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Inelastic Neutron Scattering as a Sensitive Probe of Inter-ionic Vibrational Coupling in Phase V of Ammonium Nitrate

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Summary Inelastic neutron scattering spectra indicate a strong vibrational coupling between NH_4^+ and NO_3^- ions in phase V of ammonium nitrate in the 500—1000 cm^{-1} region, although i.r. and Raman spectra show little evidence for such mixing; a variation of the coupling with the *k*-value may be indicated.

We have recently shown, by extensive isotopic studies, that the vibrational spectra of the room temperature phase (phase IV) of ammonium nitrate in the 1400 cm^{-1} region can only be explained by interionic vibrational coupling, not only between the ammonium ions and between the nitrate ions but also between these two sets.[1] Similar phenomena occur in the 1400 cm^{-1} region of the Raman spectra of phases II, III, and V of this salt. In contrast, interpretation of the 500—1000 cm^{-1} region of both the i.r. and Raman spectra does not appear to require such coupling, either in phase IV or any other phase of ammonium nitrate.

Under normal spectroscopic conditions there is no discernable coupling effect, as shown by the absence of differences between the i.r. or Raman spectra of $NH_4{}^{14}NO_3$ and $NH_4{}^{15}NO_3$ (97 atom %), with the exception of the out-of-plane deformation mode, at *ca.* 830 cm^{-1} (Table), which shows the expected shift of *ca.* 20 cm^{-1}. This observation is perhaps surprising in that the δ(ONO) peaks at *ca.* 720 cm^{-1} would be expected to show a significant low-frequency shift on ^{15}N substitution at the nitrate ion; however, the absence of this shift is common to many simple nitrates[2] and is explained by a mixing of the δ(ONO) and ν(N–O) symmetry co-ordinates. However, with the high

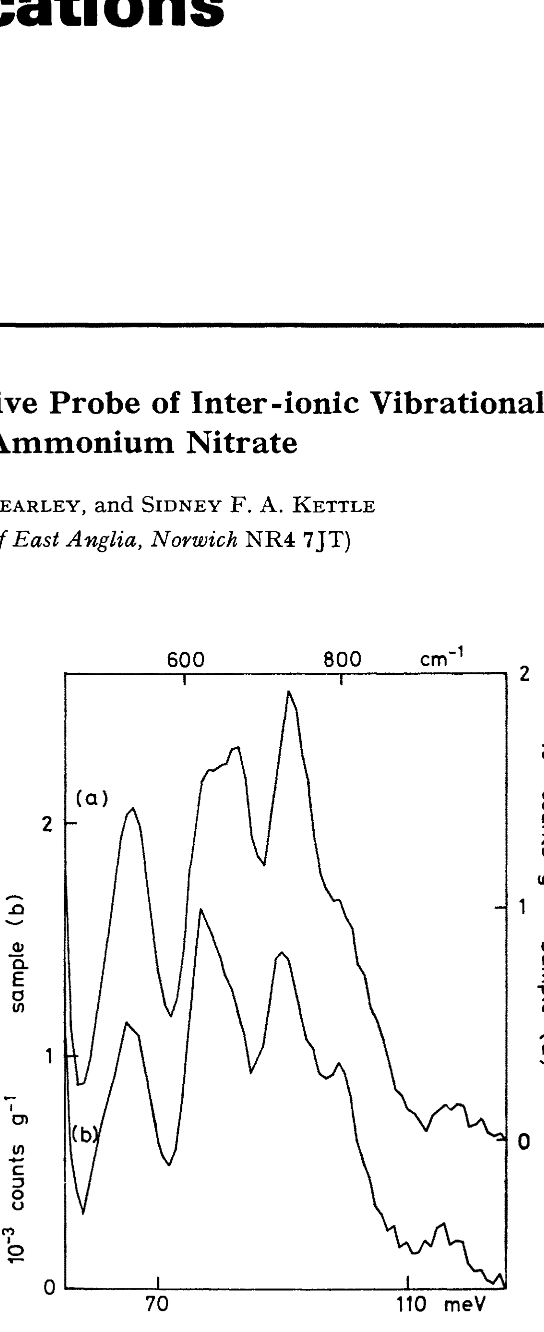

Figure. The i.i.n.s. spectra of (a) $NH_4{}^{14}NO_3$ and (b) $NH_4{}^{15}NO_3$, both recorded at 15 K and corrected for background. The intensities refer to 1·0 g of sample in each case.

Table The i.i.n.s., i.r. and Raman vibrational frequencies in the 500—1000 cm^{-1} region of $NH_4{}^{14}NO_3$ and $NH_4{}^{15}NO_3$ in phase v. Assignments refer to i.r. and Raman features only.

	$NH_4{}^{14}NO_3$			$NH_4{}^{15}NO_3$		
Assignment for i.r. and Raman spectra	i.i.n.s.[a] (cm^{-1})	i.r. (cm^{-1}	Raman (cm^{-1})	i.i.n.s.[a] (cm^{-1})	i.r. (cm^{-1})	Raman (cm^{-1})
	532			524		
	633			621		
	665					
$\nu_4(NO_3{}^-)$		706				
		712	710		708	709
		726	727		726	725
		729				
	734	733		726	733	
		739			739	
$\nu_2(NO_3{}^-)$	820	826		800	804	
		835			810	
		841				

[a] The sample interval used for the i.i.n.s. spectra was 8.0 cm^{-1}, the sampling points being matched in the two spectra to within 0·5 cm^{-1}. Although the absolute wavenumber accuracy of the i.i.n.s. spectra is much less than for i.r. or Raman spectra, the frequency differences between corresponding peaks in the two i.i.n.s. spectra have an accuracy at least comparable with the classical data. The signal to noise ratio is statistically determined and is *ca.* 1% at the peaks in the i.i.n.s. spectra.

resolution and wave-number accuracy afforded by interferometric studies small changes become apparent.

In contrast, the inelastic incoherent neutron scattering (i.i.n.s.) spectrum, recorded on the IN1 spectrometer at the I.L.L., Grenoble, (operating in the BeF mode), shows major changes on ^{15}N substitution at the nitrate ion (Table and Figure). Remembering that these spectra are completely dominated by the hydrogen atom motions (confirmed by the spectrum of the deuteriated compound), it is evident that the i.i.n.s. spectral changes can only be explained by appreciable coupling of the ammonium- and nitrate-ion vibrations. Either this coupling which presumably involves external modes and multiphonon participation, only occurs away from $k = 0$ or the apparent simplicity of the i.r. and Raman spectra in this region is deceptive. In retrospect, some of the small changes seen in the high resolution i.r. spectra may originate in such coupling. Even so, the evidence of the coupling in the i.i.n.s. spectra is very much clearer than in the classical vibrational spectra and so some k-dependence of the coupling seems probable. Indeed, if the coupling in the i.i.n.s. spectra were of the same magnitude as that in the i.r., it would not be observable using the former technique, since, despite the good wave-number repeatability of i.i.n.s. (BeF mode), the resolution is no better than *ca.* 40 cm^{-1}.

The apparent insensitivity of the conventional spectroscopic techniques to significant intermolecular vibrational coupling is a matter for some concern. It implies that the $k = 0$ limit may be unrepresentative of the whole of k-space, even in the case of internal modes, and that interaction terms may be k-dependant. In this situation there must be a real possibility that i.r. and Raman techniques alone may lead to conclusions which lack generality. A complete explanation of the phenomena which we have observed in ammonium nitrate must await triple-axis i.i.n.s. studies (which offer higher resolution) on a variety of isotopomers, studies which we plan to undertake in the near future.

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