Luminescence Spectra and Lattice Dynamics of NaNO$_2$

in the Ferroelectric Phase

By

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In order to understand the results of recent luminescence experiments harmonic lattice dynamics calculations on the ferroelectric phase of NaNO$_2$ are performed. Starting from an atom–atom potential and including the polarization of the nitrite ions by means of the shell model the phonon and vibron dispersion curves and densities of states are calculated. The calculated phonon dispersion curves are in good agreement with the inelastic neutron scattering data. The phonon density of states is compared with the phonon side band measured by luminescence. Above 15 K the measured phonon side band resembles the density of states, but at lower temperatures this resemblance is lost because of the non-uniform distribution of the excited states over the Brillouin zone. The density of states of the $v_2$-vibron band is compared with the lineshape of the $v_2$ line in luminescence spectra. It is shown that this lineshape can be explained by inclusion of the dispersion of the singlet exciton.

1. Introduction

Solid NaNO$_2$ exhibits a phase transition (at 163 °C) from a low temperature ferroelectric phase to a high temperature paraelectric phase [1]. This phase transition is rather complex [2 to 6] with an intermediate incommensurate phase. The low temperature ferroelectric phase has been the subject of several luminescence experiments [7 to 13]. The luminescence of the system that follows an electron excitation was recorded and the observed shapes of the resulting spectral lines were interpreted as to be influenced by the vibron dispersion. Also the phonon side band, which under certain conditions can be compared with the phonon density of states, has been measured in several experiment [7, 10, 13]. In order to

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understand these spectra we have performed lattice dynamics calculations, to obtain the full phonon and vibron dispersion curves, as well as the phonon and vibron densities of states. The vibron density of states is used to explain the lineshapes measured in the luminescence experiments. The calculated phonon density of states is compared with the measured phonon side band. Furthermore, we computed the Raman [14 to 20] and infrared [21, 22] frequencies and compared the calculated phonon dispersion curves with the data from inelastic neutron scattering [23, 24].

The lattice dynamics of the ferroelectric phase of NaNO$_2$ has been the subject of previous theoretical studies. In harmonic lattice dynamics calculations Castellucci and Schettino [18] calculated the angular dispersion of the vibrons in the $\Gamma$-point and the dispersion of the vibrons for wave vectors along the crystal axes. They also calculated the angular dispersion of the phonons in the $\Gamma$-point [25]. They did, however, not calculate the dispersion of the phonons in the Brillouin zone and the densities of states of the vibrons and phonons. They included the atomic polarizability by means of the shell model and showed that the rigid-ion model was inadequate to reproduce the experimental frequencies and splittings.

In the lattice dynamics calculations presented in this paper we used the site–site potential of Lynden-Bell et al. [4] who studied the lattice dynamics of NaNO$_2$ by classical molecular dynamics. However, we included the shell model as suggested by Castellucci and Schettino. We performed harmonic calculations with all the degrees of freedom so that even the (small) coupling between the phonons and the vibrons is taken into account.

2. Theory

For the calculations on NaNO$_2$ we used the harmonic lattice dynamics method for molecular solids. Because the molecular fragments, the sodium atom and the nitrite group, have an ionic character, the summation of the electrostatic interactions will not converge for the direct lattice [26]. Therefore, the Ewald method [27] had to be implemented in the summation of the electrostatic contributions to the static lattice energy and to the dynamical matrix. This method ensures a fast convergence of these electrostatic contributions.

The potential we have used in the lattice dynamics calculations on NaNO$_2$ is the exp–6 atom–atom potential with the parameters given in Table 1, supplemented by a point charge model. We assumed that the sodium atom and the nitrite group are completely ionic with charges of $+1.0e$ and $-1.0e$, respectively. The charge distribution of the nitrite ion was represented by four fractional charges: on the oxygen atoms a charge of $-0.65e$, on the nitrogen atom a charge of $1.10e$ and an additional charge of $-0.80e$ on the dipole axis,

<table>
<thead>
<tr>
<th>$x$</th>
<th>$A_{zz}$ (kJ/mol)</th>
<th>$q_{zz}$ (nm$^{-1}$)</th>
<th>$B_{zz}$ ($10^{-6}$ kJ/mol nm$^6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>40870</td>
<td>31.55</td>
<td>101.2</td>
</tr>
<tr>
<td>N</td>
<td>176000</td>
<td>37.8</td>
<td>1084.0</td>
</tr>
<tr>
<td>O</td>
<td>325000</td>
<td>41.8</td>
<td>1085.0</td>
</tr>
</tbody>
</table>

Table 1
Parameters in the atom–atom potential $V_{zz}(R_{zz}) = A_{zz} \exp \left( -q_{zz} R_{zz} \right) - B_{zz} R_{zz}^6$. The mixed interactions are given by the combination rules $A_{xz} = (A_{xx} A_{xy})^{1/2}$, $B_{xz} = (B_{xx} B_{xy})^{1/2}$, and $q_{xz} = \frac{1}{2} (q_{xx} + q_{yy})$.
Table 2
LO–TO splittings of the vibrons and amplitudes of the vibrating charges in the center of mass. The charges are +1.0e and −1.0e

<table>
<thead>
<tr>
<th>mode</th>
<th>LO–TO splitting a) (cm⁻¹)</th>
<th>amplitude (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>v₁ (sym. stretch)</td>
<td>2</td>
<td>0.0110</td>
</tr>
<tr>
<td>v₂ (bend)</td>
<td>2</td>
<td>0.0044</td>
</tr>
<tr>
<td>v₃ (asym. stretch)</td>
<td>133</td>
<td>0.0190</td>
</tr>
</tbody>
</table>

a) From Raman measurements [19]

0.080 nm from the center of mass on the nitrogen side. The work of Lynden-Bell et al. [4] shows that this is an acceptable potential for the phonon modes in NaN₃OH₂.

For the vibron modes, however, the results for this potential are rather poor. The splittings between the longitudinal and transverse optical components (LO–TO splittings) of the three vibron modes are much too large in comparison with the experimentally observed splittings [19]. In order to correct this we have adjusted the transition dipole moments of the three vibron modes by placing two opposite charges in the center of mass of the nitrite ion which vibrate along with the normal modes. The amplitude of the displacement of the two charges was fitted in order to reproduce the experimentally observed LO–TO splitting. The parameters of this fit are given in Table 2. For the intramolecular potential of the nitrite ion we used the force field of Weston and Brodasky [28] for the nitrite ion in crystalline NaN₃OH₂.

In ionic crystals the electrostatic fields are very strong and the polarizability of the ions should be taken into account. We have achieved this by implementation of the well-known shell model [29, 30]. If the polarizability of an atom equals \( \alpha \), the force constant of the core–shell interaction for that atom is given by \( f = Y^2/\alpha \). The parameter \( Y \), the charge of the shell, can be chosen freely. In the calculations on NaN₃OH₂ we neglected the polarizability of the sodium ions. The polarizability of the nitrite ions was taken from measurements of the refractive index by Hirotsu et al. [31]: \( x_{ud} = 2.240 \), \( x_{hb} = 2.716 \), and \( x_{cc} = 4.610 \times 10^{-3} \text{ nm}^3 \), where the indices label the crystallographic axes. We assumed that this polarizability is entirely localized on the oxygen atoms. Since it is anisotropic we need three different force constants for the core–shell interaction and, assuming that the charges of the oxygen atoms are completely on the shells, \( Y = -0.65e \), we obtain for these force constants: \( f_d = 0.3772 \), \( f_h = 0.3111 \), and \( f_c = 0.1833 \times 10^{-3} e \text{ nm}^{-2} \).

3. Structure

The low temperature ferroelectric phase has a body-centered orthorhombic structure with space group \( C_{2h}^{20} \). The conventional unit cell contains two NaN₃OH₂ formula units, but these units are related by a simple translation so that the primitive unit cell contains only one NaN₃OH₂ formula unit and there are twelve normal modes in the NaN₃OH₂ crystal, three translational vibrations of the sodium ions and three translational and three rotational vibrations of the nitrite ions. The remaining three vibrations are internal vibrations of the nitrite ions. In the conventional labelling of the crystal axes the \( C_{2h} \)-symmetry axis of the nitrite ion is the \( b \)-axis. In the ferroelectric phase the nitrite groups all point in the same direction along the \( b \)-axis. In the paraelectric phase these ions can point in the plus or
minus directions of the \( b \)-axis. The sodium ion is situated between two nitrite groups on the \( b \)-axis. The \( a \)-axis of the crystal is perpendicular to the plane formed by the three atoms of the nitrite ion. The \( c \)-axis is parallel to the line connecting the two oxygen atoms in the nitrite ion. The experimental [32] lattice parameters at \( 20^\circ \text{C} \) are: \( a = 0.35678 \) \( \text{nm} \), \( b = 0.55758 \) \( \text{nm} \), and \( c = 0.53919 \) \( \text{nm} \).

Before calculating the lattice excitations we have optimized the structure by minimizing the static lattice energy. The only parameters that can be varied within the space group symmetry of the structure are the lattice constants and the position of the sodium between the nitrite ions. In the minimization of the energy these nitrite ions were kept rigid. The optimized lattice parameters are \( a = 0.3709 \) \( \text{nm} \), \( b = 0.5496 \) \( \text{nm} \), and \( c = 0.5271 \) \( \text{nm} \). If we compare these parameters with the experimental values at \( 20^\circ \text{C} \) we observe that \( b \) and \( c \) are slightly too small and that \( a \) is slightly too large.

If the nitrite ions were isotropic, the position of the sodium ion would be halfway between two nitrite ions on the \( b \)-axis. But the nitrite ions are ‘arrows’ that, in the ferroelectric phase, point all in the positive \( b \)-direction. This causes the sodium ions to shift away from the centrosymmetric structure. The shift that we found in our calculations was 0.018 \( \text{nm} \) in the positive \( b \)-direction. The shift found by neutron diffraction is much larger, 0.047 \( \text{nm} \) [33], so that probably the anisotropy of the nitrite ion is underestimated.

### 4. Phonons

In the lattice dynamics calculations we have taken into account all the degrees of freedom and, therefore, in a general point in the Brillouin zone of the primitive structure we find twelve normal modes. The three internal vibrations of the nitrite ion (vibrons) are well separated in frequency from the nine external modes (phonons). The internal modes show little interaction with the external modes and we discuss them separately.

For \( \mathbf{k} = \mathbf{0} \) there are six optical phonons which are all split into a longitudinal and two transverse modes, except the phonon with \( A_2 \) symmetry which is the libration around the

| Table 3 | Phonon frequencies (in cm\(^{-1}\)) of NaN\(_2\) for \( \mathbf{k} = \mathbf{0} \) compared with Raman frequencies measured by Becucci and Castellucci [19] |
|---------|---------------------------------|---------|-------|
| mode\(^a\) | polarization | calc. | exper. b\(^b\) | c\(^c\) |
| \( A_1 \ T_b \) | TO | 200 | 190 |
| | LO | 273 | 270 |
| \( A_2 \ L_b \) | TO | 141 | 131 | 119 |
| | LO | 129 | 163 | 154 |
| \( B_1 \ L_a \) | TO | 129 | 74 | 165 |
| | LO | 218 | 218 | 236 |
| \( B_1 \ T_c \) | TO | 175 | 154 |
| | LO | 218 | 218 | 236 |
| \( B_2 \ 20\% T_a + 80\% L_c \) | TO | 170 | 149 |
| | LO | 214 | 201 |
| \( B_2 \ 80\% T_a + 20\% L_c \) | TO | 220 | 227 |
| | LO | 244 | 254 |

\(^a\) \( T_i \): translation along axis \( i \); \( L_i \): libration about axis \( i \). \(^b\) At \( T \approx 10 \text{ K} \). \(^c\) Room temperature.
In Table 3 we have given the calculated phonon frequencies in the Γ-point. All the lattice vibrations are Raman active and have been measured by Raman spectroscopy. We have compared our calculated frequencies with the recent Raman experiments of Becucci and Castellucci [19]. There are a number of other Raman and infrared measurements of the lattice frequencies of NaN$_2$O$_2$ and the spread in the results is rather large [14 to 20]. The calculated frequencies are all fairly close to the measured values, except for the mode that describes the libration about the a-axis which is off by more than 30 cm$^{-1}$. The LO–TO splitting of this mode is found to be very small (<0.5 cm$^{-1}$) while experimentally a splitting of 11 cm$^{-1}$ is observed. Our assignment of the modes with $B_2$ symmetry is different from that of Becucci and Castellucci. Both the translation along the a-axis and the libration about the c-axis have this symmetry, so these can be mixed. We find indeed a considerable mixing between these displacements. In the mode with lower frequency the libration is

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**Fig. 1.** Calculated phonon dispersion curves for the ferroelectric phase of NaN$_2$O$_2$ compared with inelastic neutron scattering results [23]. The open points refer to results taken at 23 °C and the filled points to −163 °C.
dominant and in the higher $B_2$ mode the translation. Becucci and Castellucci and also Hartwig et al. [15] assigned the lowest mode to the translation.

In Fig. 1 we show the phonon dispersion curves for wave vectors parallel to the crystal axes. The LO–TO splitting of a given mode is visible as the difference in frequency of this mode at the $\Gamma$-point for wave vectors approaching this point along the $a$-, $b$-, or $c$-axis. These dispersion curves are compared with the dispersion curves obtained by Sakurai et al. [23] from inelastic neutron scattering. For the acoustic modes the agreement between the experimental curves and the theoretical ones is good, especially in the $a$- and $b$-directions. The optical modes that have been measured show little dispersion, except for the LO branch of the $T_h$ mode that exhibits a strong dispersion for wave vectors parallel to the $b$-axis. The calculated curves show the same behaviour. The $T_h$ mode has a strong dispersion along the $b$-axis and the other optical modes show little dispersion. Our calculations show further that the dispersion of the optical modes with higher frequency depends strongly on the parametrization of the polarizability of the nitrite ion.

With the aid of a quadratic scheme for integration over the Brillouin zone developed by Wiesenekker et al. [34, 35], we have also calculated the phonon density of states for NaN$_2$. If we compare this density of states (see Fig. 2) with the phonon side band measured by Ashida et al. [10] in luminescence experiments on crystalline NaN$_2$ at 2 K, we observe, although some of the peaks correspond, that the overall resemblance is not very good. The calculated density of states is in better agreement with the phonon side band obtained by fluorescence excitation spectroscopy for crystal temperatures above 15 K. In these experiments a singlet electronic exciton of wave vector $k$ is optically excited together with a phonon of wave vector $-k$. The singlet exciton fluorescence is monitored as a function

![Fig. 2. Calculated phonon density of states](image-url)
of the energy of the exciting photon, which must be equal to the sum of the energy of the exciton and the energy of the phonon. The exciton band is very narrow (≈ 5 cm⁻¹ [10, 36]) relative to the phonon band (width ≈ 300 cm⁻¹). Moreover, it has been found [37] that, for temperatures above 15 K, the relaxation between states of different \( k \) within the exciton band is fast compared with the exciton decay time. Hence, the intensity of the fluorescence detected should be proportional to the phonon density of states. We find, indeed, that the phonon side band obtained from these experiments (see Fig. 3) agrees fairly well with the calculated phonon density of states in Fig. 2. The peak from the acoustic modes is not sharp and has a maximum around 100 cm⁻¹. There are two broad sets of peaks at about 150 and 210 cm⁻¹ separated by a gap. In the calculated phonon density of states these features are present also, but they occur at slightly lower frequencies.

5. Vibrons

The nitrite ion has three internal vibrations: the symmetric stretching mode \( v_1 \), the symmetric bending mode \( v_2 \), and the antisymmetric stretching mode \( v_3 \). In the NaN\( \text{O}_2 \) crystal these modes are well separated from the external modes. In Table 4 the calculated frequencies of the vibrons in the \( \Gamma \)-point are compared with the results of Raman measurements.

<table>
<thead>
<tr>
<th>mode</th>
<th>polarization</th>
<th>calc.</th>
<th>exper. a)</th>
<th>exper. b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 ) ( v_1 )</td>
<td>TO</td>
<td>1328</td>
<td>1329</td>
<td>1326</td>
</tr>
<tr>
<td></td>
<td>LO</td>
<td>1330</td>
<td></td>
<td>1328</td>
</tr>
<tr>
<td>( A_1 ) ( v_2 )</td>
<td>TO</td>
<td>816</td>
<td>831</td>
<td>827</td>
</tr>
<tr>
<td></td>
<td>LO</td>
<td>818</td>
<td></td>
<td>829</td>
</tr>
<tr>
<td>( B_1 ) ( v_3 )</td>
<td>TO</td>
<td>1222</td>
<td>1227</td>
<td>1225</td>
</tr>
<tr>
<td></td>
<td>LO</td>
<td>1355</td>
<td>1363</td>
<td>1358</td>
</tr>
</tbody>
</table>

a) At \( T \approx 10 \text{ K} \). b) Room temperature.
calculated frequencies are very close to the experimentally observed values. The largest discrepancy (11 cm\(^{-1}\)) occurs for the \(v_2\) mode. The LO-TO splittings are of course correct because we have fitted the transition dipole moments of the molecular vibrations to these splittings. The dispersion curves for the \(v_2\) vibron mode are drawn in Fig. 4 and for the \(v_1\) and \(v_3\) modes in Fig. 5. The \(v_2\) bending mode shows dispersion in the \(a\)- and \(c\)-direction but it is almost flat for wave vectors along the \(b\)-axis. In Fig. 5 we observe that the \(v_1\) mode and the \(v_3\) mode are mixed for wave vectors along the \(c\)-axis. The densities of states for these vibron modes are given in Fig. 6 and 7.

Fig. 4. Dispersion curves for the \(v_2\) internal mode of the nitrite ion calculated for wave vectors along the symmetry directions of the crystal.

Fig. 5. Dispersion curves for the \(v_1\) and \(v_3\) internal modes of the nitrite ion calculated for wave vectors along the symmetry directions of the crystal.
Fig. 6. Calculated density of states for the $v_2$ mode

Fig. 7. Calculated density of states for the $v_1$ and $v_3$ modes. The peak at 1330 cm$^{-1}$ is cut off
Just as the phonon density of states can be compared with the phonon side band in fluorescence experiments, the vibron density of states can be compared with the vibron band in these experiments. In that case the electronic exciton decays radiatively to a final state with a single vibron in the electronic ground state. Only the $v_1$ and $v_2$ modes can be detected in these fluorescence experiments, because the transition to the $v_3$ mode is forbidden by symmetry. The dispersion of the singlet exciton band cannot be neglected now, because it is of the same order of magnitude as the dispersion of the $v_1$ and $v_2$ vibron bands. The dispersion in the exciton band is about 5 cm$^{-1}$ and it is strongly anisotropic. There are indications that only states with wave vectors along the $a$-axis show dispersion [38]. We have assumed a model with nearest-neighbor interactions only in the $a$-direction which leads to cosine-type dispersion of the singlet exciton band, $\Delta E = 2.5 \cos (k_a 2\pi)$, where $k_a$ is the component of the wave vector along the $a$-axis. Since the exciton state is composed of $1B_1$ excited NO$_2$ molecules which have a nodal plane perpendicular to the $a$-axis, we have further assumed that the state with $k_a = 0$ has the highest energy. We subtracted this dispersion from the dispersion of the vibron band and then calculated the spectral density. If, in the experiment, the wave vectors of the singlet exciton state are distributed uniformly over the Brillouin zone and if the dispersion of the singlet exciton is correctly represented by the cosine function, then the calculated spectral density should resemble the vibron band in the fluorescence experiments. This calculated spectral density is given in Fig. 8 for the transition from the singlet exciton state to a $v_2$ vibron of the electronic ground state. This band is less peaked than the pure $v_2$ vibron density of states in Fig. 6, but it has about the same overall width. We must compare Fig. 8 with the $v_2$ vibron band in the fluorescence experiments (see Fig. 9) for temperatures above 15 K. The experimental band has a width...
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Fig. 9. Temperature dependence of the $v_2$-vibron band in singlet exciton fluorescence [11]

of about $8 \text{ cm}^{-1}$ [11] which is slightly broader than the calculated line. The experimental linewidth can be reproduced if we assume that the singlet exciton band is somewhat broader than $5 \text{ cm}^{-1}$. We noted that in order to compare the measured lineshape with our calculated shape, the energy scales in Fig. 8 and 9 are reversed.

The $v_2$ vibron band can also be measured in luminescence experiments in which the excited state is not a singlet exciton but a triplet exciton state. Because the dispersion in this triplet exciton band is very small [39] it can be neglected with respect to the dispersion of the $v_2$ mode. From these luminescence experiments the width of the $v_2$ density of states is estimated to be $3 \text{ cm}^{-1}$ [13]. This corresponds fairly well with the width at half maximum height of the density of states given in Fig. 6.

6. Conclusions

From our calculations on the lattice dynamics of the ferroelectric phase of NaNO₂ we conclude that it is possible to obtain very reasonable results with the site-site potential of
Lynden-Bell et al. extended with the effects of polarization through the shell model. For the optimization of the lattice structure and the calculation of the phonon spectrum we have chosen the charges of the shells, but we did not adjust any potential parameters to obtain better agreement with the experiments. Both the lattice parameters and the phonon frequencies in the T-point agree reasonably well with experiment. It should be noted that the phonon frequencies exhibit some temperature dependence [15, 40, 41] while the harmonic lattice dynamics calculations assume zero temperature. Also the calculated phonon dispersion curves agree well with the data obtained from neutron scattering [23].

The calculated phonon density of states does not resemble the phonon side band measured in luminescence experiments at very low temperature [10, 13]. In particular there is a gap around 115 cm\(^{-1}\) in the band measured by Ashida et al. [10] which is present neither in the calculated phonon density of states nor in the neutron scattering data. Laser fluorescence experiments [13] which have been performed as a function of temperature show that the spectrum from the phonon side band related to the singlet exciton band is temperature dependent, up to 15 K. The band measured in these experiments above 15 K agrees much better with the calculated phonon density of states. So the gap observed by Ashida et al. [10] in their measurements at 2 K is probably caused by a (strongly) non-uniform distribution of the singlet exciton states over the Brillouin zone.

For the calculation of the vibron bands we had to adjust the intermolecular potential in order to reproduce the experimental frequencies. Following Castellucci and Schettino [18], we have fitted the transition dipole moments of the molecular vibrations to the LO–TO splittings of the vibron modes. The dispersion of the \(v_1\) and \(v_3\) modes in [18] is very similar to our dispersion curves. On the scale used in [18] for the \(v_2\) mode this mode looks completely flat. The \(v_2\)-vibron band has been measured by luminescence, both from a singlet and from a triplet exciton state. The widths of the \(v_2\) bands in these experiments are rather different. It can be concluded from our calculated spectral densities, which agree reasonably well with the experiments, that this difference must be ascribed to the dispersion of the singlet exciton band.

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