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Rhenium pure quadrupole resonances have been observed in sodium, ammonium and silver perrhenates and the frequencies of both transitions for both rhenium isotopes recorded at room temperature and at 77°K, except in the case of ammonium perrhenate, where no signal is observed below about 257°K. The pure iodine quadrupole resonances in sodium and potassium periodates have also been observed. The crystals all have the scheelite structure and some distortion of the anion from a regular tetrahedron is probable. Values of the point-charge field-gradient tensors have been computed where reliable x-ray data are available. The structure of the ions and the nature of the bonding is discussed.

INTRODUCTION

It is commonly assumed that in XO_4^- ions the oxygen atoms are in a regular tetrahedral arrangement about the central X atom. One might therefore expect that the electric field gradient at the central atom would vanish for these ions, and be very small for their crystalline solid salts; accordingly, pure quadrupole resonances for the central atoms should be unobservable. However, we recently were able to observe the rhenium pure quadrupole resonance[1] in $KReO_4$ and concluded that the relatively large quadrupole coupling probably resulted from contributions to the electric field gradient tensor (FGT) from both the point charges in the tetragonal lattice and from partial covalent bonding in the ion, which is known to be distorted from tetrahedral symmetry in the crystal.[2] It seemed likely that other perrhenates would show rhenium pure quadrupole resonances and a search was made for these in the hope that the coupling constants would give information concerning the relative importance of the above two components of the electric field gradient tensor. By analogy it was concluded that iodine pure quadrupole resonances in periodates might be observable. It has indeed been possible to observe resonances in three other perrhenates and also in two periodates, and our results for these are presented here. No other NQR work on this class of substances appears to have been reported, although Weiss and Weyrich concluded from an NMR study[3] of $NaIO_4$ that the ^{127}I quadrupole coupling constant must be large.

EXPERIMENTAL

The apparatus and techniques have been described.[1] The low frequency lines of KIO_4 were observed by use of a minipulser.[4]

The sodium and ammonium perrhenates were prepared from potassium perrhenate (Alfa Chemical Co.) by passing an aqueous solution of the salt through a Dowex 50W-X2 cation-exchange column which had been converted to the acid form. The solution of $HReO_4$ was then concentrated by evaporation, neutralized with the appropriate base, and evaporated until crystals of the salt separated. The salts were all recrystallized from water except silver perrhenate which is very insoluble. Silver perrhenate was prepared by adding silver nitrate solution to perrhenic acid solution; the precipitate was washed, dried, and protected from light but not otherwise purified. Potassium and sodium periodates (J. T. Baker Chemical Co.) were recrystallized from water before use.

RESULTS

The various pure quadrupole resonance frequencies observed are listed in Table I. The asymmetry factors are zero within experimental error, as required by the crystal symmetry, so they are not listed. The temperature dependences of the NQR frequencies are normal in every case but that of ammonium perrhenate where an inverse behavior is noted (Fig. 1). A more detailed study of the temperature coefficients of the NQR frequencies in several of these compounds has been made,[5] and vibrational spectra have been reported.[6–8] Although the $\pm 3/2 \leftrightarrow \pm 1/2$ lines could be observed both at 77°K and 296°K for $NaReO_4$, we were not able to observe any signals either in the 20–40 MHz, or the 85–100 MHz, regions. A number of salts failed to give any observable resonances in the range of our spectrometers; this group includes $RbReO_4$, $TlReO_4$, $LiReO_4 \cdot 2H_2O$, NH_4IO_4, and $KClO_4$.

Point-charge field gradient tensors for the charged species in all the crystals of known structure were computed at the central nucleus (Re or I) by use of the computer program LATSUM described previously.[1,9]

CRYSTAL STRUCTURE AND SPECTROSCOPIC DATA

Interpretation of the NQR results depends to a considerable extent on having available reliable x-ray crystal structure information. Unfortunately the oxygen atoms of the perrhenates and periodates contribute relatively little to the scattering so their positions are known precisely in only a few cases. All the substances for which we report NQR resonances here have the tetragonal scheelite structure[10] with space group $I4_1/a$; loca-

TABLE I. Pure quadrupole resonance frequencies in perrhenates and periodates.

Nucleus	Transition	Temperature (°K)	Frequency (MHz)[a]
AgReO₄			
[185]Re	$\pm 5/2 \leftrightarrow \pm 3/2$	77	83.097
[187]Re	$\pm 5/2 \leftrightarrow \pm 3/2$	77	78.674
[185]Re	$\pm 5/2 \leftrightarrow \pm 3/2$	296	79.511
[187]Re	$\pm 5/2 \leftrightarrow \pm 3/2$	296	75.273
[185]Re	$\pm 3/2 \leftrightarrow \pm 1/2$	77	41.555
[187]Re	$\pm 3/2 \leftrightarrow \pm 1/2$	77	39.340
[185]Re	$\pm 3/2 \leftrightarrow \pm 1/2$	296	39.794
[187]Re	$\pm 3/2 \leftrightarrow \pm 1/2$	296	37.670
NH₄ReO₄			
[185]Re	$\pm 5/2 \leftrightarrow \pm 3/2$	257	34.092
[187]Re	$\pm 5/2 \leftrightarrow \pm 3/2$	257	32.276
[185]Re	$\pm 5/2 \leftrightarrow \pm 3/2$	296	35.140
[187]Re	$\pm 5/2 \leftrightarrow \pm 3/2$	296	33.267
[185]Re	$\pm 3/2 \leftrightarrow \pm 1/2$	257	17.050
[187]Re	$\pm 3/2 \leftrightarrow \pm 1/2$	257	16.142
[185]Re	$\pm 3/2 \leftrightarrow \pm 1/2$	296	17.578
[187]Re	$\pm 3/2 \leftrightarrow \pm 1/2$	296	16.640
NaReO₄			
[185]Re	$\pm 3/2 \leftrightarrow \pm 1/2$	77	48.620
[187]Re	$\pm 3/2 \leftrightarrow \pm 1/2$	77	46.024
[185]Re	$\pm 3/2 \leftrightarrow \pm 1/2$	296	44.997
[187]Re	$\pm 3/2 \leftrightarrow \pm 1/2$	296	42.606
NaIO₄			
[127]I	$\pm 5/2 \leftrightarrow \pm 3/2$	77	13.269
[127]I	$\pm 5/2 \leftrightarrow \pm 3/2$	296	12.723
[127]I	$\pm 3/2 \leftrightarrow \pm 1/2$	77	6.634
[127]I	$\pm 3/2 \leftrightarrow \pm 1/2$	296	6.362
KIO₄			
[127]I	$\pm 5/2 \leftrightarrow \pm 3/2$	77	6.515
[127]I	$\pm 5/2 \leftrightarrow \pm 3/2$	296	6.227
[127]I	$\pm 3/2 \leftrightarrow \pm 1/2$	77	3.258
[127]I	$\pm 3/2 \leftrightarrow \pm 1/2$	296	3.114

[a] The ratio $\nu(^{185}\mathrm{Re})/\nu(^{187}\mathrm{Re})$ is 1.056 within experimental error in each case. The probable error in the measured frequencies is ± 5 kHz.

tion of the oxygen atoms requires the determination of three parameters (x, y, z). This has been done only for potassium perrhenate[2] and sodium periodate,[11] and in both cases it is found that the oxygen atoms form a distorted tetrahedron (tetragonal bisphenoid) about the central atom, compressed along c in NaIO₄ and elongated along c in KReO₄ (Table II).

Infrared and Raman spectra[6-8] of crystalline KReO₄, NaReO₄, NH₄ReO₄, and AgReO₄ correspond to a site-group symmetry S_4 and are in agreement with (but do not require) a tetragonal bisphenoidal ReO₄⁻ group in these crystals. However, in the case of KIO₄, iodine

Mössbauer spectra have been studied, and the results are said to indicate T_d symmetry for IO₄⁻.[12,13]

Of the compounds in which we have failed to observe quadrupole resonances TlReO₄ has the (unknown) pseudoscheelite structure, KClO₄ the orthorhombic barium sulfate structure, and LiReO₄·2H₂O an unknown structure of low symmetry; only NH₄IO₄ and RbReO₄ have the scheelite structure.[10]

DISCUSSION

The observation of pure quadrupole resonances in five compounds with the scheelite structure, along with the x-ray and ir–Raman evidence discussed above, strongly suggests that in all these crystals the XO₄⁻ ions $(X = \mathrm{Re}, \mathrm{I})$ are tetragonal bisphenoidal. The quadrupole coupling could arise from the S_4 site symmetry, even if the XO₄⁻ ions were regular tetrahedra. However, the quadrupole coupling constants in the two crystals in which x-ray results have definitely established that the ions are of lower symmetry are the same order of magnitude as the others, so it is likely that in all cases the ions are distorted tetrahedra. The observed electric field gradient tensor (FGT) may then be considered, as an approximation, to be made up of two contributions. One, an electrostatic term $q(e)$, would arise from the field at a given atom of the remaining charged species throughout the lattice; the second, a "covalent" contribution $q(p)$, would arise from the distribution of the valence electrons. We can then write

$$q(\mathrm{obs}) = q(p) + q(e)[1 - \gamma_\infty], \qquad (1)$$

where γ_∞ is the Sternheimer antishielding factor, and the q's are the components in the principal axis system. Contributions from "unbalanced" d electrons are neglected.

In the case of KReO₄, where crystal structure data are available, $q(p)$ was estimated by assuming that
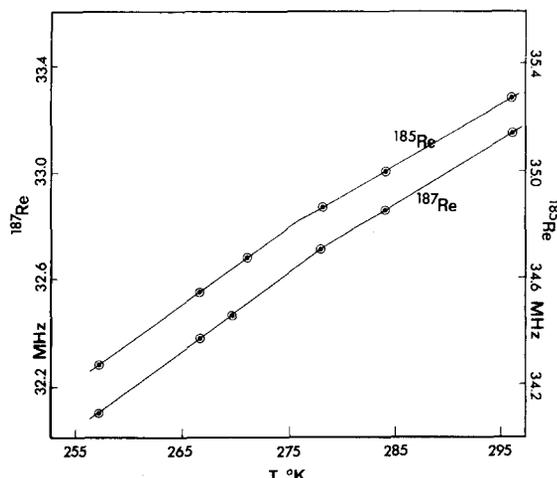

FIG. 1. Temperature dependence of the [185]Re and [187]Re NQR frequencies ($5/2 \leftrightarrow 3/2$ transition) in NH₄ReO₄.

TABLE II. Quadrupole coupling constants in perrhenates and periodates.[a,b]

Compound	eQq/h (MHz)	q(obs)$\times 10^{14}$ esu	$q(p)$ (calc)$\times 10^{14}$ esu	$q(e)$ (calc)$\times 10^{14}$ esu	γ_∞	$\angle$O–Re–O or $\angle$O–I–O°
$KReO_4$	178.75	11.2	-3.54	-0.456	-15.8	105°
$AgReO_4$	250.9	15.7				
NH_4ReO_4	110.9	6.95				
$NaReO_4$	284.0	17.75				
$NaIO_4$	42.4	7.8	-12.3	$+1.0$	-19.1 (-5.5)	114°
KIO_4	20.76	3.83				
ReO_3F	-48.4	-2.6	$+11.8$	-0.44	-28	109°30′

[a] The entries for $KReO_4$ are from Ref. 1 and for ReO_3F from J. F. Lotspeich, J. Chem. Phys. **31**, 643 (1959). The bond angle, magnitude, and sign of q(obs) for ReO_3F are from microwave spectroscopy.

[b] The calculation of $q(e)$, $q(p)$, and γ_∞ are discussed in the text.

[c] Values of $\angle$O–Re–O or $\angle$O–I–O are from crystal structure data (except ReO_3F) and refer to the angle bisected by the fourfold axis of the crystal.

rhenium forms four σ bonds, which are $sp^{9/8}d^{15/8}$ hybrids, plus two π bonds, and that each of these bonds is 50% ionic; $q(e)$ was then calculated on the point-charge model from the net charges on each atom and the atomic positions.[1] Since there is no way to calculate a reliable value of γ_∞ in this situation, at present, it was only possible to note that the reasonable value $\gamma_\infty = -15.8$ would lead to agreement between theory and experiment if the observed value has the negative sign. The experimental values of $|q(\text{obs})|$ for NH_4ReO_4 (6.95×10^{14} esu), $AgReO_4$ (15.7×10^{14} esu), and $NaReO_4$ (17.8×10^{14} esu) are somewhat similar to the value 11.2×10^{14} esu observed for $KReO_4$, and rather small changes in the oxygen parameters in the series could readily account for these variations since both $q(e)$ and $q(p)$ are very sensitive to the oxygen positions. Only precise x-ray structures for the perrhenates would permit any more meaningful analysis of the data and these are not available.

The oxygen parameters in $NaIO_4$ have been determined precisely,[11] and the tetrahedron is found to be compressed along c with $\angle$O–I–O$=114°$. With this information we may compute the terms in Eq. (1) by the same procedure as was used for $KReO_4$. Iodine is more electronegative than rhenium so the bonds to oxygen should be more covalent, as indicated in a Mössbauer investigation of KIO_4 which led to a charge distribution of $+1$ for iodine, -0.5 for oxygen, and $+1$ for potassium.[12,13] With this charge distribution the point-charge field gradient tensor was found to be $q(e)=+1.0\times10^{14}$ esu. The value $q(p)=12.3\times10^{14}$ esu was obtained by the method outlined previously[1] using the observed O–I–O bond angle of $114°$ (bisected by c) and the contribution $[q(p)]_{at}=-394\times10^{14}$ esu per p electron of iodine.[14] A value of $\gamma_\infty=-19.1$ (or -5.5) would then lead to agreement between theory and experiment depending on whether $q(\text{obs})$ is positive or negative, respectively. The sign is not determined in this work. The results of the calculations, and the experimental data, are summarized in Table II.

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