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Dynamics on an *ab Initio* Surface for Calculating J_{HH} NMR Exchange Coupling. The Case of $OsH_3X(PH_3)_2$

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Abstract: The exchange coupling J_{HH} in $OsH_3X(PH_3)_2$ (X = Cl and I) has been calculated by determining the eigenstates resulting from the coupling between the internal rotation and vibration modes, which correspond to the pairwise hydrogen exchange. The potential has been calculated by core potential *ab initio* methods at the RHF/MP2 level. The height of the barrier for exchange of two adjacent hydrogen atoms has been calculated to be 12.9 kcal·mol^{-1} (X = Cl) and 14.6 kcal·mol^{-1} (X = I). The ratio between the calculated exchange coupling constants for X = Cl and X = I is found to be in good agreement with the experimental ratio though shifted up in temperature. The temperature dependence of J_{HH} is calculated to be exponential, which is the typical behavior for such a coupling constant.

Abnormally large and temperature-dependent J_{HH} coupling constants have been observed in some transition metal trihydrides[1-4] and a pentahydride.[4] It has been suggested that this phenomenon arises from a quantum mechanical exchange of a pair of hydrides. Two models have been proposed,[5-8] and several theoretical calculations have been performed.[9-12] In particular, Jarid *et al.*[11,12] have explicitly calculated J_{HH} for $CpIrLH_3^+$ (L = PH_3 and CO) by combining an *ab initio* potential energy surface with a tunneling model.

We present a study of $OsH_3X(PH_3)_2$ (X = Cl and I) where exchange coupling has recently been observed with J_{HH} = 920 Hz (X = Cl) and 280 Hz (X = I) at 173 K.[4] We have calculated J_{HH} resulting from the coupling between the internal rotation and vibrational modes obtained from the *ab initio* calculated data. Temperature dependence has been computed from a Boltzmann distribution. To our knowledge, for the first time in the study of exchange coupling, the symmetry under permutation of the two identical particules (H) is explicitly incorporated in the determination of the nuclear wave functions. This knowledge is necessary for the understanding of the nuclear spin transitions.

$OsH_3X(PH_3)_2$ (X = Cl and I) have been fully optimized with relativistic (for Os) core potential[13-15] *ab initio* calculations at the RHF/MP2 level using Gaussian 92[16] with large basis sets.[17] The optimized structure is a minimum for Cl and I (Figure 1a).[18] The metal, the hydride atoms, and X are located in the plane Π with the phosphine ligands almost perpendicular to it. The H_a−Os−H_b angles of 56.9° (Cl) and 57.5° (I) are in excellent agreement with the experimental values.[4]

The pairwise site exchange mechanism has been represented by an out-of-plane twist of two adjacent hydrogen atoms, *e.g.* H_a and H_b. This choice is guided by the lower frequency for the out-of-plane twist of the hydrides (450 cm^{-1}) compared to the in-plane scissor motion (900 cm^{-1}) that brings H_a and H_b together. The optimized transition state found for such a site exchange corresponds to a structure with the H_a−Os−H_b plane perpendicular to the plane Π, which still contains H_c, Os, and X (Figure 1b). The H_a−Os−H_b angle has decreased to 51.5° (Cl) and 50.4° (I), which leads to a corresponding decrease of the H_a−H_b distance from 1.509 Å (Cl) and 1.524 Å (I) (ground state) to 1.381 Å (Cl) and 1.350 Å (I). H_c remains far from H_a and H_b. Notably, no H_2 complex lying either in the Π plane or perpendicular to it was found as a minimum or a saddle point on the potential energy surface. Thus, in these Os complexes, facile site exchange between hydrides can occur without the necessary formation of an H−H bond. It is important to note that the site exchange for hydrides involves simultaneously a

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(1) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909.

(2) Antinolo, A.; Chaudret, B.; Commenges, G.; Fajardo, M.; Jalon, F.; Morris, R. H.; Otero, A.; Schweitzer, C. T. *J. Chem. Soc., Chem. Commun.* **1988**, 1210.

(3) Chaudret, B.; Limbach, H. D.; Moïse, C. *C. R. Acad. Sci., Ser. 2* **1992**, *315*, 533.

(4) Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685.

(5) Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G.; Demou, P. *J. Am. Chem. Soc.* **1989**, *111*, 3088.

(6) Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G.; Neshyba, S. P.; Duchamp, J. C.; Szczyrba, J. *J. Am. Chem. Soc.* **1990**, *112*, 920.

(7) Zilm, K. W.; Millar, J. M. *Adv. Magn. Opt. Reson.* **1990**, *15*, 163.

(8) Limbach, H. D.; Scherer, G.; Maurer, M.; Chaudret, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1369.

(9) Jones, D. H.; Labinger, J. A.; Weitekamp, D. P. *J. Am. Chem. Soc.* **1989**, *111*, 3087.

(10) Barthelat, J. C.; Chaudret, B.; Daudey, J. P.; de Loth, P.; Poilblanc, R. *J. Am. Chem. Soc.* **1991**, *113*, 9896.

(11) Jarid, A.; Moreno, M.; Lledós, A.; Lluch, J. M.; Bertrán, J. *J. Am. Chem. Soc.* **1993**, *115*, 5861.

(12) Jarid, A.; Moreno, M.; Lledós, A.; Lluch, J. M.; Bertrán, J. *J. Am. Chem. Soc.*, in press.

(13) Ross, R. B.; Powers, J. M.; Atashroo, T.; Ermler, W. C.; Lajohn, L. A.; Christiansen, P. A. *J. Chem. Phys.* **1990**, *93*, 6654.

(14) Bouteiller, Y.; Mijoule, C.; Nizam, M.; Barthelat, J.-C.; Daudey, J.-P.; Pélissier, M.; Silvi, B. *Mol. Phys.* **1988**, *65*, 295.

(15) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026.

(16) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision C.4; 1992.

(17) Basis sets are of triple ζ quality for Os, triple ζ plus polarization for the hydrides, double ζ plus polarization for P, Cl, and I, and finally, single ζ quality for the phosphines hydrogen atoms. For details, see supplementary material.

(18) For Cl and I, the MP2 updated hessian for the ground state has only positive eigenvalues. In the case of X = Cl, the calculated SCF hessian for a structure essentially identical to that at the MP2 level has only positive eigenvalues. For the transition state, the hessian including all variables but ϕ has only positive eigenvalues.

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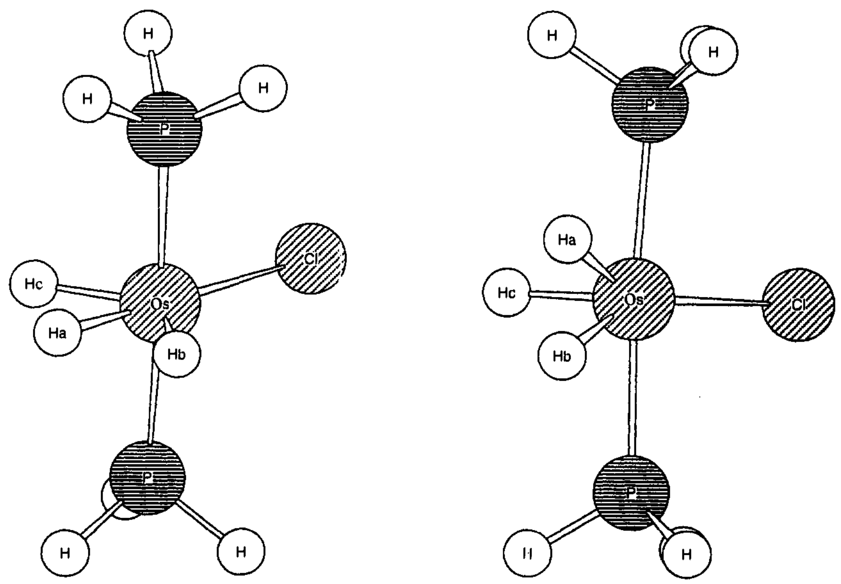

a b

Figure 1. MP2-optimized structure for $OsH_3Cl(PH_3)_2$: (a) ground state, (b) transition state.

rotation and a vibration movement. In this respect, our model differs from that of a simple rotor as discussed and rejected by Limbach.[8]

The transition state for Cl is calculated to be 12.9 kcal·mol^{-1} above the minimum, while that for I is calculated to be higher (14.6 kcal·mol^{-1}), which is in agreement with the faster rate of site exchange in the case of Cl (experimental $\Delta H^\ddagger = 8$ kcal·mol^{-1} for Cl[19] and 8.8 kcal·mol^{-1} for I[4]). Single-point calculations (Cl) at the MP4SDQ,[20] QCISD(T),[21] and CCSD(T)[22] levels give comparable energies (14.0, 14.4, and 14.3 kcal·mol^{-1}, respectively).

The reaction coordinate for hydrogen site exchange has been represented by the dihedral angle ϕ between the $H_a{-}Os{-}H_b$ and Π planes. For each ϕ, the Os$-$X bond distance, the X$-$Os$-$P angle, and all variables involving the three hydride atoms have been optimized at the MP2 level. The corresponding energy curves $V(\phi)$ are shown in Figure 2. The symmetry of the potential is described by the expansion

$$V(\phi) = \sum_{n=0}^{4} V_{2n}\cos(2n\phi) \qquad (1)$$

A fit up to $n = 4$ allowed us to accurately represent the *ab initio* data. The presence of high-order terms ($n \geq 2$) is a consequence of the flatness of the curve around the minima.

Since the $H_a{-}H_b$ distance (r) varies significantly with ϕ, a Hamiltonian explicitly incorporating ϕ and r was used. This additional degree of freedom r was taken into account according to the reaction path Hamiltonian formulation of Miller.[23] For each value of the reaction coordinate ϕ, the variation of the potential along the r coordinate is represented by quadratic $k_2(\phi)$ and cubic terms k_3. They allow for the representation of the deformation of the $H_a{-}H_b$ distance in the vicinity of the locally optimized $r_{eq}(\phi)$. The Hamiltonian resulting from the assumed planar rotor motion for H_2 can be written:[24]

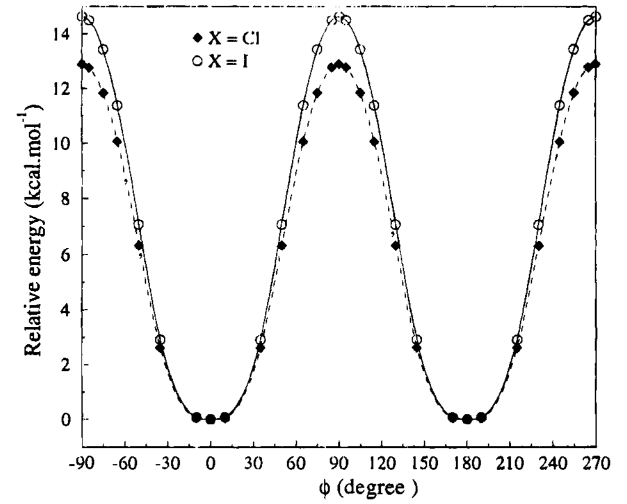

Figure 2. MP2 energy curves $E = f(\phi)$ for $OsH_3X(PH_3)_2$ (X = Cl and I) (see text for definition of ϕ).

$$\mathcal{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + {}^1/_2k_2(\phi)[r - r_{eq}(\phi)]^2 + {}^1/_6k_3[r - r_{eq}(\phi)]^3 - \frac{\hbar^2}{2\mu r^2}\frac{\partial^2}{\partial \phi^2} + V(\phi) \qquad (2)$$

where $\mu = m_H/2$ corresponds to the reduced mass of the hydrogen pair. The $k_2(\phi)$ and $r_{eq}(\phi)$ terms have been expanded in $\cos(2n\phi)$ up to first and third orders, respectively, while the averaged value ${}^1/_2[k_3(0) + k_3(\pi/2)]$ has been used for k_3. The basis set consisted of plane waves $\{e^{ik\phi}\}$ for ϕ and harmonic oscillator functions for r. The permutation symmetry has been taken into account by considering separately the even and odd

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(19) Caulton, K. G., private communication.

(20) Redmon, L. T.; Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1978**, *69*, 5386.

(21) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(22) Pople, J. A.; Head-Gordon, M.; Raghavachari, K.; Trucks, G. W. *Chem. Phys. Lett.* **1987**, *157*, 479.

(23) Miller, W. H. *J. Chem. Phys.* **1980**, *72*, 99.

(24) Eyring, H.; Walter, J.; Kimball, G. E. *Quantum Chemistry*; John Wiley & Sons: New York, 1967; pp 73–75.

k values. It should be noted that our model Hamiltonian explicitly correlates the out-of-plane motion of the two hydrides and that a full six-dimensional potential surface is necessary to confirm this hypothesis.

Diagonalizing each symmetry block of the $\hat{\mathcal{H}}$ matrix provides the corresponding eigenvalues and eigenvectors. Due to the double well nature of $V(\phi)$, levels come in pairs, symmetric (even k's) and antisymmetric (odd k's) with respect to permutation. They are thus associated with singlet and triplet nuclear spin functions, respectively. Following the model of Zilm,[6,7] the exchange coupling J_n is related to the splitting within a pair through

$$J_n = E_n^{\text{even}} - E_n^{\text{odd}} \tag{3}$$

Going from n to $n + 1$, the sign of J_n alternates. The total exchange coupling J_{HH} for a given temperature is evaluated using Boltzmann statistics:

$$J_{HH} = \frac{\sum_n J_n \exp\left(-\frac{E_n}{kT}\right)}{\sum_n \exp\left(-\frac{E_n}{kT}\right)} \tag{4}$$

Only the J's observable on the NMR time scale have been kept for the summation. The proper cutoff point in the J_{HH} sum is when J_n exceeds the inverse of the vibrational lifetime, *i.e.* 10 cm^{-1}.[25] The absolute values of J_{HH} as a function of temperature, calculated for Cl and I, are shown in Figure 3.

Several important features of the experimental data are well-reproduced although shifted up in temperature. First, even though the sign of J_n alternates, J_{HH} has an exponential behavior above a threshold temperature as observed for $Cp^*IrLH_3^+$ [1] and calculated for $CpIrLH_3^+$ (L = PH_3 and CO).[12]

J_{HH}(Cl) is calculated to be much larger than J_{HH}(I) (J_{HH}(Cl) = 950 Hz and J_{HH}(I) = 70 Hz at T = 300 K). This shows that J_{HH} is very sensitive to both the shape and height of $V(\phi)$. Actually, a simple scaling of the MP2 potential energy curve improves drastically the agreement with the experimental data. The transition state seems to be 2−3 $kcal{\cdot}mol^{-1}$ too high in energy in the calculations. Such a typical error on a barrier height is sufficient in that case to induce a 150 K shift on the temperature scale. J_{HH} reaches a non-zero plateau at low temperature and falls to almost 0 Hz for a certain temperature range.[26] This behavior has been observed recently by Heinekey in some iridium trihydrides.[27]

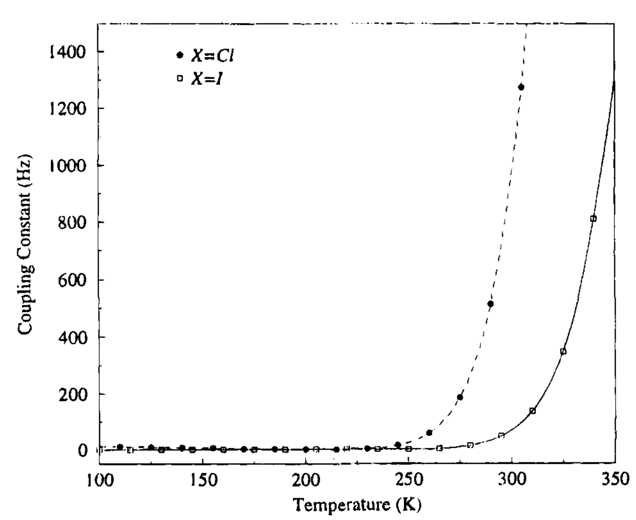

Figure 3. Calculated exchange coupling J_{HH} as a function of temperature for $OsH_3X(PH_3)_2$ (X = Cl and I).

In conclusion, this work provides a calculation of J_{HH} based on *ab initio* data consistent with a clear interpretation (in terms of permutation symmetry) of the nuclear wave function and accounting for many key experimental facts. Our model suggests that the exchange coupling in these 16-electron complexes has similar features to that of 18-electron trihydrides. Influence of an additional ligand to $OsH_3X(PH_3)_2$ is under study.

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Supplementary Material Available: A list of cartesian coordinates for the optimized ground and transition states for $OsH_3X(PH_3)_2$ (X = Cl and I), a list of selected optimized geometrical parameters for $OsH_3X(PH_3)_2$ (X = Cl and I) in the ground and transition states, and a description of basis sets (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(25) Zilm, K. W, private communication.

(26) This very small value of J results from the alternation of the sign of J_n.

(27) Heinekey, D. M., private communication.