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Effect of a Libration or Hopping Motion of the η^2-Dihydrogen Ligand on Longitudinal Nuclear Magnetic Resonance Relaxation

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In the past, H—H distances of the η^2-dihydrogen ligand in transition metal complexes have been determined in the solid state by crystallographic or NMR studies (d_{H2}^{cryst}) and have been estimated in solution from $^1J_{HD}$ coupling constants (d_{H2}^{HD}) or minimum T_1 values (d_{H2}^{slow} for slow internal motion of the H_2 or d_{H2}^{fast} for fast spinning of a free rotor H_2 where $d_{H2}^{fast} = 0.793 d_{H2}^{slow}$) as determined by ^{1}H NMR. The best estimate of the H—H distance in solution was found to be d_{H2}^{HD}. This work shows that d_{H2}^{HD} is found to lie between d_{H2}^{slow} and d_{H2}^{fast} for many dihydrogen complexes reported in the literature. In certain cases this will be true if the correlation time of the H_2 is similar to that of the molecular complex. Two other cases are considered here for the first time: (1) torsional oscillation of the H_2 in a twofold potential energy surface and (2) hydrogens undergoing rapid 90° hops between sites of unequal population in a potential surface with a fourfold component. The $^1J_{HD}$ and T_1^{min} data from the literature for 73 dihydrogen complexes are examined in light of these two other possible cases. Dihydrogen in fast rotation is proposed for 32 complexes. Six complexes appear to have an H_2 ligand with slow internal motion. Either torsional libration or fast hopping might have a significant influence on the T_1 relaxation of the remaining 35 complexes.

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INTRODUCTION

It is desirable to know the H—H distance of the η^2-dihydrogen ligand in transition metal complexes in solution. This information could then be correlated with chemical properties such as pK_a, stability or catalytic activity of dihydrogen complexes in solution.[1–4] Some progress has being made at estimating the H—H distance in solution. Originally Hamilton and Crabtree[5] described how T_1 measurements can be used. The success of the method relied on the fact that dipolar relaxation is almost solely responsible for the short T_1 values measured for η^2-H_2 ligands because of the close proximity of one H to the other (usually less than 1 Å). However H—H distances (d_{H2}^{cryst}) determined by neutron[6–13] and X-ray[6,14–16] diffraction methods and, corrected for torsional motion of the H_2, by solid-state NMR[17–19] were sometimes found to be shorter than the distance calculated (d_{H2}^{slow}) from ^{1}H NMR T_1 data on the basis of slow internal motion of the H_2 ligand.[10] A correction factor of about 0.9 was originally proposed.[5] Spin–lattice relaxation time measurements on our iron-group molecular hydrogen complexes $[M(H_2)(H)(L)_2]^+$, M = Fe, Ru, Os[9,20–24] (Fig. 1), suggested that a correction factor of 0.793 ($= 4^{-1/6}$) arises because of the fast rotational motion of the H_2 ligand in the complex, so that

$$d_{HH}^{fast} = 0.793\ d_{HH}^{slow} \qquad (1)$$

We now report that two other types of motion could also result in such a correction factor to the H—H distance calculated from solution T_1 data: libration of H_2 in a twofold potential and hopping of H of the H_2 between fourfold sites. Zilm and Millar[17] proposed that H_2 zero-point libration sweeping out an average angle of ±16° in a twofold potential well accounts for the magnitude of an effective H—H dipolar interaction in

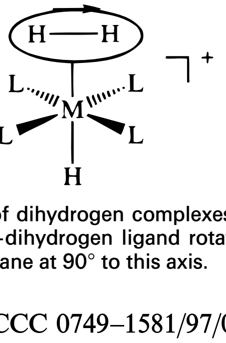

Figure 1. Structure of dihydrogen complexes with M = Fe, Ru or Os which have an η^2-dihydrogen ligand rotating freely about the H_2—M—H axis in a plane at 90° to this axis.

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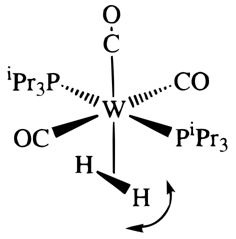

Figure 2. Structure of $W(\eta^2\text{-}H_2)(CO)_3(P^iPr_3)_2$ showing the dihydrogen ligand remaining approximately parallel to the P—W—P axis while undergoing a tortional libration about the H_2—W—CO axis in a plane at 90° to this axis.

solid $W(\eta^2\text{-}H_2)(CO)_3(P^iPr_3)_2$ below 100 K (Fig. 2). They also proposed that the temperature dependence above 100 K of the dipolar splitting can be explained by a small fourfold component to the rotational potential well. The hopping of the H_2 ligand has not been considered before.

THE H_2 LIGAND AS A FREE ROTOR

The rotation of the H_2 group in a transition metal complex can be treated in the same fashion as a methyl group spinning in a molecule. Woessner[25] has shown how the spectral density functions for a molecule tumbling anisotropically in solution can be applied to a methyl group attached to a molecule undergoing overall isotropic motion. For the case of H_2 it is assumed that relaxation along the H—H bond is perpendicular to its internal rotation. The equations then simplify to

$$J(\omega) = 0.25\,\frac{\tau_A}{(1+\omega^2{\tau_A}^2)} + 0.75\,\frac{\tau_C}{(1+\omega^2{\tau_C}^2)} \tag{2}$$

$$J(2\omega) = 0.25\,\frac{\tau_A}{(1+4\omega^2{\tau_A}^2)} + 0.75\,\frac{\tau_C}{(1+4\omega^2{\tau_C}^2)} \tag{3}$$

where

$$\frac{1}{\tau_A} = \frac{1}{\tau_{mol}} \tag{4}$$

and

$$\frac{1}{\tau_C} = \frac{1}{\tau_{H_2}} + \frac{1}{\tau_{mol}} \tag{5}$$

$$\frac{1}{T_1} = 0.3{\gamma_H}^4\hbar^2\,\frac{J(\omega)+4J(2\omega)}{d_{H2}^6} \tag{6}$$

It is assumed that the complex is sufficiently spherical for rotational diffusion to be described by a single correlation time τ_{mol}.

When purely dipolar H–H relaxation dominates then the distance d_{H2} can be calculated from the ^1H T_1^{min} value of the H_2 ligand for three different motional regimes (initially the effect of libration of the H_2 ligand will be ignored).

1. Slow-motion H_2 regime. When the dihydrogen is moving slowly so that $1/\tau_{H_2} \ll 1/\tau_{mol}$ then $\tau_C = \tau_{mol}$ and Eqns (2) and (3) just involve terms in τ_{mol}:

$$J(\omega) = \frac{\tau_{mol}}{1+\tau_{mol}^2\omega^2} \tag{7}$$

Equation (6) passes through a maximum and T_1 through a minimum value T_1^{min} when $\omega\tau_{mol} = 2\pi\nu = 0.62$. Then the expression for the distance can be derived as[24]

$$d_{H2}^{slow} = C\sqrt[6]{T_1^{min}/\nu} \tag{8}$$

with $C = 5.815$, d_{H2} in Å, T_1^{min} in s and ν, the spectrometer frequency, in MHz.

2. Fast-spinning H_2 regime. When the dihydrogen is spinning rapidly like a propeller so that $1/\tau_{H_2} \gg 1/\tau_{mol}$, then the second term in Eqns 2 and 3 is zero. Again, Eqn (6) has a maximum at $\omega\tau_{mol} = 0.62$ but now the expression for the distance is[24]

$$d_{H2}^{fast} = C\sqrt[6]{1/4}\,\sqrt[6]{T_1^{min}/\nu} = 4.611\sqrt[6]{T_1^{min}/\nu} \tag{9}$$

'Fast spinning' cannot be distinguished by this method from the case of fast 90° jumps in a fourfold potential with sites of equal population.

3. Internal motion near the Larmor frequency. When the dihydrogen is moving so that $1/\tau_{H_2} \approx 1/\tau_{mol}$, then the T_1^{min} value and the shape of the $\ln T_1$ versus $1/T$ (T = temperature) plot will be a sensitive function of both correlation times. At the temperature of minimum T_1

$$\frac{1}{\tau_{H_2}} \approx \frac{1}{\tau_{mol}} \approx \omega$$

There are well documented examples of dihydrogen complexes that fall into each of these regimes. For example, the d_{H2}^{slow} values calculated from T_1^{min} for the complexes $[Ru(H\cdots H)(C_5Me_5)(dppm)]^+$ and $[Os(H\cdots H)(en)_2(OAc)]^+$ match the d_{H2}^{cryst} value determined by neutron diffraction, 1.10(1) and 1.34(2) Å, respectively.[10] Their d_{H2}^{slow} values are also consistent with distances d_{H2}^{HD} obtained from $^1J_{HD}$ values measured on the corresponding H–D complexes. The good correlation between with d_{H2}^{cryst} and $^1J_{HD}$ is used in this calculation with the assumption that $d_{H2}^{cryst} \approx d_{H2}^{HD}$ (note that it is not clear theoretically why this correlation works so well[26]).[9,26]

$$d_{H2}^{HD} = 1.42 - 0.0167\,{}^1J_{HD} \tag{10}$$

Similarly, the complex $[Nb(H\cdots H)(C_5H_4SiMe_3)_2(PMe_2Ph)]^+$ has a slow-motion $H\cdots H$ ligand because two orientations of the corresponding $H\cdots D$ ligand with $^1J_{HD} = 15$ Hz can be frozen out.[27] Here T_1^{min}, after the approximate correction for relaxation contributions from other ligands and the metal, gives $d_{H2}^{slow} = 1.17$ Å, which is the same as the d_{H2}^{HD} value of 1.17 Å.

There are several examples of complexes with fast-spinning H_2 ligands. The complexes *trans*-$[M(H_2)(H)(dppe)_2]^+$, M = Fe, Ru, Os (Fig. 1), have

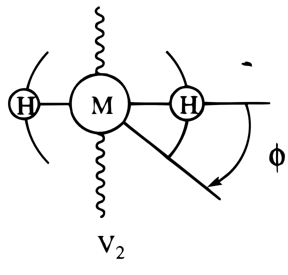

Figure 3. Definition of the parameters for the oscillation in the potential well of height V_2.

$d_{\mathrm{H2}}^{\mathrm{cryst}}$ values from crystallographic studies that are consistent with $d_{\mathrm{H2}}^{\mathrm{fast}}$ values calculated from T_1^{min} data and $d_{\mathrm{H2}}^{\mathrm{HD}}$ values.[22] The H–H dipolar coupling has been directly observed in the complex $\mathrm{Ru_2(H\cdots H)(biporphyrin)}$(*tert*-butylimidazole)$_2$ in solution because of its property to partially orient in a magnetic field. This dipolar coupling leads to an H—H distance of 1.18 Å, which is consistent with $d_{\mathrm{H2}}^{\mathrm{fast}} = 1.21$ Å from the T_1^{min} and $d_{\mathrm{H2}}^{\mathrm{HD}} = 1.17$ Å.[28]

The complex *trans*-$[\mathrm{Os(H\cdots H)(Cl)(dppe)_2}]^+$ is in the third regime where $1/\tau_{\mathrm{H_2}} \approx 1/\tau_{\mathrm{mol}}$. Here the $d_{\mathrm{H2}}^{\mathrm{cryst}}$ value [1.22(3) Å] from neutron diffraction matches $d_{\mathrm{H2}}^{\mathrm{HD}} = 1.22$ Å but is between the $d_{\mathrm{H2}}^{\mathrm{fast}}$ and $d_{\mathrm{H2}}^{\mathrm{slow}}$ values of 1.04 and 1.31 Å, respectively. Distortions from the usual V-shape of the ln T_1 versus $1/T$ plots are observed for this complex which suggest that the rotation rate of the dihydrogen ligand is close to the Larmor frequency.[9]

Table 1. Values of ζ from Eqn (13) and the derived values of C(φ) from Eqn (6)

Libration angle, $\sqrt[2]{\langle\phi^2\rangle}$ (°)	$\langle\phi^2\rangle$ (rad^2)	$\omega^2\tau^2_{\mathrm{mol}} = \zeta$	$C(\phi)$
0	0	0.386	5.82
9.05	0.025	0.390	5.74
12.8	0.05	0.402	5.66
15.7	0.075	0.417	5.57
18.1	0.1	0.434	5.48
20.2	0.125	0.455	5.37
22.2	0.15	0.480	5.26
25.6	0.2	0.5498	4.98
28.6	0.25	0.659	4.59

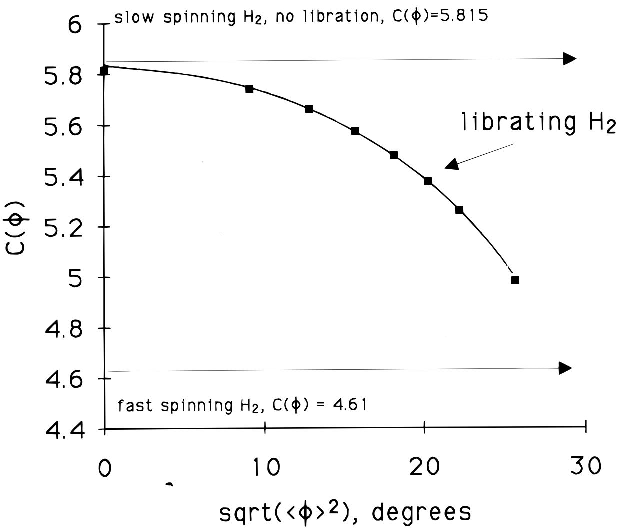

Figure 4. Plot of $C(\phi)$ versus ϕ.

Several other complexes have been identified which have $d_{\mathrm{H2}}^{\mathrm{HD}}$ or $d_{\mathrm{H2}}^{\mathrm{cryst}}$ which fall between the $d_{\mathrm{H2}}^{\mathrm{fast}}$ and $d_{\mathrm{H2}}^{\mathrm{slow}}$ values calculated from T_1^{min} data. No distortion of the ln T_1 versus $1/T$ plots has been reported for these so that they do not appear to be in regime 3 mentioned above.

INTRODUCTION OF A TWOFOLD BARRIER TO ROTATION IN THE SLOW-MOTION $\mathrm{H_2}$ REGIME

The tungsten dihydrogen complex in Fig. 2 is thought to have a barrier to rotation across the OC—W—CO axis. If a twofold potential barrier to rotation, $V = \frac{1}{2}V_2[1 - \cos(2\phi)]$, is present (Fig. 3), then the dihydrogen with correlation time τ_{C} will librate through an angle ϕ (in radians) and the spectral density functions have to be modified by a factor involving the mean square amplitude of libration $\langle\phi^2\rangle$:[29]

$$J(\omega) = 0.25\,\frac{\tau_{\mathrm{A}}}{(1+\omega^2\tau^2_{\mathrm{mol}})} + 0.75(1 - 4\langle\phi^2\rangle)\,\frac{\tau_{\mathrm{C}}}{(1+\omega^2\tau_{\mathrm{C}}{}^2)} \tag{11}$$

$$J(2\omega) = 0.25\,\frac{\tau_{\mathrm{A}}}{(1+4\omega^2\tau^2_{\mathrm{mol}})} + 0.75(1 - 4\langle\phi^2\rangle)\,\frac{\tau_{\mathrm{C}}}{(1+4\omega^2\tau_{\mathrm{C}}{}^2)} \tag{12}$$

Here it is assumed that the correlation time, τ_ϕ, of the torsional libration is much shorter than the correlation time for $\mathrm{H_2}$ motion, τ_{H2}. The barrier V_2 has to be sufficiently high so that $\langle\phi^2\rangle \ll 1$. Therefore, these expressions are valid for small angles $\phi < 1$ rad only.

If $\mathrm{H_2}$ reorientation motion is in the slow regime, then τ_{C} in Eqns (11) and (12) is equal to τ_{mol}. The T_1 values are calculated by use of Eqn (6), which has been substituted with Eqns (11) and (12) and $\tau_{\mathrm{C}} = \tau_{\mathrm{mol}}$. The maximum of Eqn (6) is obtained by setting the differentiated equation to 0. This gives a third-order polynomial in $\omega^2\tau^2_{\mathrm{mol}} = \zeta$:

$$(5 - 12\langle\phi^2\rangle) + (24\langle\phi^2\rangle - 1)\zeta + (84\langle\phi^2\rangle - 20)\zeta^2 + (48\langle\phi^2\rangle - 32)\zeta^3 = 0 \tag{13}$$

For a given value of $\langle\phi^2\rangle$, this equation can be solved to give one positive root, one negative root and one imaginary root. The positive roots for selected $\langle\phi^2\rangle$ values are listed in Table 1.

Equation (6) can now be substituted with values of $\langle\phi^2\rangle$ and τ_{mol} and rearranged to solve for d_{H2} in terms of T_1^{min} (in s) and the spectrometer frequency ν (in MHz):

$$d_{\mathrm{H2}}^{\mathrm{lib}} = C(\phi)\sqrt[6]{T_1^{\mathrm{min}}/\nu} \tag{14}$$

As expected, when there is no libration, Eqn (14) is the same as Eqn (8) with $C(0) = 5.815$. The values of $C(\phi)$ so obtained are plotted against the mean libration angle in Fig. 4. At angles above 20° it is likely that this approximate treatment breaks down. Nevertheless, it is obvious that libration can have a large effect on T_1 and therefore the d_{H2} value calculated.

COMPLEXES WHERE LIBRATION MAY AFFECT THE T_1 OF DIHYDROGEN LIGANDS

If Eqn (10) does give the 'true d_{H2}' in solution (i.e. $d_{\mathrm{H2}}^{\mathrm{HD}} = d_{\mathrm{H2}}^{\mathrm{lib}}$), then the ratio of Eqn (15) can be used to estimate the value of $C(\phi)$:

$$C(\phi) \approx 5.815\,\frac{d_{\mathrm{H2}}^{\mathrm{HD}}}{d_{\mathrm{H2}}^{\mathrm{slow}}} \qquad (15)$$

where $d_{\mathrm{H2}}^{\mathrm{HD}}$ is calculated from $^1J_{\mathrm{HD}}$ and $d_{\mathrm{H2}}^{\mathrm{slow}}$ is calculated from the T_1^{min}(corr.) of the dihydrogen ligand, corrected for dipole–dipole relaxation contributions from the metal and other nuclei nearby.[30] From values of $C(\phi)$ the mean angle of libration can be estimated by use of Fig. 4. These values are listed for a variety of dihydrogen complexes in Tables 2 and 3. The solvents used were acetone-d_6, CD_2Cl_2 or toluene-d_8. The minimum T_1 value occurred in most cases at between 180 and 240 K, depending on the size of the complex, the spectrometer frequency and the concentration of the sample. This temperature increased to 293 K for a few very large complexes.

For this case of libration in a potential well, plots of ln T_1 versus $1/T$ would be almost impossible to distinguish from the usual V-shape (Fig. 5) expected for slow motion or fast spinning H_2 regimes mentioned above.

If there is a marked temperature dependence of librational angle on temperature, then above the temperature where T_1^{min} occurs, T_1 values might be longer than expected while below this temperature they will be shorter. No examples of this behavior have been reported but the effect is subtle and might have been missed. Often complete data sets of T_1 versus temperature are not provided in literature reports, only the T_1^{min} value. Therefore, it is difficult to identify positively definite examples of this phenomenon.

The complexes in Table 2 with $C(\phi)$ values near to 4.61 appear to have fast spinning H_2 ligands. Many of these complexes have pseudo-fourfold symmetry or have H_2 *trans* to hydride, a ligand that weakens the M—H_2 bonding and presumably makes the H_2 more

Table 2. Complexes with dihydrogen in the fast-spinning regime

Complex	Ref.	MHz	$T_{1\,\mathrm{corr}}^{\mathrm{min}}$ (s)	J_{HD} (Hz)	$d_{\mathrm{HH}}^{\mathrm{slow}}$ (Å)	$d_{\mathrm{HH}}^{\mathrm{cryst}}$ (Å)	$d_{\mathrm{HH}}^{\mathrm{HD}}$ (Å)	$C(\phi)$	p_{A}
$\mathrm{Mo(H_2)(CO)(dppe)_2}$	34	200	0.02	34	1.25	0.85	0.85	3.96	0.50
$\mathrm{Ru(H_2)(biporphyrin)(Im^*)Ru(Im^*)}$	28	400	0.132	15.2	1.53	1.18	1.17	4.44	0.50
$\mathrm{Ru(H_2)(H)(PPh(OEt)_2)_4^+}$	35	80	0.005	32	1.16		0.89	4.45	0.50
$\mathrm{Ru(H_2)H(}$*meso*-tetraphos-1$)^+$	22	400	0.02	33.5	1.12		0.86	4.49	0.50
$\mathrm{Ru(H_2)H[P(C_6H_4CF_3)_2CH_2CH_2P(C_6H_4CF_3)_2]_2^+}$	36	200	0.01	33.1	1.12		0.87	4.52	0.50
$\mathrm{Ru(H_2)H[P(C_6H_4OMe)_2CH_2CH_2P(C_6H_4OMe)_2]_2^+}$	36	200	0.01	33.1	1.12		0.87	4.52	0.50
$\mathrm{Ru(H_2)H(dppe)_2^+}$	36	400	0.02	32	1.12		0.89	4.62	0.50
$\mathrm{Os(H_2)H(dppe)_2^+}$	24	400	0.04	25.5	1.25	0.95	0.99	4.62	0.50
trans-$\mathrm{Os(H_2)(I)(NH_3)_4^+}$	11, 38	400	0.129	12.5	1.52		1.21	4.63	0.50
$\mathrm{Ru(H_2)_2H[HB(Pz\text{-}3,5\text{-}Me_2)_3]}$	39, 40	250	0.021	27	1.22		0.97	4.63	0.50
cis-$\mathrm{Os(H_2)(I)(NH_3)_4^+}$	11	400	0.087	17	1.43		1.14	4.63	0.50
$\mathrm{Ru(H_2)(OEP)(THF)}$	28	400	0.025	29.5	1.16		0.93	4.66	0.57
trans-$\mathrm{Os(H_2)(CH_3CN)(NH_3)_4^{2+}}$	11, 38	400	0.062	20.3	1.35		1.08	4.67	0.57
$\mathrm{Ir(H_2)H(Nbq)(PPh_3)_2^+}$	37	500	0.03	29.5	1.15		0.93	4.69	0.59
$\mathrm{Fe(H_2)H(}$*meso*-tetraphos-1$)^+$	22	400	0.018	32	1.1		0.89	4.70	0.60
$\mathrm{Os(H_2)H(}$*meso*-tetraphos-1$)^+$	22	400	0.032	26.4	1.21		0.98	4.72	0.61
$\mathrm{Os(H_2)(Im^*)(OEP)}$	28	400	0.028	27.5	1.18		0.96	4.73	0.62
$\mathrm{Fe(H_2)H(dppe)_2^+}$	21	400	0.017	32	1.09	0.88	0.89	4.74	0.62
$\mathrm{Os(H_2)(THF)(OEP)}$	28	400	0.11	12	1.48		1.22	4.78	0.64
$\mathrm{Ru(H_2)H(dppe)_2^+}$	21	400	0.016	32	1.08		0.89	4.79	0.65
trans-$\mathrm{Os(H_2)(Cl)(NH_3)_4^+}$	11, 38	400	0.125	10.2	1.51		1.25	4.80	0.65
$\mathrm{Ru(H_2)(CO)(H)_2(P^{\mathit{i}}Pr_3)_2}$	41	200	0.008	32.4	1.06		0.88	4.81	0.65
$\mathrm{Ru(H_2)H[P(CH_2CH_2PCy_2)_3]^+}$	42	400	0.024	28	1.15		0.95	4.82	0.66
$\mathrm{Os(H_2)H[P(C_6H_4CF_3)_2CH_2CH_2P(C_6H_4CF_3)_2]_2^+}$	36	200	0.015	25.5	1.19		0.99	4.84	0.67
$\mathrm{Rh(H_2)H_2[HB(Pz\text{-}3,5Me_2)_3]}$	43–45	400	0.023	28	1.14	0.94	0.95	4.85	0.67
$\mathrm{Fe(H_2)CN(depe)_2^+}$	46	400	0.015	31.6	1.07		0.89	4.87	0.68
$\mathrm{Os(H_2)(imid)(NH_3)_4^{2+}}$(*trans* isomer)	11, 38	400	0.063	17.1	1.35		1.13	4.88	0.68
$\mathrm{Ru(H_2)H(dcype)_2^+}$ *trans*	47	80	0.003	31.5	1.06		0.89	4.89	0.69
$\mathrm{Re(H_2)(CO)_2(PMe_3)_3^+}$	48	300	0.008	33.7	1.01		0.86	4.92	0.70
$\mathrm{Cr(H_2)(CO)_3(P^{\mathit{i}}Pr_3)_2}$	19	250	0.006	35	1.99	0.89	0.84	4.92	0.70
$\mathrm{Ru(H_2)Cl(depe)_2^+}$	23	400	0.028	25.2	1.18		1	4.92	0.70
$\mathrm{Ru(H_2)Cl(dppe)_2^+}$	23	400	0.025	25.9	1.16		0.99	4.96	0.71
$\mathrm{Mo(H_2)(CO)[P(CH_2C_6H_4Me)_2CH_2CH_2(CH_2C_6H_4Me)_2]_2}$	49	250	0.01	30	1.08		0.92	4.97	0.72

Table 3. Complexes with dihydrogen ligands which might have significant librational or hopping motion

Complex	Ref.	MHz	$T_{1\,\mathrm{corr}}$ (s)	J_{HD} (Hz)	$d_{\mathrm{HH}}^{\mathrm{slow}}$ (Å)	$d_{\mathrm{HH}}^{\mathrm{cryst}}$ (Å)	$d_{\mathrm{HH}}^{\mathrm{HD}}$ (Å)	$C(\phi)$	ϕ (°)	p_{A}
$\mathrm{Ru(H_2)(dppb)(\mu\text{-}Cl_3)RuCl(dppb)}$	50, 51	300	0.012	29.4	1.08		0.93	5.03	27	0.74
$\mathrm{Ru(H_2)H(py)[HB(Pz\text{-}3,5\text{-}Me_2)_3]}$	39	250	0.013	26.7	1.12		0.97	5.04	26	0.74
$\mathrm{Os(H_2)H(depe)_2{}^+}$	24	400	0.08	11.5	1.41		1.23	5.08	26	0.75
$\mathrm{Os(H_2)H[P(CH_2CH_2PPh_2)_3]^+}$	52	300	0.022	22.5	1.19		1.04	5.11	23	0.76
trans-$\mathrm{Os(H_2)(py)(NH_3)_4^{2+}}$	38	400	0.038	19.6	1.24		1.09	5.12	23	0.77
$\mathrm{Re(H_2)(CO)_2(tripod)^+}$	53	300	0.009	30.8	1.02		0.91	5.16	23	0.78
$\mathrm{Re(H_2)(CO)_3(PMe_3)_2{}^+}$	48	300	0.007	33	0.98		0.87	5.16	23	0.78
$\mathrm{W(H_2)(CO)_3(P^iPr_3)_2}$	54	200	0.004	34	0.96	0.85	0.85	5.17	23	0.78
$\mathrm{Fe(H_2)H(dmpe)_2{}^+}$	55, 56	270	0.008	31	1.01		0.9	5.19	23	0.79
trans-$\mathrm{Os(H_2)(pyrazine)(NH_3)_4^{2+}}$	57	400	0.024	23.4	1.15		1.03	5.20	23	0.79
$\mathrm{Os(H_2)Cl(depe)_2{}^+}$	9	400	0.06	13.1	1.34		1.2	5.21	23	0.80
$\mathrm{Os(H_2)(CH_3CN)(dppe)_2^{2+}}$	58	400	0.028	21.4	1.18		1.06	5.24	22	0.81
$\mathrm{Ru(H_2)H(SC_4H_8)[HB(Pz\text{-}3,5\text{-}Me_2)_3]}$	39, 40	250	0.013	24.3	1.12		1.01	5.25	22	0.81
$\mathrm{Ta(H_2)(C_5H_5)_2(CO)^+}$	71	250	0.009	27.5	1.06		0.96	5.27	22	—[a]
$\mathrm{Os(H_2)Cl(dppe)_2{}^+}$	9	400	0.053	13.6	1.31	1.22	1.19	5.28	22	0.82
trans-$\mathrm{Os(H_2)(py)(en)_2^{2+}}$	59	400	0.032	19	1.21		1.1	5.31	21	0.83
$\mathrm{Os(H_2)_2(Cl)_2(P^iPr_3)_2}$	60	300	0.039	13.2	1.31		1.2	5.33	20	0.83
cis-$\mathrm{Os(H_2)(py)(NH_3)_4^{2+}}$	11, 38	400	0.028	20.2	1.18		1.08	5.33	20	0.83
$\mathrm{Os(H_2)(CH_3CN)_3(P^iPr_3)_2^{2+}}$	61	300	0.012	25.5	1.08		0.99	5.35	20	0.84
trans-$\mathrm{Os(H_2)(D_2O)(NH_3)_4^{2+}}$	11, 38	400	0.077	8.1	1.4		1.28	5.35	20	0.85
trans-$\mathrm{Ir(H_2)H(Br)_2(P^iPr_3)_2}$	62	200	0.004	32	0.96		0.89	5.38	20	0.85
$\mathrm{Os(H_2)({=}CCH_2CH_2CH_2CH_2O)(NH_3)_4^{2+}}$	57	400	0.021	22.7	1.13		1.04	5.38	20	0.85
$\mathrm{Ru(H_2)H(PCy_3)[HB(Pz\text{-}3,5\text{-}Me_2)_3]}$	39	250	0.015	21	1.15		1.07	5.41	19	0.86
$\mathrm{Os(H_2)(CH_3CN)(en)_2^{2+}}$	59	400	0.032	17.7	1.21		1.12	5.42	19	0.87
$\mathrm{Os(H_2)H(CH_3CN)_2(P^iPr_3)_2{}^+}$	61	300	0.052	8.4	1.37		1.28	5.42	19	0.87
cis-$\mathrm{Re(H_2)(CO)(PMe_3)_4{}^+}$	48	300	0.009	27.7	1.03		0.96	5.43	19	0.87
$\mathrm{Os(H_2)(OAc)(PPh_3)_3{}^+}$	63	400	0.041	13.7	1.26		1.19	5.51	17	0.90
$\mathrm{Ir(H_2)(H)(PMe_3)(HBPz_3)}$	64	300	0.011	24.6	1.06		1.01	5.54	16	0.90
cis-$\mathrm{Os(H_2)(py)(en)_2^{2+}}$	59	400	0.027	18	1.17		1.12	5.55	16	0.91
$\mathrm{Os(H_2)Cl(dcype)_2{}^+}$	47	80	0.01	10.5	1.3		1.24	5.57	15	0.92
$\mathrm{Ru(H_2)H[P(CH_2CH_2PPh_2)_3]^+}$	65	300	0.006	29.7	0.96		0.92	5.61	13	0.93
$\mathrm{Re(H_2)(CO)_3(P^iPr_3)_2{}^+}$	66	300	0.004	33	0.9		0.87	5.64	13	0.94
$\mathrm{Os(H_2)(CO)(Cl)_2(P^iPr_3)_2}$	67	300	0.015	20.1	1.12		1.08	5.65	13	0.94
$\mathrm{Fe(H_2)H[P(CH_2CH_2PPh_2)_3]^+}$	68	300	0.006	28.5	0.96		0.94	5.73	10	0.97

[a] This complex must have a librating but not hopping H_2 because HD in two opposite orientations is observed.

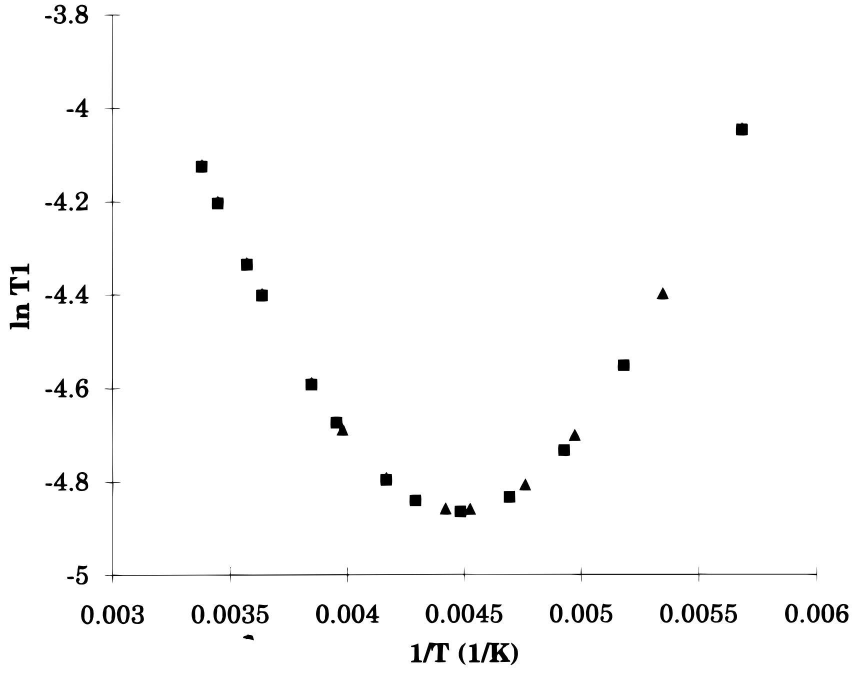

Figure 5. Comparison of the temperature dependence of ^{1}H NMR T_1 at 400 MHz of a hypothetical dihydrogen ligand with an H—H distance of 1.0 Å for the cases of (▲) no internal motion and (■) rapid libration with $\phi = 20°$.

Table 4. Dihydrogen ligands with high barriers to rotation and little libration

Complex	Ref.	MHz	$T_{1\,\mathrm{corr}}$ (s)	J_{HD} (Hz)	$d_{\mathrm{HH}}^{\mathrm{slow}}$ (Å)	$d_{\mathrm{HH}}^{\mathrm{cryst}}$ (Å)	$d_{\mathrm{HH}}^{\mathrm{HD}}$ (Å)	$C(\phi)$	ϕ (°)	p_{A}
$\mathrm{Fe(H_2)(C_5Me_5)(dppe)^+}$	69	300	0.007	27	0.98		0.97	5.73	5	0.97
$\mathrm{Os(H_2)(CO)(\eta\_^2S_2CH)(P^iPr_3)_2^+}$	70	300	0.008	25.1	1.01		1	5.79	0	1.00
trans-$\mathrm{Os(H_2)(Cl)(en)_2^+}$	11, 59	400	0.061	7.2	1.34		1.3	5.81	0	1.00
$\mathrm{Ru(C_5Me_5)(H_2)(dppm)^+}$	10	400	0.018	21.5	1.1	1.10	1.06	5.81	0	1.00
$\mathrm{Os(H_2)(OAc)(en)_2^+}$	11	400	0.061	9.1	1.34	1.34	1.27	5.81	0	1.00
$\mathrm{Nb(H_2)(C_5H_4SiMe_3)_2(PMe_2Ph)^+}$	27	300	0.020	15	1.17		1.17	5.81	0	1.00

like a free rotor (e.g. Fig. 1). It is not clear why certain complexes have $C(\phi)$ significantly less than 4.6. An explanation is that Eqn (10) only gives an approximate d_{HH} value.

The complexes in Table 3 might have H_2 librating in a twofold potential well. They are ordered in increasing value of $C(\phi)$ and decreasing angles ϕ. Several of these complexes have pseudo-twofold symmetry (e.g. Fig. 2). For most of these complexes the height of the barrier is not known. The value of $C(\phi) = 5.17$ for $\mathrm{W(\eta^2\text{-}H_2)(CO)_3(P^iPr_3)_2}$ in solution at 180 K corresponds to an average angle ϕ of 22°, in keeping with the value of 16° (at 100 K) determined by Zilm and Millar[17] (see above). The value of V_2 for this complex has been determined to be 2.4 kcal $\mathrm{mol^{-1}}$.[31] There may be reasons other than librational motion why the $C(\phi)$ value is intermediate for the complexes of Table 3. Motion of the H_2 with frequency near to the Larmor frequency (see above) and fast hopping (see below) could also produce this effect.

In Table 4 are six complexes in which the dihydrogen ligand apparently has a high barrier to rotation and small libration angle. This situation has been discussed previously.[10]

COMPLEXES WITH DIHYDROGEN UNDERGOING FAST 90° HOPS IN A FOURFOLD POTENTIAL

A fourfold potential surface for rotation of the η^2-dihydrogen ligand might arise if the ligand has a preference to orient parallel to the *cis*-ligand to metal bond axes as in Fig. 2 or between these bond axes as in Fig. 6.

The spectral density function for hydrogens of the H_2 hopping between sites A and B at 90° to each other (90° flips; see Fig. 6) superimposed on isotropic molecular reorientation is derived from Latanowicz's Eqn (11) in Ref. 32 to be

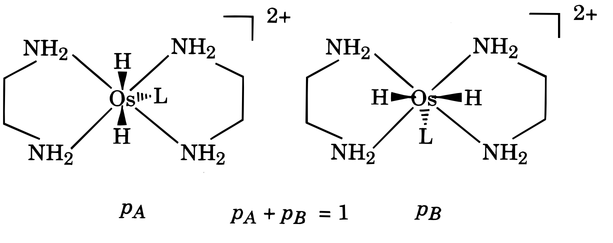

Figure 6. Possible example of a dihydrogen complex with L = py or $\mathrm{CH_3CN}$ (see Table 3) with H_2 hopping between sites of different population. Site A with H atoms staggered between the N atoms which are not connected by the ethylene group is probably favored in this case over site B with the H atoms between the connected N atoms (i.e. $p_A > p_B$).[11]

$$J(\omega) = ({p_A}^2 - p_A p_B + {p_B}^2)\frac{\tau_{\mathrm{mol}}}{1 + \tau_{\mathrm{mol}}^2\omega^2} + (3p_A p_B)\frac{\tau_{\mathrm{mol}} + (k_A + k_B)\tau_{\mathrm{mol}}^2}{[1 + (k_A + k_B)\tau_{\mathrm{mol}}]^2 + \tau_{\mathrm{mol}}^2\omega^2} \tag{16}$$

where τ_{mol} is the rotational correlation time of the complex (τ_0 in Ref. 32), ω is the Larmor frequency, k_A and k_B are the forward and reverse rates for the 90° hops and p_A and p_B are the populations of the two sites ($p_A + p_B = 1$). Some correspondences between Latanowicz's notation and this work are $\tau_{\mathrm{mol}} = \tau_0$, $\theta = 90°$, $d_{\mathrm{HH}} = R_{ik\mathrm{A}} = R_{ik\mathrm{B}}$. In real complexes these two distances may not be exactly equal. Equation (16) was also derived from first principles by one of us.[33]

In the case of no internal flips ($k_A = k_B = 0$), $J(\omega)$ reduces to the standard isotropic reorientation expression of Eqn (7).

In the case of very rapid internal flips ($k_A + k_B \gg 1/\tau_{\mathrm{mol}}$), the second term goes to zero and $J(\omega)$ becomes

$$J(\omega) = A\frac{\tau_{\mathrm{mol}}}{1 + \tau_{\mathrm{mol}}^2\omega^2} \tag{17}$$

where $A = {p_A}^2 - p_A p_B + {p_B}^2$. When $p_A = p_B = 0.5$ then $A = 0.25$, which is equivalent to the case of fast internal rotation or spinning of H_2.[20] The interesting cases occur for $p_A \neq p_B$ because the value of A can then range from 0.25 to 1 depending on the population difference of the two sites. The significance of this is that if rapid flipping or hopping is occurring between sites of different population then the minimum T_1 of the protons will depend on p_A as well as $d(\mathrm{HH})^6$.

Therefore, the observed ratio of the distance expected from the T_1^{min} if there were no fast 90° hops to the distance observed (estimated by use of $d_{\mathrm{H2}}^{\mathrm{HD}}$) is C^{hop}, which is equivalent to $C(\phi)$ above:

$$C^{\mathrm{hop}} \approx 5.815\frac{d_{\mathrm{H2}}^{\mathrm{HD}}}{d_{\mathrm{H2}}^{\mathrm{slow}}} \tag{18}$$

Therefore, if fast hopping is the explanation for a shorter distance being observed than expected on the basis of the no-motion T_1^{min} calculation ($d_{\mathrm{H2}}^{\mathrm{slow}}$), then p_A (and $p_B = 1 - p_A$) can be obtained by solving the equation

$$C^{\mathrm{hop}} = 5.815\sqrt[6]{{p_A}^2 - p_A p_B + {p_B}^2} \tag{19}$$

Values of p_A calculated from $C(\phi) = C^{\mathrm{hop}}$ values are also listed in Tables 2–4. Complexes in Table 3 with p_A

between 0.7 and 0.9 are the most likely to have this type of motion, but they could have librational motion or H_2 motion near to the Larmor frequency instead (as above).

The temperature dependence of ln T_1 for this type of motion would not be distinctive compared with the usual V-shape discussed above unless there were a large temperature dependence in the equilibrium constant $K = p_A/p_B$.

CONCLUSIONS

Three types of internal motion of the H_2 ligand have been considered. The first is H_2 rotation. Depending on the frequency of spinning relative to the reorientation frequency of the complex, three regimes might be observed for this type of motion: H_2 fast spinning as a free rotor, slow-motion H_2 and H_2 moving with a frequency near to the ^{1}H Larmor frequency. The last can be identified by its distinctive temperature dependence of T_1. Table 2 lists 33 complexes which appear to have fast-spinning dihydrogen ligands on the basis of their $C(\phi)$ value near to 4.6. Table 4 lists six complexes which appear to have slow-motion H_2 ligands and small angle librational motion on the basis of $C(\phi)$ values near to 5.8. The H—H distance calculated from T_1^{min} for the fast-spinning H_2 regime, $d_{\text{HH}}^{\text{fast}}$, is a factor of 0.793 shorter than $d_{\text{HH}}^{\text{slow}}$ of the slow-motion H_2 regime and these two values are the lower and upper limits of possible distances calculated from the T_1^{min} value (assuming pure dipolar relaxation exclusive of other contributions). The second type of motion is torsional libration of H_2 in a deep twofold potential well. A method is proposed to estimate the root-mean-square angle of libration. This type of behavior might be identified by the temperature dependence of the T_1 data. Table 3 lists increasing $C(\phi)$ values and decreasing angles ϕ for 35 complexes which might be relevant. The final type of motion is rapid hopping between unequally populated sites at 90° in a rotational potential with a fourfold component. Again, the dihydrogen ligands of the complexes in Table 3 might be undergoing fast hopping. The temperature dependence in this case is indistinguishable from that in the free rotor case. Therefore, it is not clear at this stage which motion or combination of motions is contributing to produce the T_1^{min} values reported in the literature and more work needs to be done to resolve these questions.

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