

Isotope Shifts in Ammonium Perrhenate*

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Isotope shifts in the NQR and Raman spectra of ammonium perrhenate due to ^{15}N and ^2H substitution are reported. The effect of isotopic substitution at the nitrogen on the NQR spectrum is zero; in the Raman spectrum the translational lattice modes of the ammonium ion are clearly differentiated from the torsional modes.

The effect of deuteration on the NQR frequency has been measured to high accuracy and confirms that to a moderately good approximation the effect of deuteration is equivalent to the application of pressure. The effect of deuteration on the lattice parameters has been measured. NQR spectra of slightly deuterated ammonium perrhenate show a shoulder with a characteristic shift due to short range influence of NH_3D^+ .

The spectroscopic, structural and thermodynamic properties of NH_4ReO_4 have been studied for about ten years but the underlying reason for its peculiar behaviour has not been identified. In this work, the effects of isotopic substitution of nitrogen and hydrogen are investigated.

1. Experimental Methods

Ammonium perrhenate was deuterated by repeated recrystallization from D_2O , or from a $\text{D}_2\text{O}/\text{H}_2\text{O}$ mixture in the case of partially deuterated samples. Infra-red spectra were used to check qualitatively that deuteration was essentially complete. Isotopic substitution at nitrogen was obtained by distilling ammonia from a sample of $^{15}\text{NH}_4\text{Cl}$, to which base had been added, into a solution of Re_2O_7 , followed by evaporation and recrystallization.

Spectra were recorded on a Novex FT spectrometer. The very large temperature coefficient of the resonances makes the observation of spectra very difficult in the region of 200 K unless care is taken to avoid temperature gradients. In the gas flow cryostat the gas was lead through an axial labyrinth in the aluminum sample block to avoid temperature gradients along the axis of the sample. For some spectra coaxial samples containing two isotopically different salts were used to avoid errors

due to non-reproducible temperatures and temperature gradients, but low signal/noise made it impossible to do this at all temperatures. When coaxial samples could not be used, care was taken to ensure reproducible thermocouple placement; a high order polynomial was then fitted to the frequency-temperature graphs by a Simplex least squares procedure, and the deuteration shift was determined by subtracting each point from the other curve.

Lattice parameters were determined by X-ray diffraction using a CSS/STOE STADI 2/PL two circle diffractometer and accompanying software. Silicon was used as an internal standard, and temperatures were estimated to be constant within a 1 K range.

2. Spectra of $^{15}\text{NH}_4\text{ReO}_4$

The effect of isotopic substitution of nitrogen on the Re NQR frequency was found to be zero, with an upper limit of about 1/10 of a linewidth, which is about 15 kHz. A coaxial sample of the ^{15}N and ^{14}N salts showed no measurable splitting at room temperature, and at several temperatures down to 240 K.

Nitrogen isotopic substitution does not change the moment of inertia of the cation, and it is reasonable to assume that there is no effect on the rotational motion. However the cation mass does change, and the translational vibrations of the cation are affected. Figure 1 shows the the Raman spectra of this salt in the region of the lattice modes. At 10 K, lines at about 275 cm^{-1} and 266 cm^{-1} are not significantly shifted, and are therefore libra-

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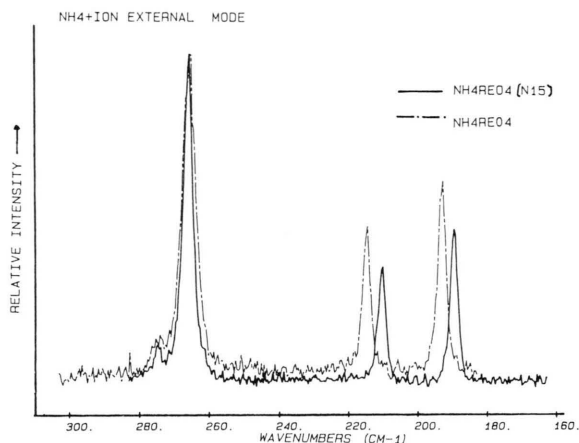


Fig. 1. The ammonium ion lattice modes in the Raman spectrum of $^{14}\text{NH}_4\text{ReO}_4$ and $^{15}\text{NH}_4\text{ReO}_4$, at temperature 10 K.

tional in nature; lines at 214 cm^{-1} and 192 cm^{-1} are shifted down by about 4 cm^{-1} , which is consistent with the square root of the ratio of cation masses. Any coupling of translational modes into the average electric field gradient at the Re site would be reflected in a shift of the Re NQR frequency. No such shift is seen, and so it can be concluded that there is no coupling to the translational modes.

3. NQR Deuteration Shift

The shift of the Re NQR frequency upon deuteration has been reported before [1], but the data were taken from a variety of experimental data sets which were not totally consistent. It was clear however that the temperature dependence of the deuteration shift was similar to that of the pressure coefficient $(\partial\nu/\partial P)_T$. If this is true, it implies that the effect of deuteration can be mimicked by the application of a suitable hydrostatic pressure. This recalls the observations that the phase transition [2] and elastic constants [3] of NH_4Cl are affected by deuteration in a way which is equivalent to the application of hydrostatic pressure. Thus it is of interest to see whether more accurate data for NH_4ReO confirms the earlier data.

The deuteration shift is plotted against temperature in Figure 2. The shift increases rapidly as temperature is lowered from room temperature, and at about 200 K a peak is reached; at lower temperatures, the shift decreases somewhat, whereas the pressure coefficient decreases only very slightly below 200 K [4]. In Fig. 3 the deuteration shift is

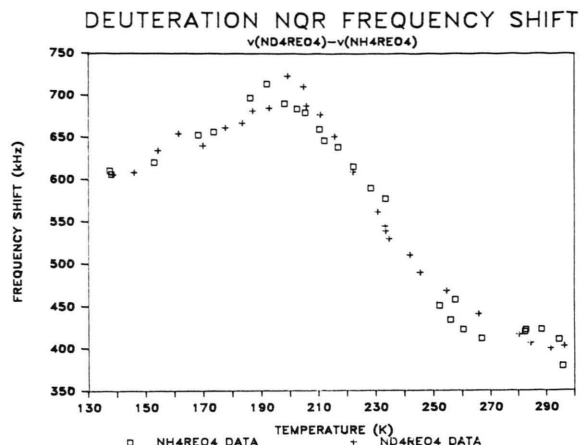


Fig. 2. Shift of the $3/2-5/2$ NQR frequency in $\text{NH}_4^{187}\text{ReO}_4$ due to deuteration.

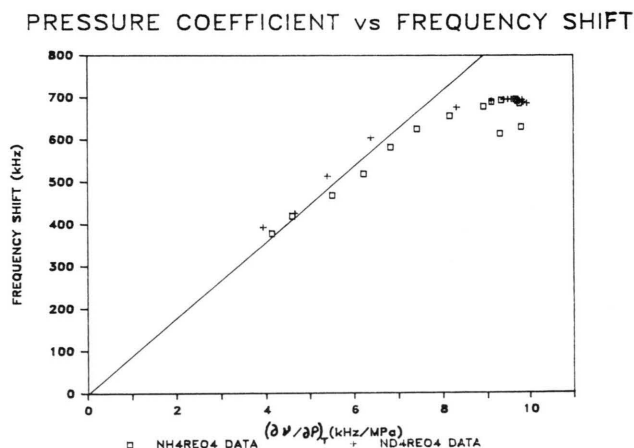


Fig. 3. Re NQR frequency shift due to deuteration plotted against the pressure coefficient of the NQR frequency, for a range of temperatures. The straight line corresponds to a pressure of 900 bar.

plotted against the pressure coefficient, and it is seen that while the relationship is not strictly linear, the effect of deuteration is equivalent to a pressure of approximately 90 MPa (900 bar). This is comparable to the pressure equivalent of deuteration in NH_4Cl .

4. Change of Lattice Parameter upon Deuteration

It has been pointed out in several studies of perrhenates that there is a correlation between the Re NQR frequency and the lattice geometry [5, 6]. The deuteration shift could be due to either the direct influence of the change in the properties of the ammonium ion, but it could also be simply the

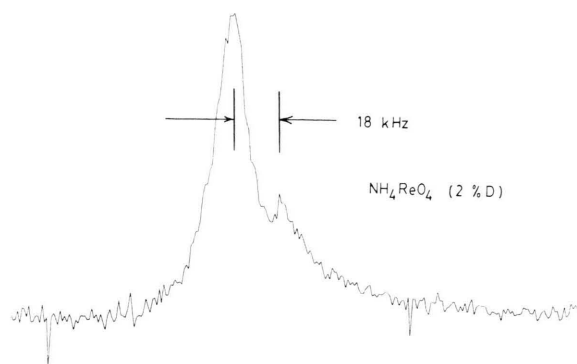


Fig. 4. The $3/2-5/2$ Re NQR line in $\text{NH}_4^{187}\text{ReO}_4$ containing approximately 2 per cent deuterium.

Table 1. Lattice parameters of ammonium perrhenate at 295.5(5) K.

	a (Å)	c (Å)	V (Å ³)
NH_4ReO_4	5.8841 (6)	12.974 (2)	449.2 (1)
ND_4ReO_4	5.8793 (4)	12.978 (2)	448.6 (1)

result of a change in lattice geometry caused in some way by the change in the properties of the ammonium ion. In order to test this, the lattice parameters of the deuterated salt were determined to high precision by X-ray diffraction. The results are shown in Table 1. Taking the observed shift in the a -parameter with the slope of -80 MHz/Å for the $5/2-3/2$ transition frequency correlation seen for ammonium perrhenate [5], the predicted shift in the $3/2-5/2$ transition frequency is 380 kHz, with an uncertainty of about 20%. This is in agreement with the observed deuteration shift at room temperature (Figure 2). This constitutes further support for the theory that it is the a -parameter which is of dominant importance in determining the Re NQR frequency; the deuteration shift can be interpreted as a result of a change in lattice dimensions rather than as the direct effect of the change in ammonium ion motion.

This interpretation suggests that since the deuteration shift increases as the temperature is lowered,

the effect of deuteration on the lattice parameters ought to be enhanced at low temperatures.

5. NQR of Partially Deuterated NH_4ReO_4

Partial deuteration of an ammonium salt ought to yield a single phase material which can be regarded as a solid solution of the various possible phases formed from the five individual pure $\text{NH}_{4-x}\text{D}_x$ salts. Thus the lattice parameters ought to be smooth functions of the degrees of deuteration. If the Re NQR frequency is a primarily a function of the lattice parameters, then partial deuteration should cause a partial shift. We have therefore investigated the NQR of partially deuterated samples.

For appreciable degrees of deuteration, no NQR signal at all was observed. However, when samples with only a few percent of deuterium were examined, it was found that a line of low intensity appeared approximately 18 kHz above the main line, independent of the degree of deuteration. A typical spectrum is shown in Figure 4. Measurements on a coaxial double sample showed that the main line is not measurably shifted or broadened. In a slightly deuterated sample, the only significant deuterated species is NH_3D^+ , and these ions will be widely separated. The observed spectra can be interpreted as indicating a short-range effect of a small concentration of substitutional impurities. The mechanism of the effect is unclear; it can be noted that the effective size of this cation is larger than the normal ion since the centre of mass is shifted by approximately 0.058 Å from the nitrogen atom, and the ion presumably rotates about its centre of mass. This effect is similar to that observed in solid solutions of chlorobenzene in bromobenzene [7].

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