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Nuclear Dynamics Discrete Variable Representation Study of the Equilibrium Isotope Effect on H_2 Binding in $M(\eta^2\text{-}H_2)L_n$ Complexes: An Effective Theoretical Way To Account for Anharmonicity

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Equilibrium isotope effects (EIE) on the binding of H_2 and D_2 to transition metal complexes are calculated for a modeled version of $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$, $[Ru(H\cdots H)(C_5Me_5)(dppm)]^+$ and *trans*-$[Os(H\cdots H)Cl(dppe)_2]^+$. Being probably unsatisfactorily described by the harmonic approach (specially in the elongated dihydrogen complexes), the thermodynamic contribution of the H−H stretching related modes is evaluated by means of nuclear motion quantum calculations. The Discrete Variable Representation (DVR) methodology is applied to obtain the anharmonic vibrational spectrum on the bidimensional B3LYP potential surface. From these results, the associated partition function is calculated and used to correct the harmonic EIE and other thermodynamic magnitudes. In agreement with experimental results, the anharmonically corrected EIE for the W complex turns out to be inverse (0.534 at 300 K). On the contrary, the corrected EIE for the Ru and Os complexes is clearly normal (1.217 and 1.685 at 300 K, respectively), predicting an unusual behavior for ML_nH_2 compounds. Comparison with the pure harmonic EIE's leads to the conclusion that the harmonic approach is inadequate to describe the properties of the elongated dihydrogen complexes.

I. Introduction

Isotope effects provide useful information about the molecular properties (structure and reactivity) of the organometallic compounds,[1] specially in fluxional (nonrigid) transition-metal complexes involving dihydrogen or/and hydride ligands. In particular, isotope effects have become a very important tool in the mechanistic study of the reversible oxidative addition of molecular hydrogen to transition-metal complexes, one of the most interesting and characteristic reactions of transition-metal chemistry. Several papers have recently appeared concerning deuterium equilibrium isotope effects (EIE's) for the addition of H_2 and D_2 to various transition-metal complexes in solution to form either metal dihydride/dideuteride complexes[2] or dihydrogen/dideuterium complexes.[3] EIE's are defined as K_H/K_D, where K_H is the equilibrium constant for the perprotio reaction and K_D stands for the equilibrium constant of the isotopically substituted reaction. By definition, an EIE is normal if it is greater than unity, whereas it is inverse if it is less than unity. Observed EIE's for H_2 versus D_2 addition turn out to be usually inverse,[4] with typical values of K_H/K_D around 0.50 or less, showing that metal complexes bind D_2 better than they do H_2 over a large temperature range.

Of special interest is the very recent study[4] of the EIE on H_2 binding to the dihydrogen complex $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$, one of the so-called Kubas complexes (the first isolable dihydrogen complexes). In that paper Bender, Kubas, Hoff and co-workers use the measured vibrational frequencies arising from the corresponding infrared spectra to obtain the molecular translational, rotational and vibrational partition functions ratios as described in the general treatment of equilibrium isotope effects by Bigeleisen and Goeppert-Mayer.[5] From their calculations they get a modest inverse EIE value of 0.78 at 300 K. In addition, by comparison of the equilibrium constants for displacement of N_2 by H_2 or D_2 in the complex $W(CO)_3(PCy_3)_2(N_2)$ in THF solution they obtain an EIE value of 0.70 ± 0.15 at 295 K. At first glance these results seem counterintuitive because the large decrease in the H−H (D−D) stretching frequency due to the H_2 (D_2) binding to the complex should produce a large normal EIE. However, Bender, Kubas, Hoff and co-workers show that the contributions of the five new vibrational modes that appear in the addition product (coming from the original five translational and rotational degrees of freedom in the free hydrogen molecules) overcome the normal contributions of the H−H (D−D) stretching mode and the translational and rotational degrees of freedom, this way leading to an overall inverse EIE.

At this point, an inverse deuterium EIE seems the rule rather than the exception for the addition of molecular hydrogen to suitable metal complexes to form either dihydride or dihydrogen transition-metal complexes. However, we wondered what the EIE would be for the formation of the particular group of transition-metal dihydrogen complexes known as elongated dihydrogen complexes.[6] These complexes fill the gap between classical polyhydrides (with H−H distances at or above 1.6 Å) and nonclassical dihydrogen complexes (which have H−H distances below 1.0 Å). Some of us[7a,b] have recently used a combined electronic Density Functional Theory plus nuclear dynamics study of two complexes to prove that the existence and several properties of the elongated dihydrogen complexes can be explained taking into account the quantum vibrational motion of the hydrogen nuclei on a very anharmonic potential energy surface.

The first purpose of this paper is to theoretically study the deuterium equilibrium isotope effect for the addition of molecular hydrogen to a complex leading to an elongated dihydrogen transition-metal complex. To this aim we will calculate the equilibrium constants of the several equilibria of the type pictured in Scheme 1. Concretely, we will study the EIE corresponding to the formation of the elongated dihydrogen

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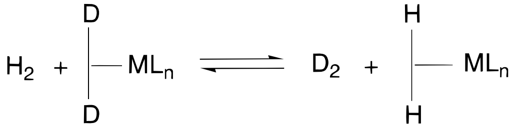
SCHEME 1



complexes [Ru(H···H)(C_5Me_5)(dppm)]$^+$ and *trans*-[Os(H···H)-Cl(dppe)$_2$]$^+$ (dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane). For the sake of comparison, the case corresponding to the formation of the dihydrogen complex W(CO)$_3$(PCy$_3$)$_2$(η^2-H_2) will also be considered. On the other hand, it has to be emphasized that, as mentioned above, the interesting properties of the elongated dihydrogen complexes arise from the high anharmonicity of the H−H stretching and that the related vibrational modes are very sensitive to it. As a consequence, any theoretical calculation of the EIE for these complexes should include vibrational anharmonicity in a reliable way. So, the second purpose of this paper is to devise an effective strategy which allows for the practical calculation of the anharmonic vibrational levels that influence the EIE in dihydrogen transition-metal complexes, so that the vibrational partition functions (and the EIE) can be reliably computed at a reasonable cost.

II. Calculational Details

As stated in the Introduction, this work is devoted to obtain equilibrium isotope effects. To this aim we have used a statistical thermodynamic formulation[8] as described in the next section. The molecular partition functions were first computed within the ideal gas, rigid rotor, and harmonic oscillator models. Then a treatment to introduce anharmonicity was employed. A pressure of 1 atm and a temperature of 300 K have been assumed in all the calculations. Two different types of quantum results are required. Electronic structure calculations provide the geometry of the minimum energy structures and permits to build up a sizable part of the potential energy surface (PES). Nuclear motion calculations have been carried out to determinate vibrational (anharmonic) energy levels and their associated vibrational wave functions. Some technical details of both sets of calculations follows.

A. Electronic Structure Calculations. For saving computational effort some modeling has been made on the experimental complexes. The three cyclohexyl groups in the Kubas complex were changed by three hydrogen atoms; the C_5Me_5 unit and the four phenyl groups in the dppm ligand were substituted by a cyclopentadienyl and four hydrogen atoms, respectively, in the ruthenium complex; finally, in the osmium complex the four phenyl groups in the dppe ligand were changed by four hydrogen atoms. As a result the dihydrogen complexes that have actually been studied are W(CO)$_3$(PH$_3$)$_2$(η^2-H_2), [Ru(H···H)(C_5H_5)($H_2PCH_2PH_2$)]$^+$ and *trans*-[Os(H···H)Cl-($H_2PCH_2CH_2PH_2$)$_2$]$^+$.

All electronic structure calculations have been carried out with the GAUSSIAN 98 series of programs.[9] To solve the electronic Schrödinger equation, the density-functional theory (DFT)[10] methodology has been used. This methodology meets the requirements of high accuracy and reasonable cost, and has been employed with great success to study several organometallic systems, including dihydrogen and polyhydride complexes.[7a,7b,11] The three-parameter hybrid functional of Becke and the Lee, Yang and Parr's correlation functional, widely known as Becke3LYP,[12] have been used.

To reduce the cost of the computations an effective core operator has been used to replace the 60 innermost electrons of the tungsten atom in the Kubas complex. For the 14 outer electrons of the metal atom the basis set was that associated with the pseudopotential of Hay and Wadt[13] with a standard valence double-ξ LANL2DZ contraction.[14] The basis set for the hydrogen atoms directly attached to the metal was a double-ξ supplemented with a polarization p shell.[15,16] A 6-31G basis set[15] was used for the H atoms attached to a P or a C atom, as well as for carbon and oxygen atoms. The phosphorus atoms were described with the 6-31G(d) basis set.[17]

Most of the electronic results for the two elongated dihydrogen complexes have been taken from our previous papers.[7a,7b,18] However, a few new electronic calculations have been carried out for these two complexes using the same level of calculation described there. That is, an effective core operator replacing the inner electrons (28 and 60 in the ruthenium and osmium atoms, respectively), and the basis set associated with the pseudopotential of Hay and Wadt[13] with a standard valence double-ξ LANL2DZ contraction[14] for the 16 outer electrons in both ruthenium and osmium atoms.The basis set for the hydrogen atoms directly attached to the metal was a double-ξ supplemented with a polarization p shell.[15,16] A 6-31G basis set[15] was used for the H atoms attached to a P or a C atom, as well as for carbon atoms. The phosphorus atoms were described with the 6-31G(d) basis set.[17] For the chlorine atom in the osmium complex a 6-31G(d) basis set[17] was used. Finally, a 6-31G(p) basis set was used for the free hydrogen molecule whose geometry has been optimized.

The Z-matrices of the minimum energy structures corresponding to the Kubas complex and the elongated dihydrogen complexes have been obtained from the authors of the ref 19 and from our previous results, respectively.[7a,b] Geometry optimizations have been performed using the Schlegel gradient optimization algorithm using redundant internal coordinates.[14,20]

For each minimum energy structure analytical second derivatives of the energy with respect to the Cartesian coordinates have been computed to obtain the frequencies and eigenvectors associated with each vibrational normal mode within the harmonic approximation. For complexes described by means of pseudopotentials this is a new feature included in GAUSSIAN 98.[9] For those systems GAUSSIAN 94[14] and previous versions only allow numerical second derivatives calculation by finite differences of analytically computed first derivatives, this way involving very time-consuming calculations. The fact that all the frequencies turn out to be real confirms that the located points are actual minima of the PES.

The normal modes have been recalculated for each dideuterated minimum energy structure in order to obtain the frequencies and eigenvectors corresponding to the isotopically substituted species.

B. Nuclear Motion Calculations. As explained in the next section, introducing the anharmonicity effects in the elongated dihydrogen transition-metal complexes requires the solution of the nuclear Schrödinger equation (vibrational energy levels and wave functions) over a suitable PES built up from electronic calculations. Concretely, we have chosen a two-dimensional PES as a function of the interatomic distance between the two hydrogen (deuterium) atoms of the H_2 (D_2) unit of the complex and the distance between the metal atom and the point halfway between those two hydrogen (deuterium) atoms. These two parameters behave as orthogonal coordinates, in such a way that no coupled terms between them appear in the nuclear kinetic operator of the corresponding nuclear Schrödinger equation, that is,

$$\hat{T} = \frac{-\hbar^2}{2\mu_x}\frac{\partial^2}{\partial x^2} + \frac{-\hbar^2}{2\mu_y}\frac{\partial^2}{\partial y^2} \tag{1}$$

where x and y stand for the H−H and $M-H_2$ distances, respectively.

When calculating the PES, global relaxation of the rest of geometrical parameters has been allowed. Some additional details concerning the PES are given in the next section.

To solve the nuclear Schrödinger equation a discrete variable representation (DVR)[21,22] has been used. This method has already been applied with success in the field of organometallic chemistry.[7] Computationally, the DVR has great advantages over the more traditional variational basis representation, in which the energy levels are obtained by diagonalization of the matrix representation of the projection of the Hamiltonian operator on a given basis set. In short, the DVR is a grid-point representation instead of a basis set representation, and thus it facilitates the calculation of the potential energy integrals V_{ij}. In this representation, the potential energy matrix is diagonal,

$$V_{ii'} = \delta_{ii'}V(x_i) \tag{2}$$

and the kinetic energy matrix is very simple,

$$T_{ii'} = \frac{\hbar^2(-1)^{i-i'}}{2m\Delta x^2}\begin{Bmatrix} \pi^2/3 & i = i' \\ \dfrac{2}{(i-i')^2} & i \neq i' \end{Bmatrix} \tag{3}$$

leading to a very sparse Hamiltonian matrix easier to diagonalize than those coming from a basis set representation,

$$H_{ij,i'j'} = T_{ii'}\delta_{jj'} + T_{jj'}\delta_{ii'} + \delta_{ii'}\delta_{jj'}V(x_i, y_j) \tag{4}$$

In this paper the generic DVR proposed by Colbert and Miller[22] has been used. Once the grid-point representation of the nuclear Hamiltonian has been built up, the nuclear energy levels and wave functions are found through diagonalization of this matrix. The nuclear wave functions Ψ_i are obtained as a linear combination of associated basis functions ϕ_j

$$\Psi_i = \sum_{j=1}^{N_p} c_{ij}\phi_j \tag{5}$$

where N_p is the total number of points in the grid. In a general two-dimensional case whose two dimensions are labeled x and y, ϕ_j are functions of the form

$$\phi_j(x, y) = \frac{\sin\left(\dfrac{\pi(x - x_m)}{\Delta x}\right)}{\pi(x - x_m)} \cdot \frac{\sin\left(\dfrac{\pi(y - y_m)}{\Delta y}\right)}{\pi(y - y_m)} \tag{6}$$

being x_m and y_m the (x, y) coordinates of the grid point associated with the basis function ϕ_j, and Δx and Δy the spacings in the x and y directions of the grid. The wave function has to be normalized prior to any calculation involving it.

III. Results and Discussion

According to the well-known formulas of the statistical thermodynamics,[8] we will calculate the deuterium equilibrium isotope effect as the equilibrium constant (K_H/K_D) of the equilibrium displayed in Scheme 1. For the three cases studied in this work ML_n stands for $W(CO)_3(PH_3)_2$, $[Ru(C_5H_5)(H_2PCH_2PH_2)]^+$ and *trans*-$[OsCl(H_2PCH_2CH_2PH_2)_2]^+$.

A. Harmonic EIE. First of all, within the harmonic approximation, we have used the molecular partition functions provided by GAUSSIAN 98 for each chemical species in Scheme 1 to evaluate the harmonic EIE's. In addition, we have decomposed each EIE as the product of three factors: the translational-rotational contribution (TRANSROT); the factor corresponding to the contribution of the ground vibrational states, that is, only including the zero-point energy levels (ZPE); and the factor that appears when the excited vibrational energy levels are taken into account (EXC). The corresponding results are shown in Table 1. Our harmonic EIE for the complex $W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$ turns out to be inverse, although numerically is somewhat lesser (that is to say, the isotope effect turns out to be more intense) than the value calculated by Bender, Kubas, Hoff and co-workers[4] from the infrared spectra. The difference stems fundamentally from the ZPE factor, which is the main responsible of the inverse behavior. On the other hand, the complexes $[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$ and *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$ also give inverse harmonic EIE's, with figures that do not qualitatively differ from those corresponding to the Kubas complex. Then, our theoretical results seem to confirm the inverse deuterium EIE as a rule for the formation of the transition-metal dihydrogen complexes, at least within the harmonic approximation.

B. Anharmonic EIE. We wondered what the effect of the anharmonicity on the EIE's would be, specially for the elongated dihydrogen complexes. Theoretical harmonic vibrational frequencies are, in general, overestimated[23] because of incomplete incorporation of electron correlation, the use of finite basis sets and, as a major source of error, the neglect of anharmonicity effects. For this reason, scaling factors are often applied prior to the use of the frequencies in the EIE calculations. Scaling factors for obtaining fundamental vibrational frequencies, low-energy vibrations, zero-point vibrational energies and thermal contributions to enthalpy and entropy from theoretical harmonic frequencies have been determined by Scott and Radom[24] by fitting to experimental values. To our knowledge, no scaling factors have been explicitly developed for calculating isotope effects through vibrational partition functions. Perhaps the scaling factors recommended for the prediction of the zero-point vibrational energies or the thermochemical quantities, at the Becke3LYP/6-31G(d) level, could be appropriate (0.9806, 0.9989, and 1.0015 for the zero-point vibrational energies, the thermal contribution to enthalpy and the thermal contribution to entropy, respectively).[24] Note that in this formalism we are looking for anharmonically corrected frequencies that provide good results when used in the harmonic expression of the vibrational partition function. As a matter of fact this is the approach adopted by Bender, Kubas, Hoff and co-workers[4] when introducing the measured vibrational frequencies from the infrared spectra (and so including anharmonicity) in the harmonic treatment of Bigeleisen and Goeppert-Mayer.[5] However, we decided not to use any scaling factors in this paper for two reasons. First of all, the above indicated scaling factors are very close to one and they do not appreciably modify the calculated EIE's indicated in Table 1. Second, those scaling factors have not been fitted to reproduce properties of transition metal complexes and even less to account for the high degree of anharmonicity found in the elongated dihydrogen complexes.

Instead of calculating anharmonically corrected frequencies, in the present paper we will try to determine directly the anharmonic vibrational energy levels. Assuming an independent normal-mode framework (i.e., no mode−mode coupling), the vibrational partition function of the molecule is separable as a

TABLE 1: Harmonic EIE's and Contributions to Them

	$W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$	$[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$	*trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$
TRANSROT	5.519 (5.77)	5.470	5.553
ZPE	0.131 (0.20)	0.135	0.189
EXC	0.675 (0.67)	0.729	0.665
EIE	0.486 (0.78)	0.538	0.696

Numbers in parentheses correspond to the values calculated by Bender, Kubas, Hoff and co-workers from the infrared spectra.

product of the contributions corresponding to each individual normal mode. The potential energy along a single mode could be expanded in a series of powers of the associated normal coordinate with coefficients given by the second, third, fourth and higher numerical directional derivatives of the potential energy along the normal-mode direction. If the vibrational energy levels E_i^m of the one-dimensional potential energy along the mode m can be determined in some way, the vibrational partition function for mode m (q_m) can be calculated as

$$q_m = \sum_i e^{-E_i^m/k_BT} \qquad (7)$$

where k_B is the Boltzmann's constant. To avoid the calculation of high numerical derivatives (with the associated lack of accuracy) it is better to build up a one-dimensional potential energy surface as a function of each normal coordinate. Then we can solve the nuclear Schrödinger equation by means of the DVR method to find the vibrational energy levels, which incorporate the anharmonicity associated with each normal mode in a natural way.

Our three dihydrogen transition-metal complexes have between 17 and 28 nuclei, what implies dealing with 45−78 vibrational normal modes. Application of the above outlined procedure to each normal mode is a task out of reach. Instead, to account for the anharmonicity in a practical way, we propose an attainable strategy that works in the following fashion:

(a) The most anharmonic vibrational normal modes are previously chosen (they will be called anharmonic modes from here on).

(b) For each anharmonic normal mode a one-dimensional PES as a function of the corresponding normal coordinate is built up.

(c) The DVR method is used to solve the nuclear Schrödinger equation over the PES associated with each anharmonic normal mode, therefore obtaining the corresponding anharmonic vibrational energy levels.

(d) The anharmonic vibrational partition function for each anharmonic normal mode is computed through eq 7.

(e) The anharmonic vibrational partition function of the molecule is calculated as a product of the anharmonic vibrational partition functions corresponding to the anharmonic normal modes and the harmonic vibrational partition functions corresponding to the remaining normal modes (the ones that can be considered harmonic modes). As a matter of fact, this is done by substituting the original harmonic contributions of the anharmonic modes in the totally harmonic vibrational partition function of the molecule by their corresponding anharmonic vibrational partition functions.

What are the main sources of anharmonicity in the dihydrogen transition-metal complexes that can influence the EIE's? Indeed they will be associated with the dihydrogen ligand. Owing to the large mass difference between the light hydrogen (or deuterium) nuclei and the heavy rest of the complex, the normal modes involving the hydrogen (or deuterium) nuclei consist fundamentally of their motion. There are 6 such vibrational modes.[4] The associated normal coordinates can be defined from suitable displacement coordinates adapted to symmetry, which are pictured in Figure 1. These symmetry coordinates correspond to the unique vibrational mode (the H−H stretching) and the lost translational and rotational degrees of freedom for free hydrogen. Assuming that the hydrogen nuclei move under the field of a heavy point center (ML_n) formed by the rest of the complex, their symmetry point group is C_{2v}. Figure 1 also shows the irreducible representation to which each symmetry coordinate belongs. There are two totally symmetrical coordinates (A_1), two coordinates with symmetry species B_1, one B_2 symmetry coordinate and one A_2 symmetry coordinate. Each normal coordinate has to be a linear combination of the symmetry coordinates that belong to the same irreducible representation of this normal coordinate. For instance, the normal coordinates of the two A_1 modes are linear combination of the two A_1 symmetry coordinates (the H−H stretching and the symmetric $M-H_2$ stretching).

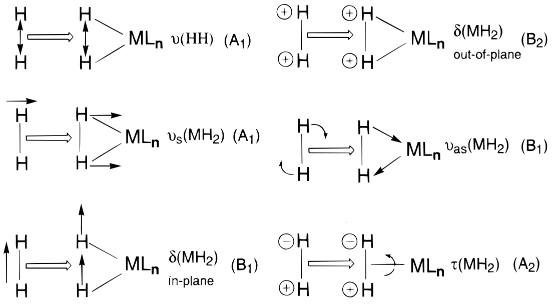


Figure 1. Symmetry coordinates associated with the dihydrogen ligand along with their irreducible representation in a C_{2v} symmetry point group. For the three cases studied in this work ML_n stands for $W(CO)_3(PH_3)_2$, $[Ru(C_5H_5)(H_2PCH_2PH_2)]^+$ and *trans*-$[OsCl(H_2PCH_2CH_2PH_2)_2]^+$.

The major anharmonicity effect is probably related to the H−H stretching (specially for the elongated dihydrogen complexes), which participates in the two A_1 normal modes. Then both A_1 normal modes have to be considered as anharmonic modes in the sense defined above. In addition, it is expected that anharmonicity couples significantly the two modes of the same symmetry. Therefore, we will assume the independent normal-mode framework neglecting all the mode−mode couplings but the coupling between the two A_1 modes, that will not be separated in our treatment. This assumption slightly modifies the above introduced a−e working scheme, in the sense that both anharmonic normal modes are studied together over a two-dimensional PES as a function of the two symmetry coordinates that define the corresponding normal coordinates. This leads to a two-dimensional anharmonic vibrational partition function that will substitute the two original one-dimensional harmonic contributions of the anharmonic modes in the harmonic vibrational partition function of the molecule, in this way leading to the anharmonic vibrational partition function of the molecule.

A series of electronic structure calculations have been performed to construct the two-dimensional PES for the complex $W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$. A collection of 120 points, each corresponding to a different set of H−H and $W-H_2$ distances, has

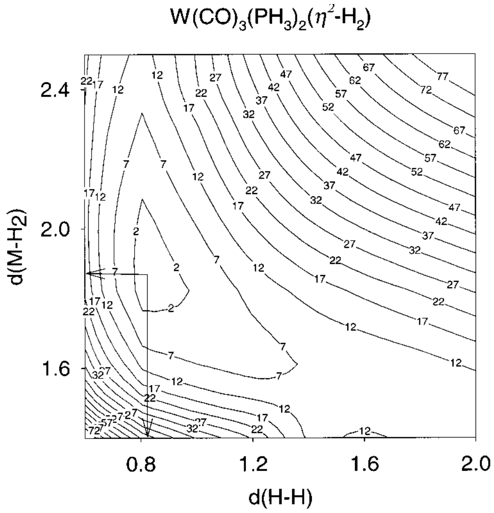


Figure 2. Contour plot of the two-dimensional potential energy surface for the complex $W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$. Distances are given in Å. Energy contours appear every 5 kcal/mol. The arrows indicate the position of the minimum energy structure (d(H−H) = 0.832 Å and $d(M-H_2)$ = 1.872 Å).

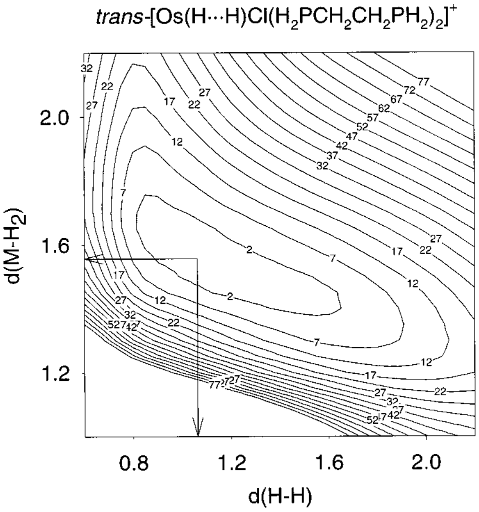


Figure 3. Contour plot of the two-dimensional potential energy surface for the complex *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$. Distances are given in Å. Energy contours appear every 5 kcal/mol. The arrows indicate the position of the minimum energy structure (d(H−H) = 1.071 Å and $d(M-H_2)$ = 1.567 Å).

been calculated. The ranges covered have been from 0.6 to 2.0 Å for the H−H distance, and from 1.4 to 2.5 Å for the distance between the tungsten atom and the midpoint halfway between the two hydrogen atoms. The resulting points have been fitted into a two-dimensional cubic splines functional form,[25] which is a smooth and continuous function. Figure 2 depicts the two-dimensional PES as a contour plot.

Analogous two-dimensional PES′ were built up for the two elongated dihydrogen complexes in two previous papers.[7a,b] For the complex $[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$ the range for the H−H distance covered from 0.59 to 2.29 Å, while the $Ru-H_2$ distance covered from 1.00 to 2.20 Å. As for the complex *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$, the intervals were from 0.6 to 2.2 Å and from 1.0 to 2.2 Å for the H−H and the $Os-H_2$ distances, respectively. From those two works we have borrowed the corresponding fitted two-dimensional cubic splines. The PES′ for the complexes $[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$ and *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$ turn out to be qualitatively similar and for the sake of conciseness only the second one has been pictured in Figure 3.

Comparison between Figures 2 and 3 discloses important differences. The first one concerns to the position of the minimum energy structure. For the Kubas complex it is found at d(H−H) = 0.832 Å and $d(W-H_2)$ = 1.872 Å, whereas the corresponding values of the minimum energy structure for the complex *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$ are 1.071 and 1.567 Å, respectively. However, the most important point is the shape of the PES in the region next to the minima. Around the minimum energy structure of the Kubas complex, a normal dihydrogen complex, the potential energy valley is quite parallel to the $W-H_2$ axis with a trend to curve along the H−H direction as the $W-H_2$ distance shortens (Figure 2). As a consequence, the two normal modes of A_1 symmetry, although mixed to some extent (as already pointed out by Bender, Kubas, Hoff and coworkers[4]), can be still identified, respectively, with the two A_1 symmetry coordinates. That is to say, one normal mode is basically the H−H stretching and the other one is essentially the symmetric $M-H_2$ stretching. This is, probably, a common feature of the normal dihydrogen transition-metal complexes. The scenario for the *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$ clearly differs (Figure 3). In this case the potential energy valley surrounding the minimum energy structure is oblique, in such a way that none of the two A_1 normal modes can be identified at all with one of the A_1 symmetry coordinates depicted in Figure 1. Along the normal mode that is roughly parallel to the energetically smooth oblique valley, the stretching of the H−H bond leads to shortening of the $M-H_2$ distance, and vice versa. On the other hand, the other normal mode is orthogonal to the first one and consists of the simultaneous stretching (or compression) of both the H−H bond and the $M-H_2$ distance. Apart from the obliqueness of the two A_1 normal modes that imposes a global treatment, this valley is highly anharmonic, this being a crucial factor in determining the interesting properties of the elongated dihydrogen transition metal-complexes.

Once the two-dimensional cubic splines that define the PES′ have been obtained, the corresponding nuclear Schrödinger equations can be solved using the DVR method. First of all, a certain reduced mass has to be assigned to each degree of freedom in the Hamiltonian. As in our previous works,[7a,b,18] the reduced masses for the motion along the symmetry coordinates have been calculated (for the perprotio complexes) as

$$\frac{1}{\mu_{\mathrm{d(H-H)}}} = \frac{1}{m_{\mathrm{H(A)}}} + \frac{1}{m_{\mathrm{H(B)}}}$$

$$\frac{1}{\mu_{d(\mathrm{M-H_2})}} = \frac{1}{m_{\mathrm{H_2}}} + \frac{1}{m_{[\mathrm{ML}_n]}} \tag{8}$$

Note that the reduced masses of the dideuterated complexes can be calculated in an analogous way. Then, the matrix representation of the nuclear Hamiltonian over a rectangular grid of equally spaced points has been constructed. Different sizes of each grid have been tested until convergence of the energy levels has been achieved. The characteristics of the final grids chosen for the different systems have been as follows: 35 × 27 = 945 for both the perprotio and the dideuterated complexes $W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$; 29 × 21 = 609 for both the perprotio and the dideuterated complexes $[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$; and 33 × 25 = 825 and 37 × 27 = 999 for the perprotio and the dideuterated complexes *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$, respectively (the format used is: number of points along the H−H coordinate × number of points

TABLE 2: Anharmonic EIE's (see text) and Contributions to Them

	$W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$	$[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$	*trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$
TRANSROT	5.519	5.470	5.553
ZPE	0.143	0.323	0.505
EXC	0.676	0.689	0.601
EIE	0.534	1.217	1.685

TABLE 3: Thermodynamic Functions (300 K) Corresponding to the Equilibria of the Type Pictured in Scheme 1[a]

	$W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$		$[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$		*trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$	
	har	anhar	har	anhar	har	anhar
ΔH^b	0.906	0.871	0.912	0.350	0.688	0.041
ΔS^c	1.587	1.663	1.806	1.555	1.584	1.157
ΔG^b	0.431	0.373	0.370	−0.117	0.216	−0.314

[a] Har and Anhar stand for the Harmonic and Anharmonic aproximations, respectively. [b] In kcal·mol^{-1}. [c] In cal·mol^{-1}·K^{-1}

along the $M-H_2$ coordinate = total number of points). Diagonalization of the corresponding 6 matrices provides the 6 sets of vibrational wave functions (eigenvectors) and anharmonic energy levels (eigenvalues). These energy levels permit the calculation of the anharmonic vibrational partition function of each molecule according to the procedure outlined above and then the anharmonic EIE's are obtained.

Table 2 exhibits the anharmonic EIE's and their decomposition in factors (evidently the TRANSROT contribution is the same as in Table 1). Comparison of Tables 1 and 2 shows that anharmonicity does not significantly alter the EXC factor. The important changes only concern the ZPE factor. For the complex $W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$ anharmonicity augments just slightly the ZPE contribution and, therefore, the EIE. The anharmonic EIE, still clearly inverse, is somewhat closer to the experimental values than the harmonic EIE. Taking into account the range of uncertainty of the experimental values[4] (0.78 from infrared spectra or 0.70 ± 0.15 from displacement of N_2) and that anharmonicity has been only partially incorporated, the agreement is rather good. Anyway, we have shown that anharmonicity tends to favor the addition of H_2. This effect is magnified in the two highly anharmonic elongated dihydrogen complexes. The anharmonic EIE's for the complex $[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$ and, specially, for the complex *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$ (even more anharmonic than the complex of ruthenium) become clearly normal. Then, we predict theoretically that the deuterium equilibrium isotope effect for the addition of molecular hydrogen to a transition-metal complex leading to the formation of $[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$ or *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$ is clearly normal. That is to say, H_2 binds better than D_2 to both $[Ru(C_5H_5)(H_2PCH_2PH_2)]^+$ and $[OsCl(H_2PCH_2CH_2PH_2)_2]^+$, and this conclusion is probably general for the formation of any elongated dihydrogen transition metal complex.

Why anharmonicity tends to favor the addition of H_2? Isotopic substitution by deuterium lowers the vibrational energy levels corresponding to normal modes that consist fundamentally of motion of hydrogen nuclei, that is, the 6 normal modes associated with the dihydrogen ligand (Figure 1). The key is that the larger the anharmonicity of the normal modes sensitive to the isotopic substitution in the dihydrogen complex, the smaller the gap between the equivalent HH and DD vibrational energy levels. Along the addition, the change in the HH/DD zero-point energy gap for the normal mode corresponding originally to the H−H (D−D) stretching in the free hydrogen molecule gives a normal ZPE factor (a value greater than unity). This effect is larger as the HH/DD gap is smaller in the dihydrogen complex. On the contrary, conversion of the 5 translational and rotational modes in free hydrogen to vibrational normal modes in the dihydrogen complex leads to an inverse ZPE factor (a value smaller than unity), this effect being smaller as the HH/DD gap is more reduced in the dihydrogen complex. As a consequence of all this, anharmonicity increases the numerical values of the ZPE factors associated with the dihydrogen ligand (the normal and inverse factors become more normal and less inverse, respectively), so tending to produce a normal EIE. This effect is so important in the highly anharmonic elongated dihydrogen transition-metal complexes that the EIE becomes normal.

Finally, we have to remark that the anharmonic corrections calculated in this paper are based on a two-dimensional approach. Indeed, this reduction of dimensionality is a limitation. However, the results obtained at the 2D approximation sounds reasonable. As a matter of fact, the major source of anharmonicity is related with the H−H stretching, which participates in the two A_1 normal modes. Given the size of the systems, inclusion of more dimensions (B_1 normal modes) would be out of reach. On the other hand, incorporation of coupling would be desireable but it is not probably necessary in order to obtain a reasonable prediction that can be useful for experimentalists.

C. Thermodynamic Functions. We have calculated the thermodynamic functions at 300 K corresponding to the equilibria of the type pictured in Scheme 1. The harmonic values are obtained from the harmonic molecular partition functions according to the suitable statistical thermodynamic formulas.[8] We have determined the anharmonic values by substituting in the corresponding expressions the contributions of the two original one-dimensional harmonic vibrational partition functions of the two anharmonic modes by the contribution of the two-dimensional anharmonic vibrational partition function. Results are shown in Table 3. Note that ΔH also gives the reaction enthalpy difference ($\Delta\Delta H$) between the addition of H_2 to a transition-metal complex leading to the formation of a dihydrogen complex and the corresponding addition of D_2. The same is true for the entropy and the Gibbs energy.

For the complex $W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$ it is clear that, as already found by Bender, Kubas, Hoff and co-workers,[4] D_2 binding is enthalpically favored over H_2 binding, but it is disfavored entropically. Anharmonic values are somewhat closer to the experimental thermodynamic functions ($\Delta H = 0.64$ kcal mol^{-1} and $\Delta S = 1.7$ cal mol^{-1} K^{-1}), the agreement being excellent. Our corresponding EIE's (see above) have been apparently not so good in comparison with the experimental results, but it has to be recalled that EIE's are measured as equilibrium constants, that is, as exponential functions of ΔG and, indeed, they are much more sensitive to small errors (theoretical or experimental). On the other hand, anharmonicity lowers the endothermicity of equilibria indicated in Scheme 1

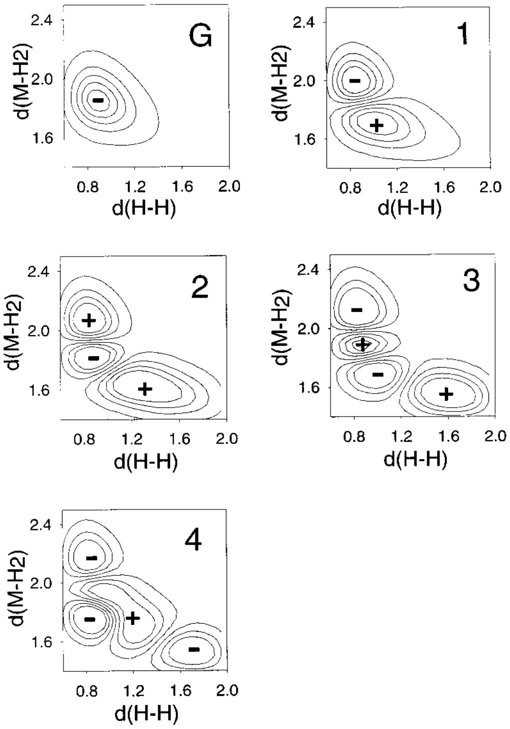


Figure 4. Contour plots of the vibrational wave functions associated with the ground vibrational state (G) and the first (1), second (2), third (3) and fourth (4) excited states for the complex $W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$. Distances are given in Å. (+) and (−) refer to the sign of the vibrational wave function in order to indicate where the nodes are.

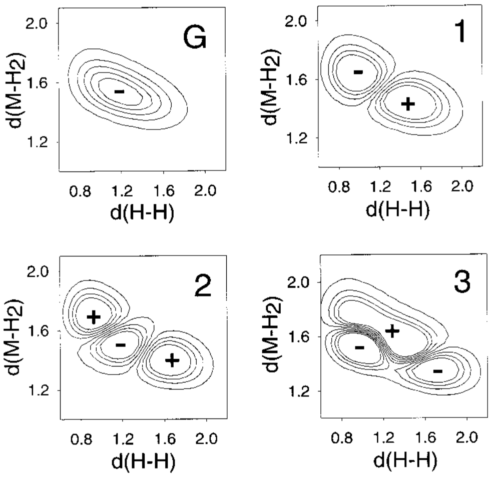


Figure 5. Contour plots of the vibrational wave functions associated with the ground vibrational state (G) and the first (1), second (2) and third (3) excited states for the complex *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$. Distances are given in Å. (+) and (−) refer to the sign of the vibrational wave function in order to indicate where the nodes are.

because it also reduces the gap among the equivalent HH and DD vibrational energy levels in the dihydrogen complexes. This effect is again highly amplified in the two elongated dihydrogen complexes, for which that endothermicity becomes quite small (only when anharmonicity is introduced). In these cases the entropic term ($-T\Delta S$) dominates at this temperature and the EIE becomes normal. It becomes manifest that anharmonicity is cleary required to describe correctly the thermodynamic of the process for the elongated dihydrogen transition-metal complexes.

D. Anharmonic Vibrational Wave Functions. A final point concerns the anharmonic vibrational wave functions obtained as eigenvectors of the DVR matrices. For the sake of brevity, we will only comment the vibrational wave functions corresponding to the perprotio complexes $W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$ and *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$. Figures 4 and 5 present the contour plots of the wave functions associated with the ground vibrational state and the first excited states for both the Kubas complex and the elongated dihydrogen complex, respectively. The ground wave function spreads on the low-energy basin around the minimum energy structure on the PES. Conversely, excited wave functions tend to progressively expand toward higher energy regions. As a matter of fact the wave functions reflect the shape of the corresponding PES. So, the ground wave function for the Kubas complex surrounds rather symmetrically the minimum (compare Figures 2 and 4), showing a slight deviation along the H−H direction as the W−H_2 distance shortens. The wave functions associated with the first, second and third excited states present one, two and three nodal lines, respectively. These states are all vibrationally excited states corresponding to progressive excitations of the normal mode that is basically the W−H_2 stretching which is the direction with smoothest slope around the minimum on the PES. However, the progressive expansion of the excited wave functions along the H−H direction suggests that the symmetric W−H_2 stretching normal mode mixes more and more with the H−H stretching normal mode as the order of the excitation grows. On the other hand, the fourth excited state displays only one (although somewhat sinuous) nodal line and corresponds to the first excitation of the H−H stretching normal mode (the steepest direction around the minimum on the PES). In this case an important mixing with the symmetric W−H_2 stretching normal mode is present as indicated by the expansion of the wave function along the W−H_2 direction.

The scenario is different for the complex *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$. In this case, the ground and the excited wave functions spread along the energetically smooth, long oblique valley (compare Figures 3 and 5). The first and second excited states possess one and two nodal lines, respectively, roughly perpendicular to the major axis of the almost elliptic valley. These states are vibrationally excited states corresponding to progressive excitations of the normal mode roughly parallel to the valley. On the other hand, the third excited state has only one nodal line approximately along the major axis of the valley and corresponds to the first excitation of the second A_1 normal mode (the one that vibrates along the steepest direction). It has to be underlined that, for the elongated dihydrogen complexes, the degree of coupling between both A_1 normal modes does not seem to change as the order of the excitation goes up, at least for the lower excited states analyzed here.

IV. Conclusions

In this paper we have theoretically calculated the deuterium equilibrium isotope effect for the binding of H_2 and D_2 to three dihydrogen transition-metal complexes: $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$, $[Ru(H\cdots H)(C_5Me_5)(dppm)]^+$ and *trans*-$[Os(H\cdots H)Cl(dppe)_2]^+$. Concretely, we have taken the complexes $W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$, $[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$ and *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$, respectively, as realistic models of them. The last two complexes are known to be elongated dihydrogen complexes for which the high anharmonicity related to the H−H stretching is a crucial feature that determines many of their special properties. In this paper, we propose an attainable strategy to account for the effects of anharmonicity in a practical and reliable way. In short, the procedure consists of using a discrete variable representation to solve the nuclear Schrödinger equation on the potential energy surface built up along the most anharmonic vibrational normal modes. This provides the corresponding anharmonic vibrational energy levels and, from them, an anharmonically corrected vibrational partition function of the molecule can be calculated. This partition function is not the complete anharmonic partition function of the molecule yet, but it contains the anharmonicity contributions corresponding to the considered modes.

We have proven, within the pure harmonic approach, that an inverse deuterium equilibrium isotope effect is found for the three complexes. However, anharmonicity tends to favor the H_2 binding. Anharmonicity in the complex $W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$ is not important enough to change the preference for D_2 binding (in good agreement with the experimental results), but the deuterium equilibrium isotope effect is clearly normal for the binding in $[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$ and *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$. This is the first time that the preference for the binding of H_2 is predicted in elongated dihydrogen transition-metal complexes. This result opens new possibilities to separate hydrogen isotopes at room temperature on metal complexes that reversibly bind molecular hydrogen so that experimental work devoted to proving that theoretical prediction would be very interesting

Finally, it has to be emphasized that anharmonicity has to be taken into account in order to reproduce and theoretically predict the experimental results concerning many properties of dihydrogen and, probably, polyhydride transition-metal complexes, specially in what concerns the isotope effects. Since experimental results in this field are not easy to obtain, we think that the theoretical procedure we propose here can be very useful to clarify many related problems as, for instance, whether deuterium favors a classical versus a nonclassical site in transition metal complexes. Work on this topic is now in progress in our laboratory.

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