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Deuterium Quadrupole Coupling Constants and Asymmetry Parameters in Metal Hydrides: Calculations of Model Systems Representing Three Modes of Metal-Hydrogen Bonding

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The electric field gradient at the hydrogen atom site has been calculated in three model systems: M-H (M = Li, Na, K, Rb, and Cs), $[Na-H-Na]^+$, $[Na-H_2]^+$, and $[Rb-H_2]^+$. The effect of metal hydride geometry on the deuterium quadrupole coupling constant was examined with an extended basis set by using restricted Hartree-Fock methods. For the terminal M-H bonds (M = K, Rb, and Cs), the deuterium quadrupole coupling constant is about 20 kHz. Formation of a bridging metal-hydrogen bond reduces the value of the quadrupole coupling constant; nonlinearity reduces the quadrupole coupling constant further. For the $[M-H_2]^+$ system, the value of the deuterium quadrupole coupling constant is strongly affected by H-H bonding. These results can be used in the assignment and interpretation of solid-state deuterium NMR spectra of metal-hydrogen bonds in organometallic complexes.

Introduction

Recent solid-state deuterium NMR experiments have shown that the deuterium quadrupole coupling constant, $e^2q_{zz}Q/h$, is a sensitive function of the metal-hydride bond geometry, with characteristics similar to those observed in the solid-state deuterium NMR spectra of O-D···O bonds. An amorphous polymeric solid, bis(cyclopentadienyl)zirconium dideuteride, has two inequivalent deuterium sites.[1] On the basis of the solid-state deuterium NMR spectrum, the existence of a terminal metal hydride and a bridging metal hydride was deduced; integration of the peak areas quantified the results.

The interpretation of solid-state deuterium NMR spectra has been aided by the results of molecular orbital calculations done on model systems. With use of extended Gaussian basis sets, relationships between molecular geometry and the electric field gradient at deuterium have been established. In small molecules, C-H, N-H, and O-H bonds have been studied and the dependence noted between the deuterium quadrupole coupling constant and the atom to which deuterium is bound and the bond length.[2,3] Variations in the hydrogen bond length or angle (O-H···O bonds) affect the deuterium quadrupole coupling constant and asymmetry parameters; ab initio molecular orbital calculations were used to study the casual factors. The assignment of major factors has been confirmed by solid-state deuterium NMR and ADLF spectroscopy.[4]

Structural information comes about from the fact that, in the solid state, the deuterium NMR spectrum is determined by the electric field gradient at the deuterium nuclear site. The electric field gradient is a tensor quantity with a trace of zero. When solid-state deuterium NMR data are reported, the common convention is to identify an axis system that diagonalizes the electric field gradient tensor; the largest diagonal element of the tensor, eq_{zz}, gives the quadrupole coupling constant, $e^2q_{zz}Q/h$. The quadrupole coupling constant is a direct function of the charge distribution in the close vicinity (within about 3 Å) of the deuterium nucleus, as shown in eq 1. Note that only occupied

$$eq_{zz} = \sum_n K_n \frac{3z_n^2 - r_n^2}{r_n^5} - e\langle\Psi^*|\sum_i \frac{3z_i^2 - r_i^2}{r_i^5}|\Psi\rangle \qquad (1)$$

molecular orbitals contribute to the electric field gradient; the absence of contributions from excited states greatly simplifies the calculations required to compute quadrupole coupling constants by using ab initio molecular orbital calculations. The other major elements of the electric field gradient tensor, eq_{xx} and eq_{yy}, are obtained by a similar summation of neighboring charge with a $1/r^3$ distance dependence. Also specified in solid-state deuterium NMR is the asymmetry parameter, η, of the electric field gradient tensor:

$$\eta = \frac{eq_{xx} - eq_{yy}}{eq_{zz}} \qquad (2)$$

The asymmetry parameter is useful since a terminal $X-^2H$ or linear $X\cdots{}^2H-Y$ bond should have a near-zero value for η; non-zero values are characteristic of nonlinear $X\cdots{}^2H-Y$ bonds.

Solid-state deuterium NMR spectroscopy can be applied to a large range of metal hydride chemistry. In homogeneous transition-metal complexes,[5-8] and on catalytic surfaces,[9,10] structures of metal-hydrogen bonds are quite varied, ranging from terminal metal-hydride bonds to several types of bridging geometries. One method of synthesizing transition-metal hydrides proceeds by the oxidative addition of dihydrogen to a coordinatively unsaturated metal center. The addition process is presumed to involve, at some point along the reaction pathway, nonclassical coordination of the dihydrogen molecule to the metal center.[11] Recently, sterically constrained metal complexes have been isolated that contain weakly coordinated dihydrogen molecules.[12]

Herein, we report the results of three series of calculations. Terminal metal hydrides are modeled by diatomic metal deuterides. Bridging metal hydrides are modeled by a $[Na-H-Na]^+$ system. Finally, the interaction of dihydrogen with a metal center

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Table I. Deuterium Quadrupole Coupling Constants for Alkali-Metal Deuterides and Comparison to Vibration Force Constants

atom	M–H, Å[a]	k,[b] 10^5 dyn/cm	$e^2q_{\mathrm{nucl}}Q/h$, kHz	$e^2q_{zz}Q/h$, kHz[c]	e^2q_{zz}/k[d]
LiH	1.595	1.02	147.16	36.80	0.8298
NaH	1.887	0.78	325.89	24.84	0.7351
KH	2.244	0.56	334.88	20.60	0.8486
RbH	2.376	0.51	549.37	19.74	0.8867
CsH	2.494	0.46	680.44	21.04	1.0410

[a] From ref 18. [b] k is calculated from ω_e values.[18] [c] Values from the results of the Gaussian-82 calculations. [d] Calculated by following the procedure of ref 27.

has been followed with $[Na–H_2]^+$ and $[Rb–H_2]^+$ complexes.

Calculations

Gaussian-82 and the associated properties package was used for all SCF-HF calculations.[13] The cesium metal atom basis set was taken from the compilation of Huzinaga and consisted of the nominal basis set enhanced with a two-membered p-type polarization function.[14] For the purpose of comparing results between the alkali-metal hydrides, the basis sets for lithium, sodium, potassium, and rubidium were restricted to the same form as available for cesium. The hydrogen atom basis set was (1s2p1d).[15] In this work, we have taken the deuterium nuclear quadrupole moment, Q, as 2.86×10^{-27} cm^2.[16] The convention used herein for reporting the electric field gradient is $|q_{zz}| \geqslant |q_{yy}| \geqslant |q_{xx}|$.[17]

For the terminal metal hydrides, the M–H bond distances and vibrational stretching force constants were taken from Herzberg.[18] In the linear bridging metal hydride model $[Na–H–Na]^+$, the hydride was constrained to be symmetrically situated between the metal atoms. In the nonlinear bridging hydride model, the Na–H distance was fixed at 2.0 Å. For the $[M–H_2]^+$ systems, all geometries were optimized by using as input the M–(H_2 centroid) distance.

No corrections for vibrational effects were made to the calculated electric field gradients. In the cases when calculated electric field gradients have been corrected for vibration, the general effect is to slightly reduce the magnitude of the electric field gradient tensor elements.[19]

Results and Discussion

Terminal Metal Hydrides. The quality of the basis set was evaluated by comparing the results obtained here for LiH with other calculations and with the results of gas-phase microwave spectroscopy. Hameka and co-workers have evaluated the effect of basis sets on the electronic contribution to the electric field gradient, q_{el}, for the hydride site in LiH, $q_{\mathrm{el}} = -0.1642$ (this work) and $q_{\mathrm{el}} = -0.1615$ (Hameka et al.).[20,21] Adding to the electric field gradient tensor the positive contribution due to the lithium nucleus, we calculate a deuterium quadrupole coupling constant, $e^2q_{zz}Q/h$, of 36.8 kHz, in good agreement with the experimental value of 33 (1) kHz.[22] Unfortunately, experimental values of the deuterium quadrupole coupling constant are not available for the other alkali-metal hydrides. However, a correlation has been noted between the vibrational stretching force constant, k, and the deuterium quadrupole coupling constant;[23-27] the correlation is used here to show that the calculated deuterium quadrupole coupling constants, especially for larger metals, do not suffer from any gross errors. The ratio e^2q_{zz}/k should be near unity,[23,27] as is found for all of the alkali-metal hydrides reported herein. Table I lists the M–H distance, the vibrational force constant, the nuclear contribution to the deuterium quadrupole coupling constant, the calculated deuterium quadrupole coupling constant, and the ratio e^2q_{zz}/k for the alkali-metal hydrides.

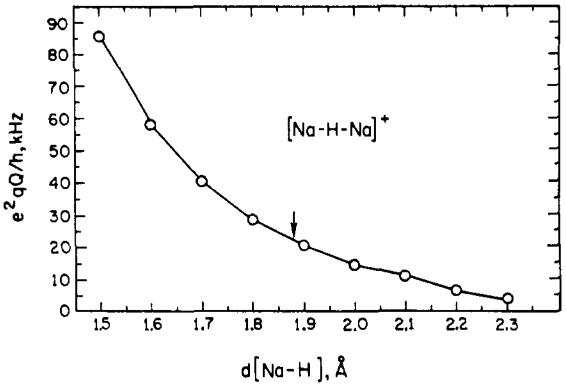

Figure 1. Deuterium quadrupole coupling constants in the bridging metal hydride $[Na–H–Na]^+$. Also shown (arrow) is the Na–H bond distance for the neutral diatomic hydride. The values shown for the deuterium quadrupole coupling constant are corrected for the net positive charge on the model complex by using a point charge mode.

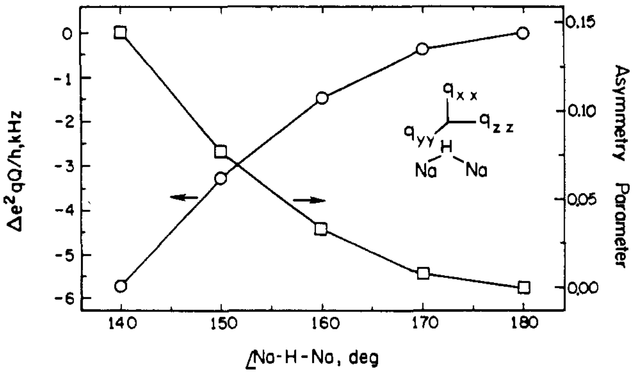

Figure 2. Effect of a nonlinear bond on the deuterium quadrupole coupling constants and asymmetry parameters in $[Na–H–Na]^+$. The Na–H distance is held constant at 2 Å. The orientation of the electric field gradient tensor principal axis system relative to that of the molecular system is shown with the convention $|q_{zz}| \geqslant |q_{yy}| \geqslant |q_{xx}|$. The deuterium quadrupole coupling constants are shown relative to the calculated value at ∠Na–H–Na = 180°.

The results shown in Table I lead to two important conclusions. First, for terminal metal hydrides, the smallest value of the deuterium quadrupole coupling constant is on the order of 20 kHz. Since the alkali-metal hydrides KH, RbH, and CsH have smaller vibrational force constants than typical organometallic transition-metal hydrides,[26,28,29] 20 kHz represents a lower bound for the deuterium quadrupole coupling constant. In a recent survey of organometallic hydrides, the smallest value yet found is 46.7

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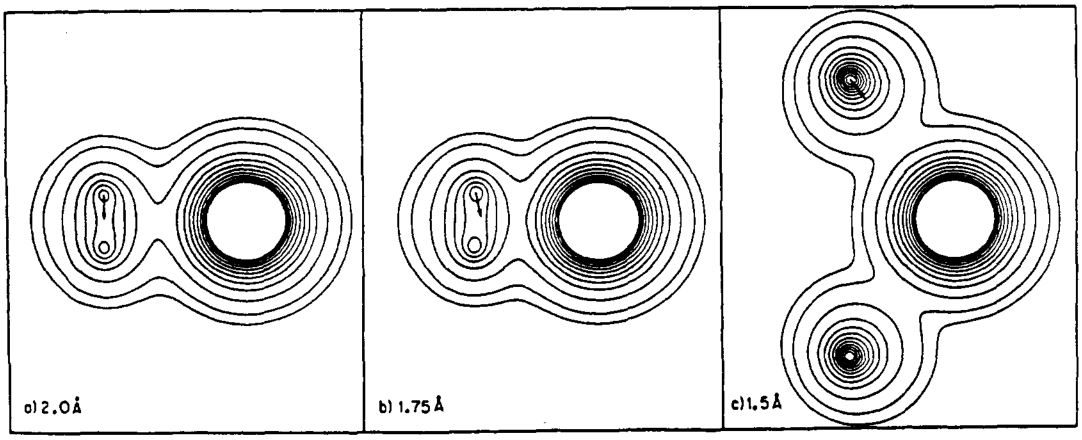

Figure 3. Plots representing the electron density (contour) and the orientation (arrow) of the electric field gradient major axis for $[Rb-H_2]^+$. $Rb-(H_2)$ distances are (a) 1.50, (b) 1.75, and (c) 2.00 Å. The outermost contour shown is at 0.01 e/Å^3, the next contour is at 0.02 e/Å^3, and the next 10 contours start at 0.05 e/Å^3 with 0.05 e/Å^3 steps.

(5) kHz.[1] Second, as one proceeds from lithium to cesium, the alkali-metal core electrons are quite effective at shielding the increased nuclear charge from contributing to the total electric field gradient at the hydride site. This second conclusion has been previously discussed in a different format on the basis of a comparison of the similar origins for vibrational force constants and electric field gradients in hydrides.[23]

Bridging Metal Hydrides. The model bridging metal hydride $[Na-H-Na]^+$ was studied over a range of Na–Na distances, ranging from 3 to 4.6 Å; at all points, equal Na–H bond distances were maintained. While generally satisfactory in most features, the $[Na-H-Na]^+$ model, because of the net positive charge, yields values for the deuterium quadrupole coupling constants that are forced to be more positive than would be expected for an organometallic complex. A point charge model, with +0.5 e charge situated at each sodium nuclear site, was used to correct the calculated deuterium quadrupole coupling constants. The $[Na-H-Na]^+$ data are plotted in Figure 1 with the corrected deuterium quadrupole coupling constants.

The most notable feature in Figure 1 is the large reduction in the value of the deuterium quadrupole coupling constant with increasing metal–metal distance. The reduction is caused by the decreasing nuclear contribution to the electric field gradient and is exactly analogous to the reduction calculated and observed in symmetric O–H–O bonds.[4a,30] Also noted on the graph is the Na–H bond distance for the neutral diatomic hydride. Since formation of a bridging hydride bond causes an increase in the Na–H distance, from Figure 1 we would predict that bridging metal hydrides should have a deuterium quadrupole coupling constant smaller than that of a comparable terminal metal hydride.

The deuterium quadrupole coupling constants of nonlinear bridging metal hydrides were investigated with a fixed Na–H bond distance of 2.0 Å. Fixed O–H distances were also used in a study of O–H···O bond angles and the correlation with deuterium quadrupole coupling constants.[4a] Figure 2 shows the effect bending the bridging metal–hydride bond has upon the deuterium electric field gradient. Relative to the case for a linear system, bent metal–hydride bonds have a reduced deuterium quadrupole coupling constant. Also, the asymmetry parameter becomes large upon bending; the relative orientation of the electric field gradient principal axis system is shown in Figure 2.

The solid-state deuterium NMR spectrum of bis(cyclopentadienyl)zirconium dideuteride shows two deuterium sites with deuterium quadrupole coupling constants of 46.7 (5) and 32.7 (20) kHz.[1] The site with the smaller value for the deuterium quadrupole coupling constant was assigned, partly on the basis of the known trends for O–H···O bonds, to a bridging metal hydride site.

Dihydrogen Adducts. In this model, a dihydrogen molecule is brought near an alkali-metal ion that is acting as a Lewis acid.[11i] As the dihydrogen molecule is brought closer to the metal, the H–H bond is broken and two new M–H bonds are formed. In this work the geometry of the complex was determined by an energy minimization process. The principal coordinates of the complex are as follows: (1) the $M-(H_2)$ distance, the distance between the metal and the centroid of the dihydrogen system, and (2) the H–H distance, the distance between the two hydrogen atoms. For example, little interaction between the metal ion and the dihydrogen molecule occurs with $d(M-(H_2))$ = 4 Å and $d(H-H)$ = 0.85 Å. At the other extreme, a linear $[H-M-H]^+$ complex corresponds to $d(M-(H_2))$ = 0 Å and $d(H-H)$ = 4.2236 Å, the sum of the two M–H bond distances. Figure 3 shows representations of the electron density in the $[Rb-(H_2)]^+$ complex for three $M-(H_2)$ distances in the region where the H–H bond is being broken.

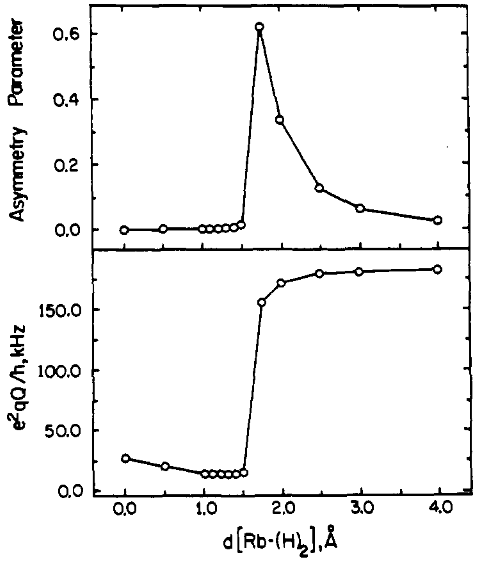

Figure 4. Evolution of the deuterium quadrupole coupling constant and asymmetry parameter in the addition of dihydrogen to a Rb^+ center.

In spite of the complexity of the dihydrogen addition process, it is possible to describe, in relatively simple terms, the evolution of the deuterium quadrupole coupling constant and asymmetry parameter. In the dihydrogen molecule prior to interaction with a metal, the deuterium quadrupole coupling constant is +225 kHz and is dominated by the relatively unshielded neighboring hydrogen nucleus only 0.79 Å distant. After an alkali-metal–hydride bond is formed, the deuterium quadrupole coupling constant is on the order of 20 kHz but is still positive and is dominated by the nuclear charge of the alkali-metal atom. Having established the limiting cases, one would expect intermediate regions of the dihydrogen addition process to show a smooth evolution of deuterium quadrupole coupling constant and reorientation of the electric field gradient major axis. The arrow in Figure 3 shows

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Table II. Calcualted Deuterium Quadrupole Coupling Constants and Asymmetry Parameters for $[Rb-H_2]^+$

$Rb-(H_2)$, Å	H-H, Å	θ, deg[a]	η	e^2qQ/h, kHz
4.00	0.8500	0.103	0.0250	181.770
3.00	0.8492	0.378	0.0627	179.965
2.50	0.8452	1.061	0.1250	178.867
2.00	0.8386	4.665	0.3372	171.082
1.75	0.8450	12.905	0.6228	155.373
1.50	3.9545	36.733	0.0170	14.775
1.40	4.2200	32.931	0.0080	13.565
1.30	4.3840	29.974	0.0046	13.156
1.20	4.4912	27.393	0.0031	13.123
1.10	4.5582	25.019	0.0022	13.343
1.00	4.5936	22.769	0.0017	13.779
0.50	4.4346	12.003	0.0007	19.634
0.00	4.2236	0.000	0.0000	26.902

[a] Angle between the H-H vector and the major axis of the electric field gradient tensor (*z* axis).

the orientation of the electric field gradient major axis; Figure 4 shows the evolution of the deuterium quadrupole coupling constant and asymmetry parameters. The $[Rb-(H_2)]^+$ data are summarized in Table II. The $[Na-(H_2)]^+$ system behaved similarly to $[Rb-(H_2)]^+$, differing mainly in having a shorter $M-(H_2)$ distance in the M-H bond-breaking region.

The evolution of the minor axes of the electric field gradient tensor is not as predictable as for the major axis. For $Rb-(H_2)$ distances of 1.75 Å and greater, q_{yy} is normal to the $Rb-(H_2)$ plane. After the H-H bond is broken, q_{yy} lies in the $Rb-(H_2)$ plane.

The solid-state deuterium NMR spectrum of a tungsten dihydrogen complex gives a deuterium quadrupole coupling constant of about 124 kHz,[12c] in good agreement with the trends found herein. Due to motional averaging, the asymmetry parameter could not be obtained from the spectrum but would be expected to be non-zero.

Conclusions

Terminal Metal Hydrides. From the calculations on the alkali-metal hydrides and subsequent comparison to vibrational stretching force constants, two general statements can be made:

1. A lower limit for the deuterium quadrupole coupling constant in organometallic hydrides is 20 kHz.
2. Metal core electrons effectively shield the deuteron from the electric field gradient generated by large nuclear charges.

Bridging Metal Hydrides. Formation of a bridging metal-hydride bond causes a reduction in the deuterium quadrupole coupling constant relative to the value found for a terminal metal-hydride bond to the same metal.

Dihydrogen Adducts. In the addition of dihydrogen to a d^0 metal center, the major features of the electric field gradient at the hydrogen site evolve in a straightforward manner.

1. The value of the deuterium quadrupole coupling constant is reduced, with the most rapid reduction occurring as the H-H bond is being broken.
2. The orientation of the electric field gradient major axis, aligned along the H-H bond in the dihydrogen molecule, rotates toward alignment with the M-H bond as the H-H bond is broken.
3. At structures corresponding to intermediate H-H and M-H bonds, the asymmetry parameter is non-zero.

Given the occasional experimental difficulties in acquiring solid-state deuterium NMR spectra, it can be highly beneficial to the spectroscopist to optimize the instrumental parameters on the basis of estimates of the deuterium quadrupole coupling constant and the asymmetry parameter. Also, there is a clear and definitive connection between the observed solid-state deuterium NMR spectrum and structural features of the metal-hydrogen bond, making solid-state deuterium NMR spectroscopy a potentially unique and valuable asset for physical organometallic chemistry.

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Registry No. $[Na-H-Na]^+$, 101985-62-0; $[Na-H_2]^+$, 109552-64-9; $[Rb-H_2]^+$, 109552-65-0; LiH, 7580-67-8; NaH, 7646-69-7; KH, 7693-26-7; RbH, 13446-75-8; CsH, 13772-47-9; deuterium, 7782-39-0.

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Exchange Reactions and Microscopic Reversibility

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The principle of microscopic reversibility as applied to the kinetics and stereochemistry of the CO-exchange reactions of compounds of the type $Mn(CO)_5X$ is reviewed, and some fundamental errors in the literature are exposed.

Introduction

The proper interpretation of the kinetics of the fundamental exchange reaction

$$MX_n + {}^*X \rightarrow MX_{n-1}{}^*X + X \qquad (1)$$

is important in its own right, and also for the extrapolation of the results to the kinetics of the related substitution process[1,2]

$$MX_n + Y \rightarrow MX_{n-1}Y + X \qquad (2)$$

The correct application of the principle of microscopic reversibility (hereafter PMR), which is relevant to not only exchange processes but all reactions, has on occasions proved troublesome.[1] Likewise, the related principle of detailed balance (hereafter PDB)[3-5] has sometimes been overlooked in correctly interpreting mechanism. Herein these principles are applied to the classic exchange reactions of $Mn(CO)_5X$, processes that have received a great deal of experimental attention using ^{13}CO, ^{14}CO, or $C^{18}O$ as isotopic labels.[6-12] Recently[13] we have given detailed con-

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