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Isotopic Product Rule for Solid State Lithium Nitrate

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The *Teller-Redlich* type isotopic product rule within the harmonic approximation is found to be satisfactorily applicable to solid state vibrations of anhydrous lithium nitrate, $^6LiNO_3$ and $^7LiNO_3$.

(Keywords: Isotopic product rule; $^6Li/^7Li$ *isotopic effect; Lithium nitrate)*

Die isotopische Produktenregel für Lithiumnitrat im Festzustand

Es wurde festgestellt, daß die Isotopenproduktenregel vom *Teller-Redlich*-Typ innerhalb der harmonischen Näherung für die Vibrationen von wasserfreiem Lithiumnitrat ($^6LiNO_3$ und $^7LiNO_3$) im festen Zustand befriedigende Ergebnisse bringt.

Recently the *Teller-Redlich* type isotopic product rule was tentatively applied to the solid state problems of vibration. Although the product rule was originally advanced to isolated molecules within the harmonic oscillator approximation [1], the results for the adapted form were quite satisfactory for lithium hydroxide [2, 3] and lithium oxalate [4]. In both cases, the lithium ions are surrounded almost tetrahedrally by four oxygen atoms in their crystal structures. According to *Tarte* [5], lithium compounds are mostly classified into two types based on the site configurations of lithium ions: one is the most general tetrahedral type where the Li^+ bands appear in the 800–300 cm^{-1} region and another is the octahedral type where the Li^+ bands are expected in the lower region. Therefore, it is very interesting to examine a validity of the isotopic product rule for the second kind.

As an example of the second type, lithium nitrate seems to be the ideal one because all the *Raman* and infrared active fundamentals are already known [6] and the vibrational and crystallographic structures are moderately simple to investigate.

Table 1. *Observed fundamental wavenumbers*[a] *for* $LiNO_3$ (cm^{-1})

	$^6LiNO_3$	$^7LiNO_3$
a_{1g}	1 069	1 069
e_g	1 383, 734, 235, 123	1 382, 734, 235, 123
a_{2u}	838, 314[b], 153	838, 300[b], 152
e_u	1 392, 737, 314[b], 275, 168	1 392, 738, 300[b], 265, 167

[a] Fundamental wavenumbers from Ref. [6]

[b] Accidental degeneracy between symmetry species a_{2u} and e_u

Table 1 gives the experimentally observed fundamental wavenumbers of $^6LiNO_3$ and $^7LiNO_3$. Since lithium nitrate crystallizes in space group R$\bar{3}$c and the unit cell contains two formula units, the structure of the reduced representation of the 27 normal vibrations is found to be $\Gamma = 1\,a_{1g} + 3\,a_{2g} + 4\,e_g + 2\,a_{1u} + 3\,a_{2u} + 5\,e_u$, in which the normal modes of species a_{1g} and e_g are *Raman* active only, while those of species a_{2u} and e_u are infrared active only. For each symmetry block the isotopic product ratio is calculated by

$$\prod_i \frac{\omega_i(1)}{\omega_i(2)} = \prod_j \left(\frac{m_j(2)}{m_j(1)}\right)^{t_j/2} \left(\frac{M(1)}{M(2)}\right)^{T/2},$$

where the index i denotes all normal vibrations of a given symmetry block, the index j all non-equivalent isotopic atoms, t_j the number of normal modes which these isotopic atoms contribute to this representation, M the total mass of the formula unit and T the number of hindered translations within the representation.

The product ratios thus obtained theoretically between $^6LiNO_3$ and $^7LiNO_3$ are given in Table 2, together with those obtained experimentally from the fundamental bands. The results are satisfactorily acceptable. No Li^+ site translations belong to the *Raman* active species. For the infrared active species, the intense and broadened bands at 314 cm^{-1} of $^6LiNO_3$

Table 2. *Isotopic product ratios for* $^6LiNO_3/^7LiNO_3$

	a_{1g}	a_{2g}	e_g	a_{1u}	a_{2u}	e_u
Theor.	1.000	1.000	1.000	1.000	1.072	1.072
Obsd.	1.000	—	1.001	—	1.054	1.091

and at 300 cm^{-1} of $^7LiNO_3$ are assigned doubly as the Li^+ bands of species a_{2u} and e_u. This accidental degeneracy may cause a slight discrepancy between the theoretical and experimental product ratios for these symmetry species. On the assumption that the central band positions (given in Table 1) of these broadened absorptions are nearly the average of two fundamentals, the product ratios are also obtained for the combined symmetry block of a_{2u} and e_u, of course, taking into account the degeneracy of the species e_u. The theoretical ratio 1.232 reproduces well the experimental value 1.254. Consequently, it is concluded that the *Teller-Redlich* type isotopic product rule is also reasonably applicable to the solid state vibrations of the octahedral type of lithium compounds.

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