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Lattice dynamics of the orthorhombic phase of $KClO_4$: Ewald's method in molecular coordinates

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The algorithm of the Ewald lattice sums is formulated in a form suited for application to lattice dynamics calculations for ionic molecular crystals, employing molecular coordinates and a discrete-charges representation of the Coulomb interactions. The method is used for a lattice dynamics calculation of $KClO_4$ crystal, including external and internal degrees of freedom. An atom/atom plus charge/charge potential is used, providing a remarkably good agreement with the experimental data. The calculation is extended also to the anharmonic properties: the calculated linewidths of the external phonons compare satisfactorily to the observed values.

1. Introduction

Lattice dynamics (LD) calculations, both in the harmonic and in the anharmonic approximation, are commonly used in studies involving molecular crystals. In fact, they have proved to be a powerful to in the interpretation of vibrational data; at the same time, they provide a useful means of testing potential models [1].

Crystals containing molecular and atomic ions have been the subject of a number of computational studies, in which the different role played by short-range repulsive and long-range electrostatic interactions between particles has been investigated. Molecular Dynamics simulations [2] have shown that many properties of ionic molecular crystals can be explained on the basis of simple potential expressions, including a rigid ion model for Coulomb interactions. The same models have been adopted in a few LD calculations about such crystals [3–11].

In this paper we present the results of LD calculations of the orthorhombic, low temperature modification of $KClO_4$. Internal and external modes of this crystal have been extensively studied in recent years by means of IR and Raman spectroscopy [12–15]. In this paper we show that a good description of the observed vibrational modes, including a discussion of anharmonic effects, can be reached using a potential of the type atom–atom plus charge–charge.

In LD calculations involving an electrostatic potential one is faced with slowly converging lattice sums. The most common solution to this problem is represented by the well-known Ewald transformations [16–18]. Since in ionic molecular crystals it is convenient to use a set of molecular coordinates, which allow a separate description of translations, rotations and vibrations of ions [1], expressions of Ewald's formulas in this formalism have been developed. Although the general theory is well described in the literature, we have reported here the basics steps, along with the final formulas; we believe this will give also the reader who is not familiar with the subject a precise idea of the implications of the treatment. Section 2 deals with LD expressions for ionic molecular crystals; section 3 with the corresponding Ewald formulas.

Results concerning the $KClO_4$ crystal are reported in sections 4 and 5.

2. Lattice dynamics of ionic molecular crystals

The dynamics of crystals containing mono- and polyatomic ions is best studied by making use of a set of molecular coordinates, extending the treatment originally developed for molecular crystals [1]. To each ion q of N_q atoms the following $3N_q$ coordinates are associated: 3 mass-weighted Cartesian displacements of the center of mass, 3 inertia-weighted rotations about the ion's principal axes of inertia (these are 2 or 0 for a linear or monatomic ion, respectively), and $3N_q-6$ ($3N_q-5$ or 0) internal vibrations (normal modes).

The vibrational problem is solved, in the harmonic approximation, by diagonalizing the matrix **D** of second derivatives of the crystal potential V with respect to the molecular coordinates. If cyclic boundary conditions are imposed and a set of delocalized symmetry coordinates is used [1], the elements of **D** take the form

$$D_{\boldsymbol{k}}\begin{pmatrix} fqi \\ f'q'i' \end{pmatrix} = \sum_l \frac{\partial^2 V}{\partial R^{0fqi}\,\partial R^{lf'q'i'}} \exp[\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{l}] , \tag{2.1}$$

where R^{lfqi} is molecular coordinate i of ion q belonging to formula unit f in cell l; $\boldsymbol{l}$ is the position of cell l in a fixed Cartesian frame ($l=0$ indicates the origin cell). The wave vector $\boldsymbol{k}$ contains the factor 2π.

If $f'=f$ and $q'=q$ it is convenient to separate the contribution of the origin cell from those of the rest of the lattice

$$D_{\boldsymbol{k}}\begin{pmatrix} fqi \\ fqi' \end{pmatrix} = \sum_{l\neq 0} \frac{\partial^2 V}{\partial R^{0fqi}\,\partial R^{lfqi'}} \exp[\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{l}] + \frac{\partial^2 V}{\partial R^{0fqi}\,\partial R^{0fqi'}} . \tag{2.2}$$

V can be divided into an intramolecular part V_{M} and an intermolecular part V_{I}. The former contributes only to the second term to the right in eq. (2.2) by

$$\frac{\partial^2 V_M}{\partial R^{0fqi}\,\partial R^{0fqi'}} = \omega_i^2 \delta_{ii'} , \tag{2.3}$$

where ω_i is the frequency of isolated-ion vibration I.

V_{I} is well approximated by a sum of pairwise potentials between centers n,n' belonging to two different ions:

$$V_{\mathrm{I}} = \tfrac{1}{2} \sum_{lfqn} \sum_{l'f'q'n'} W\begin{pmatrix} lfqn \\ l'f'q'n' \end{pmatrix} , \tag{2.4}$$

where $(l'f'q') \neq (lfq)$.

Limiting ourselves to the contribution of V_{I} to **D**, the elements (2.1) and (2.2) of **D** are easily related to derivatives of the two-center potential W with respect to the particles' Cartesian coordinates x_σ^{0fqn}, $x_\tau^{lf'q'n'}$ (σ, $\tau=$x, y, z):

$$D_{\boldsymbol{k}}\begin{pmatrix} fqi \\ f'q'i' \end{pmatrix} = \sum_l \sum_{nn'} \sum_{\sigma\tau} W''^{+}_{\sigma\tau}\begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix} \xi\begin{pmatrix} fqn \\ \sigma i \end{pmatrix} \xi\begin{pmatrix} f'q'n' \\ \tau i' \end{pmatrix} \exp[\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{l}] , \quad (q' \neq q \text{ if } f'=f) \tag{2.5}$$

and

$$\begin{aligned} D_{\boldsymbol{k}}\begin{pmatrix} fqi \\ fqi' \end{pmatrix} = {} & \sum_{l\neq 0} \sum_{nn'} \sum_{\sigma\tau} W''^{+}_{\sigma\tau}\begin{pmatrix} 0fqn \\ lfqn' \end{pmatrix} \xi\begin{pmatrix} fqn \\ \sigma i \end{pmatrix} \xi\begin{pmatrix} fqn' \\ \tau i' \end{pmatrix} \exp[\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{l}] \\ & + \sum_{lf'q'} \sum_{nn'} \left[\sum_{\sigma\tau} W''^{-}_{\sigma\tau}\begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix} \xi\begin{pmatrix} fqn \\ \sigma i \end{pmatrix} \xi\begin{pmatrix} fqn \\ \tau i' \end{pmatrix} + \sum_\sigma W'_\sigma\begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix} \xi\begin{pmatrix} fqn \\ \sigma ii' \end{pmatrix} \right] , \end{aligned} \tag{2.6}$$

where

$$W'_{\sigma}\begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix} = \partial W\begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix} / \partial x_{\sigma}^{0fqn} , \tag{2.7}$$

$$W''^{+}_{\sigma\tau}\begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix} = \partial^2 W\begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix} / \partial x_{\sigma}^{0fqn}\, \partial x_{\tau}^{lf'q'n'} , \tag{2.8}$$

$$W''^{-}_{\sigma\tau}\begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix} = \partial^2 W\begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix} / \partial x_{\sigma}^{0fqn}\, \partial x_{\tau}^{0fqn} , \tag{2.9}$$

$$\xi\begin{pmatrix} fqn \\ \sigma i \end{pmatrix} = \frac{\partial x_{\sigma}^{0fqn}}{\partial R^{0fqi}} \tag{2.10}$$

and

$$\xi\begin{pmatrix} fqn \\ \sigma i i' \end{pmatrix} = \frac{\partial^2 x_{\sigma}^{0fqn}}{\partial R^{0fqi}\, \partial R^{0fqi'}} , \quad \{=\emptyset \text{ if } i \text{ or } i' = \text{translation}\} \tag{2.11}$$

(The condition { } in eq. (2.11) reflects the fact that translations depend linearly on Cartesian coordinates and vice versa.)

The ξ's are known constants which depend on the particles' masses and positions, while W', W'' can be computed from an analytical form of W.

If W is spherical, like the atom/atom and charge/charge interactions used in this research, W'_{σ}, $W''_{\sigma\tau}$ can be expressed as a function of explicit derivatives of W with respect to the particle/particle scalar distance

$$S\begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix}$$

and of derivatives of S with respect to x_{σ}^{0fqn}, etc. These expressions are reported in Appendix A, where it is also shown that

$$W''^{-}_{\sigma\tau}\begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix} = -W''^{+}_{\sigma\tau}\begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix} . \tag{2.12}$$

3. Ewald's formulas for harmonic LD of ionic molecular crystals

In actual LD computations, the infinite lattice sums that appear in the lattice energy expression and in $\mathbf{D}_k$ matrix elements (2.5) and (2.6) are truncated at a distance $r_{\max}$ where the value of the potential becomes negligible. For the atom–atom potential, which depends on r^{-n} with $n > 5$, $r_{\max}$ is of the order of 10 Å. Electrostatic interactions, instead, depend on r^{-1} and consequently extend to a much wider range. However, a fast convergence of the corresponding lattice sums can be achieved, following Ewald's method, by transforming a direct lattice sum of r^{-1} (and its derivatives) into one sum over the direct lattice of a "damped" function plus one sum over the reciprocal lattice of an exponential, both rapidly converging.

Let us consider point charges e_{qn}, $e_{q'n'}$ in lattice positions $\boldsymbol{x}^{0fqn}$, $\boldsymbol{x}^{lf'q'n'}$. The distance between them can be written

$$\boldsymbol{x}^{lf'q'n'} - \boldsymbol{x}^{0fqn} = \boldsymbol{l} + \boldsymbol{x} , \tag{3.1}$$

where $\boldsymbol{l}$ is the vector position of cell l and

$$\boldsymbol{x} = \boldsymbol{x}^{lf'q'n'} - \boldsymbol{x}^{lfqn} , \tag{3.2}$$

is a distance inside the cell.

The Coulomb potential between the two charges is (neglecting constants)

$$W\begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix} = \frac{e_{qn} e_{q'n'}}{|\boldsymbol{l}+\boldsymbol{x}|} \tag{3.3}$$

and the electrostatic energy per cell of a crystal of L cells is

$$E = \frac{1}{2L} \sum_{l}{}' \sum_{f'q'n'} \sum_{fqn} \frac{e_{qn} e_{q'n'}}{|\boldsymbol{l}+\boldsymbol{x}|} , \tag{3.4}$$

where the symbol $\sum'_l$ means that the term $l=0$ is to be omitted when $(f', q', n') = (f, q, n)$, that is $\boldsymbol{l} \neq \boldsymbol{0}$ if $\boldsymbol{x} = \boldsymbol{0}$; this excludes self-interaction of charges.

Note that eq. (3.4) includes intramolecular (intra-ion) interactions (see below).

The contribution of the Coulomb potential to the dynamical matrix elements (2.5) and (2.6) is contained in derivatives (2.7)–(2.9) that can be directly related to derivatives of W with respect to the components of $\boldsymbol{l}+\boldsymbol{x}$ – see eq. (3.1).

The following identity is used [17,18]

$$\sum_{l}{}' \frac{1}{|\boldsymbol{l}+\boldsymbol{x}|} \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{l}+\boldsymbol{x})] = \sum_{l}{}' \frac{1}{|\boldsymbol{l}+\boldsymbol{x}|} \operatorname{erfc}(\alpha|\boldsymbol{l}+\boldsymbol{x}|) \exp(\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{l}+\boldsymbol{x})]$$
$$+ \frac{4\pi}{V_c} \sum_{h} \frac{\exp(-|\boldsymbol{h}-\boldsymbol{k}|^2/4\alpha^2)}{|\boldsymbol{h}-\boldsymbol{k}|^2} \exp[\mathrm{i}\boldsymbol{h}\cdot\boldsymbol{x}] - 2\alpha\pi^{-(1/2)}\delta(\boldsymbol{x}) , \tag{3.5}$$

where V_c is the volume of the unit cell, $\sum_h$ indicates the sum over the reciprocal lattice, $\boldsymbol{h}$ is a vector in the reciprocal lattice (including the factor 2π), $\delta(\boldsymbol{x})$ is Dirac's delta function and

$$\operatorname{erfc}(y) = 1 - \operatorname{erf}(y) = \frac{2}{(\pi)^{1/2}} \int_{y}^{\infty} \mathrm{d}t \exp(-t^2) . \tag{3.6}$$

α is a positive constant whose value, while not affecting the result, determines how rapidly one or the other sum converges; to obtain a balanced effect, it is usually taken of the order of the inverse of a nearest-neighbor distance.

Using eq. (3.5) and substituting for shortness

$$\boldsymbol{r} = \boldsymbol{l}+\boldsymbol{x} \tag{3.7}$$

and

$$r = |\boldsymbol{r}| , \tag{3.8}$$

one obtains

$$\sum_{l}{}' \frac{1}{r} = \sum_{l}{}' \frac{1}{r} \operatorname{erfc}(\alpha r) + \frac{4\pi}{V_c} \sum_{h} \frac{\exp(-|\boldsymbol{h}|^2/4\alpha^2)}{|\boldsymbol{h}|^2} \exp(\mathrm{i}\boldsymbol{h}\cdot\boldsymbol{r}) - 2\pi^{-1/2}\alpha\,\delta(\boldsymbol{r}) , \tag{3.9}$$

$$\sum_{l}{}' \frac{\partial}{\partial r_\sigma}\left(\frac{1}{r}\right) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) = \sum_{l}{}' \frac{\partial}{\partial r_\sigma}\left(\frac{1}{r}\operatorname{erfc}(\alpha r)\right) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) + \frac{4\pi}{V_c} \sum_{h} \frac{i(\boldsymbol{h}-\boldsymbol{k})_\sigma}{|\boldsymbol{h}-\boldsymbol{k}|^2} \exp[|\boldsymbol{h}-\boldsymbol{k}|^2/4\alpha^2] \exp(\mathrm{i}\boldsymbol{h}\cdot\boldsymbol{r}) . \tag{3.10}$$

$$\sum_{l}{}' \frac{\partial^2}{\partial r_\sigma \partial r_\tau}\left(\frac{1}{r}\right) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) = \sum_{l}{}' \frac{\partial^2}{\partial r_\sigma \partial r_\tau}\left(\frac{1}{r}\operatorname{erfc}(\alpha r)\right) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})$$
$$- \frac{4\pi}{V_c} \sum_{h} \frac{(\boldsymbol{h}-\boldsymbol{k})_\sigma(\boldsymbol{h}-\boldsymbol{k})_\tau}{|\boldsymbol{h}-\boldsymbol{k}|^2} \exp[|\boldsymbol{h}-\boldsymbol{k}|^2/4\alpha^2] \exp(\mathrm{i}\boldsymbol{h}\cdot\boldsymbol{r}) . \tag{3.11}$$

From eqs. (3.4) and (3.9) the Coulombic crystal energy is

$$E=\frac{1}{2L}\sum_{fqn}\sum_{f'q'n'} e_{qn}e_{q'n'}\left(\sum_{l}{}' \frac{1}{|\boldsymbol{l}+\boldsymbol{x}|}\operatorname{erfc}(\alpha|\boldsymbol{l}+\boldsymbol{x}|)+\frac{4\pi}{V_{\mathrm{c}}}\sum_{h\neq 0}\frac{\exp(-|\boldsymbol{h}|^2/4\alpha^2)}{|\boldsymbol{h}|^2}\exp[\mathrm{i}\boldsymbol{h}\cdot\boldsymbol{x}]-2\alpha\pi^{-(1/2)}\,\delta(\boldsymbol{x})\right). \tag{3.12}$$

Note that the singular ($\boldsymbol{h}=\boldsymbol{0}$) term in the second member to the right of this equation is omitted, being identically zero due to the charge neutrality of the formula unit.

The lattice sums contained in $\mathbf{D}_{\boldsymbol{k}}$ matrix elements (2.5) and (2.6) can also be transformed, using eqs. (3.10) and (3.11). According to these equations, there are two contributions to $\mathbf{D}_{\boldsymbol{k}}$, one arising from the direct lattice sum, and the other one from the reciprocal lattice sum

$$\mathbf{D}_{\boldsymbol{k}}=\mathbf{D}_{\boldsymbol{k}}^{\mathrm{D}}+\mathbf{D}_{\boldsymbol{k}}^{\mathrm{R}}\,. \tag{3.13}$$

As it can be seen from eqs. (3.10) and (3.11), the *direct lattice contribution* $\mathbf{D}_{\boldsymbol{k}}^{\mathrm{D}}$ can be obtained straightly from eqs. (2.5) and (2.6) by replacing W with a "damped" potential U where the following substitution is made:

$$\frac{1}{r}\rightarrow\frac{1}{r}\operatorname{erfc}(\alpha r)\,. \tag{3.14}$$

The *reciprocal lattice contributions* to eqs. (2.5) and (2.6) are respectively

$$D_{\boldsymbol{k}}^{\mathrm{R}}\begin{pmatrix} fqi \\ f'q'i' \end{pmatrix}=\frac{4\pi}{V_{\mathrm{c}}}\sum_{nn'} e_{qn}e_{q'n'}\sum_{\sigma\tau}\xi\begin{pmatrix} fqn \\ \sigma i \end{pmatrix}\xi\begin{pmatrix} f'q'n' \\ \tau i' \end{pmatrix}\exp[-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}^{0f'q'n'}-\boldsymbol{x}^{0fqn})]$$

$$\times\sum_{h}\frac{(\boldsymbol{h}-\boldsymbol{k})_{\sigma}(\boldsymbol{h}-\boldsymbol{k})_{\tau}}{|\boldsymbol{h}-\boldsymbol{k}|^2}\exp[-|\boldsymbol{h}-\boldsymbol{k}|^2/4\alpha^2]\exp[\mathrm{i}\boldsymbol{h}\cdot(\boldsymbol{x}^{0f'q'n'}-\boldsymbol{x}^{0fqn})]\,,\quad (q'\neq q \text{ if } f'=f) \tag{3.15}$$

and

$$D_{\boldsymbol{k}}^{\mathrm{R}}\begin{pmatrix} fqi \\ fqi' \end{pmatrix}=\frac{4\pi}{V_{\mathrm{c}}}\sum_{nn'} e_{qn}e_{q'n'}\sum_{\sigma\tau}\xi\begin{pmatrix} fqn \\ \sigma i \end{pmatrix}\xi\begin{pmatrix} fqn' \\ \tau i' \end{pmatrix}\exp[-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}^{0fqn'}-\boldsymbol{x}^{0fqn})]$$

$$\times\sum_{h}\frac{(\boldsymbol{h}-\boldsymbol{k})_{\sigma}(\boldsymbol{h}-\boldsymbol{k})_{\tau}}{|\boldsymbol{h}-\boldsymbol{k}|^2}\exp[-|\boldsymbol{h}-\boldsymbol{k}|^2/4\alpha^2]\exp[\mathrm{i}\boldsymbol{h}\cdot(\boldsymbol{x}^{0fqn'}-\boldsymbol{x}^{0fqn})]$$

$$-\frac{4\pi}{V_{\mathrm{c}}}\sum_{f'q'}\sum_{nn'} e_{qn}e_{qn'}\left[\sum_{\sigma\tau}\xi\begin{pmatrix} fqn \\ \sigma i \end{pmatrix}\xi\begin{pmatrix} fqn \\ \tau i' \end{pmatrix}\sum_{h\neq 0}\frac{\boldsymbol{h}_{\sigma}\boldsymbol{h}_{\tau}}{|\boldsymbol{h}|^2}\exp[-|\boldsymbol{h}|^2/4\alpha^2]\exp[\mathrm{i}\boldsymbol{h}\cdot(\boldsymbol{x}^{0f'q'n'}-\boldsymbol{x}^{0fqn})]\right.$$

$$\left.+\sum_{\sigma}\xi\begin{pmatrix} fqn \\ \sigma ii' \end{pmatrix}\sum_{h\neq 0}\frac{\boldsymbol{h}_{\sigma}}{|\boldsymbol{h}|^2}\exp[-|\boldsymbol{h}|^2/4\alpha^2]\exp[\mathrm{i}\boldsymbol{h}\cdot(\boldsymbol{x}^{0f'q'n'}-\boldsymbol{x}^{0fqn}+\pi/2)]\right]. \tag{3.16}$$

In these equations, the exponential factors placed out of the reciprocal lattice sum arise from the difference between phase factors in the last terms of eqs. (3.10), (3.11) and in eqs. (2.5), (2.6).

Like in lattice energy (3.12), also in deriving the last two equations care must be taken about singular terms. Two cases can be examined separately

(1) In the second and third reciprocal lattice sum of eq. (3.16) the $\boldsymbol{h}=\boldsymbol{0}$ terms would not be defined. However, these are identically zero for the charge neutrality condition and have therefore been omitted.

(2) In the first reciprocal lattice sum in eq. (3.16) and in the reciprocal lattice sum in eq. (3.15) the $\boldsymbol{h}=\boldsymbol{0}$ terms are not defined if $\boldsymbol{k}=\boldsymbol{0}$. However, they have a finite value. In fact

$$\lim_{k->0}\frac{k_{\sigma}k_{\tau}}{|\boldsymbol{k}|^2}=\boldsymbol{u}_{\sigma}\cdot\boldsymbol{u}_{\tau}\,, \tag{3.17}$$

where $\boldsymbol{u}$ is a unit vector in the direction of $\boldsymbol{k}$. The ($\boldsymbol{h}=\boldsymbol{0}$, $\boldsymbol{k}=\boldsymbol{0}$) terms can be interpreted as the contribution of the macroscopic field [17]. Their effect on $\boldsymbol{k}=\boldsymbol{0}$ (optical) frequencies depends on the angle between $\boldsymbol{k}$ and the polarization associated to the mode, which can be 0 (LO modes), $\pi/2$ (TO modes), or a generic angle.

One last remark regards *intramolecular* (*intra-ion*) *interactions* (0*fqn*, 0*fqn'*) which, in the present model, have no physical meaning but are implicitly contained in the reciprocal lattice sums for $f'=f$ and $q'=q$ [first term in eq. (3.16)]. If (as it is customary) these interactions are excluded from the direct lattice sum, a correction $\mathbf{D}'_{\boldsymbol{k}}$ must be added to the corresponding $\mathbf{D}_{\boldsymbol{k}}$ elements

$$\mathbf{D}_{\boldsymbol{k}}=\mathbf{D}^{\mathrm{D}}_{\boldsymbol{k}}+\mathbf{D}^{\mathrm{R}}_{\boldsymbol{k}}+\mathbf{D}'_{\boldsymbol{k}}\ . \tag{3.18}$$

This correction must balance the second term to the right in eqs. (3.8)–(3.10) and is therefore:

$$D'_{\boldsymbol{k}}\begin{pmatrix} fqi \\ fqi' \end{pmatrix}=\sum_{n,n'\neq n}\sum_{\sigma\tau}Z''^{+}_{\sigma\tau}\begin{pmatrix} 0fqn \\ 0fqn' \end{pmatrix}\xi\begin{pmatrix} fqn \\ \sigma i \end{pmatrix}\xi\begin{pmatrix} fqn \\ \tau i' \end{pmatrix}$$
$$+\sum_{n,n'\neq n}\left[\sum_{\sigma\tau}Z''^{-}_{\sigma\tau}\begin{pmatrix} 0fqn \\ 0fqn' \end{pmatrix}\xi\begin{pmatrix} fqn \\ \sigma i \end{pmatrix}\xi\begin{pmatrix} fqn \\ \tau i' \end{pmatrix}+\sum_{\sigma}Z'_{\sigma}\begin{pmatrix} 0fqn \\ 0fqn' \end{pmatrix}\xi\begin{pmatrix} fqn \\ \sigma ii' \end{pmatrix}\right]. \tag{3.19}$$

Where Z', Z'' are defined similarly to W', W'' with

$$Z\begin{pmatrix} 0fqn \\ 0fqn' \end{pmatrix}=e_{qn}e_{qn'}\left(\frac{1}{r}\operatorname{erfc}(\alpha r)-\frac{1}{r}\right)=e_{qn}e_{q'n'}\frac{1}{r}\operatorname{erfc}(\alpha r) \tag{3.20}$$

and

$$r=|\boldsymbol{x}^{0fqn'}-\boldsymbol{x}^{0fqn}|\ . \tag{3.21}$$

In Appendix B is shown that this correction is zero when one of molecular coordinates i, i' is a translation.

4. Harmonic LD of orthorhombic $KClO_4$

Lattice dynamics calculations of the orthorhombic crystal of $KClO_4$ were carried out using the formulas described in the preceding sections.

4.1. Orthorhombic $KClO_4$: structure and spectral data

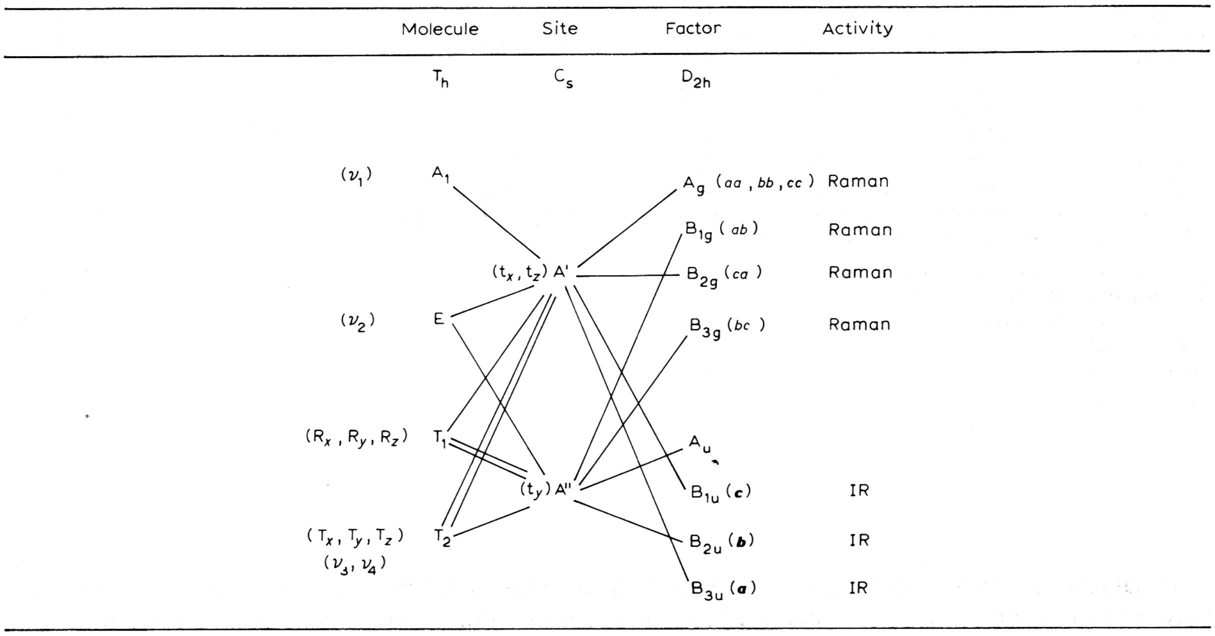
Two crystal modifications of potassium perchlorate are known. A cubic, orientationally disordered phase, belonging to space group O^5_h, is stable at $T>483$ K. Below this temperature, $KClO_4$ crystallizes in an orthorhombic form, with four formula units per cell, belonging to space group D^{16}_{2h}. In this phase both ClO_4^- and K^+ ions occupy sites of C_s symmetry.

The correlation diagram between molecule, site and factor group in the orthorhombic crystal is shown in table 1. Three translations of K^+ plus three translations and three rotations of ClO_4^- generate $4\times9-3=33$ optical lattice modes. $5A_g+4B_{1g}+5B_{2g}+4B_{3g}$ of them are Raman active, $4B_{1u}+3B_{2u}+4B_{3u}$ are IR active, and $4A_u$ are optically inactive; the three acoustic modes at $\boldsymbol{k}=\boldsymbol{0}$ have B_{1u}, B_{2u} and B_{3u} symmetry.

In aqueous solution, ClO_4^- is a tetrahedral ion with 4 normal modes of vibration [19]: $\nu_1(A_1)$, symmetrical stretching; $\nu_2(E)$, bending; $\nu_3(F_2)$, with prevalent stretching character; $\nu_4(F_2)$, with prevalent bending character. Each component of these normal modes generates, in the crystal, two Raman active 'g' vibrations and two 'u' vibrations, all of which are IR active except A_u ones.

Lattice bands have a rather weak intensity; however, all predicted bands (except one B_g) have been observed in polarized Raman spectra at room temperature [13], while IR bands are not resolved in the spectra reported by the same authors. High resolution Raman spectra in the lattice region have been recently recorded in our laboratory [20] at 20 K; stronger bands can be unambiguously assigned, in good agreement with the results of

Table 1
Correlation diagram between molecular (ClO_4^-), site and factor group in $KClO_4$. T: translations of ClO_4^-; R: rotations of ClO_4^-; t: translations of K^+. The plane formed by molecular axes x, z is parallel to the crystallographic $\boldsymbol{a}$, $\boldsymbol{c}$ plane. The symmetry of translations along crystal axes and of elements of the crystal polarizability tensor is also shown



ref. [13], and their widths contain valuable information about the anharmonicity of the intermolecular potential (see section 5).

Internal modes of ClO_4^- have been observed in the liquid and in both solid phases [12,13,21]. In the orthorhombic crystal the ν_1 mode has a small dispersion ($\approx 1\ cm^{-1}$) and is in Fermi resonance with the $2\nu_2$ harmonic mode [15]. The ν_2 and ν_4 modes show moderate dispersion (5 to 20 cm^{-1}) [12,15]. The very intense ν_3 band extends over more than 100 cm^{-1} [12].

Low-temperature decay times of totally symmetric components of all internal modes have been measured recently by time-resolved CARS spectroscopy [14,22]. These measurements show that population decay plays a fundamental role in determining phonons' lifetime.

4.2. Intermolecular potential and lattice modes

Both static and dynamical properties of $KClO_4$ can be satisfactorily reproduced with the atom/atom and charge/charge potential model described in section 2. Such a model has been used in a molecular dynamics simulation of the cubic phase of the same compound [23]. The potential parameters used in the present work were fitted to the lattice energy [24], crystal structure [25], and lattice frequencies [13,20] of the low-T phase. They are listed in table 2.

The atom/atom part of the potential is in the Buckingham form

$$W_{ij}(r) = A_{ij}\exp(-B_{ij}r) - C_{ij}r, \qquad (4.1)$$

where i and j label atomic species, A, B, C are constants and r is the atom/atom distance. This part of the

Table 2
Intermolecular potential for orthorhombic $KClO_4$.

Atom/atom potential: $V(r)=Ae^{-Br}-Cr^{-6}$ [a]

Species	A	B	C
K–K	14000	2.970	250
Cl–Cl	79100	3.305	800
O–O	100000	4.070	220
K–Cl	53591	3.138	520
K–O	40000	3.520	260
Cl–O	79686	3.688	450

[a] Units: A(kcal mol^{-1}), B($Å^{-1}$), C(kcal mol^{-1} $Å^6$)

Electrostatic potential: $V(r)=q_iq_j/r$
(q in units of proton charge)
$q(K)=+1.00$
$q(Cl)=+0.40$
$q(O)=-0.35$

Table 3
$KClO_4$ minimum energy structure [a]

	Calculated	Experimental
E(exp. struct.)	−148.788	−143.248 [b]
E (minimum)	−148.811	
a	8.938	8.866 [c]
b	5.703	
c	7.254	7.254 [c]
cell volume	369.7611	364.4029

[a] Units: kcal mol^{-1} and Å.
[b] Ref. [25].. [c]Ref. [24].

potential gives the largest contribution to the lattice frequencies, which were indeed found to be particularly sensitive to K/O and O/O first contacts. The K/O parameters adopted in this work compare will with K/O parameters used in the literature (see, for example, ref. [26] and references therein).

Effective point charges are placed on the nuclei. The adopted fractional charge on oxygen atoms is $-0.35\ e$, a value that is in agreement with lattice energy computations of a series of perchlorates [24], and is virtually identical to the one of the cubic phase simulations [23]. Statical properties, however, are not very sensitive to this quantity.

The computed lattice energy and minimum energy structure compare very well with experimental data (see table 3).

The calculated lattice frequencies at $\boldsymbol{k}=\boldsymbol{0}$ are reported in table 4, along with experimental data. The results refer to a lattice of 5×5×5 cells with an atom/atom cut-off radius of 6 Å. A reciprocal lattice of 27 cells with $\alpha^{-1}=5$ Å was used in Ewald's sum. Mixing of translations of both ions and of rotations of ClO_4^- is allowed by symmetry rules (see table 1). However, many of the modes have a prevalent translational or rotational character (see fig. 1, where the height of the bars is proportional to the square of the eigenvectors' components). Polar (IR) modes show angular dispersion. LO frequencies are systematically higher than TO ones, the difference being larger for high frequency modes. This TO/LO splitting is probably overestimated by our model, which does not take into account polarizability effects. Unfortunately, the corresponding experimental data are not available.

Fig. 2 shows the density of states in the lattice region, calculated with a sample of 343 wavevectors uniformly distributed in the reduced Brillouin zone (1/8 of the full zone). As expected, vibrations of higher frequency involve mainly translations of K^+ (whose mass is smaller than that of ClO_4^-), while modes below 110 cm^{-1} have a mixed character. The shape of the density of states is very similar to that of a side-band of ν_4 observed in the IR spectrum [27], with one central and two side peaks separated by approximately 100 cm^{-1}. Dispersion curves along the axes of the reciprocal lattice are shown in fig. 3.

Table 4
Orthorhombic KClO$_4$ lattice frequencies at $\boldsymbol{k}=\boldsymbol{0}$ (cm^{-1})

	Experimental		Calculated	
	ref. [13]	ref. [20]	TO	LO
A_g	140		141.4	
	116	120.0	102.3	
	87	92.0	83.1	
	72	72.6	76.3	
	52		43.2	
B_{1g} (*ab*)	138		126.1	
	114		108.4	
	73	72.4	80.8	
	55		63.2	
B_{2g} (*ac*)	147		161.5	
	128	136.0	132.7	
	112		101.6	
	97	99.2	95.0	
	79	76.6	87.3	
B_{3g} (*bc*)	116		110.8	
	101		93.6	
	69		76.9	
			62.9	
A_u			117.7	
			81.3	
			68.5	
			50.7	
B_{1u}			137.3	189.7
			132.3	136.6
			111.8	112.1
			78.5	83.9
B_{2u}			129.3	185.9
			101.8	104.7
			58.3	65.1
B_{3u}			144.2	197.6
			133.1	133.1
			73.2	73.2
			64.0	71.4

4.3. Intramolecular potential and internal modes

The vibrational analysis of isolated ClO_4^- was carried out using a basis of internal coordinates, namely four Cl–O stretching coordinates and six O–Cl–O bending coordinates.

We used the force constants of table 5, which were fitted to the frequencies of ClO_4^- in solution [13] (see table 6).

The atomic Cartesian dispacements obtained in this way were used as the definition of internal (normal) coordinates in the lattice dynamics calculation (that is, the ξs in (2.5) and (2.6)), while isolated ion frequen-

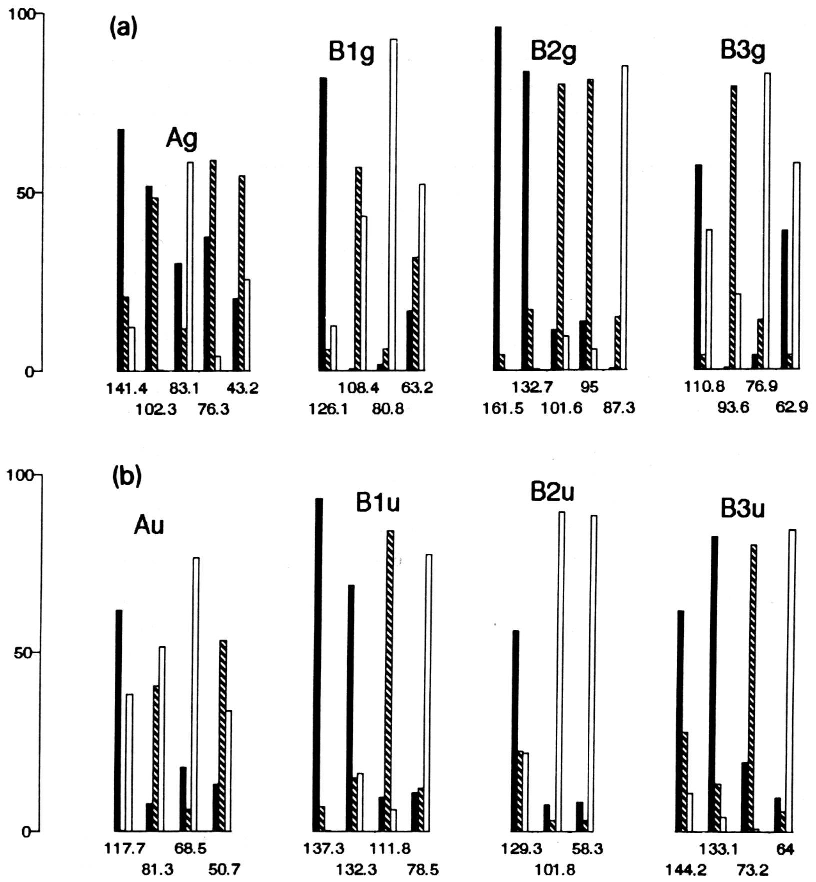


Fig. 1. Percent translational/rotational character of lattice modes of $KClO_4$ at $\boldsymbol{k=0}$. The height of the bars is proportional to the sum of the square of the eigenvectors' components relative to: K^+ translations (■), ClO_4^- translations (▨), ClO_4^- rotations (☐). Only the TO component of polar modes is shown.

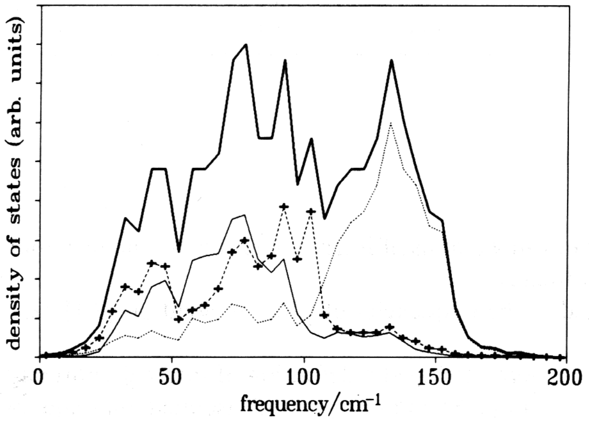


Fig. 2. One phonon density of states of $KClO_4$ in the lattice region. Bold line: total states. Thin lines: partial densities of states (the density of states has been weighted with the square of eigenvectors) for K^+ translations (—), ClO_4^- translations (...), ClO_4^- rotations (----).

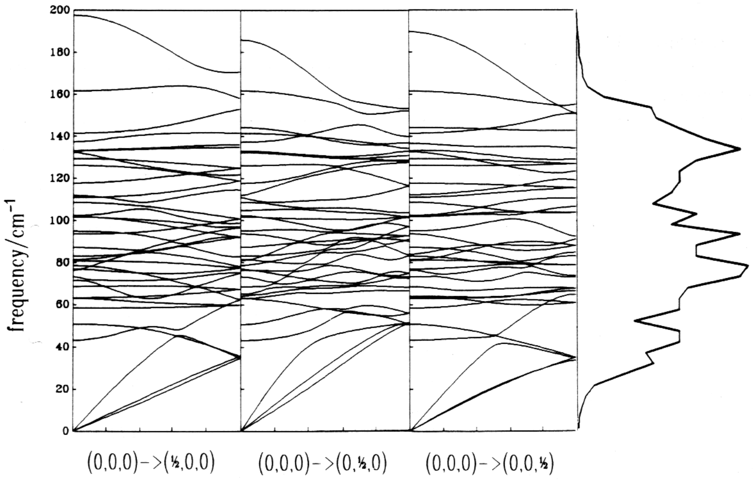


Fig. 3. Dispersion of lattice mode frequencies along the axes of the reciprocal lattice. The curve to the right of the figure is the total density of states of fig. 2.

Table 5
Intramolecular force constants for $KClO_4$

Type of force constant [a]	Value	Units
rr	7.0	mdyne/Å
rr'	6.5	mdyne/Å
$\alpha\alpha$	1.5	mdyne Å
$\alpha\alpha'$	0.7	mdyne Å
$\alpha\alpha''$	-0.2	mdyne Å

[a] r=Cl–O stretching; α=O–Cl–O bending. α' is opposite to α, while α'' is adjacent to it (the two bendings share one Cl–O bond).

cies ω_i in eq. (2.3) were adjusted in order to give the best agreement with observed crystal frequencies.

The perturbation due to the intermolecular potential results in a splitting of internal frequencies which compares very well with observed spectra (table 6). The case of ν_3 requires, however, a separate discussion. If the charges of table 2 are used, the dispersion of ν_3 is only 10 cm^{-1}, while the observed value is about 100 cm^{-1}. It is well known that the Davydov splitting of very strong IR bands, like this one, is largely affected by the transition dipole–transition dipole interactions [28,29]. Our model contains a dipolar contribution, originating from the motion of effective atomic charges; however, it does not include any variation of such charges during an internal motion. Within the same model, a good agreement with the observed splitting can be obtained if an effective transition dipole is introduced. This can be achieved by increasing the charge on O atoms to $-1.14\,e$. However, since such a high charge causes lattice frequencies to vary considerably from the values of table 4, only the block of **D** relative to ν_3 was computed using this value for the charge on oxygens.

Table 6
Experimental and calculated internal frequencies of ClO_4^-

	Isolated ion		Crystal				
	exp. a)	calc. b)	spec.	exp. c)	exp. d)	calc. TO	calc. LO
ν_4	460	441	A_g		463.4	466.2	
			B_{1g}		464.8	462.9	
			B_{2g}		461.4	463.2	
			B_{3g}		465.4	466.1	
			A_u			470.1	
			B_{1u}		468.5	465.8	465.8
			B_{2u}		466.0	463.0	463.0
			B_{3u}		471.5	469.2	469.2
ν_2	630	603	A_g	636.5		635.1	
						639.2	
			B_{1g}	627.5		628.0	
			B_{2g}	634.0		634.1	
				643.5		639.9	
			B_{3g}	627.5		629.9	
			A_u			624.4	
			B_{1u}			630.5	632.7
				626.0		637.1	637.1
			B_{2u}	629.5		626.6	628.9
			B_{3u}	637.5		635.4	635.5
						639.8	641.9
ν_1	935	950	A_g	943.5	942.6	943.9	
			B_{2g}	943.5		942.1	
			B_{1u}	942.0	943.0	944.0	944.0
			B_{3u}		943.7	941.8	941.8
ν_3	1050–1170	1125	A_g	1127.5		1077.2	
						1116.6	
			B_{1g}			1117.1	
			B_{2g}	1127.5		1123.8	
				1148.5		1172.8	
			B_{3g}	1089.0		1092.9	
			A_u	1071.0		1075.1	
			B_{1u}	1083.0		1102.3	1107.3
				1090.0		1181.6	1181.6
			B_{2u}	1116.0		1094.9	1099.9
			B_{3u}	1149.0		1095.0	1096.9
				1182.0		1115.7	1118.7

a) ClO_4^- in solution, room temperature [13]. b) See section 4.3. c) IR and Raman, 90 K [12]. d) IR and Raman, 20 K [15].

5. Anharmonic LD calculations

In sections 2 and 3 we have considered only the harmonic part of the crystal potential. The anharmonic part, which contains third and higher order derivatives of the potential is responsible for phonons' finite lifetime and, consequently, for the broadening of phonon spectral lines.

The contribution of anharmonic terms to phonon bandwidths can be calculated in the framework of linear response theory, following a perturbative approach [1]. Calculations involving several molecular crystals have shown that the lowest order term in the perturbative expansion can account for lattice phonon bandwidths [30,31,33–37] (for a recent review of theory and results see ref. [32]). This term depends on third derivatives of V and for the optical mode $(j, \boldsymbol{0})$ it can be written [32]

$$\gamma_{j0} = 36\pi\hbar^{-2} \sum_{\boldsymbol{k}} \sum_{j'} \sum_{j''} \left| B\begin{pmatrix} j0 \\ j'\boldsymbol{k} \\ j'' -\boldsymbol{k} \end{pmatrix} \right|^2 \left[(n_{j'} + n_{j''} + 1)\, \delta(\omega_{j0} - \omega_{j'\boldsymbol{k}} - \omega_{j''-\boldsymbol{k}}) + 2(n_{j''} - n_{j'})\, \delta(\omega_{j0} - \omega_{j'\boldsymbol{k}} + \omega_{j''-\boldsymbol{k}}) \right], \tag{5.1}$$

where the coupling coefficients B are given by

$$B\begin{pmatrix} j0 \\ j'\boldsymbol{k} \\ j'' -\boldsymbol{k} \end{pmatrix} = \frac{1}{3!} \left(\frac{\hbar^3}{2^3 \omega_{j0} \omega_{j'\boldsymbol{k}} \omega_{j''-\boldsymbol{k}}} \right)^{1/2} \frac{\partial^3 V}{\partial q_{j0}\, \partial q_{j'\boldsymbol{k}}\, \partial q_{j''-\boldsymbol{k}}} \tag{5.2}$$

and $n_{j\boldsymbol{k}}$ is the average occupation number of the state $(j, \boldsymbol{k})$

$$n_{j\boldsymbol{k}} = \frac{1}{\exp(\hbar\omega_{j\boldsymbol{k}}/k_B T) - 1}\,. \tag{5.3}$$

The widths of lattice bands in $KClO_4$ have been calculated using eq. (5.1) and the potential described in the previous section. A sample of 64 wavevectors $\boldsymbol{k}$ in the reduced Brillouin zone was used.

The results at $T = 10$ K are compared in table 7 to experimental data. The agreement is very good, and this indicates that cubic terms of the potential give a good estimate of global anharmonicity. Nor attempt has been made to reproduce the room temperature results of ref. [13] since these seem to be largely affected by instrumental resolution.

We have also investigated the variation of the average coupling coefficient among different phonons. In eq. (5.1), the squared coefficient can be replaced by its average value $\langle B_{j0}^2 \rangle$; furthermore, in the vicinity of zero temperature all occupation numbers vanish. Thus one has

Table 7
Full width γ of some lattice bands of $KClO_4$ (cm^{-1})

Species	Experimental [20] (20 K)		Calculated (10 K)	
	ω	γ	ω	γ
A_g	72.6	1.6	76.2	0.9
A_g	92.0	0.9	83.0	0.4
A_g	120.0	1.6	102.3	2.2
B_{1g}	72.4	0.9	80.8	1.9
B_{2g}	76.6	2.3	87.3	1.2
B_{2g}	99.2	1.8	101.5	2.0
B_{2g}	136.0	4.1	132.4	6.1

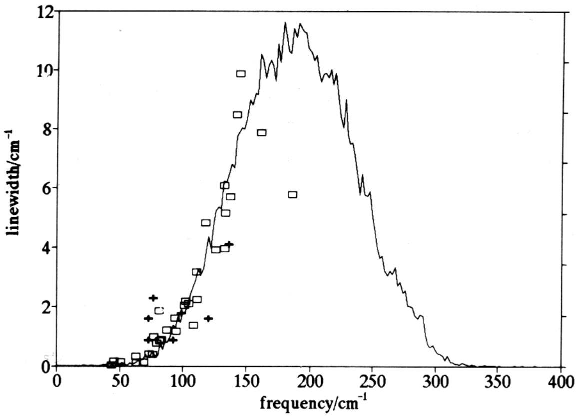


Fig. 4. Width of optical lattice bands in KClO$_4$. Squares: calculated; crosses: experimental [20]. The solid curve is the profile of the two-phonon density of sum states (see eq. (5.4)), in arbitrary units.

$$\gamma_{j0} \approx \langle B_{j0}^2 \rangle \sum_{\boldsymbol{k}} \sum_{j'} \sum_{j''} \delta(\omega_{j0} - \omega_{j'\boldsymbol{k}} - \omega_{j''-\boldsymbol{k}}) \,. \tag{5.4}$$

Our results show that in KClO$_4$ $\langle B^2 \rangle$ is independent of the decaying phonon $(j, \boldsymbol{0})$, so according to the previous expression γ is simply proportional to the density of sum states at the frequency ω_{j0}. This is illustrated in fig. 4, which refers to modes with $\boldsymbol{k}$ parallel to the crystal $\boldsymbol{b}$ axis. Only the highest frequency mode, of symmetry B_{2u} (LO), deviates significantly from the pattern of two phonon density of states, indicating that this mode is less coupled to the phonon bath than the others.

Similar results have been obtained for lattice bands of molecular crystals [33–37].

6. Conclusions

In this paper, we report Ewald formulas for lattice dynamics of ionic molecular crystals using a base of molecular coordinates and a charge/charge potential. The expressions are extensively commented and can be easily implemented in a computer program.

The algorithm has been used for the calculation of vibrational frequencies of orthorhombic KClO$_4$. In spite of its simplicity, the atom/atom and charge/charge potential presented in this research appears to reproduce well the statics and dynamics of the system. It also remarkable that its parameters differ only slightly from those used in studies regarding this crystal and its cubic modification.

Third-order terms of the potential account well for the low temperature width of the lattice bands. In analogy with several molecular crystals, the average third-order coupling coefficient is nearly constant for all lattice phonons.

Appendix A. Complete expressions for derivatives of the particle/particle spherical potential *W*

Let us consider the potential between particles a and b

$$W(\mathrm{ab}) = W[S(\mathrm{ab})] \,, \tag{A.1}$$

where $S(\mathrm{ab})$ is the absolute value of the distance between a and b

$$S(\mathrm{ab}) = \Big(\sum_{\sigma} (x^{\mathrm{a}}_{\sigma} - x^{\mathrm{b}}_{\sigma})^2 \Big)^{1/2} . \tag{A.2}$$

Let $W'_{\sigma}(\mathrm{ab})$, $W''_{\sigma\tau}(\mathrm{ab})$ be the first and second derivatives of $W(\mathrm{ab})$ with respect to x^{a}_{σ} etc., in accordance with definitions (2.7)–(2.9) – and

$$W'(\mathrm{ab}) = \frac{\partial W(\mathrm{ab})}{\partial S(\mathrm{ab})} , \tag{A.3}$$

$$W''(\mathrm{ab}) = \frac{\partial^2 W(\mathrm{ab})}{[\partial S(\mathrm{ab})]^2} . \tag{A.4}$$

We have

$$W'_{\sigma}(\mathrm{ab}) = W'(\mathrm{ab}) \frac{\partial S(\mathrm{ab})}{\partial x^{\mathrm{a}}_{\sigma}} , \tag{A.5}$$

$$W''^{+}_{\sigma\tau}(\mathrm{ab}) = W''(\mathrm{ab}) \frac{\partial S(\mathrm{ab})}{\partial x^{\mathrm{a}}_{\sigma}} \frac{\partial S(\mathrm{ab})}{\partial x^{\mathrm{b}}_{\tau}} + W'(\mathrm{ab}) \frac{\partial^2 S(\mathrm{ab})}{\partial x^{\mathrm{a}}_{\sigma} \partial x^{\mathrm{b}}_{\tau}} , \tag{A.6}$$

$$W''^{-}_{\sigma\tau}(\mathrm{ab}) = W''(\mathrm{ab}) \frac{\partial S(\mathrm{ab})}{\partial x^{\mathrm{a}}_{\sigma}} \frac{\partial S(\mathrm{ab})}{\partial x^{\mathrm{a}}_{\tau}} + W'(\mathrm{ab}) \frac{\partial^2 S(\mathrm{ab})}{\partial x^{\mathrm{a}}_{\sigma} \partial x^{\mathrm{a}}_{\tau}} . \tag{A.7}$$

and from eq. (A.2)

$$\frac{\partial S(\mathrm{ab})}{\partial x^{\mathrm{a}}_{\sigma}} = \frac{(x^{\mathrm{a}}_{\sigma} - x^{\mathrm{b}}_{\sigma})}{S(\mathrm{ab})} , \tag{A.8}$$

$$\frac{\partial S(\mathrm{ab})}{\partial x^{\mathrm{b}}_{\tau}} = - \frac{\partial S(\mathrm{ab})}{\partial x^{\mathrm{a}}_{\tau}} , \tag{A.9}$$

$$\frac{\partial^2 S(\mathrm{ab})}{\partial x^{\mathrm{a}}_{\sigma} \partial x^{\mathrm{b}}_{\tau}} = \frac{(x^{\mathrm{a}}_{\sigma} - x^{\mathrm{b}}_{\sigma})(x^{\mathrm{a}}_{\tau} - x^{\mathrm{b}}_{\tau})}{S(\mathrm{ab})^3} - \frac{\delta_{\sigma\tau}}{S(\mathrm{ab})} , \tag{A.10}$$

$$\frac{\partial^2 S(\mathrm{ab})}{\partial x^{\mathrm{a}}_{\sigma} \partial x^{\mathrm{a}}_{\tau}} = - \frac{\partial^2 S(\mathrm{ab})}{\partial x^{\mathrm{a}}_{\sigma} \partial x^{\mathrm{b}}_{\tau}} . \tag{A.11}$$

From eqs. (A.7), (A.9) and (A.11) it results

$$W''^{-}_{\sigma\tau}(\mathrm{ab}) = - W''^{+}_{\sigma\tau}(\mathrm{ab}) . \tag{A.12}$$

Appendix B. Zero elements of correction (3.19) to the dynamical matrix

Proof of the statement: if one of the coordinates i, i' in eq. (3.19) is a translation, then the corresponding correction to $\mathbf{D}_{\boldsymbol{k}}$ is zero.

If i or i' is a translation the last term in eq. (3.19) is zero according to eq. (2.11); furthermore, in analogy with eq. (2.12):

$$Z''^{-}_{\sigma\tau} \begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix} = - Z''^{+}_{\sigma\tau} \begin{pmatrix} 0fqn \\ lf'q'n' \end{pmatrix} . \tag{B.1}$$

Thus eq. (3.19) becomes

$$D_{\mathbf{k}'}\begin{pmatrix}0fqi\\0fqi'\end{pmatrix} = -\sum_{n}\sum_{n'\neq n} Z''^{+}_{\sigma\tau}\begin{pmatrix}0fqn\\0fqn'\end{pmatrix}\xi\begin{pmatrix}fqn\\\sigma i\end{pmatrix}\left[\xi\begin{pmatrix}fqn'\\\tau i'\end{pmatrix}-\xi\begin{pmatrix}fqn\\\tau i'\end{pmatrix}\right]. \tag{B.2}$$

If i' is a translation this quantity is zero because in this case

$$\xi\begin{pmatrix}fqn'\\\tau i'\end{pmatrix}=\xi\begin{pmatrix}fqn\\\tau i'\end{pmatrix}, \tag{B.3}$$

i.e. ions move rigidly during a translation.

Finally, if i is a translation, when the summation over atoms in eq. (B.2) is performed the $(n=N, N'=M)$ term cancels out with the $(n=M, n'=N)$ term

$$Z''^{+}_{\sigma\tau}\begin{pmatrix}0fqN\\0fqM\end{pmatrix}\xi\begin{pmatrix}fqN\\\sigma i\end{pmatrix}\left[\xi\begin{pmatrix}fqM\\\tau i'\end{pmatrix}-\xi\begin{pmatrix}fqN\\\tau i'\end{pmatrix}\right]=-Z''^{+}_{\sigma\tau}\begin{pmatrix}0fqM\\0fqN\end{pmatrix}\xi\begin{pmatrix}fqM\\\sigma i\end{pmatrix}\left[\xi\begin{pmatrix}fqN\\\tau i'\end{pmatrix}-\xi\begin{pmatrix}fqM\\\tau i'\end{pmatrix}\right]. \tag{B.4}$$

In fact

$$Z''^{+}_{\sigma\tau}\begin{pmatrix}0fqN\\0fqM\end{pmatrix}=Z''^{+}_{\sigma\tau}\begin{pmatrix}0fqM\\0fqN\end{pmatrix} \tag{B.5}$$

and

$$\xi\begin{pmatrix}fqM\\\sigma i\end{pmatrix}=\xi\begin{pmatrix}fqN\\\sigma i\end{pmatrix}. \tag{B.6}$$

Equations (B.3) and (B.6) do not hold for rotations or vibrations, since during a rotation or vibration different atoms or charges undergo different displacements.

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