inlet system can be very deceptive if the temperature range is below the ion-chamber temperature.

(3) Reactions which occur in the mass spectrometer may be more pronounced than expected from other experimental evidence. For example, $Mn(CO)_5Cl$ can be purified by vacuum sublimation in a clean apparatus at 60° where gross amounts are transferred onto a cold glass surface. Yet this material will decompose in a few minutes after introduction into a previously used molecular-leak reservoir heated to only 50°.

INSTITUTE FOR ATOMIC RESEARCH AND
THE DEPARTMENT OF CHEMISTRY
IOWA STATE UNIVERSITY
AMES, IOWA 50010

HARRY J. SVEC
GREGOR A. JUNK

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Transition Metal Nuclear Quadrupole Resonance. II. Interpretation of the Rhenium Nuclear Quadrupole Resonance Spectra in Dirhenium Decacarbonyl

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 author's knowledge the only pure Re^{185} and Re^{187} nqr have been detected[4] in dirhenium decacarbonyl. 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 I) were obtained on a high-power superregenerative spectrometer[5] and all frequency measurements were made utilizing spectrum-analyzing techniques.[6]

TABLE I

RHENIUM NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES

Nucleus	Transition	Temp, °C	Signal to noise ratio	Freq (±0.05), MHz
Re^{185}	$\pm^1/_2 \rightarrow \pm^3/_2$	26.5	11:1	28.94
Re^{187}	$\pm^1/_2 \rightarrow \pm^3/_2$	26.5	24:1	27.35
Re^{185}	$\pm^3/_2 \rightarrow \pm^5/_2$	26.5	44:1	39.93
Re^{187}	$\pm^3/_2 \rightarrow \pm^5/_2$	26.5	92:1	37.70
Re^{185}	$\pm^1/_2 \rightarrow \pm^3/_2$	−196	~10:1	35.67
Re^{187}	$\pm^1/_2 \rightarrow \pm^3/_2$	−196	~20:1	33.75
Re^{185}	$\pm^3/_2 \rightarrow \pm^5/_2$	−196	~30:1	39.80
Re^{187}	$\pm^3/_2 \rightarrow \pm^5/_2$	−196	~60:1	37.51

The rhenium field gradient, q_{zz}, and the asymmetry parameter, η, defined in terms of its irreducible tensor

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

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. This is totally unexpected in view of the symmetry[11] of $Re_2(CO)_{10}$. 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 $Mn_2(CO)_{10}$[12] and $Tc_2(CO)_{10}$[13] 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.[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 one-tenth the coulombic contributions and thus would account[14] for less than 1% 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

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(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.

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(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.

factors shows significant differences in thermal motion of the carbonyls *cis* to each other. In $Mn_2(CO)_{10}$, 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 in the y direction. Assuming a similar behavior in $Re_2(CO)_{10}$, the over-all effect, therefore, of the large anisotropic vibration is to leave q_{zz} relatively unchanged in both direction (along the Re–Re bond) and magnitude but to make $|q_{yy}/q_{xx}|$ much larger than 1. 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 η 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 η 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, σ, in a Gaussiun distribution, *i.e.*, rms amplitude = $(1/2\sigma)^{1/2}$ the expectation value of r^{-3} centered at the metal nucleus can be calculated, *i.e.*

$$\langle r^{-3}\rangle = (\sigma/\pi)^{1/2}\int_{-\infty}^{+\infty} r^{-3}e^{-\sigma(r-R_0)^2}\,dr \qquad (1)$$

where R_0 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, the expectation values of r^{-3} are calculated with R_0 = 1.83 Å as 0.157 and 0.161 $Å^{-3}$. Because the 5d radial wave functions of Re are so diffuse[17] (*cf.* Figure 2), the effect of a carbonyl vibration is transmitted the Re nucleus as a dynamical variation in the $\langle r^{-3}\rangle$ of the d electrons. One must consider the two electrons 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 effects of all π electrons are about equal to those of the σ electrons. Thus eq 2 can be written, where N is the number of effective

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

electrons projected on the Re–C bond and $(1 - \gamma_\infty)$ is the Sternheimer factor[18] for inner-core polarizations. The dynamical q_{xx} and q_{yy} are calculated as 0.753 × 10^{14} and 0.772 × 10^{14} esu/cm^3, respectively, using the calculated $\langle r^{-3}\rangle_{x,y}$. N is equal to 4 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 to show that dynamical vibration anisotropy can in a credible fashion account for a sizable η.

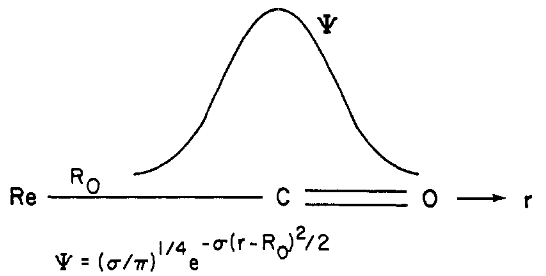

Figure 1.—Coordinate system for $\langle r^{-3}\rangle$ and its relation to the CO vibrational amplitude.

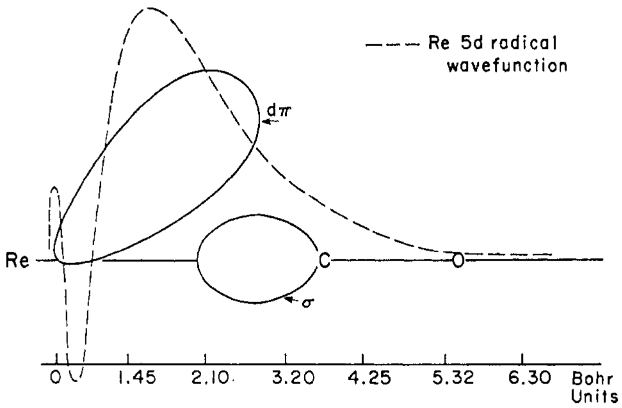

Figure 2.—Radial 5d wave function for Re and its relation to the σ and π electrons in an Re–CO bond.

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DEPARTMENT OF CHEMISTRY OF
THE UNIVERSITY OF CALIFORNIA AND
THE INORGANIC MATERIALS RESEARCH
DIVISION OF THE LAWRENCE RADIATION
LABORATORY
BERKELEY, CALIFORNIA 94720
CHARLES B. HARRIS

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Mössbauer Experiments on Iron(II) Phthalocyanine

Sir:

We wish to report the results of Mössbauer spectroscopic experiments on iron(II) phthalocyanines. Our independent experiments are very similar to those of