The M–H Bond Stretching Frequencies of μ_2-Bridged Metal Hydrides and their Relationship to the M–H–M Interbond Angle

By M. W. Howard, U. A. Jayasooriya, S. F. A. Kettle, D. B. Powell, and N. Sheppard
(*School of Chemical Sciences, University of East Anglia, Norwich* NR4 7TJ)

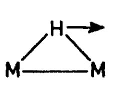
Summary A successful theoretical correlation is made of experimental data on the M–H bond stretching modes of μ_2-bridged metal hydrides with the M–H–M interbond angle, based on the application of central or valence force fields to the MHM unit.

The direct location of the hydrogen atom in metal clusters containing μ_2-hydrogen bridges has been successfully determined by neutron diffraction[1] and by *X*-ray diffraction[2,3] for only a few compounds. Neither of these techniques is routine. For example neutron diffraction requires a single crystal of some 10 mm^3 volume and in *X*-ray diffraction there are major difficulties caused by the uniquely low electron density of hydrogen atoms.

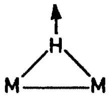
We report here a method of estimating the M–H–M interbond angle from the measurements, and particularly the ratio, of the asymmetric and symmetric metal–hydrogen bond stretching vibrational frequencies, v_{as} and v_s (or $\tilde{v}_{as}$ and $\tilde{v}_s$ in wavenumbers) respectively.

We have been systematically investigating the nature and frequencies in μ_2-hydrogen containing cluster compounds and have successfully characterised the v_{MH} frequency regions.[4] Our studies have enabled the identification of ν_{MH} bands which shift by *ca.* $1/\sqrt{2}$ in deuterium containing analogues. This shows that, in considerable measure, the ν_{MH} and ν_{MD} modes are independent vibrators in agreement with the conclusions of Knox *et al.*[5] However, the bands observed often have associated substructure and in some cases the latter may be partially caused by weak coupling between ν_{MH} and the very low frequency ν_{MM} bond stretching modes. The absorption bands are also often broad and hence relatively weak, but sharpen up markedly on cooling to liquid nitrogen temperatures.[6] These effects and the H/D shifts enable reliable assignments to be made.

A hydrogen atom bridging two metal atoms has two stretching vibrations, an asymmetric mode (A) and a symmetric mode (B), assuming that the heavy metal framework remains stationary.



(A)



(B)

If the standard vibration equations for an XY_2 molecule are taken using either a simple valence or central force field,[7] with the approximations (a) that the mass of the Y atoms, m_Y are taken as infinite and that of the X atoms, m_X, is equal to the mass of a hydrogen atom, m_H and (b) that, for the valence force field, the angle bending force constant, k_θ, is much smaller than that for bond-stretching, k_r, we obtain relationships (1) and (2), where θ is the M–H–M

$$\nu_{as}^2 = k_r \sin^2(\theta/2)/2\pi^2c^2m_H \quad (1)$$

$$\nu_s^2 = k_r \cos^2(\theta/2)/2\pi^2c^2m_H \quad (2)$$

interbond angle, and c is the velocity of light. These give the simple relationship (3).

$$(\nu_{as}/\nu_s) = (\tilde{\nu}_{as}/\tilde{\nu}_s) = \tan(\theta/2) \quad (3)$$

A non-zero stretch–stretch interaction constant would lead to slightly different values for the force constant controlling $\tilde{\nu}_{as}$ and $\tilde{\nu}_s$. As interaction constants are usually small, this would have the effect in equation (3) of multiplying $\tan(\theta/2)$ by a factor slightly different from unity. Qualitatively, equation (3) requires that at $\theta = ca.\ 90°$ the ratio should be near unity, *i.e.* the separation between $\tilde{\nu}_{as}$ and $\tilde{\nu}_s$ becomes small. As $\theta \rightarrow 180°$, the ratio and frequency separation increases. On the central force model when there is a truly linear bridge with $\theta = 180°$, $\tilde{\nu}_s$ is zero. However, for the valence force model, this extreme situation is never reached because the angle bending force constant k_θ becomes important; hence, as θ becomes larger, the observed ratio will tend to a value that is less than that indicated by the simple relationship of equation (3).

In the case where θ approaches 180°, the bond-stretching contribution to the hydrogen motion becomes negligible and the valence force field then gives the limiting value as in equation (4). This leads to the limiting ratio shown in equation (5).

$$\nu_s^2 = k_\theta \sin^2(\theta/2)/\pi^2c^2m_H \quad (4)$$

$$(\nu_{as}/\nu_s) = (k_r/2k_\theta)^{\frac{1}{2}} \quad (5)$$

TABLE. The observed wavenumbers $\tilde{\nu}_{as}$ and $\tilde{\nu}_s$, and the M–H–M interbond angles for a number of μ_2-bridged metal hydrides.

No.	Compound	$\tilde{\nu}_{as}$/cm^{-1}	$\tilde{\nu}_s$/cm^{-1}	θ/°
1	$H_2Os_3(CO)_{10}$[a]	1228	1177	92·6
2	$HOs_3(CO)_{10}CH:CH_2$[a]	1392	1286	101·5
3	$H_2Os_3(CO)_9C:CH_2$[a]	1411	1313	103·5
4	$[Ph_4P]^+[HW_2(CO)_{10}]^-$[b]	1520	1022	123·3
5	$H_3Mn_3(CO)_{12}$[c]	1660 (av)	888 (av)	131 (av)
6	$[Et_4N]^+[HW_2(CO)_{10}]^-$[d]	1680	875	137·2
7	$[Et_4N]^+[HCr_2(CO)_{10}]^-$[e]	1720	818	158·9

[a] G. Sheldrake, personal communication. [b] R. Bau, personal communication. [c] Ref. 2; (av = average over multiple absorptions or multiple angles). [d] Ref. 1. [e] J. Roziere, J. M. Williams, R. P. Stewart, J. L. Peterson, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **99**, 4497.

The Table shows the list of observed $\tilde{\nu}_{as}$ and $\tilde{\nu}_s$ wavenumbers for those compounds which we have studied, whose M–H–M angles have also been measured.[1,2] The ν_{as} bands tend to be more prominent in the i.r. and the $\tilde{\nu}_s$ bands more prominent in the Raman spectra. Where multiple maxima are observed, the mean values for $\tilde{\nu}_{as}$ and $\tilde{\nu}_s$ are listed. It can be seen qualitatively that the separation of $\tilde{\nu}_{as}$ and $\tilde{\nu}_s$ does indeed increase with increasing values of θ and that the ratio is approximately unity in $H_2Os_3(CO)_{10}$, where $\theta = ca.$ 90°. This finding differs substantially from some earlier experimental studies.[8] The wavenumber range of $\tilde{\nu}_{as}$ is very large and the experimental results were difficult to understand until the relationship between this and the interbond angle became apparent.

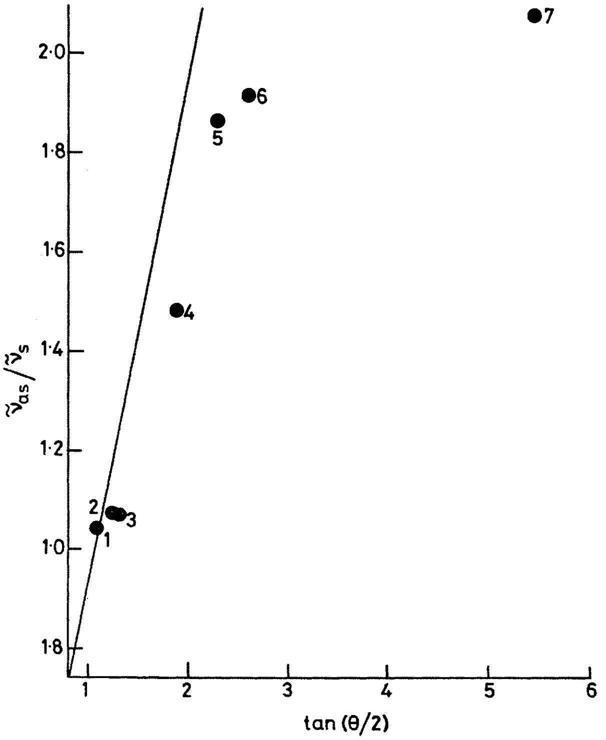


FIGURE 1. Comparison of experimental data with the theoretical line predicted by equation (3).

Figure 1 shows the experimental data and the 'theoretical' curve of gradient unity expected from equation (3). The relationship given in equation (3) has the advantage, if the

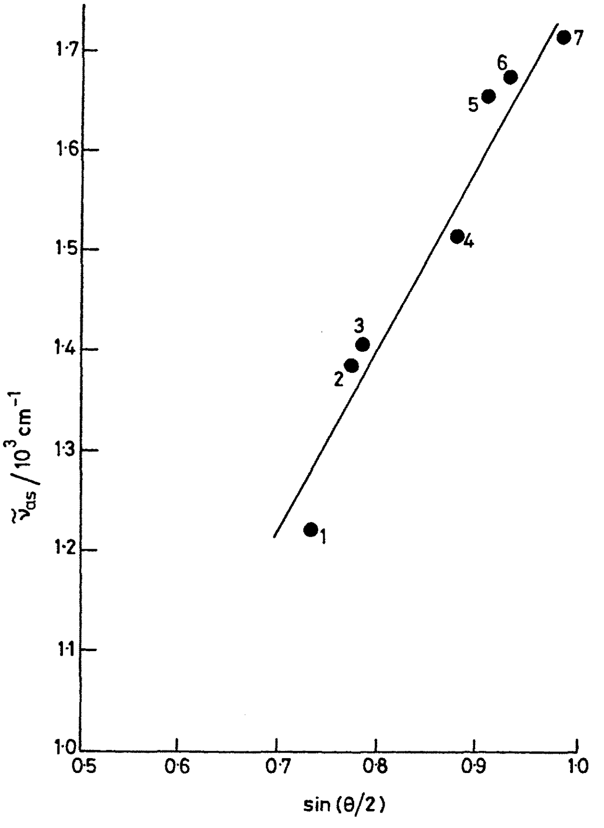


FIGURE 2. A plot of $\tilde{\nu}_{as}$ against sin(θ/2) in accordance with equation (2).

model is adequate, that it is independent of the individual values of the metal hydrogen force constant and requires no empirically determined parameters. The points show that for larger values of θ the deviation from the theoretical line increases rather rapidly due to the effect of k_θ on $\tilde{\nu}_s$. Expectation based on equation (5) would lead to deviations similar to that observed for $[Et_4N]^+[HCr_2(CO)_{10}]^-$ but more experimental data on such high-angle complexes are needed before further analysis is justified. The relationships implied in the separate equations (1) and (2) are only of any value if k_r is essentially constant, *i.e.* independent of the metal or the specific compound studied. Because $\tilde{\nu}_{as}$ is readily available from i.r. measurements ($\tilde{\nu}_s$ is sometimes impossible to obtain from Raman studies for highly coloured compounds) we show graphically the relationship between $\tilde{\nu}_{as}$ and sin(θ/2) in Figure 2. In fact, a reasonably good straight line is obtained with a slope corresponding to a value for k_r of *ca.* 108 N m^{-1}. In this plot the root mean square deviation from the straight line is 4·7°, with a maximum error of 6° in θ. Although this apparent accuracy probably exceeds that associated with the experimental data in θ, and so must be taken with caution, it does seem that this alternative empirical plot may be of predictive value.

Until more experimental data are available it is not clear whether an empirical curve drawn through the points of Figure 1 or the empirical line drawn in Figure 2 would give the better estimate of θ. With regard to Figure 2, the value of the force constant k_r may be compensated by the fact that, on the simple harmonic force field, it is independent of k_θ.

(*Received*, 23*rd August* 1978; *Com.* 929.)

---

[1] R. Bau, personal communication, to be published in *Accounts Chem. Res.*

[2] $H_3Mn_3(CO)_{12}$: S. W. Kirtley, J. P. Owen, and R. Bau, *J. Amer. Chem. Soc.*, 1973, **95**, 4532.

[3] $[Et_4N^+]_2[H_2W_2(CO)_8]^{2-}$: M. R. Churchill and W. S.-Y. N. Chang, *Inorg. Chem.*, 1974, **13**, 2413; $[(\pi\text{-}C_5Me_5)RhCl]_2{\cdot}HCl$: M. R. Churchill and S. W.-Y. Ni, *J. Amer. Chem. Soc.*, 1973, **95**, 2150; $HRu_3(CO)_{10}(C{:}NMe_2)$: M. R. Churchill, B. G. DeBoer, and F. J Rotella, *Inorg. Chem.*, 1976, **15**, 843; $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$: M. R. Churchill and B. G. DeBoer, *ibid.*, 1977, **16**, 1141; $H_2Os_3(CO)_{10}(PPh_3)$: *ibid.*, p. 2397.

[4] J. R. Andrews, M. W. Howard, U. A. Jayasooriya, M. A. Chesters, S. F. A. Kettle, D. B. Powell, and N. Sheppard, unpublished work.

[5] S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1975, **97**, 3942.

[6] D. C. Harris and H. B. Gray, *J. Amer. Chem. Soc.*, 1975, **97**, 3073; D. F. Shriver, personal communication.

[7] G. Herzberg, 'Infrared and Raman Spectra,' Van Nostrand, New York, 1945, p. 168.

[8] S. W. Kirtley, Ph.D. thesis, University of California at Los Angeles, 1972.