

Peculiarities of the Ionic Dynamics of Molten Nitrites

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Polarization measurements in the Raman spectra of molten sodium nitrite have shown that the reorientational line widths of the ν_1 and ν_2 bands (both of the A_1 symmetry type) of NO_2^- are different. Possible reasons are discussed. Also, the line widths of NO_2^- for various molten nitrites are found to depend on R^{-4} , the closest approach distance in the melt, and on Z , the cation charge number. This dependence agrees with theoretical predictions for the coupling of vibrational and reorientational dephasing caused by ion-dipole interactions.

1. Introduction

The usual assumption that for a given vibrational mode the vibrational correlation functions in infrared, isotropic and anisotropic Raman are equal was shown to be invalid in two kinds of experiments. When studying different Raman bands of the same symmetry type for the same molecule one may find the reorientational part of line widths to vary from band to band, although reorientation about the same molecular axis is probed [1]. Differences of the vibrational parts of infrared and Raman line widths for the same normal mode can also exist [2]. This phenomenon was discussed in several papers (see, e.g., [3–6]).

Such a phenomenon appears to be unknown for molten salts, the systems involving strong interparticle interactions. Nevertheless, the examination of recent spectroscopic data proves its existence for molten alkali nitrates. Derivation of τ_{1R} and τ_{2R} correlation times from IR [7] and Raman [8] spectra using τ_v from isotropic Raman band contours for the same $\nu_1(A'_1)$ normal mode of NO_3^- gives erroneous results: $\tau_{1R} \ll \tau_{2R}$ for all salts studied excepting CsNO_3 . The aim of this work is to study the differences of the reorientational line width probing the different ν_1 and ν_2 bands of the same A_1 symmetry type for the same entity, NO_2^- , in a single Raman experiment.

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2. Experimental

Owing to the instability of molten nitrites, Raman spectra of sufficiently high quality were obtained for sodium nitrite only. The chemically pure (USSR) salt under investigation was first recrystallized, its hot solution was filtered and dried. Raman spectra were collected on a JEOL JRS-S1 spectrometer equipped with the RS-HT2 high temperature Raman cell device. The 514.5 nm line of an argon ion laser (ILA 120) was used at an incident power output of 150 mW at the sample. For scattered radiation with different polarization vector orientations, the isotropic and anisotropic scattering components were isolated according to the relations

$$I_{\text{aniso}}(\nu) = I_{\perp}(\nu),$$

$$I_{\text{iso}}(\nu) = I_{\parallel}(\nu) - \frac{4}{3} I_{\perp}(\nu).$$

The depolarization ratio of the nitrite ion ν_2 line was 0.050. The tentative depolarization ratio of the ν_1 line was 0.24 (0.31 according to [9]). A more accurate estimation is difficult since this polarized line and the depolarized line $\nu_3(E)$ overlap on the small wave number side. This circumstance does not allow the whole $I_{\text{aniso}}(\nu)$ contour to be found with good accuracy and forces to use the overlap-free side only. The spectra are shown in Fig. 1 and the line widths are summarized in Table 1. Clearly the reorientational line widths $\delta_{2R} = \delta_{\text{aniso}} - \delta_{\text{iso}}$ from ν_1 and ν_2 are different.

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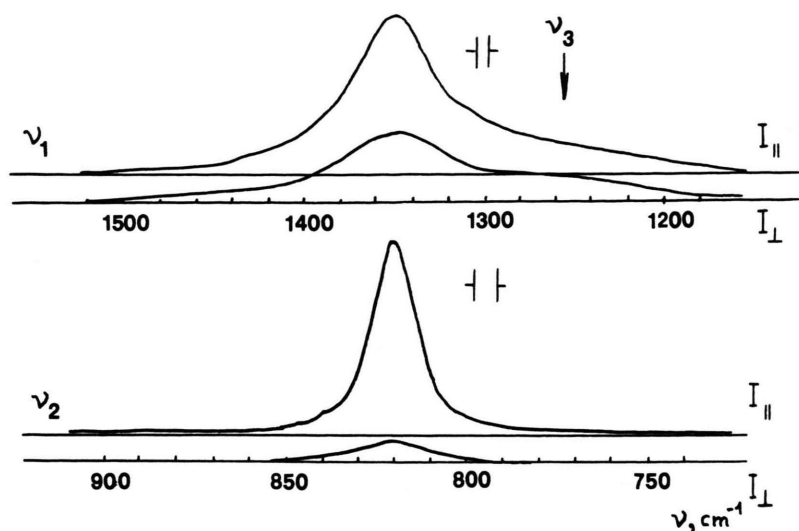


Fig. 1. Raman spectra of NaNO_2 at 573 K.

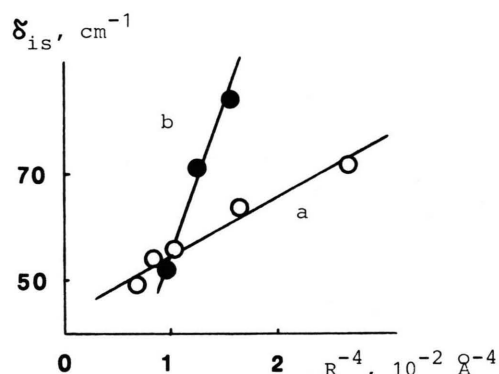


Fig. 2. Raman line widths of the ν_1 mode of NO_2^- ion in molten alkali (a) and alkaline earth (b) nitrites plotted against R^{-4} . All data taken from [9], cationic radii according Bat-sanov [14], $R_{\text{NO}_2^-} = 1.8 \text{ \AA}$ [15].

3. Discussion

According to Lynden-Bell, the difference between the vibrational contributions to the infrared, isotropic and anisotropic Raman line contours can arise either from the existence of cross terms between the “self” and “distinct” parts of the vibrational correlation function [3] or from the coupling of vibrational and reorientational dephasing [4]. The former appears to be of no importance for melts. Expanding the inter-particle potential F in a Taylor series with respect to normal coordinates Q , Lynden-Bell distinguishes between two terms which contribute to the secular broadening: The diagonal term, $\frac{1}{2} \frac{\partial^2 F}{\partial Q_i^2} Q_i^2$, and

Table 1. Line widths (full widths at half heights in cm^{-1}) in the Raman spectra of molten NaNO_2 . $\partial\mu/\partial Q_i$ were calculated in arbitrary units using the IR intensity data for solid solutions of nitrites in KCl [10].

Mode	δ_{iso}	δ_{aniso}	δ_{2R}	$\frac{\partial\mu}{\partial Q_i}$
ν_1	54.4	80.0	25.6	1.9
ν_2	14.8	21.2	6.4	1

the off diagonal exchange (resonant transfer) term, $\frac{1}{2} \frac{\partial^2 F}{\partial Q_i \partial Q_j} Q_i Q_j$, where i and j label the particle of interest and its surroundings. If the interionic potential is divided, following Hills and Madden [11], into cation-anion and anion-anion parts, one may conclude that the former gives no contribution to the exchange term. However, the contribution of anion-anion interaction is negligibly small for melts since anions are surrounded by cationic layers. As follows from recent reviews [12, 13], resonant transfer is not actually the cause of line shifts and broadening in melts even for the lines which are most intense in infrared. If the vibration is anharmonic there exists another self term which is proportional to the first derivative of the interaction potential: $(\partial F / \partial Q_i)_0 Q_i$. In real cases it can be of the same order of magnitude as the second derivative term.

If one follows Lynden-Bells theory of coupling of vibrational and reorientational dephasing [4, 5], the magnitude of such coupling may be measured with the square of the orientationally dependent contribution

of the interionic potential. Therefore one can expect a strong coupling in the case of the ion-dipole contribution. The first and second derivative diagonal terms are then proportional to

$$\left(\frac{\partial^n \mu_i}{\partial Q_i^n}\right)_0 \frac{Z e}{R^2} Q_i^n \quad \text{with } n=1 \text{ or } 2,$$

where μ_i is the anion dipole moment, Z the cation charge number, e the electron charge and R the distance of closest approach. The slope of δ_{iso} against R^{-4} for divalent cations is actually almost four times as large as for univalent ones (Figure 2). This observation confirms the assumption that the isotropic width is mainly due to ion-dipole interaction, because in the fast modulation limit the width is proportional to the

2nd moment, the averaged square of the spectroscopically active interionic potential. The fact that the larger $(\partial \mu / \partial Q_i)_0$, the broader the isotropic part of the bands studied (Table 1) could indicate at a first sight that the first derivative term of the interaction potential is more important in these cases than the second derivative term. Indeed that is true for NO_2 -because the first overtone of the ν_1 mode is undetectable in IR (see [10] and references cited therein).

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