## Title
TRANSITION METAL NUCLEAR QUADRIPOLE RESONANCE. II. INTERPRETATION OF THE RHENIUM NUCLEAR QUADRUPOLE RESONANCE SPECTRA IN DIRHENIUM DECACARBONYL

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# University of California

# Ernest O. Lawrence Radiation Laboratory

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# TRANSITION METAL NUCLEAR QUADRUPOLE RESONANCE.

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Charles B. Harris

February 1968

Contribution from the Department of Chemistry of the
University of California and the Inorganic Materials Research Division
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# Transition Metal Nuclear Quadrupole Resonance.
# II. Interpretation of the Rhenium Nuclear Quadrupole Resonance Spectra in Dirhenium Decacarbonyl.

Charles B. Harris

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.

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(1) F. A. Cotton and C. B. Harris, Inorg. Chem., **4**, 330 (1965).

(2) F. A. Cotton, ibid., **4**, 334 (1965).

Although quadrupole coupling has been observed in the microwave spectrum of rhenium compounds,[3] to the authors knowledge the only pure

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(3) J. F. Lotspeich, J. Chem. Phys., 31, 633 (1959); 31, 643 (1959).

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$Re^{185}$ and $Re^{187}$ nqr have been detected[4] in dirhenium decacarbonyl.

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(4) S. L. Segel and R. G. Barnes, Phys. Rev., 107, 638 (1957).

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Because of the unusual nature of the results no explanation has heretofore been proposed. This communication reports the low temperature rhenium quadrupole coupling constant and offers a credible explanation for the anomalies.

All resonances (Cf. Table) were obtained on a high power super-regenerative spectrometer[5] and all frequency measurements were made

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(5) C. B. Harris, unpublished work; G. E. Peterson, private communication.

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utilizing spectrum analyzing techniques.[6]

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(6) G. E. Peterson and P. M. Bridenbaugh, Rev. Sci. Instr., 37, 1081 (1966).

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The rhenium field gradient, $q_{zz}$ and the asymmetry parameter $\eta$ defined,

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

in terms of its irreducible tensor components(7) can be calculated using solutions(8) of the secular equation for a nucleus with a spin of 5/2 and the value for the electric quadrupole moment of Re$^{187}$.(9) The room temperature values are $q_{zz} = -6.9 \times 10^{14}$ esu/cm$^3$ and $\eta = 0.63 \pm 0.03$ while the liquid nitrogen temperature values are $q_{zz} = -7.1 \times 10^{14}$ esu/cm$^3$ and $\eta = 0.88 \pm 0.03$. These results show that the "average"(10) field gradient tensor in the y-direction is twice as large as the "average" field gradient tensor in the x-direction at room temperature.

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(7) T. P. Das and E. L. Hahn, Solid State Phys., Suppl. 1, 4 (1958).

(8) M. H. Cohen, Phys. Rev., 96, 1278 (1954).

(9) H. Schüler and H. Korsching, Z. Physik, 105, 168 (1937).

(10) 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.

This is totally unexpected in view of the symmetry[11] of $Re_2(CO)_{10}$.

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(11) L. F. Dahl, E. Ishishi, and R. E. Rundle, J. Chem. Phys., 26, 1750 (1957).

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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 $Mn_2(CO)_{10}$ [12] and

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(12) L. F. Dahl and R. E. Rundle, Acta Cryst., 16, 419 (1963).

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$Tc_2(CO)_{10}$ [13] are very small. In fact, all the measured bond angles and

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(13) M. F. Bailey and L. F. Dahl, Inorg. Chem., 4, 1140 (1965).

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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.[11] 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 cannot 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 and thus would account[14] 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 $Re_2(CO)_{10}$.[15]

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 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 Mn $C_{4v}$ site symmetry to $C_{2v}$, e.g. the CO's in the x-direction have 30% less thermal displacement than the CO's

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(14) T. P. Das and E. L. Hahn, Solid State Phys., Suppl. 1, 165 (1958).

(15) $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ but not $Re_2(CO)_{10}$ crystal structures were refined anisotropically. The anisotropic temperature factors of both $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ indicate the same relative amplitude of anisotropic thermal motion in the same directions. It seems safe to assume that $Re_2(CO)_{10}$ should be similar to isomorphs in this respect.

in the y-direction. Assuming a similar behavior in $Re_2(CO)_{10}$, the overall effect, therefore, of the large anisotropic vibration 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 than one. 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.

The increase in the low temperature $\eta$ may be due to a decrease in the x and y motion but a greater decrease in the x-direction. Low temperature $Re_2(CO)_{10}$ anisotropic thermal parameters are needed to verify this point.

The room temperature $\eta$ can be estimated theoretically as follows. Consider the vibration of a carbonyl attached to a rhenium as depicted in Figure 1. Under the harmonic oscillator approximation the RMS component of vibration along the M-CO bond can be calculated[16] from the anisotropic temperature tensors. In the case of $Mn_2(CO)_{10}$ there is a 30% difference between CO's cis to each other. Relating the RMS amplitude to the exponentional function, $\sigma$, in a gaussium distribution, i.e. RMS = $(1/2\sigma)^{1/2}$, the expectation value of $r^{-3}$ centered at the metal nucleus can be calculated.

i.e. $$< r^{-3} > = (\sigma/\Pi)^{1/2} \int_{-\infty}^{+\infty} r^{-3} e^{-\sigma(r-R_o)^2} dr \qquad (1)$$

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[16] R. W. James, *The Optical Principles of the Diffraction of X-rays*, G. Bell and Sons Ltd., London, 1962.

where $R_o$ is the distance from the metal to the carbon. Using RMS values for CO's in the x and y directions respectively as 0.26 and 0.18 $Å^2$ the expectation values of $r^{-3}$ are calculated with a $R_o$ = 1.83 Å as 0.157 and 0.161 $Å^{-3}$. Because the 5d radial wave functions of Re are so diffuse[17]

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(17) F. Herman and S. Skillman, Atomic Structure Calculations, Prentice-Hall, Englewood Cliffs, N.J., 1963.

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(Cf. Figure 2) the effect of a carbonyl vibration is transmitted the Re nucleus as a dynamical variation in the $< r^{-3} >$ of the d electrons. One must consider the two electron forming the Re-C σ bond as well as the four electrons participating in the Re-C Π bond. These are depicted in Figure 2. Note that the Π electrons are localized in a region of space about 45° off the Re-C bond. Because of the angular dependence in the field gradient tensor the effect of all Π electrons are about equal to the σ electrons. Thus Equation 2 can be written,

$$\eta = \frac{(q_{xx} - q_{yy})\ \text{dynamical}\ \ N\ (1-\gamma_\infty)}{q_{zz}} \qquad (2)$$

where N is the number of effective electrons projected on the Re-C bond and $(1-\gamma_\infty)$ is the Sternheimer factor[18] for inner core polarizations.

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(18) R. M. Sternheimer, Phys. Rev., 84, 244(1951); 86, 316(1952); 95, 736(1954); 130, 1423(1963).

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The dynamical $q_{xx}$ and $q_{yy}$ are calculated as 0.753 x $10^{14}$ esu/$cm^3$ and 0.772 x $10^{14}$ esu/$cm^3$ respectively using the calculated $< r^{-3} >_{x,y}$. N is equal to four and a $(1-\gamma_\infty)$ of 28 is used[19] to calculate an η equal to 0.31. This compares favorably to the observed η of 0.63. It should be emphasized that the above is only a qualitative argument meant only to show that dynamical vibration anisotropy can in a credible fashion account for a sizeable η.

Acknowledgment. The author acknowledges the assistance in this work of M. D. Fayer and the U.S. Atomic Energy Commission under the auspices of the Inorganic Materials Research Division, Lawrence Radiation Laboratory for financial support.

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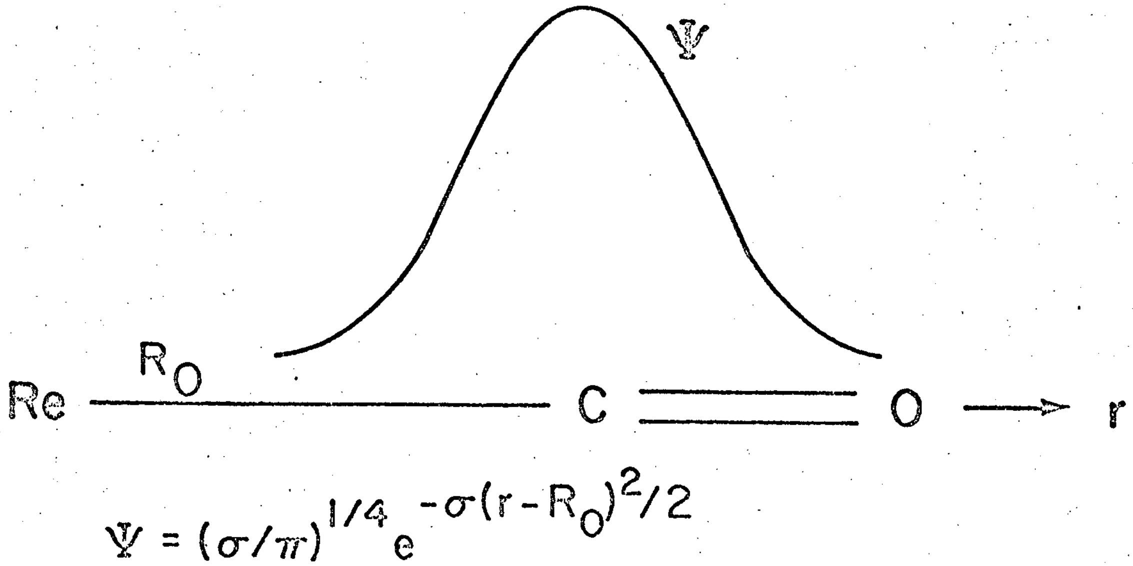
(19) J. F. Lotspeich, J. Chem. Phys., 31, 643(1959).

Table 1. Rhenium Nuclear Quadrupole Resonance Frequencies

| Nucleus | Transition | Temperature | Signal to Noise Ratio | Frequency (MHz ± 0.05) |
|---|---|---|---|---|
| $Re^{185}$ | ± 1/2 → ± 3/2 | 26.5°C | 11:1 | 28.94 |
| $Re^{187}$ | ± 1/2 → ± 3/2 | 26.5°C | 24:1 | 27.35 |
| $Re^{185}$ | ± 3/2 → ± 5/2 | 26.5°C | 44:1 | 39.93 |
| $Re^{187}$ | ± 3/2 → ± 5/2 | 26.5°C | 92:1 | 37.70 |
| $Re^{185}$ | ± 1/2 → ± 3/2 | -196°C | ~10:1 | 35.67 |
| $Re^{187}$ | ± 1/2 → ± 3/2 | -196°C | ~20:1 | 33.75 |
| $Re^{185}$ | ± 3/2 → ± 5/2 | -196°C | ~30:1 | 39.80 |
| $Re^{187}$ | ± 3/2 → ± 5/2 | -196°C | ~60:1 | 37.51 |



$$\Psi = (\sigma/\pi)^{1/4} e^{-\sigma(r-R_O)^2/2}$$

Figure 1. Coordinate system for $< r^{-3} >$ and its relation to the CO vibrational amplitude.

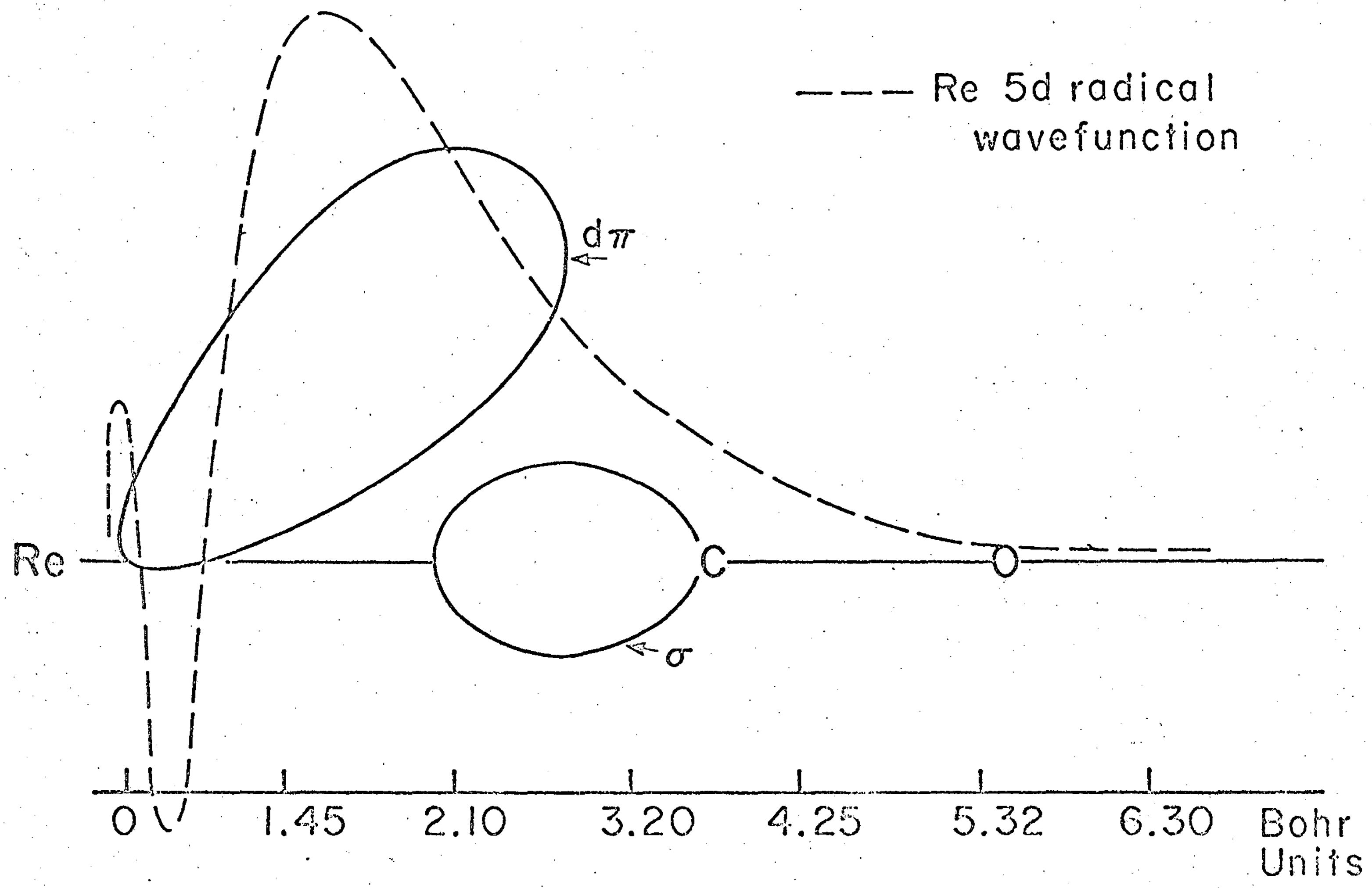


Figure 2. Radial 5d wave function for Re and its relation to the sigma and $\Pi$ electrons in a Re-CO bond.