The Metal–Hydrogen Bond Lengths in $HMn(CO)_5$ and $HCo(CO)_4$

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THE n.m.r. spectra of solid $HMn(CO)_5$ and $HCo(CO)_4$ at low temperatures have been interpreted by Farrar *et al.*,[1,2] in terms of metal–hydrogen bond lengths of 1·28 and 1·42 (or 1·2) Å, respectively. We suggest that these authors were not justified in ignoring quadrupole effects. The analysis presented here gives the values 1·44 ±0·03 and 1·59 ± 0·04 Å respectively, and has the advantages that the values of the Co–H bond lengths obtained from the second moment of the absorption line and from a line shape analysis are found to be consistent, and that it is not necessary to assume that part of the spectrum of $HCo(CO)_4$ has been lost in the noise.

Van Vleck's formula,[3] used by the above authors, assumes that the quantization of the nucleus interacting with that at resonance is defined by the direction of the applied magnetic field. Since the energies of interaction of the nuclear electric quadrupoles of ^{55}Mn and ^{59}Co with the electric-field gradients are probably much greater than the energies of interaction of the magnetic dipoles of these nuclei with the magnetic field, the quantization of these nuclei will be determined by the direction of the electric-field gradient at the nucleus. If we assume that a quadrupolar nucleus M is quantized with respect to the M–H bond direction, the component of the magnetic field due to M in the direction of the external field at the hydrogen nucleus will be $\delta H = m\gamma\hbar\cos\theta/r^3$, where

r is the M–H distance and θ the angle between the M–H vector and the applied field. γ is the magnetogyric ratio of M, and m takes the values $I, I\text{-}1, \ldots, \text{-}I$, where I is the nuclear spin of M. The second moment of the powder spectrum is given by the average over all values of m and θ.

$$\langle \delta H^2 \rangle = \frac{4\gamma^2\hbar^2}{r^6}\left(\frac{\Sigma m^2}{2I + 1}\right)\int_0^{\pi} \frac{\cos^2\theta \cdot 2\pi \sin\theta \cdot d\theta}{4\pi} = \frac{4\gamma^2\hbar^2 I(I + 1)}{9r^6} \tag{1}$$

This differs from Van Vleck's formula for non-identical nuclei only in that the spherical average of $4\cos^2\theta$ is 4/3, whereas that of $(3\cos^2\theta - 1)^2$ is 4/5. However this formula is not quite correct for half-integral I because a magnetic field in any direction causes appreciable mixing of the $m = \pm \frac{1}{2}$ states. The necessary theory will be given elsewhere; the result is that the numerical term $4I(I + 1)/9$ must be replaced by a complicated expression which takes the values 1·760346, 4·199363, and 7·511911 for $I = 3/2$, 5/2, and 7/2, respectively. Hence for $HMn(CO)_5$, since it is necessary to consider the nearby Mn′–H′ bond,

$$\langle \delta H^2 \rangle = \frac{9\gamma_{H}^2\hbar^2}{20r_{HH'}{}^6} + 4{\cdot}19936\gamma_{Mn}^2\,\hbar^2\left\{r_{MnH}{}^{-6} + \frac{(1 + 3\cos^2\beta)^2 r_{HMn'}^{-6}}{16}\right\}$$

where β is the angle between the MnH and MnH′ vectors. The term involving β is a good approximation, and only makes a 0·2% contribution to the second moment.

Including information from the crystal structure[4] and placing the hydrogen atoms on the fourfold axes, the value $\langle \delta H^2 \rangle = 26{\cdot}6 \pm 0{\cdot}6$ gauss^2 leads to the two solutions $r_{MnH} = 1{\cdot}42 \pm 0{\cdot}01$ or $1{\cdot}94 \pm 0{\cdot}01$ Å, corresponding to $r_{HH} = 2{\cdot}55 \pm 0{\cdot}01$ or $1{\cdot}58 \pm 0{\cdot}01$ Å. The second solution is rejected because the non-bonded H–H′ distance is too short.

Ignoring all intermolecular broadening, we obtain $r_{CoH} = 1{\cdot}57 \pm 0{\cdot}02$ Å from the observed second moment of $22{\cdot}5 \pm 1{\cdot}0$ gauss^2 in $HCo(CO)_4$. Since in $HMn(CO)_5$ the directly bonded manganese nucleus contributes 95% of the second moment, the correction to r_{CoH} for intermolecular interactions should lie in the range 0 to +0·03 Å. The observed fine structure arises from molecules in which the Co–H bond is almost parallel to the magnetic field, since there is little contribution to the second moment when the Co–H bond is exactly perpendicular to the magnetic field. The presence of the outer pair of the 8-line spectrum provides good evidence that the observed second moment is reliable. The assignment as "parallel" instead of "perpendicular" requires that the value of r_{CoH} calculated by Farrar *et al.*,[2] from the separation of this pair of lines is in error by a factor of $2^{1/3}$, leading to the result $r_{CoH} = 1{\cdot}5 \pm 0{\cdot}1$ Å, in good agreement with the above figure.

Four possible sources of error in these bond-length determinations are (1) zero-point vibrational amplitudes, since $\langle r^{-3}\rangle^{1/3}$ is the bond length actually determined, (2) zero-point torsion, (3) deviation of the M–H vector from the quantization direction, and (4) the influence of a chemical shift anisotropy. A combined estimated correction of $+0{\cdot}02 \pm 0{\cdot}02$ Å for (1) and (2) has been applied in both examples. As a result of (3), a correction factor of approx. $[(3\cos^2\delta + 1)/4]^{1/3}$ must be applied to r, where δ is the angle between the M–H vector and the quantization direction. This differs very little from unity for small δ. The effect of (4) is difficult to estimate without a detailed line-shape analysis.

The second moment $8{\cdot}1 \pm 1{\cdot}0$ gauss^2 reported[5] for $H_2Fe(CO)_4$ is by no means inconsistent with an Fe–H bond length in the region $1{\cdot}5 \pm 0{\cdot}1$ Å; with an intermolecular H–H distance of $2{\cdot}6 \pm 0{\cdot}4$ Å this would require an H–Fe–H angle of 80 ± 8°. When the energy of the quadrupole interaction of M with the electric-field gradient is smaller than that of the magnetic dipole interaction with the applied magnetic field, Van Vleck's formula still applies; an elegant example of this has been given in the analysis of the spectrum of $HB(OCD_3)_2$ at low temperature.[6]

(*Received, May* 31*st*, 1967; *Com.* 538.)

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