Nuclear Quadrupole Resonance Spectra of Tantalum-181 in Tantalum(v) Halides, Ta_2X_{10}

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Summary The first ^{181}Ta pure nuclear quadrupole resonance spectra have been detected in Ta_2X_{10} (X = Cl and Br).

The first ^{181}Ta pure nuclear quadrupole resonance (n.q.r.) spectra are important for two reasons. First, ^{181}Ta possesses a nuclear spin $I = 7/2$. Nuclei possessing $I > 3/2$ are inherently more appropriate for study using n.q.r. techniques than those with $I = 3/2$ because both the quadrupole coupling constant (e^2Qq/h) and the asymmetry parameter (η) can be directly determined from the observed resonance frequencies. Second, studies of the n.q.r.

resonances of ^{181}Ta will supplement those of other transition-metal nuclei[1–3] such as ^{55}Mn, ^{59}Co, ^{185}Re, and ^{187}Re which have provided insight into the bonding in transition-metal complexes.

TABLE

^{181}Ta *Resonance frequencies in* Ta_2X_{10} ($X = Cl, Br$)

Compd.	Assignment	Frequency (MHz)[a]	η	e^2Qq/h (MHz)
Ta_2Cl_{10}	ν_1 ($\pm 1/2 \longleftrightarrow \pm 3/2$)	177·6	0·36	1786[b]
	ν_1 ($\pm 1/2 \longleftrightarrow \pm 3/2$)	183·0	0·38	1795
	ν_2 ($\pm 3/2 \longleftrightarrow \pm 5/2$)	241·4		
Ta_2Br_{10}	ν_1 ($\pm 1/2 \longleftrightarrow \pm 3/2$)	156·7	0·45	1421[c]
	ν_1 ($\pm 1/2 \longleftrightarrow \pm 3/2$)	161·1	0·46	1436
	ν_2 ($\pm 3/2 \longleftrightarrow \pm 5/2$)	190·0		

[a] Measured at room temperature, ±0·2 MHz. [b] ±3·0 MHz. [c] ±6·0 MHz.

Resonance frequencies and tentative assignments of the ^{181}Ta resonances detected are listed in the Table. The assignments, which must be considered as tentative until the third allowed transitions have been detected, are based in part on the close correspondence of the values of η, obtained using Cohen's tables,[4] to those exhibited by ^{93}Nb in Nb_2Cl_{10}, 0·32, and Nb_2Br_{10}, 0·40.[5,6] Other potential assignments would imply values of $\eta > 0{\cdot}60$. Such widely variant values for η would be hard to rationalize because Nb_2Cl_{10} and Ta_2Cl_{10} are known to be iso-structural from *X*-ray structural studies,[7] and Nb_2Br_{10} and Ta_2Br_{10} are assumed to be structurally similar to the chlorides from *X*-ray powder diffraction[7] and vibrational studies.[8] Also, other potential assignments would require the third transitions to be at frequencies at which no resonances have been detected, *i.e.* <300 MHz. The assignments indicated in the Table require the third transitions to occur at >300 MHz, a region we have been unable to search satisfactorily because of instrumentation problems. It should also be noted that the frequencies of these detected resonances do not correspond to frequencies reported for halogen atom resonances.[9]

The fact that in both cases only one ν_2 transition and two ν_1 transitions were recorded is interesting. As is evident from Cohen's tables,[4] the frequencies of ν_1 transitions are more dramatically affected by small changes in η than those of ν_2 transitions. Also, molecules of Nb_2Cl_{10} are known to be located at two different symmetry sites.[7] Even very subtle differences between those sites could be manifested in slightly different values of η for the metal atoms in molecules of different site symmetry. The effect of the different values of η on the frequencies of the ν_2 transitions could be too small to be detected. The values of η and e^2Qq/h listed in the Table are very approximate as they must be until the frequencies for the $\nu_3(\pm 5/2 \rightarrow \pm 7/2)$ transitions have been determined.

Samples were used as prepared without further purification and sealed in evacuated Pyrex tubes. An annealing procedure was employed in which the sample was lowered very slowly through a temperature gradient in a vertically mounted tube furnace. The temperature of the furnace was set at a temperature such that the material was completely sublimed from one end of the sample tube to the other. N.q.r. spectra were obtained using a Wilks NQR-1A spectrometer and frequency measurements were made employing spectrum analysing techniques.[10]

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