}^{(0)} | \hat{q}_i^4 | \Psi_{ni}^{(0)} \rangle \right|}{\hbar \omega_{ni,ni-2}} + \frac{\left| \langle \Psi_{ni+2}^{(0)} | \hat{q}_i^4 | \Psi_{ni}^{(0)} \rangle \right|}{\hbar \omega_{ni,ni+2}} + \frac{\left| \langle \Psi_{ni+4}^{(0)} | \hat{q}_i^4 | \Psi_{ni}^{(0)} \rangle \right|}{\hbar \omega_{ni,ni+4}} \right) \quad (20)$$

which finally gives Eq. (10).

## SAŽETAK

### **Iterativan perturbacijski algoritam za računanje dijagonalnih konstanti sile $\nu_3$ modova u kvazi-tetraedarskim sustavima niske anharmoničnosti**

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Na temelju stacionarne teorije smetnje razvijen je novi iterativan algoritam za izračunavanje dijagonalnih konstanta sile za  $\nu_3$  vibracijske modove u tetraedarskim i kvazi-tetraedarskim sustavima niske anharmoničnosti. Dijagonalni elementi u izrazu za potencijalnu energiju izračunani su samoskladnim postupkom na temelju valnih brojeva prijelaza (fundamentalnih i drugog reda). Korekcije za smetnju do drugog reda uključene su u model. Postupak brzo konvergira, jednostavan je i lako se implementira u kompjutorski program. Izračunane dijagonalne konstante sile slažu se s izmjerenim valnim brojevima prijelaza (fundamentalnih i drugog reda). Predloženi je model primijenjen na nekoliko izomorfno izoliranih (iskrivljeno tetraedarskih) sulfatnih nečistoća u selenatnim i kromatnim matricama. Eksperimentalni podatci za te sustave dobiveni su s pomoću FT-IR spektroskopije.