

H–D Spin–Spin Coupling in Stretched Molecular Hydrogen Complexes of Osmium(II): Density Functional Studies of J_{HD}

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Abstract: Using density functional techniques the H–D spin–spin coupling constant J_{HD} has been calculated for a range of osmium(II)–dihydrogen complexes $[\text{Os}(\text{NH}_3)_4\text{L}^z(\eta^2\text{-H}_2)]^{(z+2)+}$ in which properties of the H–H bond are modulated by variation of the *trans* ligand L^z ($\text{L}^z = (\text{CH}_3)_2\text{CO}$, H_2O , CH_3COO^- , Cl^- , H^- , $\text{C}_5\text{H}_5\text{N}$, CH_3CN , NH_3 , NH_2OH , and CN^-). The results of the calculations are compared with the available experimental values. A high degree of correlation between the calculated J_{HD} , H–H bond length r_{HH} , and Os– H_2 interaction energy is demonstrated. Consistent with the experimentally established trends in a wide variety of complexes, J_{HD} varies inversely with r_{HH} . This behavior, opposite to that in free HD, is explained in terms of the metal–dihydrogen bonding mechanism.

Introduction

The measurement and interpretation of hydrogen–deuterium coupling constants (J_{HD}) have played an important role in the structural characterization of many transition metal–dihydrogen complexes, providing a probe for both hydride and $\eta^2\text{-H}_2$ coordination. More specifically, an inverse correlation between J_{HD} and the H–H distance in a range of dihydrogen complexes has been experimentally established.^{1–3} The relationship between J_{HD} and r_{HH} appears to be essentially linear, with slopes of approximately -0.01 to -0.025 Å/Hz, depending on the interpretation of the experimental data. In the absence of definitive neutron diffraction data the H–H distance is most often deduced from the study of the spin–lattice relaxation times (T_1) in solution NMR experiments. Depending on the assumptions made in the interpretation of T_1 data, such as the rate of (internal) rotation of H_2 relative to the overall rotation of the complex, there is some uncertainty associated with the inferred H–H distances, which at times may be considerable.⁴ Consequently, the scatter in the plots of “experimental” r_{HH} versus J_{HD} is generally attributed to the uncertainty in r_{HH} .

Intuitively, one may expect the H–H distance dependence of the coupling constant to reflect the degree of H–H bonding in the dihydrogen ligand. Similar relationships, such as that between proton–proton coupling constant and bond order, are well established in organic chemistry^{5–7} and are commonly used as a chemical rule of thumb, although such relationships have been demonstrated for protons not directly bonded to each other. In free H_2 , however, careful quantum chemical studies have shown that the coupling constant actually *increases* with H–H distance.⁸ The explanation for this initially unexpected behavior is that as the H–H bond becomes weaker, *i.e.*, longer, the

nuclear magnetic moments perturb the electronic wave function to a successively greater degree, resulting in an increase in the coupling constant. (In the limit of complete dissociation the coupling constant does, of course, decay to zero.)

The observed inverse relationship between J_{HD} and r_{HH} in molecular hydrogen complexes, opposite to that in free H_2 , reflects the effects of the metal–hydrogen interaction and one of the aims of this work is to provide an explanation for it in terms of the bonding mechanism in these systems.

The work reported in this paper is concerned with the quantum chemical calculation of H–D coupling constants using density functional theory (DFT) in the series of osmium–dihydrogen complexes $[\text{Os}(\text{NH}_3)_4\text{L}^z(\eta^2\text{-H}_2)]^{(z+2)+}$ in which the nature of the Os(II)– H_2 bond is modulated by variation of the *trans* ligand L^z ($\text{L}^z = (\text{CH}_3)_2\text{CO}$, H_2O , CH_3COO^- , Cl^- , H^- , $\text{C}_5\text{H}_5\text{N}$, CH_3CN , NH_3 , NH_2OH and CN^-). The general structure of the complexes is shown in Figure 1. The equilibrium geometries and the binding energies of the ligands H_2 and L^z in these complexes have already been reported.^{9–11} Our current study complements and extends previous theoretical work on these complexes that included the calculation of coupling constants at the SCF and MP2 levels of theory,⁹ which were actually the first *ab initio* calculations of J_{HD} in transition metal complexes.

The calculation of coupling constants using DFT is a relatively new area of research. However, the recent work of Malkin *et al.*^{12,13} on a range of small organic molecules has shown that DFT is capable of providing an accurate description of spin–spin coupling and therefore it holds considerable promise for the calculation of coupling constants in large organic and biological molecules.

Theory and Computational Details

The nuclear spin–spin constant J_{AB} is a measure of the interaction

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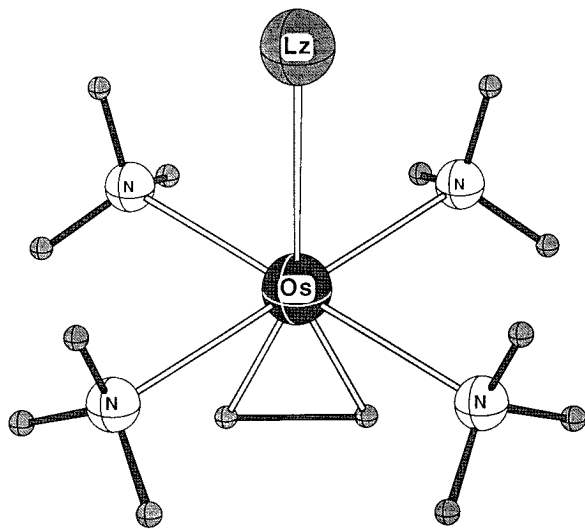


Figure 1. The general stereochemistry of the $[\text{Os}(\text{NH}_3)_4\text{L}^z(\eta^2\text{-H}_2)]^{(z+2)+}$ complexes.

between two magnetic dipolar nuclei A and B,

$$\Delta E_{AB} = hJ_{AB}\mathbf{I}_A \cdot \mathbf{I}_B = \frac{4\pi^2}{h\gamma_A\gamma_B} J_{AB}\boldsymbol{\mu}_A \cdot \boldsymbol{\mu}_B \quad (1)$$

where ΔE_{AB} is the interaction energy, \mathbf{I}_A and \mathbf{I}_B are the nuclear spin angular momenta (in units of \hbar), $\boldsymbol{\mu}_A$ and $\boldsymbol{\mu}_B$ are the corresponding magnetic moments, γ_A and γ_B are the gyromagnetic ratios, and h is Planck's constant. In the case of H and D nuclei the dominant coupling mechanism is generally believed to be the Fermi contact term; this is supported by work where all contributions have been calculated.^{12,14,15} The perturbed molecular Hamiltonian is then written in the form

$$\hat{H}(\mu_A, \mu_B) = \hat{H}_0 + \mu_A \hat{V}_A + \mu_B \hat{V}_B \quad (2)$$

where the perturbing terms $\mu_A \hat{V}_A$ and $\mu_B \hat{V}_B$ represent the Fermi contact interaction between the electrons and the nuclear magnetic moments. Thus,

$$\hat{V}_A = \frac{2}{3}\mu_0 g_s \mu_B \sum_e \delta(\mathbf{r}_{eA}) \hat{S}_z(e) \quad (3)$$

where (using SI notation) μ_0 is the permeability of free space, μ_B is the Bohr magneton (not the magnetic moment of nucleus B), g_s is the free-electron g value, \mathbf{r}_{eA} is the position coordinate of electron e relative to nucleus A, and $\hat{S}_z(e)$ is the z -component of the spin angular momentum operator of electron e . The standard perturbation theory expression for the coupling constant is then¹⁶

$$J_{AB} = \frac{h\gamma_A\gamma_B}{2\pi^2} \sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{V}_A | \Psi_n \rangle \langle \Psi_n | \hat{V}_B | \Psi_0 \rangle}{E_n - E_0} \quad (4)$$

where Ψ_0 and $\{\Psi_n\}$ represent the ground and excited electronic states of the molecule with energies E_0 and $\{E_n\}$.

The practical approach to the quantum chemical calculation of coupling constants is by the techniques of finite perturbation theory.^{17–20}

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If the magnetic moments are treated as continuous variables, the coupling constant can be defined as a gradient, *viz.*

$$J_{AB} = \frac{h\gamma_A\gamma_B}{4\pi^2} \frac{\partial E(\mu_A, \mu_B)}{\partial \mu_A \partial \mu_B} \Big|_{\mu_A=0, \mu_B=0} \quad (5)$$

where $E(\mu_A, \mu_B)$ is the perturbed energy of the molecule, *i.e.*, the expectation value of the Hamiltonian of eq 2. If the Hellmann–Feynman theorem is obeyed, as in the case of (single reference) SCF and DFT wave functions, the simpler formula

$$J_{AB} = \frac{h\gamma_A\gamma_B}{4\pi^2} \frac{\partial}{\partial \mu_A} \langle \Psi(\mu_A) | \mu_B \hat{V}_B | \Psi(\mu_A) \rangle \Big|_{\mu_A=0} \quad (6)$$

can be used, where $\Psi(\mu_A)$ is a wave function calculated using the perturbed Hamiltonian $\hat{H}(\mu_A, 0)$.^{17–19} The differentiation in eq 6 is performed numerically.

The sum over states formula (4) is nevertheless very useful, as it enables one to interpret the coupling constant and its variation in terms of simple chemical concepts via molecular orbital (MO) theory. For a molecule with a closed shell singlet ground state, approximating the ground and excited state wave functions by the SCF determinant and its singly excited triplet spin-coupled configurations respectively results in the expression⁶

$$J_{AB} = -\Lambda_{AB} \sum_i \sum_a \frac{\langle \phi_i | \delta(\mathbf{r}_A) | \phi_a \rangle \langle \phi_a | \delta(\mathbf{r}_B) | \phi_i \rangle}{{}^3\Delta E_{i \rightarrow a}} \quad (7)$$

where $\{\phi_i\}$ and $\{\phi_a\}$ are the occupied and virtual MO's of the molecule, $\{{}^3\Delta E_{i \rightarrow a}\}$ are the appropriate singlet to triplet excitation energies, and

$$\Lambda_{AB} = \frac{1}{\pi^2} \left(\frac{2}{3} \mu_0 g_s \mu_B \right)^2 \gamma_A \gamma_B \quad (8)$$

In H_2 the most important excited state wave function corresponds to the lowest ${}^3\Sigma_u^+$ state, described by the configuration $1\sigma_g 1\sigma_u$, hence

$$J_{HD} \approx -\Lambda_{HD} \frac{\langle 1\sigma_g | \delta(\mathbf{r}_A) | 1\sigma_u \rangle \langle 1\sigma_u | \delta(\mathbf{r}_B) | 1\sigma_g \rangle}{{}^3\Delta E(1\sigma_g \rightarrow 1\sigma_u)} \quad (9)$$

The dominant contributions to the matrix elements in eq 9 are due to the hydrogen 1s atomic orbitals (AO), *e.g.*,

$$\langle 1\sigma_g | \delta(\mathbf{r}_A) | 1\sigma_u \rangle \approx c(A, \sigma_g) c(A, \sigma_u) |1s_A(\mathbf{r}_A)|^2 \quad (10)$$

where $c(A, \sigma_g)$ and $c(A, \sigma_u)$ are the coefficients of the $1s_A$ AO in the $1\sigma_g$ and $1\sigma_u$ MO's.

In the molecular hydrogen complexes of Os(II), the metal–hydrogen interaction is described in terms of σ -donation by H_2 to an empty d_σ Os orbital and d_π back-donation by Os to the H_2 σ^* MO.⁹ In other words, the $1\sigma_g$ and $1\sigma_u$ MO's of H_2 mix strongly with the appropriate metal orbitals, reducing their hydrogenic 1s character and thereby decreasing the numerator in eq 9. Assuming that the relative change in the energy ${}^3\Delta E(1\sigma_g \rightarrow 1\sigma_u)$ is small on complex formation, the variation in the HD coupling constant could be correlated with the strength of the metal–dihydrogen interaction, *i.e.*, predict a decrease in J_{HD} with increasing metal–hydrogen bond strength.

As in our previous studies,^{9–11} the calculations described here were performed using the effective core potentials (ecp) and basis sets of Stoll *et al.*²¹ to describe the heavy atoms. The osmium ecp is parametrized so as to allow for relativistic effects and the valence basis is a [5s4p3d] Gaussian set, to accommodate the valence ns , np , and nd ($n = 5$) electrons of Os^{2+} . For the carbon, nitrogen, oxygen, and chlorine atoms [2s,2p] Gaussian bases have been used. A double- ζ basis set has been chosen for the hydrogen atoms,²² which was augmented with a set of 2p polarization functions ($\zeta = 0.8$) for the

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Table 1. Calculated (BLYP) and Observed Values of H–D Coupling Constant, J_{HD} (Hz), the H_2 Binding Energy ($-\Delta E(H_2)$ kcal/mol), and H–H and Os–H Distances (Å) for the Various $[Os(NH_3)_4L^z(\eta^2-H_2)]^{(z+2)+}$ Complexes

L^z	J_{HD}		$-\Delta E(H_2)(\text{calc})$	$r_{HH}(\text{calc})$	$r_{OSH}(\text{calc})$
	calc	obs			
$(CH_3)_2CO$	6.6	4.0 ^a	45.9	1.249	1.612
H_2O	6.6	8.1 ^a	49.7	1.250	1.613
CH_3COO^-	4.8	10.0 ^a	44.5	1.316	1.635
Cl^-	5.3	10.2 ^a	45.0	1.314	1.630
H^-	22.7		22.9	0.978	1.751
C_5H_5N	20.0	19.6 ^a	32.3	0.998	1.689
CH_3CN	20.8	20.3 ^a	33.0	0.985	1.691
CN^-	22.9		23.7	0.953	1.746
NH_2OH	17.2		36.5	1.031	1.670
NH_3	16.3	15.0 ^b	37.5	1.057	1.659
H_2 (free molecule)	51.1	43.0 ^d		0.766	
	39.4 ^c				

^a Reference 26. ^b Reference 27. ^c Cl value including zero-point vibrational effects, ref 8. ^d Reference 28.

molecular hydrogen and hydride ligands. The density functional calculations reported are based on the BLYP functional, which utilizes the Becke gradient corrected exchange functional²³ and the Lee, Yang, and Parr correlation functional,²⁴ as implemented in the GAUSSIAN 94 software package.²⁵

The geometries used in this work were obtained by optimization of all geometric parameters, using analytic gradients, except those that define the intramolecular geometries of L^z and NH_3 which were frozen at their monomeric SCF values. C_s symmetry was assumed, so that the hydrogen atoms of the dihydrogen ligand are symmetry equivalent. More complete details of the geometries can be found in our previous work,¹¹ where the effects of the constrained geometry optimizations (found to be small) are also discussed.

The H–D coupling constants, in the Fermi contact approximation, were calculated by application of eq 5.

The calculations were performed using the GAUSSIAN 94 programs on HP700 series workstations.

Results and Discussion

The calculated and observed (where known) values of J_{HD} for the $[Os(NH_3)_4L^z(\eta^2-H_2)]^{(z+2)+}$ complexes are given in Table 1 along with the corresponding binding energies of H_2 , and the H–H and Os–H distances. The calculated and observed coupling constants are also compared in Figure 2. In the case of neutral *trans* ligands the agreement between the observed and calculated values of J_{HD} is excellent. For the two anionic ligands CH_3COO^- and Cl^- , the agreement is not as good, with the calculated J_{HD} values being approximately 5 Hz below the observed values. Nevertheless, these results indicate that DFT calculations for these rather large molecules are capable of providing reasonable estimates of the H–D coupling constants. The current level of agreement between experiment and theory is gratifying since previous calculations of J_{HD} for these complexes⁹ obtained by Hartree–Fock and MP2 methods yielded considerably less satisfactory agreement with experiment. The superior performance of DFT methods is attributed

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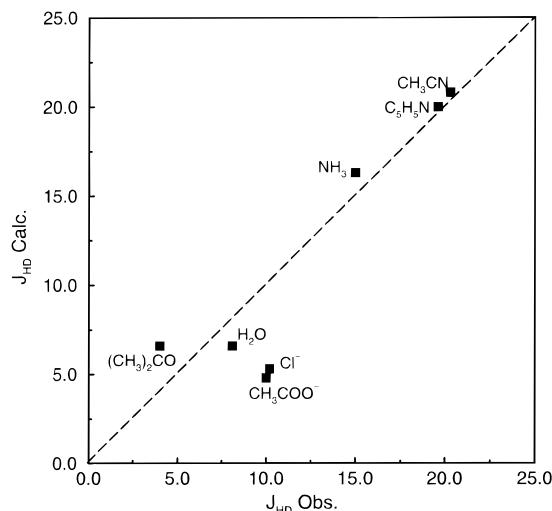


Figure 2. Comparison of the calculated and observed J_{HD} values (Hz) for a range of *trans* ligands L^z in $[Os(NH_3)_4L^z(\eta^2-H_2)]^{(z+2)+}$ complexes. (Note that the broken line is not a line of best fit but one with unit slope.)

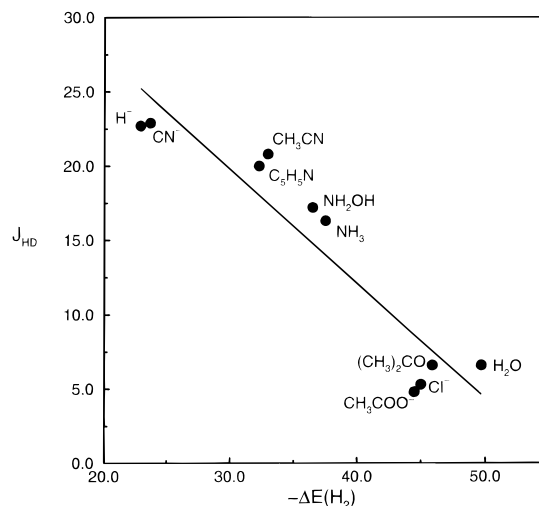


Figure 3. Correlation of the calculated H–D coupling constants (Hz) with the Os– H_2 bond strength (defined as the energy associated with the removal of the H_2 ligand from the complex ($\Delta E(H_2)$ kcal/mol) for a range of *trans* ligands L^z .

to a more accurate description of electron correlation effects in these systems than at the MP2 level.

The correlation between the calculated H–D coupling constant and metal–dihydrogen bond strength is demonstrated by the plot in Figure 3. The coupling constant decreases as the bond becomes stronger, as expected on the basis of σ -donation by H_2 and π -back-bonding by the osmium ion. The variation in Os– H_2 bond strength is also manifested in the H–H and Os–H distances. As expected, they increase and decrease respectively with the magnitude of the Os– H_2 binding energy. These relationships have been explored and discussed in considerable detail in our previous work.¹¹

The resulting correlation between the calculated H–D coupling constants and the dihydrogen bond lengths, shown in Figure 4, is very significant indeed and considerably more convincing than that between J_{HD} and the Os– H_2 bond strengths. Over the range studied the relationship is effectively linear with a slope of $-0.002 \pm 0.001 \text{ \AA/Hz}$, consistent with the experimentally observed relationships in other systems. Once the coupling constant in free HD is also considered, however, it is likely that over the full range of r_{HH} , *viz.* 0.74–1.3 Å, the

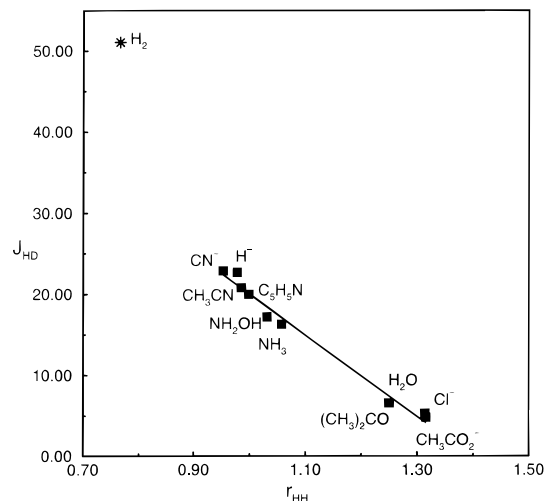


Figure 4. Correlation of the calculated J_{HD} values (Hz) with the H–H distance, r_{HH} (Å), for a range of *trans* ligands L^2 in the $[\text{Os}(\text{NH}_3)_4L^2(\eta^2\text{-H}_2)]^{(z+2)+}$ complexes.

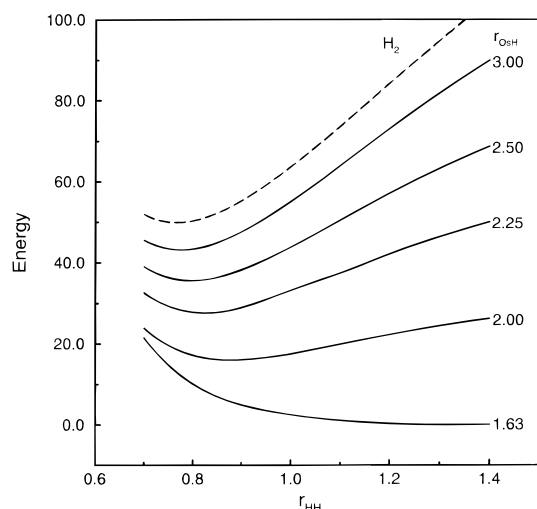


Figure 5. Variation in energy (kcal/mol) with H–H distance, r_{HH} (Å), at various values of the Os–H separation, r_{OsH} (Å), for the $[\text{Os}(\text{NH}_3)_4\text{Cl}(\eta^2\text{-H}_2)]^+$ complex (relative to the energy at equilibrium) and comparison with the energy of free H_2 (broken line, shifted by 50 kcal/mol, for ease of comparison).

relationship would be nonlinear, with a smaller $r_{\text{HD}}/J_{\text{HD}}$ gradient at the smaller H–D separations.

The influence of the osmium ion on the H–D coupling constant has been investigated in more detail for a single complex, $[\text{Os}(\text{NH}_3)_4\text{Cl}(\eta^2\text{-H}_2)]^+$, for which the H–H distance dependence of J_{HD} has been studied for a range of Os–H distances, keeping all other geometrical parameters fixed at their equilibrium values. By varying the Os–H bond lengths the corresponding bond strength is readily altered, as shown in Figure 5. As the Os–H bond becomes longer and weaker, the behavior of the molecular potential energy as a function of the H–H distance more and more resembles that in free H_2 , with the equilibrium H–H distance dropping rapidly to its free molecule value. The corresponding behavior of the HD coupling constant is shown in Figure 6. As the Os– H_2 bonds are weakened, the coupling constants become larger and the dependence on the H–H distance also gradually changes such that the decreasing trend with distance becomes less pronounced and eventually the monotonic increase with distance, as in free H_2 , becomes evident.

Given the sensitivity of J_{HD} to the bond length of the dihydrogen ligand one may speculate that, to some extent at

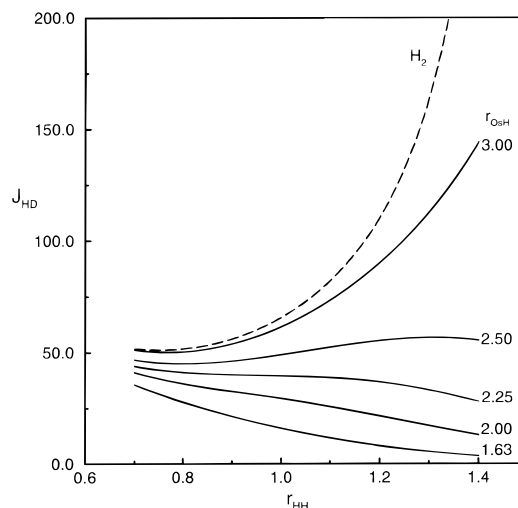


Figure 6. Variation in H–D coupling constant, J_{HD} (Hz), with H–H distance, r_{HH} (Å), at various values of the Os–H distance, r_{OsH} (Å), for the $[\text{Os}(\text{NH}_3)_4\text{Cl}(\eta^2\text{-H}_2)]^+$ complex and comparison with J_{HD} for free H_2 (broken curve).

least, the discrepancy between the predicted and observed coupling constants in the case of the anionic *trans* ligands, Cl^- and CH_3COO^- , is due to overestimation of the predicted H–H distance. In the case of Cl^- the H–H bond length would need to be ≈ 0.15 Å shorter than the calculated equilibrium value of 1.314 Å to result in a value of ≈ 10 Hz for J_{HD} . An error of that magnitude however is considered unlikely, especially since the variation in the computed H–H distances with method used, *viz.* BLYP, B3LYP, and MP2, is considerably smaller.¹¹ Another possible source of error is the neglect of solvation in this study, specifically its effect on geometries and hence coupling constants. Finally, we recognize that a definitive calculation of J_{HD} needs to include the nuclear dipole–electron orbital and spin dipolar terms that have been thus far neglected.

The variations in H–H bond length, Os– H_2 binding energy, and J_{HD} result from modulation of the nature of the H_2 binding by the *trans* ligand. We have shown elsewhere that these effects correlate,¹¹ as anticipated from the angular overlap model,²⁹ with the σ - and π -donor/acceptor properties of the ligand, measured by its experimental spectrochemical parameter.³⁰

Conclusions

The results of this study demonstrate that density functional approaches are capable of predicting the H–D spin–spin coupling constants in dihydrogen complexes fairly accurately. In agreement with the experimentally established trends, J_{HD} varies inversely with r_{HH} and hence with the strength of the Os–dihydrogen interaction. The J_{HD} versus r_{HH} correlation is opposite to that noted in free HD, indicating that in these complexes the H–D coupling constant is largely determined by the nature of the metal–dihydrogen bond.

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