874. *Proton Chemical Shifts in the Nuclear Magnetic Resonance Spectra of Transition-metal Hydrides: Square-planar Platinum(II) Complexes.*

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The recent theory [1] of the very large high-field shifts in the proton magnetic resonance spectra of transition-metal hydrides is applied to square-planar d^8 complexes, with special attention to platinum(II) compounds. The high-field shifts in *trans*-PtHX(PEt$_3$)$_2$ complexes are attributed mainly to paramagnetic shielding of the proton by the Pt $5d$-electrons. Shifts ~20 p.p.m. are obtained for a Pt–H bond length $R \sim 3$ a.u. (atomic units). Chemical shifts are chiefly caused by changes in R associated with variations in the "*trans*-effect" of the ligand X. Large low-field shifts are predicted for protons above the molecular plane. Somewhat different shielding constants are expected for the deuterium analogues of the transition-metal hydrides.

IN another Paper [1] we suggested an explanation of the very large high-field shifts in the proton magnetic resonance spectra of octahedral transition-metal hydrides. The shift was attributed mainly to paramagnetic shielding by the incomplete d-electron subshell. The same general theory is here applied to square-planar low-spin platinum(II) hydrides.

Theory.—The mean shielding constant σ, of a proton H at a distance R along the x-axis from a metal atom M can be written [eqns. (3) and (4) in ref. 1]

$$\sigma = \sigma^d + \sigma^p$$

where

$$\sigma^d = \frac{e^2}{3\,mc^2} \langle 0 \,|\, \sum_j r_{Hj}^{-3} (r_{Hj}^2 + Rx_{Hj}) \,|\, 0 \rangle$$

$$\sigma^p = \tfrac{1}{3}(\sigma^p_{xx} + \sigma^p_{yy} + \sigma^p_{zz}) \tag{1}$$

$$\sigma^p_{xx} = -\frac{e^2}{2m^2c^2} \sum_{n \neq 0} (E_n - E_o)^{-1} [\langle 0 \,|\, \sum_j l_{Mxj} \,|\, n \rangle \langle n \,|\, \sum_k r_{Hk}^{-3}\, l_{Hxk} \,|\, 0 \rangle +$$
$$\langle 0 \,|\, \sum_k r_{H_k}^{-3}\, l_{Hxk} \,|\, n \rangle \langle n \,|\, \sum l_{Mxj} \,|\, 0 \rangle]$$

with analogous expressions for σ^p_{yy} and σ^p_{zz}. $|0\rangle$ and $|n\rangle$ are ground and excited state molecular wave-functions of energies E_o and E_n, respectively, and l_H and l_M are the one-electron angular momentum operators relating to motion about the proton and M.

The platinum d-electron contribution to σ is evaluated using the ligand-field theoretical description of the ground and excited states. Only one-electron excitations to singlet states contribute to σ^p; spin–orbit coupling and configuration interaction are neglected. For a PtH$_4^{2-}$ ion of D_{4h} symmetry, the d-orbital splitting and the relevant states are shown in Figs. 1 and 2. The wave-functions of the states are

$$^1A_{1g}a_1 = |\, d_{z^2}{}^2 d_{yz}{}^2 d_{zx}{}^2 d_{xy}{}^2 \rangle$$
$$^1A_{2g}a_2 = |\, d_{z^2}{}^2 d_{yz}{}^2 d_{zx}{}^2 d_{xy} d_{x^2-y^2} \rangle$$
$$^1E_g x \;\;= |\, d_{z^2}{}^2 d_{yz} d_{zx}{}^2 d_{xy}{}^2 d_{x^2-y^2} \rangle$$
$$^1E_g y \;\;= |\, d_{z^2}{}^2 d_{yz}{}^2 d_{zx} d_{xy}{}^2 d_{x^2-y^2} \rangle \tag{2}$$
$$^1B_{1g}b_1 \;= |\, d_{z^2} d_{yz}{}^2 d_{zx}{}^2 d_{xy}{}^2 d_{x^2-y^2} \rangle$$

where $|\, d_{z^2}{}^2 d_{yz}{}^2 d_{zx}{}^2 d_{xy} d_{x^2-y^2} \rangle$ is short for $\dfrac{1}{\sqrt{2}}[\,|d_{z^2}{}^2 d_{yz}{}^2 d_{zx}{}^2 d_{xy}{}^+ d_{x^2-y^2}{}^- \rangle - |d_{z^2}{}^2 d_{yz}{}^2 d_{zx}{}^2 d_{xy}{}^- d_{x^2-y^2}{}^+ \rangle],$

$|\,\rangle$ indicates a normalised determinantal wave-function, $\phi^2 = \phi^+\phi^-$ and $+$ and $-$ denote

[1] Buckingham and Stephens, *J.*, 1964, 2747.

α and β spins, respectively. The symmetry notation follows Griffith.[2] In C_{2v} complexes of type *trans*-$PtHXY_2$ (the only type for which n.m.r. data exist) the degeneracy of d_{yz} and d_{zx}, and hence of the ^1E state, is lifted.
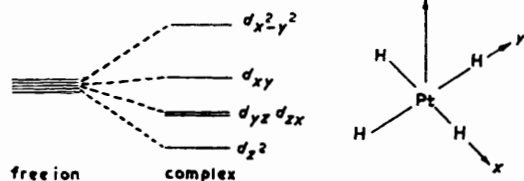

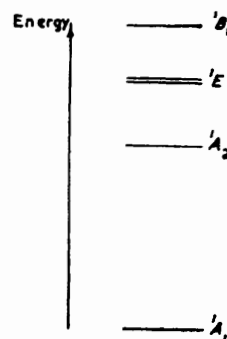FIG. 1.   Splitting of d orbitals in a square-planar D_{4h} platinum(II) complex.

FIG. 2.   Singlet energy levels in a square-planar D_{4h} platinum(II) complex.

We assume that the d-orbitals can be represented by single Slater orbitals of exponent k (the same for all d-orbitals of the same shell); the required matrix elements can then be derived from the general expressions of Pitzer, Kern, and Lipscomb.[3] Substituting (2) in (1) we obtain *

$$\sigma^d = \frac{2e^2}{3mc^2R}\left\{\frac{180}{7\rho^2} + \frac{75240}{7\rho^4} + e^{-\rho}\left[\frac{\rho^8}{32256} + \frac{\rho^7}{4608} + \frac{\rho^6}{5376} - \frac{79\rho^5}{5376} - \frac{37\rho^4}{168} - \frac{235\rho^3}{112}\right.\right.$$
$$\left.\left. - \frac{31\rho^2}{2} - \frac{1307\rho}{14} - \frac{3225}{7} - \frac{12720}{7\rho} - \frac{5400}{\rho^2} - \frac{75240}{7\rho^3} - \frac{75240}{7\rho^4}\right]\right\}$$

$$\sigma^P_{xx} = \frac{-2e^2\hbar^2}{m^2c^2R^3\Delta E_E}\left\{1 - \frac{270}{7\rho^2} + e^{-\rho}\left[\frac{\rho^5}{1344} + \frac{5\rho^4}{336} + \frac{53\rho^3}{336} + \frac{31\rho^2}{28} + \frac{38\rho}{7}\right.\right.$$
$$\left.\left. + \frac{128}{7} + \frac{270}{7\rho} + \frac{270}{7\rho^2}\right]\right\}(3)$$

$$\sigma^P_{yy} = \frac{e^2\hbar^2}{m^2c^2R^3\Delta E_E}\left\{1 + \frac{1215}{7\rho^2} - e^{-\rho}\left[\frac{\rho^8}{5376} + \frac{\rho^7}{896} + \frac{19\rho^6}{2688} + \frac{31\rho^5}{672} + \frac{97\rho^4}{336}\right.\right.$$
$$\left.\left. + \frac{34\rho^3}{21} + \frac{433\rho^2}{56} + \frac{419\rho}{14} + \frac{1229}{14} + \frac{1215}{7\rho} + \frac{1215}{7\rho^2}\right]\right\}$$

$$\sigma^P_{zz} = \frac{2e^2\hbar^2}{m^2c^2R^3\Delta E_A}\left\{2 + \frac{405}{7\rho^2} - e^{-\rho}\left[\frac{\rho^8}{5376} + \frac{\rho^7}{896} + \frac{17\rho^6}{2688} + \frac{23\rho^5}{672} + \frac{59\rho^4}{336} + \frac{139\rho^3}{168}\right.\right.$$
$$\left.\left. + \frac{191\rho^2}{56} + \frac{163\rho}{14} + \frac{433}{14} + \frac{405}{7\rho} + \frac{405}{7\rho^2}\right]\right\}$$

where $\rho = 2kR$, $\Delta E_A = E(^1A_2) - E(^1A_1)$, and $\Delta E_E = E(^1E) - E(^1A_1)$. The $^1B_1$ state does not contribute to σ^P. Eqns. (3) reduce in the limit of $k \to \infty$ to the results obtained by the near-neighbour approximation (NNA) [with the same wave-functions [1]] and in the limit of $R = 0$ to the d-electron contribution to the shielding of the Pt nucleus, namely,

$$\sigma^P_{xx} = \sigma^P_{yy} = -\frac{2e^2\hbar^2\overline{r^{-3}}}{m^2c^2\Delta E_E} = -\frac{e^2\hbar^2k^3}{21m^2c^2\Delta E_E}; \ \sigma^P_{zz} = -\frac{8e^2\hbar^2\overline{r^{-3}}}{m^2c^2\Delta E_A} \qquad (4)$$

* σ^d and σ^P henceforth represent only the Pt d-electron contribution to the total shielding.

[2] Griffith, " The Theory of Transition-metal Ions," Cambridge University Press, 1961.
[3] Pitzer, Kern, and Lipscomb, *J. Chem. Phys.*, 1962, **37**, 267.

It is interesting that here even the NNA predicts a high-field shift (unlike octahedral d^6 complexes) since the paramagnetic susceptibility due to $d \longrightarrow d$ excitations is greater (actually 4 times) perpendicular to the plane than in the plane. Eqn. (3) has been
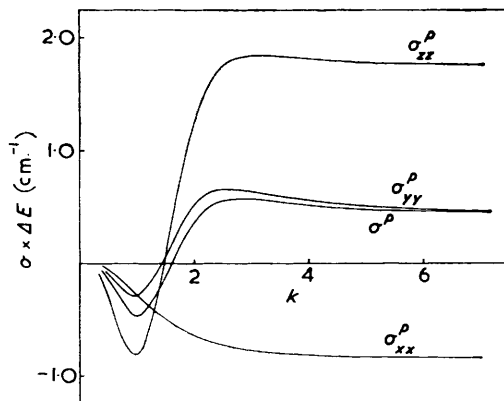
FIG. 3. σ^p_{zz}, σ^p_{yy}, σ^p_{zz}, and σ^p at $R = 3$ a.u.
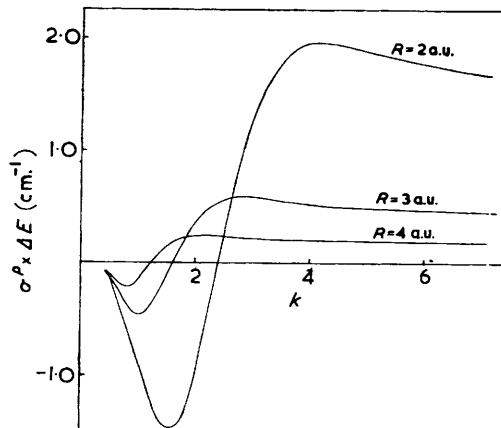
FIG. 4. σ^p at $R = 2, 3, 4$ a.u.

FIG. 5. σ^p at $R = 2, 3, 4$ a.u.
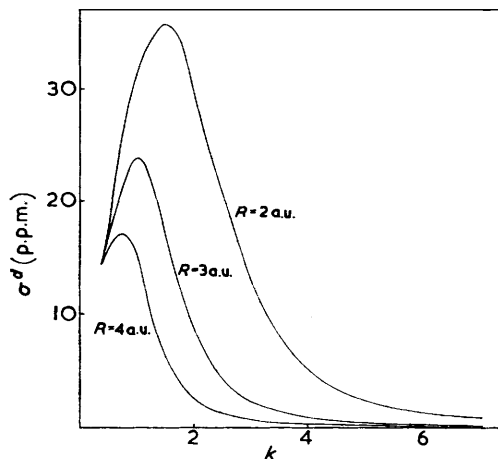
evaluated numerically for $R = 2$, **3**, and **4** a.u. as functions of ΔE and k and the results are illustrated in Figs. 3—5; σ^p was calculated assuming all ΔE values to be equal.

Application.—The available [7] n.m.r. data on platinum(II) hydrides are in the Table.

τ for *trans*-PtHX(PEt$_3$)$_2$.

X	NO$_3$	Cl	Br	I	NO$_2$	NCS	CN
τ	33·8	26·9	25·6	22·7	29·7	23·2, 27·9	17·8

We assume that local shielding alone gives $\tau = 5$ and the shift to be explained is therefore $\tau - 5$. Before estimating σ, R, k, and ΔE must be considered:

(i) R: R has not been measured in a platinum(II) complex, although it is hoped to do this, using the effect of partial molecular orientation on the n.m.r. spectrum.[4] At present, $R \sim 3$ a.u. seems likely.

(ii) k: reliable calculations of wave-functions for third series transition-metals have not been made. In the earlier Paper,[1] k for Os^{2+} and Ir^{3+} was estimated to be between 3 and 4 and this is reasonable for Pt^{2+} also.

[4] Buckingham and Lovering, *Trans. Faraday Soc.*, 1962, **58**, 2077.

(iii) ΔE: so far, there are no spectral data on platinum(II) hydrides and ΔE must be estimated by extrapolation. Unfortunately, even when the spectrum is known there is ambiguity in assigning the $d \longrightarrow d$ bands, and three different assignments of the $PtCl_4^{2-}$ spectrum have been proposed.[5] However, in all of these $\Delta E_A < \Delta E_E$. In *trans*-$PtHX(PEt_3)_2$, ΔE_A is unlikely to be <40,000 cm.[-1]. Splitting of d_{yz} and d_{zx} is expected to be small and no splitting of the ^1E band has been observed. Since taking $\Delta E_E = \Delta E_A$ only slightly affects σ^p, it can be adequately estimated by assuming all ΔE values to be equal.

σ^p calculated for $\Delta E = 40,000$ cm.[-1] and $R = 2, 3,$ and 4 a.u. is shown in Fig. 6. For $3 < k < 4$, $\sigma \sim 20$ p.p.m. at the reasonable R value of 3 a.u., σ^p being the main contributor to σ.
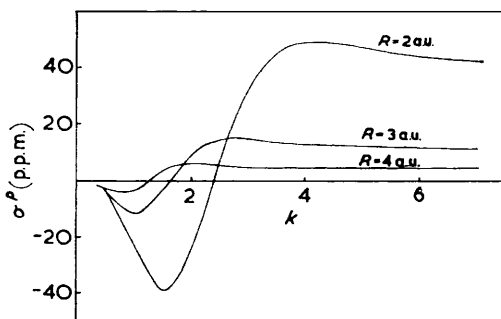

FIG. 6. σ^p at $R = 2, 3, 4$ a.u. with $\Delta E = 40,000$ cm.[-1].

The changes in τ with ligand X trans to H could be due to variations in R, k, or ΔE. Crystallographic data show that the Pt–L bond length in square-planar Pt^{II} complexes increases with increasing *trans*-effect of the *trans*-ligand, the observed variations being [6] over a range ~ 0.5 a.u. This variation in R could change σ^p by 5—10 p.p.m., though this depends sensitively on k. The *trans*-effect of X is [7] in order $NO_3 < Cl < Br < I < NO_2 < NCS < CN$ which is also the order of decreasing τ, except for NO_2 and NCS. The variation in *trans*-effect from NO_3 to CN is also larger than in the complexes studied crystallographically. Changes in R thus probably contribute appreciably to shifts in τ. The size of the d-orbitals might vary with X, but for $R \sim 3$ a.u. and $3 < k < 4$, σ varies slowly with k (see Figs. 4 and 6), so it seems unlikely that changes in k affect τ significantly (unless R is substantially smaller than 3 a.u.).

Varying ΔE from 40,000 to 55,000 cm.[-1] decreases $\sigma^p_{max.}$ at $R = 3$ a.u. from 15 to 11 p.p.m. Since the change in ΔE from X = NO_3 to CN is probably <10,000 cm.[-1], this is unlikely to be the major cause of the τ variations.

On the basis of our model (which separates the R, k, and ΔE contributions to σ) it seems that the changes in τ can be attributed mainly to changes in R. It would be interesting to check this by a direct measurement of R in a series of complexes. The above calculations apply strictly only to complexes with an orthogonal arrangement of ligands around the metal atom. However, X-ray analysis of *trans*-$PtHBr(PEt_3)_2$ showed [8] that the Br–Pt–P angle is 94°. This distortion might make a small additional contribution to σ.

It was shown for octahedral d^6 hydrides that measurement of the anisotropy in σ would provide a check of the theory; $(\sigma^p_{xx} - \sigma^p_{zz})$ was predicted to be ~ -500 p.p.m. For square-planar Pt^{II} hydrides, $[\sigma^p_{xx} - \frac{1}{2}(\sigma^p_{yy} + \sigma^p_{zz})]$ for $R = 3$ a.u. and $\Delta E = 40,000$ cm.[-1]

[5] Chatt, Gamlen, and Orgel, *J.*, 1958, 486; Fenske, Martin, and Ruedenberg, *Inorg. Chem.*, 1962, **1**, 441; Gray and Ballhausen, *J. Amer. Chem. Soc.*, 1963, **85**, 260.

[6] Basolo and Pearson, "Progress in Inorganic Chemistry," ed. Cotton, Interscience, 1962, **4**, 381.

[7] Chatt and Shaw, *J.*, 1962, 5075.

[8] Owston, Partridge, and Rowe, *Acta Cryst.*, 1960, **13**, 246.

is only ~ -50 p.p.m., when $3 < k < 4$, and is therefore of the same order of magnitude as the anisotropy in σ^d and the local shielding.

A prediction of the theory is that protons situated *above* the plane should have large low-field shifts. Suitable structures might be achieved either by protonation with a strong protonating agent (as has been effected for many carbonyl and cyclopentadienyl complexes [9]) the proton being most likely to co-ordinate to the full d_{z^2} orbital, or by using multidentate ligands with alkyl chains connecting *trans*-co-ordinating atoms analogous to the method used in investigating the shielding by the ring current in benzenoid molecules.[10] Protonation might also assist in spectral assignment since the bands would be expected to show shifts in order $^1A_2 < {}^1E < {}^1B_1$.

Isotope Effects.—The strong dependence of σ on R suggests that the substitution of D for H might appreciably affect the shielding. The shielding constant can be expanded as a series in $\xi = (R - R_e)/R_e$, where R_e is the equilibrium separation: $\sigma_e + \sigma_e'\xi + \frac{1}{2}\sigma_e''\xi^2 + \ldots \ldots$ For the ground vibrational state $\sigma = \sigma_e + \dfrac{B_e}{2\omega_e}(\sigma_e'' - 3a\sigma_e') + \ldots \ldots$ where a is the cubic anharmonic constant, B_e the rotational constant, and $c\omega_e$ the harmonic oscillator frequency. σ_e' and σ_e'' can be estimated using $\sigma^p \sim 250/R^3$ which approximately fits our calculated results in the k regions of interest. With $a = -3$ and $\omega_e = 2000$ and 1414 cm.$^{-1}$ for H and D, respectively, $\sigma_H{}^p - \sigma_D{}^p = -0.51$ and -0.08 p.p.m. at $R = 2$ and 3 a.u. (The contributions of σ^d and σ^{local} to $\sigma_H - \sigma_D$ are negligible.) This difference would be readily measurable if $R \sim 2$ a.u.; the contributions of bending vibrations to σ have been neglected.

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[9] Curphey, Santer, Rosenblum, and Richards, *J. Amer. Chem. Soc.*, 1960, **82**, 5249; Green, McCleverty, Pratt, and Wilkinson, *J.*, 1961, 4854; Davison, McFarlane, Pratt, and Wilkinson, *J.*, 1962, 3653.

[10] Waugh and Fessenden, *J. Amer. Chem. Soc.*, 1957, **79**, 846.