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IN DIRHENIUM DECACARBONYL

Charles B. Harris

October 1967

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THE RHENIUM NUCLEAR QUADRUPOLE RESONANCE
SPECTRA IN DIRHENIUM DECACARBONYL

C. B. Harris

October, 1967

Sir:

Since nuclear quadrupole resonance spectroscopy provides a sensitive measure of the charge and electron distribution in molecules, Re^{185} and Re^{187} nqr may be useful in the study of rhenium-rhenium^{1,2} and rhenium-ligand bonds.

Although quadrupole coupling has been observed in the microwave spectrum of rhenium compounds,³ to the authors knowledge no pure Re^{185} and Re^{187} nqr have heretofore been detected. This communication reports the rhenium quadrupole coupling constant in dirhenium decacarbonyl in the solid state.

All resonances (Cf. Table) were obtained on a high power super-regenerative spectrometer⁴ and all frequency measurements were made utilizing spectrum analyzing techniques.⁵

The rhenium field gradient, q_{zz} and the asymmetry parameter η defined,

$$\eta = (q_{xx} - q_{yy})/q_{zz}$$

in terms of its irreducible tensor components⁶ can be calculated using solutions⁷ of the secular equation for a nucleus with a spin of 5/2.

The room temperature values are $q_{zz} = -6.9 \times 10^{14}$ esu/cm³ and $\eta = 0.63 \pm 0.03$ while the liquid nitrogen temperature values are $q_{zz} = -7.1 \times 10^{14}$ esu/cm³ and $\eta = 0.88 \pm 0.03$. These results show that the "average"⁸ field gradient tensor in the y-direction is twice as large as the "average" field gradient tensor in the x-direction. This is totally unexpected in view of the symmetry⁹ of $\text{Re}_2(\text{CO})_{10}$. The D_{4d} "ideal" molecular symmetry requires C_{4v} site symmetry at the Re nucleus. Under a fourfold rotation axis q_{xx} should be the same as q_{yy} , i.e. $\eta = 0$.

The deviations from ideal C_{4v} site symmetry in $Mn_2(CO)_{10}^{10}$ and $Tc_2(CO)_{10}^{11}$ are very small. In fact, all the measured bond angles and bond distances in both molecules are within three standard deviations of ideal D_{4d} molecular symmetry.

Unfortunately, precise structural parameters for $Re_2(CO)_{10}$ are not available from a two dimension crystal structure.⁹ However, it is difficult to imagine the $Re_2(CO)_{10}$ structure deviating enough from its $Tc_2(CO)_{10}$ and $Mn_2(CO)_{10}$ isomorphs to produce such a large asymmetry parameter.

Since the molecules are neutral there can be no point charge lattice sum contributions to the field gradient in any direction. Induced dipole-induced dipole interactions can not contribute any appreciable field gradient at the Re nucleus. At a distance of ~ 2 Å the induced-dipole interactions are about ten times less than the coulombic contributions which, in favorable cases,¹² account for less than 1 per cent of the total field gradient in neutral molecules.

There does appear to be a credible explanation for the large asymmetry parameter if one accepts structural isomorphism and assumes that the anisotropic temperature factors, B_{ij} of the form $\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$ are similar for $Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$.

It is interesting to note that in both $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ an analysis of the anisotropic temperature factors shows significant differences in the thermal motion of the carbonyls cis to each other. In the $Mn_2(CO)_{10}$, for instance, the root-mean-square component of the thermal displacement lowers the Re C_{4v} site symmetry to C_{2v} , e.g. the CO's in the x-direction

have 30% less thermal displacement than the CO's in the y-direction. Assuming a similar behavior in $\text{Re}_2(\text{CO})_{10}$, the overall effect, therefore, of the large anisotropic motion is to leave q_{zz} relatively unchanged in both directions (along the Re-Re bond) and magnitude but to make $|q_{yy}/q_{xx}|$ much larger. In other words, the "average" electron density around the Re is distributed more by thermal motion along the y-direction than the x-direction; thus, a large asymmetry parameter may be observed.

Finally, the increase in the low temperature η may be due to a decrease in the x and y motion but a greater decrease in the x-direction.

A temperature dependent single crystal nqr study has been initiated to explicitly investigate these possibilities. A molecular electronic interpretation of q_{zz} must necessarily be deferred until the single crystal study is completed.

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Table 1. Rhenium Nuclear Quadrupole Resonance Frequencies

Nucleus	Transition	Temperature	Signal to Noise Ratio	Frequency (MHz \pm 0.02)
Re ¹⁸⁵	$\pm 1/2 \rightarrow \pm 3/2$	26.5°C	11:1	28.94
Re ¹⁸⁷	$\pm 1/2 \rightarrow \pm 3/2$	26.5°C	24:1	27.35
Re ¹⁸⁵	$\pm 3/2 \rightarrow \pm 5/2$	26.5°C	44:1	39.93
Re ¹⁸⁷	$\pm 3/2 \rightarrow \pm 5/2$	26.5°C	92:1	37.70
Re ¹⁸⁵	$\pm 1/2 \rightarrow \pm 3/2$	-196°C	~10:1	35.67
Re ¹⁸⁷	$\pm 1/2 \rightarrow \pm 3/2$	-196°C	~20:1	33.75
Re ¹⁸⁵	$\pm 3/2 \rightarrow \pm 5/2$	-196°C	~30:1	39.80
Re ¹⁸⁷	$\pm 3/2 \rightarrow \pm 5/2$	-196°C	~60:1	37.51

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- (8) The phrase "average" field gradient connotes the field gradient from contributions of electron distributions averaged over the dynamical properties of the solid, e.g., large thermal or molecular vibrations in the lattice. The term molecular field gradient denotes the idealized field gradient of a nucleus at its zero point vibrational energy.
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- (13) $\text{Mu}_2(\text{CO})_{10}$ and $\text{Tc}_2(\text{CO})_{10}$ but not $\text{Re}_2(\text{CO})_{10}$ crystal structures were refined anisotropically. The anisotropic temperature factors of both $\text{Mu}_2(\text{CO})_{10}$ and $\text{Tc}_2(\text{CO})_{10}$ indicate the same relative amplitude of anisotropic thermal motion in the same directions. It seems safe to assume that $\text{Re}_2(\text{CO})_{10}$ should be similar to isomorphs in this respect.

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