Microscopic Model of $NaNO_2$ Based on Reorientations and Translations

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Starting from an atomistic sterical hindrance potential, translational and orientational motion of the NO_2 group in the deformable lattice are described. The reorientations of the NO_2 group in the paraelectric phase occur essentially by rotations around the crystallographic $\vec{c}$ axis, in agreement with slow or zero-frequency experiments. It is explained why high-frequency optical methods lead to the incorrect conclusion that reorientations take place around the $\vec{a}$ axis. The collective interaction of translations and rotations is discussed.

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Since the discovery of ferroelectricity[1] in $NaNO_2$, this substance has been the subject of numerous investigations.[2] Neutron[3] and infrared[4] data indicate the absence of soft phonons in the region of the ferroelectric transition. This distinguishes $NaNO_2$ from displacive ferroelectrics.[5] The changes in the ferroelectric fluctuations[3,6] occur far more slowly than the lattice vibrations. Critical behavior was also found in x-ray diffuse scattering.[7] Although an Ising model can be used formally to describe the right and left positions of the NO_2 group along the crystallographic $\vec{b}$ axis (see, e.g., Ref. 7), it does not give much insight into the dynamics on a microscopic level. Stimulated by a discussion with Dolling, we have undertaken the construction of an atomistic model which combines the local-mode lattice-dynamical and order-disorder aspects in a unified way.

Our dynamical variables are first the displacements of both the Na ions and the rotation centers D of the NO_2 groups. Secondly, each NO_2 group is treated as a rigid body ("molecule") having full orientational freedom. Inspection of the lattice parameters[8] as well as of the ionic radii of all particles shows that the available space for each NO_2 molecule surrounded by the cage of six Na ions in the paraelectric phase is sterically restricted. Figure 1 shows the scale of dimensions along the $\vec{b}$ axis. In analogy with previous work[9] on KCN, we describe the interaction of a NO_2 group at lattice site $\vec{n}$ with a Na ion at site $\vec{n}'$ in nearest-neighbor position (n.n.) by a sum of three Born-Mayer potentials:

$$V(\vec{n},\vec{n}') = \sum_{l=1}^{3} C_1 \exp\{-C_2 |\vec{R}[\vec{n}(l)] - \vec{R}(\vec{n}')|\}. \qquad (1)$$

For a given position $\vec{R}(\vec{n}) = X(\vec{n}) + \vec{u}(\vec{n}, D)$ of the rotation center D of the NO_2 molecule, the l sum runs over the three constituting atoms, say $l = 1 \to N$, $l = 2 \to O^+$, and $l = 3 \to O^-$. The plus and minus indices are used only to distinguish the two O atoms. Explicitly

$$\vec{R}[\vec{n}(l)] = \vec{X}(\vec{n}) + \vec{u}(\vec{n}, D) + \vec{r}(\vec{n}, l), \qquad (2a)$$

$$\vec{R}(\vec{n}') = \vec{X}(\vec{n}') + \vec{u}(\vec{n}', \mathrm{Na}). \qquad (2b)$$

Here $\vec{X}(\vec{n})$ denotes the equilibrium positions of D and Na in the orthorhombic lattice. The translational lattice displacements are denoted by $\vec{u}(\vec{n}^{(\prime)}, \kappa)$, where $\kappa = D$ or Na, respectively. Finally, $\vec{r}(\vec{n}, l)$ accounts for the positions of the atoms N, O^+, O^- relative to the rotation center D. One

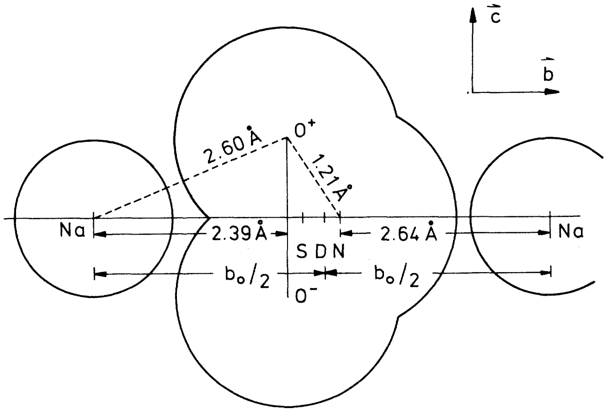

FIG. 1. The NO_2 molecule and two Na ions along the $\vec{b}$ axis, distances $\overline{SD} = 0.26$ Å, $\overline{DN} = 0.21$ Å, and $b_0/2 = 2.85$ Å.

passes from the molecular frame to the crystallographic axes ($\vec{b}, \vec{a}, \vec{c}$) chosen, respectively, as x, y, and z axes, by using the Euler angles $\Omega \equiv (\alpha, \beta, \gamma)$. The rotation center D does not coincide with the center of mass, S, of the NO_2 molecule (Fig. 1). This distinction ensures that two opposite orientations of the NO_2 group along the $\vec{b}$ axis are equivalent. It also accounts, in agreement with experiment, for the displacement of the center of mass[10] as well as for the relative displacement between Na and NO_2 ions.[11] The complete sterical hindrance potential (s.h.) is given by

$$V^{\mathrm{s.h.}} = \sum_{\vec{n}} \sum_{\vec{n}'} V(\vec{n}, \vec{n}') . \tag{3}$$

For a given $\vec{n}$, one sums over the six neighboring Na atoms $\vec{n}'$.

We expand the right-hand side of Eq. (3) in series of displacements $\vec{u}(\vec{n}^{(\prime)}, \kappa)$. The zeroth-order term corresponds to a sum of single-particle potentials:

$$V^0(\vec{n}) \equiv \sum_{\vec{n}'} V(\vec{n}, \vec{n}')\big|_{u=0} = V^0(\Omega(\vec{n})), \tag{4}$$

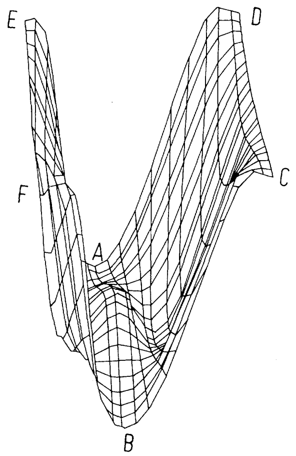

FIG. 2. Single-particle potential V^0 for $\Omega = (\psi, \varphi)$. The points A–F correspond to the values $(\psi, \varphi) = (0°, 0°)$, $(0°, 180°)$, $(90°, 180°)$, $(90°, 0°)$, $(-90°, 0°)$, and $(-90°, 180°)$, respectively.

for the rotation of the NO_2 molecule in the rigid lattice (crystal field). The first-order term yields, for each $\vec{n}$,

$$V^1(\vec{n}) \equiv \sum_{\vec{n}'} [\partial V(\vec{n}, \vec{n}')/\partial u_i]_{u=0} [u_i(\vec{n}', \mathrm{Na}) - u_i(\vec{n}, D)], \tag{5}$$

where the coefficient $[\partial V/\partial u]_{u=0}$ is a function of $\Omega(\vec{n})$.

We have studied numerically the variation of V^0 as a function of the molecular orientation Ω. Rotations around the $\vec{b}$ axis are energetically improbable and can be excluded. The variation of the potential as a function of rotations around the $\vec{c}$ axis ($\sphericalangle\varphi$) and around the $\vec{a}$ axis ($\sphericalangle\psi$) is given in Fig. 2. We conclude from this that reorientations of the NO_2 groups in the paraelectric phase occur essentially by rotations around the $\vec{c}$ axis. However, during the process of reorientation, the molecular $\vec{c}'$ axis (O^+-O^- line) deviates by an angle ψ from the $\vec{c}$ axis. Determining numerically the energetically most favorable path for reorientations along the valley in Fig. 2, we find that ψ varies continuously as a function of φ. For the pair of angles (ψ, φ), we quote in degrees the values (0, 0), (10, 40), (30, 70), (40, 90), (30, 110), (10, 140), and (0, 180). Optical methods with frequencies ≥ 10 THz are able to follow instantaneously the path of the NO_2 molecule during the short process of reorientation and during the torsional oscillations around the $\vec{a}$ axis when the molecule is trapped in the potential minima (Fig. 2) at $\varphi = 0°$ and 180°. The observed infrared spectra in $\vec{c}$ polarization[12] indicate variations of the angle ψ. However, in our opinion, it is an overinterpretation of experiments to conclude that the reorientation of the NO_2 group between two sterically opposite positions along the $\vec{b}$ axis occur through reorientations around the $\vec{a}$ axis. The same remark applies to Raman experiments[11, 13] from which one has deduced that reorientations would take place predominantly about the $\vec{a}$ axis. On the other hand, zero- or low-frequency methods such as diffraction experiments (neutrons[8, 14-16] and x rays[15]) and magnetic resonance results,[16] respectively, indicate that the reorientations occur about the $\vec{c}$ axis. This is essentially the case according to the present theory.

For a description of ferroelectric fluctuations (1–10 GHz) associated with the phase transition, the details of the motion during the short time of reorientation are irrelevant. It is then a meaningful approximation to assume that $\psi = 0$ and to consider only the angular variable φ which describes rotations around the $\vec{c}$ axis. Since we are dealing with large-amplitude motions (reorientations), we expand the angle-dependent functions in Eqs. (4) and (5) in terms of symmetry-adapted functions $\cos m\varphi$, $\sin\varphi$, where m and n are integers.

Symmetry arguments for the single-particle potential (crystal field) yield the expression

$$V^R = \sum_{\vec{n}} V^0(\vec{n}) = \sum_{\vec{n}} c_2 \cos[2\varphi(\vec{n})]. \tag{6}$$

Here we have dropped an irrelevant angle-independent term. Numerical calculations show that the series converges well with $m = 2$; therefore we retain only $\cos 2\varphi$.

Expanding the first-order term (5), we obtain

$$V^{TR} = \sum_{\vec{n}} V^{(1)}(\vec{n}) = \sum_{\vec{n},\vec{n}'} v_{i\alpha}(\vec{\tau}) Y_\alpha(\vec{n})[u_i(\vec{n}', \mathrm{Na}) - u_i(\vec{n}, D)]. \tag{7}$$

Here the vector $\vec{\tau}$ stands for $\vec{X}(\vec{n}') - \vec{X}(\vec{n})$, the expansion coefficients $v_{i\alpha}$ from a 3×4 matrix ($i = x, y, z$), and Y_α, with $\alpha = 1-4$, labels the symmetry-adapted functions $\cos\varphi$, $\sin\varphi$, $\sin 2\varphi$, and $\cos 2\varphi$, respectively, with $\varphi \equiv \varphi(\vec{n})$. The symmetry-adapted functions $Y_\alpha(\varphi)$ are the dynamic variables of our problem. Note that the crystal-field term (6) is invariant with respect to reorientation ($\varphi = 0° \rightarrow \varphi = 180°$). On the other hand, Y_1 takes the values ± 1 while $Y_2 = 0$ for these two extreme positions. For an arbitrary rotation around the $\vec{c}$ axis, Y_α, $\alpha = 1$ and 2, are the two components of an orientational-order parameter. The Ising spin description[7] is recovered as a particular case of our description. We can show that the variable $\sin 2\varphi$ couples to shear motion and affects the elastic constant c_{66}. The components Y_α, $\alpha = 3$ and 4, are not relevant for the ferroelectric and antiferroelectric phase transitions.

Expression (7) constitutes the bilinear interaction between translational and rotational motion. In order to study the nature of this coupling, we separate the matrix $\tilde{v}(\vec{\tau})$ into a symmetric and an antisymmetric part,

$$\tilde{v}(\vec{\tau}) = \tilde{v}^s(\vec{\tau}) + \tilde{v}^a(\vec{\tau}), \tag{8}$$

with $\tilde{v}^s(\vec{\tau}) = \tilde{v}^s(-\vec{\tau})$ and $\tilde{v}^a(\vec{\tau}) = -\tilde{v}^a(-\vec{\tau})$. From symmetry arguments it follows that $\tilde{v}^s(\vec{\tau})$ possesses only nonzero elements coupling to Y_α, $\alpha = 1$ and 2, i.e., to the order-parameter components, while $\tilde{v}^a(\vec{\tau})$ has only nonzero elements for $\alpha = 3$ and 4. In addition we find that in the long-wavelength limit ($\vec{q} \rightarrow 0$), the coupling $\tilde{v}^s(\vec{\tau})$ is different from zero only for optical phonons while $\tilde{v}^a(\vec{\tau})$ corresponds to a coupling to acoustical phonons. Therefore in the long-wavelength limit the order parameter does not couple to acoustical phonons. This explains the absence of any acoustical soft mode in the experimental results.[3,4] On the other hand, since the ferroelectric fluctuations are several orders of magnitude slower than the optical vibrations, we are in the slow relaxation regime as far as the coupled dynamics of translations and rotations is concerned.[17] Therefore there appears also no softening of the optical modes in the neutron experiments.[3]

Introducing Fourier transforms of the lattice displacements, $\vec{u}(\vec{n}^{(\prime)}, \kappa) = (N m_\kappa)^{-1/2} \sum_{\vec{q}} \vec{u}(\vec{q}, \kappa) \times \exp[i\vec{q}\cdot\vec{X}(n^{(\prime)}, \kappa)]$, where N denotes the number of unit cells, we consider the six-dimensional space of displacements $\{u_\rho(\vec{q})\} = \{u_i(\vec{q}, \mathrm{Na}), u_j(\vec{q}, D)\}$, $i, j = 1-3$. Here $\rho = 1-3$ and $\rho = 4-6$ label, respectively, the displacements of the Na and the $\mathrm{NO_2}$ ions. Retaining only the coupling to the order parameter ($\alpha = 1, 2$) in the bilinear interaction (7), we can write

$$V_{1,2}{}^{TR} = \sum_{\vec{q}} \hat{v}_{\rho\alpha}{}^s(\vec{q}) Y_\alpha{}^\dagger(\vec{q}) u_\rho(\vec{q}), \tag{9}$$

with summation over repeated indices α and ρ. The matrix $\tilde{\tilde{v}}^s(\vec{q})$ is given by the transpose of

$$(m_{\mathrm{Na}}{}^{-1/2} \tilde{v}^s(\vec{q}), \; -m_D{}^{-1/2} \tilde{v}^s(\vec{q} = 0)), \tag{10}$$

with $v_{\alpha i}{}^s(\vec{q}) = \sum_{\vec{\tau}} v_{\alpha i}{}^s(\vec{\tau}) \cos(\vec{q}\cdot\vec{\tau})$. The function $Y_\alpha{}^\dagger(\vec{q})$ is given by $N^{-1/2} \sum_{\vec{n}} Y_\alpha \exp[-i\vec{q}\cdot\vec{X}(\vec{n})]$.

The bilinear interaction (9) leads to an effective interaction $V = -\sum Y\tilde{C}Y$ between reorienting $\mathrm{NO_2}$ groups. Here $\tilde{C} = \tilde{\tilde{v}}\tilde{M}^{-1}\tilde{\tilde{v}}$, where $\tilde{M}$ is the dynamical matrix of the unperturbed phonons. This lattice-mediated interaction is relevant in addition to dipolar forces if one wants to study the phase transitions in $\mathrm{NaNO_2}$. A detailed numerical study is being carried out at present.

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