Theory of the Normal Modes of Vibrations in the Lanthanide type Crystals

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Abstract. For the lanthanide type crystals, a vast and rich, though incomplete amount of experimental data has been accumulated, from linear and non linear optics, during the last decades. The main goal of the current research work is to report a new methodology and strategy to put forward a more representative approach to account for the normal modes of vibrations for a complex N-body system. For illustrative purposes, the chloride lanthanide type crystals \(\text{Cs}_2\text{NaLnCl}_6\) have been chosen and we develop new convergence tests as well as a criterion to deal with the details of the \(\Gamma\)-matrix (potential energy matrix). A novel and useful concept of natural potential energy distributions (NPED) is introduced and examined throughout the course of this work. The diagonal and non diagonal contributions to these NPED-values, are evaluated for a series of these crystals explicitly. Our model is based upon a total of seventy two internal coordinates and ninety eight internal Hooke type force constants. An optimization mathematical procedure is applied with reference to the series of chloride lanthanide crystals and it is shown that the strategy and model adopted is sound from both a chemical and a physical viewpoints. We can argue that the current model is able to accommodate a number of interactions and to provide us with a very useful physical insight. The limitations and advantages of the current model and the most likely sources for improvements are discussed in detail.

1. Introduction

Although, the experimental data available, from linear and non linear optics, is rather scarce or incomplete, is does not seem obvious to claim that some relevant problems in the solid state spectroscopy for these systems have been solved adequately. Indeed, we have been working on systems such as \(\text{Cs}_2\text{NaLnCl}_6\) for \(\text{Ln} = \text{Pr}, \text{Eu}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}\) and \(\text{Tm}\), aiming to advance our understanding in those electronic and vibrational factors, upon which the one photon electronic transitions depend upon. In this work, we report a novel strategy to rationalize the normal coordinate analysis so as to get a closer and more realistic approach, to deal with those contributions which determine what we regard as a natural potential energy distribution (NPED). It is essential to agree on the conditions upon which, we develop our convergence tests based on a physical view, so as to discern between a selections of experimental assignments from a more comprehensive viewpoint. As a starting point, we review the outstanding contribution put forward by Lentz\(^1\), who may claim priority in this area of the vibrational spectroscopy for the cryolite and elpasolite compounds.
Subsequently other authors, have introduced some correction terms in the description of the vibrational force field. It is indeed a major task to produce a better description for this interacting potential, based upon a maximum of ten vibrational frequencies. In the current work, our description is based upon a total of seventy two internal coordinates and an initial number of ninety eight internal force constants. We show that the potential energy matrix $F$ may be symmetrized by reducing the number of these latter to eighty one internal force constants. For each of the elpasolite type systems, we have considered a total of three representative $F$-matrices, and have calculated both the diagonal and non-diagonal contributions to the observed vibrational wave numbers, $\sqrt{\lambda_i} = (\nu_i/1303.16)$ for each of the experimental data and have managed to understand the sensitivity of the mixing between the symmetry coordinates for the same symmetry species with reference to a given vibrational frequency.

2. Vibrations

In this section, we aim to put forward a model to help the understanding of both, the advantages and disadvantages, when a normal coordinates analysis is performed for these systems. At the very best, we know that, this interacting potential operator is a function of the relative distances between the particles of the system. At starting point, we need to work out the well known vibrational equations of motion: $GFL = LA$.

When the systems is stable, for a given nuclear configuration, then the $G$ matrix is known and can be worked out from structural parameters and the masses of the nuclei ions of the crystal. All of this, is certainly referred to some nuclear equilibrium configuration ($Q \rightarrow \bar{Q}^{(0)}$). Also the $L$-matrix plays a crucial role in the theory since it does relate the symmetry coordinates to the normal coordinates of the system ($S = LQ$).

The $L$-matrices represent the amplitudes of vibrations and are functions of the chosen force field $F$ (the details of the force field should be considered with extreme care and accuracy). The amplitudes are normalized to the kinetic matrix by means of the transformation: $LL^t = G$. This kind of normalization condition is solely determined by the geometry and the equilibrium configuration of the system. It should be kept in mind that for any $L$-matrix (i.e. for a choice of the force field), the kinetic matrix $G$ is fixed. Also, from the normalization condition, given above, it follows that the $G$-matrix must be positive, then its eigenvalues must be positive.

Next, let $B$ be factorization matrix of the transformation attributed to Cholesky$^2$ for the $L$-matrix, then we write: $G = B'B$. Also: $GFL = LA$, then if follows: $F = G^{-1}(LA)L^{-1} = (LL^t)^{-1}(LA)L^{-1}$. After some algebra, we arrive to the chain of identities: $F = (L^{-1})^t(L^{-1})(LA)L^{-1} = (L^{-1})^tLAL^{-1} = (L^{-1})L(L^{-1})$. It is interesting to observe that the $F$-matrix obtained using this method, will be symmetric and that the associated eigenvalues corresponding to the matrix product $GF$ will be the same as those reported by the experiment (input values). Next, to work out a suitable $F$-matrix, it is relevant to define the amplitudes of vibrations matrix $L$ in an appropriate form, and as a consequence, this latter matrix must be non singular and its columns should provide a basis set in the whole space $R^n$. Let us introduce, the transformation: $L = B'A$, where the $B$-matrix has been defined previously and $A$ stands for a matrix whose columns constitutes an orthonormal basis set in the $R^n$-space, i.e. $A^t = A^{-1}$. 

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It follows that: \( G = L' L = (B' A') (B' A') = (AB)(AB)' \). Also, \( F = (L^{-1}) A (L^{-1}) \) and \( L = B' A' \) and \( A' = A^{-1} \). Thus, we write: \( L = B' A' \rightarrow L' = AB \rightarrow L'' = B^{-1} A^{-1} \). In terms of these identities, we write, the chain of identities as given below:

\[
F = \left\{ [B' A']^{-1} \right\} \Lambda \left\{ [B' A']^{-1} \right\} = (\left\{ [AB]^{-1} \right\} \Lambda \left\{ [BA]^{-1} \right\})^{-1} = (AB)^{-1} \Lambda (BA)^{-1} = B^{-1} A' \Lambda [AB]^{-1} \]

We have employed the identity: \((AB)^{-1} = B^{-1} A^{-1} = (B^{-1}) A'\), since the A-matrix is orthogonal. Also, we may write the chain of identities, such as:

\[
\left\{ [AB]^{-1} \right\} = (B' A')^{-1} = (B^{-1} A')^{-1} = (B^{-1} A') \]

therefore, we end up with the matrix transformation to be employed to get a modeled force field for these systems. Thus, we write: \( F = (B^{-1}) A' \Lambda A (B^{-1}) \) and hence from this matrix transformation, we observe that the \( F \)-matrix depends solely on the details of the \( A \)-matrix, which must be orthogonal \((A^{-1} = A')\). Next, we shall introduce an algorithm so as to put some restrictions upon the \( F \)-matrix; all its matrix elements should be positive and the following constrains should be fulfilled simultaneously:

The restrictions imposed upon this energy potential matrix are as described below:

\( f_{ij} > 0 \), for all \( i, j = 1, 2, ..., n \)

\( f_{ij} > f_{ij} \), for all \( i, j = 1, 2, ..., n \)

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Within the 10-atoms system model for these elpasolite type systems, the \( \tau_{\mu} \)-symmetry block is 4 x 4 and the symmetry coordinates have been labeled as: \( S_{i} (i = 6, 7, 8, 9) \). Next, the experimental evidence indicates that for these \( Cs_{2}NaLnCl_{6} \) systems, the trend is as follows: \( \nu_{6} > \nu_{8} > \nu_{7} > \nu_{9} \). A small but useful piece of help, may be obtained from the vibrational behavior of, say some diatomic molecule, such as: \( AB \)-type. We find that the allowed vibrational frequencies, corresponding to the optical branch are those given by the identity: \( \nu = \frac{1}{2\pi} \sqrt{k\mu^{-1}} \), where the reduced mass is denoted by \( \mu \), whereas the Hooke type force constant is labeled as \( k \). It is then straightforward to observe that for a set of given masses, it follows some kind of trend as follows: \( \nu \propto \sqrt{k} \), and hence we might expect for the 4x4 symmetry block and for the diagonal matrix elements a given patterns as: \( f_{66} > f_{88} > f_{77} > f_{99} \). This is, indeed our starting point, for the most probably ordering for the diagonal matrix elements. The conditions to be fulfilled by the \( F \)-matrix are somehow written as given below:

\[
\text{Conditions upon the } F \text{ -matrix} = \begin{cases} 
\text{true} & \text{if all conditions are satisfied} \\
\text{false} & \text{otherwise}
\end{cases}
\]
Algorithm:

Be \( G \) and \( F \), two given matrices

\( B \) is the factorization matrix of the \( G \)-matrix (Cholesky)

While: Conditions upon \( F = false \)

\( \hat{A} \)-matrix (random)

if \( |A| \neq 0 \) , then

\( A \) is an orthogonal matrix generated by \( \hat{A} \)

\( F = (B^{-1})A' \Lambda A(B^{-1}) \)

If these conditions upon \( F \) are fulfilled , then

Stop

\( F \) is feasible

end(If)

end(If)

end(While)

The assignment criteria are discussed in terms of the following strategy:

The short range contributions to the dynamic matrix obey the vibrational equation of motion:

\( GFL = \Lambda \), where \( G = LL' \). Thus, we write the general identity: \( \Lambda = L'FL \), and the elements of the diagonal matrix \( \Lambda \) are denoted by \( \lambda_i \), \( i = 1,2,...,s \), being \( s \) the number of normal modes of vibrations for the system. It is known, that these eigenvalues of the \( H = GF \)-matrix may be expressed as:

\( \vec{v} = 1303.16 \sqrt{\lambda} \).

In this notation, the wave numbers associated with each of the normal modes of vibrations for the systems have been denoted as \( \vec{v} \left( cm^{-1} \right) \).

From the identity: \( \Lambda = L'FL \), we write the general identity:

\( \lambda_i = \sum_{i=1}^{1} \sum_{k=1}^{2} L_{i,k} f_{k,i} = \sum_{k=1}^{2} L_{k,i} f_{k,k} + \sum_{k \neq i} L_{r,i} L_{k,k} f_{k,j} \).

These non diagonal contributions may be regarded as an interference term, which needs to be considered in detail (based solely upon the fact, that the diagonal components of the \( F \)-matrix is expected to be bigger than the non diagonal elements. It has been customary, in the literature, to neglect these terms from the start and subsequently to proceed in such a way that a renormalizing procedure is undertaken for each \( \lambda_i \).

It is, therefore assumed that the approximate expression is fulfilled:

\( \frac{1}{\lambda_i} = 1 \). For a series of compounds and transitions of the type \( d \rightarrow d \) and \( f \rightarrow f \), we have studied the above assumption and have found no reason to believe that this approximation should be considered and taken into account in the general theory of the normal modes of vibrations for a N-body system.

We have instead, considered the complete identity as given below:

\( 1 = [\sum_{i=1}^{2} L_{k,k} f_{k,i} / \lambda_i] + [\sum_{k \neq i} L_{r,i} L_{k,k} f_{k,j} / \lambda_i] \)

and therefore for each \( \lambda_i \), we may write:
At his point of the discussion, it is convenient to introduce a more general notation, suitable for computing calculations as given below:

\[ (1) \]

\[ 1 = \left( \sum_{k=1}^{N} \left( L_{i,j} f_{k,k} \right) / \lambda_{k} \right) + \left( \sum_{k \neq i} \left( L_{k,i} f_{k,j} / \lambda_{k} \right) \right) = \left( PED \right)^{d}_{i,j} + \left( PED \right)^{n-d}_{i,j} \]

and also:

\[ (2) \]

\[ [M_{\text{diagonal}}]_{i,j} = L_{i,j}^{2} f_{i,j} \]

In this approach, as we mentioned earlier on in the text, we may proceed to sum the above two matrices (2) and (3) to produce the \( M^{d+n-d}_{d+n-d} \). It is straightforward to realize that the summation over all the matrix elements along the various columns of the \( M^{d+n-d}_{d+n-d} \) matrix will produce as result the eigenvectors associated with the \( H = GF \) matrix for each and all of the symmetry blocks. Similarly, it is relevant to notice that from the above defined matrices (2) and (3), we may obtain the matrix elements corresponding to the natural potential energy distribution (in percentage) to give the general expression:

\[ (6) \]

\[ (PED)_{i,j} = 100 \left( \frac{\left( M^{d+n-d}_{d+n-d} \right)_{i,j}}{\lambda_{j}} \right) \]

A complete set of calculations have been carried out for the series \( Cs_{2}NaLnCl_{6} \) for \( Ln = Pr, Eu, Tb, Dy, Ho, Er \) and \( Tm \) and detailed results will be published somewhere else. For the sake of brevity, we have chosen to underline the methodology of the calculation method rather than the actual results, since many pages would be necessary to achieve this formidable task. Further requirements may be fulfilled upon request to RA.

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References
[1] A.Lentz. J.Phys.Chem.Solids, 35,827(1974)
[2] J.E.Gentle. “Cholesky Factorization” 3.2.2. In Numerical Linear Algebra for Applications in Static. Berlin. Spring-Verlag. pages: 93-95, 1998