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Empirical corrections for anharmonic zero-point vibrations of hydrogen and deuterium in geometric hydrogen bond correlations

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Dedicated to Prof. Dr H.D. Lutz on the occasion of his 70th birthday

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Abstract

In this paper, empirical corrections for anharmonic ground-state vibrations of hydrogen and deuterium in the hydrogen bridges A–L···B, L = H, D are introduced into the geometric hydrogen bond correlation analysis based on the empirical Pauling valence bond orders. The method is verified using the examples of the hydrogen bonded anions in $[(CO)_5Cr{-}C{\equiv}N{\cdots}H{\cdots}N{\equiv}C{-}Cr(CO)_5]^-$ $As(Ph)_4^+$ (**1h**), in $[(CO)_5Cr{-}C{\equiv}N{\cdots}H{\cdots}N{\equiv}C{-}Cr(CO)_5]^-$ $N(n\text{-propyl})_4^+$ (**2h**), in the model system $[C{\equiv}N{\cdots}H{\cdots}N{\equiv}C]^-$ Li^+ (**3h**), and their deuterated isotopologs (**1d**, **2d** and **3d**) studied previously by dipolar NMR and theoretical methods by H. Benedict et al. [J. Am. Chem. Soc. 120 (1998) 2939]. The new corrections are able to describe isotope effects on hydrogen bond geometries from the weak to the strong hydrogen bond regime, taking into account single and double-well situations.

Keywords: Hydrogen bond; Geometric isotope effect; Valence bond order; Empirical correction; Ground-state vibration

1. Introduction

In the recent years, Steiner et al. [1] have established geometric hydrogen bond correlations based on low-temperature neutron diffraction studies. These correlations imply that the two distances r_1 of the diatomic unit AH and r_2 of the diatomic unit H···B in a hydrogen bonded system A–H···B are correlated with each other. This finding has been rationalized in terms of the valence bond model of Pauling [2] and Brown [3]. These bond orders are defined as

$$p_1 = \exp\{-(r_1 - r_1^0)/b_1\},$$
$$p_2 = \exp\{-(r_2 - r_2^0)/b_2\}, \quad (1)$$

where b_1 and b_2 characterize the decrease of the bond orders with increasing distances and r_1^0 and r_2^0 the distances of the non-hydrogen bonded diatomic units AH and HB. According to the assumption of Brown [3], the total valence, i.e. the sum of the two bond orders, is unity,

$$p_1 + p_2 = 1. \quad (2)$$

It follows that r_1 and r_2 cannot be varied independently of each other. The same is true of the hydrogen bond coordinates $q_1 = 1/2(r_1 - r_2)$ and $q_2 = r_1 + r_2$. For a linear hydrogen bond, q_1 represents the distance of H from the hydrogen bond center and q_2 the distance between atoms A and B. When H is transferred from one heavy atom to the other, q_1 increases from negative values to positive values; q_2 goes through a minimum which is located at $q_1 = 0$ for AHA and near 0 for AHB systems. These findings have been supported by *ab initio* calculations of the equilibrium geometries [4,5]. However, note that the hydrogen bond angle does not appear in Eq. (1).

Recently, some of our group have used this model to describe the geometries of polycrystalline homoconjugated anions in **1h**, **2h** studied by dipolar NMR, in their deuterated

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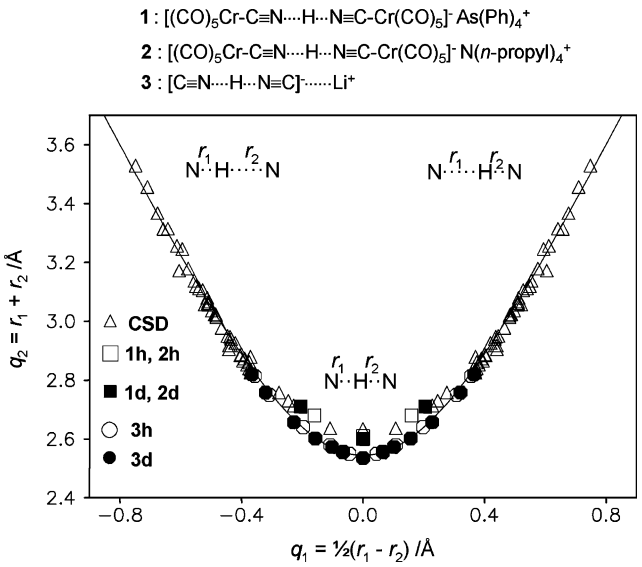

Fig. 1. Correlation of the hydrogen bridge length $q_2 = r_1 + r_2$ with the proton transfer coordinate $q_1 = 1/2(r_1 - r_2)$, adapted from Ref. [6]. CSD: neutron diffraction data of various NHN hydrogen bonds from the Cambridge Structural Database [13] listed in Ref. [6]; additional data points around $q_1 = 0$ were added (BEXROL, GUNHUS, PYCBZN01, TEHNAV, XUNCUE). The solid line was calculated in terms of Eq. (1), (2) with a single set of parameters $b = 0.404$ Å and $r^0 = 0.992$ Å.

analogs **1d** and **2d** as well as in the model complex **3h** and **3d,** for which *ab initio* calculations including quantum corrections for zero-point vibrations were performed [6]. The hydrogen bond correlation obtained is depicted in Fig. 1, which also includes literature data for other NHN-hydrogen bonds collected by Steiner [1b], data from our group [6], and some new data for short NHN hydrogen bonds from the Cambridge Structural Database. The dynamically corrected hydrogen bond geometries of **3** were well reproduced by Eq. (1), (2) with a single set of parameters $b_1 = b_2 = b = 0.404$ Å and $r_1^0 = r_2^0 = r^0 = 0.992$ Å for the protonated and the deuterated systems, in spite of small systematic differences between the data points of **3h** and of **3d**. The data points of **1** and **2** showed significant isotope-dependent deviations from the correlation as depicted in Fig. 1; it was not clear in Ref. [6] whether this finding was significant. However, the new neutron diffraction data of short NHN-hydrogen bonds in the range between $q_1 = -0.3$ and $+0.3$ Å (Fig. 1) convinced us that these deviations are significant.

Therefore, in this paper we introduce empirical corrections into the valence bond model which are able to take into account anharmonic zero-point stretching vibrations of H and D in the hydrogen bond, and which are able to explain the above-mentioned deviations. Moreover, these corrections allow one to calculate the correlation curves not only for the protonated, but also for the deuterated systems, where both the double-well and single-well situations are taken into account.

2. Results and discussion

The starting point of the corrections we propose is the well-known features of the one-dimensional potentials for the H and D motions in hydrogen bonds. These potentials are depicted schematically in Fig. 2 for a sequence of configurations where the proton is shifted from A towards B. The squared wave functions of the lowest vibrational states are included, i.e. where the vertical bars correspond to the average hydrogen positions $\langle q_1 \rangle^{\mathrm{L}} \equiv q_1^{\mathrm{L}}$, L = H, D. A look at the different configurations indicates that deuteration in the asymmetric configurations shifts D away from the H-bond center and increases the A···B bond length. The same is true in a configuration of a symmetric double well. When the two maxima are well separated, two proton positions can be identified by neutron diffraction, and for each position the hydrogen bond correlation may be fulfilled. However, as ellipsoids are often used to fit the proton locations, an average proton position $q_1^{\mathrm{H}} = 0$ may result when the maxima are close to each other. Then, the value of

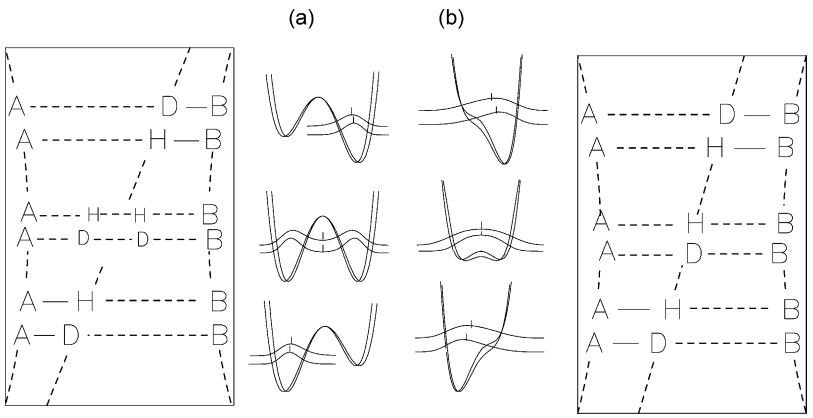

Fig. 2. One-dimensional hydron (H and D) potentials and geometric changes during the transfer of a hydron from A to B. The squares of the wave functions of the vibrational ground states for H and D, i.e. the proton and deuteron distribution functions are included. When at the quasi-symmetric midpoint the barrier is high, the maximum of the wave function for D is shifted with respect to that for H (case a), leading to a small H/D isotope effect on the geometry. This effect is absent if the barrier is low (case b). Adapted from Ref. [14].

q_2^H will be larger than predicted by the correlation curve; furthermore, the deviations will be larger for D than for H. On the other hand, in a symmetric single-well potential D will be confined more to the hydrogen bond center, leading to a smaller value of q_2 for D as compared to H.

In order to take into account zero-point stretching vibrations in the valence bond model, we assume that Eq. (2) is valid only for a 'classical' system exhibiting an 'equilibrium' geometry corresponding to the minimum of the potential energy surface. In other words, p_1 and p_2 are essentially equilibrium bond orders. A real hydrogen bond ALB, L = H, D, exhibiting anharmonic zero-point vibrations of H and D, is then characterized by the real average bond orders p_1^L and p_2^L. For the latter, Eq. (2) is no longer valid in the strong hydrogen bond regime, and we assume that

$$p_1^L + p_2^L < 1. \tag{3}$$

More specifically, we propose the following relations between the classical and real bond orders, which are only subsequently justified by comparison with experimental data. We assume that

$$\begin{aligned} p_1^L &= p_1 - c^L(p_1p_2)^f(p_1 - p_2) - d^L(p_1p_2)^g, \\ p_2^L &= p_2 + c^L(p_3p_2)^f(p_1 - p_2) - d^L(p_1p_2)^g, L = H, D \end{aligned} \tag{4}$$

The corresponding average distances are calculated from the real bond orders using Eq. (1). The parameters c^L and d^L as well as the values of the powers f and g are empirical and have to be adjusted to a given data set. The term $d^L(p_1p_2)^g$ is a correction term describing the flattening of the real correlation curves in the minimum. If d^L is set to zero, the classical and the real correlation curves of AHB and ADB coincide. The 'correlation' term $c^L(p_1p_2)^f(p_1 - p_2)$ indicates then by how much the geometry of ALB is shifted on the correlation curve as compared to the classical value.

Eq. (4) also allows one to calculate the so-called [6] primary geometric hydrogen bond isotope effect (primary GIE)

$$\Delta q_1 = q_{1D} - q_{1H}, \tag{5}$$

and the secondary geometric hydrogen bond isotope effect (secondary GIE)

$$\Delta q_2 = q_{2D} - q_{2H}. \tag{6}$$

The secondary effect has also been called the 'Ubbelohde effect', as it was observed by the eponymous author for a number of hydrogen bonded systems [7]. A negative value of Δq_2 has also been called an 'inverse' Ubbelohde effect. Generally, secondary effects can be observed quite easily by X-ray crystallography, as hydron positions do not need to be determined. The primary geometric isotope effects are, however, difficult to study by X-ray diffraction, and neutron diffraction is needed. Indirect spectroscopic methods such as IR, Raman or NMR [8–10] can give more precise results after a suitable calibration of the spectroscopic parameters. Naturally, theoretical methods can also be used to calculate these geometric isotope effects [11].

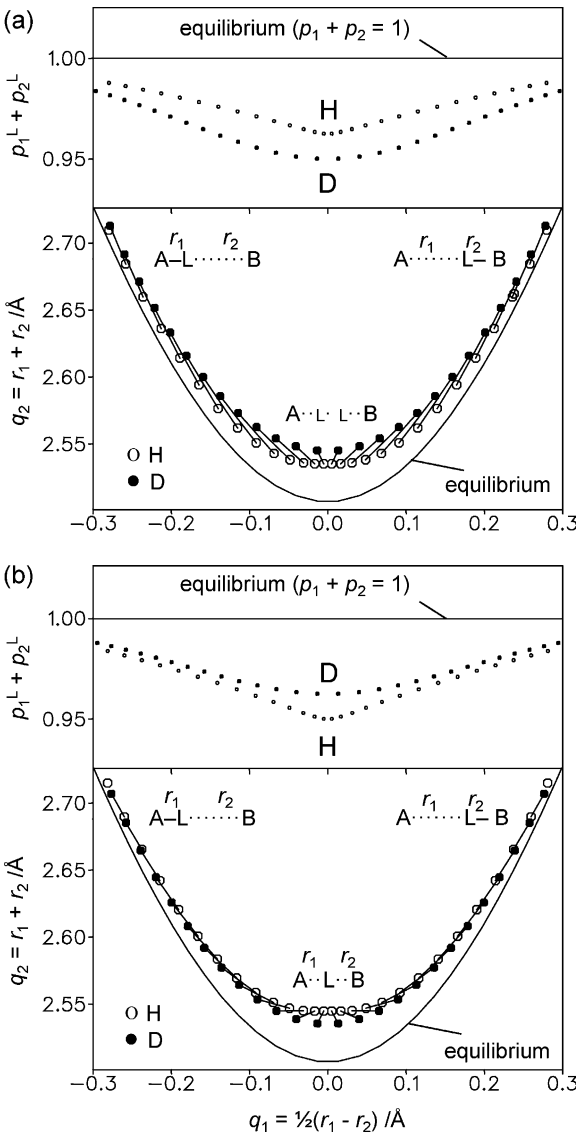

Fig. 3. Geometric hydrogen bond correlations according to Eq. (4) for a system with a strong hydrogen bond, i.e. in the region around $q_1 = 0$. The solid line represents the equilibrium geometries (a) for systems with double-well proton potential at the symmetric midpoint (according to Fig. 2a) and (b) for systems with single-well proton potential at the symmetric midpoint (according to Fig. 2b). Bond order sum as a function of q_1 is shown for H and D particles both for cases (a) and (b). Note that bottom part of the equilibrium curve on (a) does not correspond to a stationary point, but represents an average H-bond geometry. The parameters used to calculate the curves are included in Table 1. For further explanation, see text.

The performance of Eq. (4) is depicted qualitatively in Fig. 3 for two arbitrary sets of parameters listed in Table 1. Fig. 3a corresponds to the series of hydrogen bond configurations of Fig. 2a, exhibiting a double well in the symmetric case. At all geometries, Δq_2 is positive, i.e. the hydrogen bond is widened upon deuteration. Δq_1 is negative for negative values of q_1^L but changes sign

Table 1
Parameters of the anharmonic correction in Eq. (4)

Figure	System	b (Å)	r^0 (Å)	f	g	c^H	d^H	c^D	d^D
Fig. 1	**1**, **2**, **3**	0.404	0.992	–	–	–	–	–	–
Fig. 3a		0.370	0.997	5	2	330	0.3	30	0.4
Fig. 3b		0.370	0.997	5	2	330	0.4	30	0.3
Fig. 4	**3**	0.370	0.997	5	2	330	0.4	30	0.3
Fig. 5	**1**, **2**	0.370	0.997	5	2	330	1.2	30	1.1

when the latter becomes positive. D is always farther away from the H-bond center than H. The bond order sum $p_1^L + p_2^L$ predicted by Eq. (4) is shown on top of Fig. 3a for the protonated and the deuterated hydrogen bonds. The deviation from unity is well pronounced in the strong hydrogen bond region; the reduction is stronger for D than for H. This reduction of the bond order sum is responsible for the larger q_2^L values as compared to the equilibrium geometries, where the bond order sum is always unity.

The behavior of a series of hydrogen bonded complexes exhibiting a single-well potential also in the symmetric configuration is shown in Fig. 3b. In contrast to Fig. 3a, in the symmetric case Δq_2 is negative, i.e. the hydrogen bond is shortened upon deuteration as is well established for ions such as FHF^- [12]. Again, we have included the sum $p_1^L + p_2^L$ for H and D in Fig. 3b. Now, the hydrogen bond shortens in the symmetric case after deuteration, whereas in the asymmetric cases the contrary is found. We note that we only needed to exchange the values of the parameters d^H and d^D in order to describe the change of the effective correlation curves between Fig. 3a and b.

We now apply Eq. (4) to the homoconjugated anionic systems **1** to **3**. In Figs. 4 and 5 we have plotted the geometric hydrogen bond correlations q_2 and the primary and the secondary geometric isotope effects Δq_1 and Δq_2 as a function of q_1. The dotted lines were calculated using Eq. (4), where

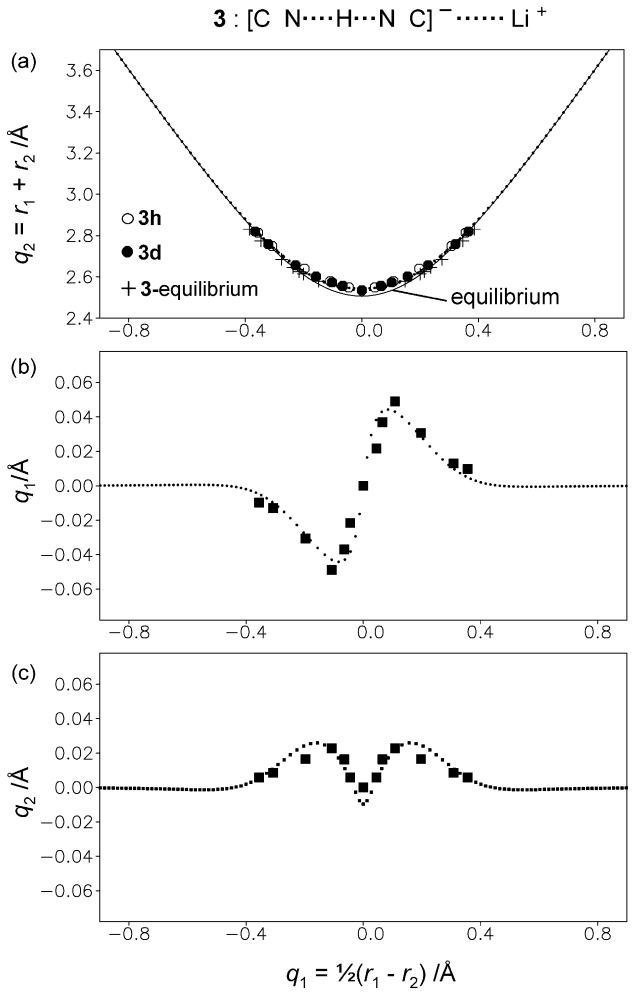

Fig. 4. (a) Hydrogen bond correlations adapted to **3h** and **3d** using the correction of Eq. (4) and the parameters listed in Table 1. The solid line was fitted to the equilibrium geometries of **3** listed in Table 2 of Ref. [6], included as crosses in the graph. (b) Primary geometric isotope effects Δq_1, (c) secondary geometric isotope effects Δq_2. The parameters of the dotted curves are included in Table 1. For further explanation, see text.

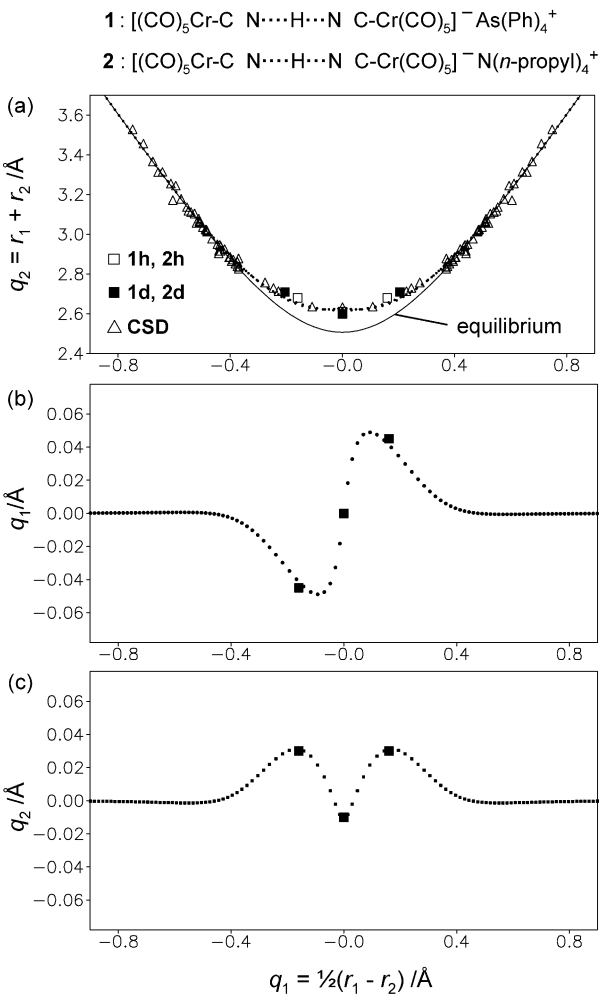

Fig. 5. (a) Hydrogen bond correlations adapted to the data of **1**, **2** published in Ref. [6] and to the CSD data of Fig. 1, using the correction of Eq. (4) and the parameters listed in Table 1. (b) Primary geometric isotope effects Δq_1, (c) secondary geometric isotope effects Δq_2. The parameters of the dotted curves are included in Table 1. For further explanation, see text.

the parameters used are included in Table 1. The data points of Fig. 1 are included separately in Figs. 4a and 5a; in addition, we have included in Fig. 4a the equilibrium distances of **3** as crosses, as calculated in Ref. [6] without dynamic correction.

As the parameters $b = 0.404$ Å and $r^0 = 0.992$ Å of the correlation curve of Fig. 1 were derived mainly for protonated systems [6], they cannot be directly used for the calculation of the equilibrium geometry correlation. Therefore, in Fig. 4a we have used the equilibrium geometries of **3** for this purpose. The parameters $b = 0.370$ Å and $r^0 = 0.997$ Å reproduced these geometries in a satisfactory way, as indicated by the crosses and the solid line in Fig. 4a. However, we anticipate that these parameters might be subject to changes in the future.

The computational data of the model compound **3h** and **3d** need a relatively small correction for the anharmonic zero-point vibration, as indicated by the dotted line in Fig. 4a; the primary GIE and the secondary GIE are well reproduced. Our model predicts negative secondary isotope effect at $q_1 = 0$. However, the crude adiabatic approximation used for data points of system **3** does not predict any GIE at $q_1 = 0$, because, in contrast to the expectations of Fig. 2b, it uses the same potential for H and D for the symmetric complex. A more-dimensional treatment would probably reveal a negative secondary GIE, found experimentally for **1** as depicted in Fig. 5a and c. In the cases of **1** and **2**, the correction terms (Table 1) are larger than for **3**; Fig. 5 shows that the GIE are well reproduced. But most important point is that the increase in the q_2^{L} values of both compounds as compared to the values calculated from the equilibrium correlation is now well reproduced.

3. Conclusions

We conclude that the deviations of the geometries of strong hydrogen bonds from the classical hydrogen bond correlation can be reproduced by introducing appropriate correction terms into the valence bond analysis. If these terms are ignored, the fit parameters and r^0 of the classical correlation will depend on how many data points of the strong hydrogen bond regime are included in the data analysis. The correction terms are needed for the description of geometric H/D isotope effects and can take into account both single or double-well situations.

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