Temperature dependent deuterium quadrupole coupling constants of short hydrogen bonds

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Abstract

Very short hydrogen bonds universally show large positive dependences of the deuterium NMR quadrupolar coupling constant with temperature. We present temperature dependent NMR data for eight such systems, with O····O distances of between 238 and 250 pm, and show we can model the temperature dependences by density functional methods, as long as proper attention is paid to intermolecular effects and intermode couplings.

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1. Introduction

The hydrogen bond, or ‘hydrogen bridge’, as it was originally known, seems to have been independently conceived twice within a single year at the University of California at Berkeley, by Maurice Huggins, in an undergraduate thesis, and by Latimer and Rosebush [1]. Shortly thereafter, Bragg [2] proposed that a network of these bonds could explain the tetrahedral arrangement of oxygen atoms in water ice. Huggins, who seems to be the unacknowledged father of the hydrogen bond, also first proposed another seminal idea [3]: that if the distance between the two oxygens in an ice-like hydrogen bond (which we will denote, in the notation first proposed by Huggins [4], as O–H····O) becomes short enough, the ‘central hump’ in the potential for displacement of the hydrogen parallel to the hydrogen bond direction will disappear, and there will be a single energy minimum, in the center. Thus, was born the idea of the experimentally elusive single-minimum hydrogen bond.

Huggins, using a primitive Morse potential, estimated the ‘hump’ would disappear at r_{OO} ~ 265 pm. Speakman [5], in his early X-ray crystallographic characterization of potassium hydrogen bis-phenylacetate, the seminal member of the hydrogen dicarboxylate class of strong hydrogen bonds, observed that the twin oxygens of the O–H····O system were symmetrically displaced about a crystallographic center, approximately 255 pm distant, and astutely noted that this could be explained either by a Huggins-type single minimum potential, or by disordered hydrogens with 50% occupancy in a double potential minimum. While the structures of many significantly shorter O–H····O systems have since been determined, we can seldom if ever unequivocally distinguish between Speakman’s two alternatives, even by neutron crystallography; hydrogen bonds with r_{OO} distances as short as 239 pm [6] often yield centered, anisotropic thermal ellipsoids, which could in principle be consistent either with a single, highly anisotropic single well potential, or a low-barrier double well. Thus, nearly 70 years since Huggins first sketched a set of double-well potentials merging into single wells as r_{OO} decreases, the question of how short the O····O distance has to be to create a true single well potential is still a controversial one.

Since structural methods have been surprisingly impotent regarding this issue, spectroscopy has instead come to the force. Any survey of the early work in the field must note
the observation of the vibrational 0–1 transition of a symmetric
O–H⋯O system, by Hadzöö in 1961; the observation of
infrared absorptions between 120 and 150 cm$^{-1}$ in potassium
dihydrogenphosphate and isomorphs, phenylphosphinic acid,
and potassium hydrogen bis-4-nitrobenzoate clearly showed
these systems to be low-barrier double-wells, with frequencies
considerably higher than conventional tunneling frequencies
of ‘normal’ hydrogen bonds, but far lower than would be expected
for a hydrogen in a single minimum. Where direct observation
of infrared transitions has been difficult or impossible, inelastic
neutron scattering has often served as a substitute.

It is clear that measurement of a full set of vibrational
transitions allows an exact delineation of the potential surface;
in fact, given the constraints on the possible vibrational
potentials for a hydrogen bond, even a single correctly-
assigned 0–1 vibrational frequency gives an excellent
indication of the height of the barrier, although interpretation
is made more difficult by mode-coupling, particularly with the
soft and strongly coupled O⋯O mode. The rub is, of course,
the measurement and assignment of this vibrational spectrum
may not be straightforward.

Other spectroscopic measurables, therefore, have instead
been sought. NMR provides several possibilities. It has been
known for many years that, both in solution[7], by multiple
pulse solid-state NMR [8], and most recently by high-speed
magic-angle spinning $^1$H NMR [9] that the chemical shift of
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The deuterium quadrupole coupling constant, which we will
denote by $\text{eq}_{\text{V}_{zz}}$, which is directly proportional to the electric
field gradient at the nuclear site, and can therefore simply be
calculated from the electronic ground state electron density,
similarly has a strong monotonic dependence on hydrogen bond
quadrupole coupling constants over a range of $r_{\text{OO}}$ values from
243.7 pm to effectively infinity (the isolated O–H group in
hydroxyl hydrate structure (H–O–H$^\cdot$). The observation of
the O–H proton depends strongly on the hydrogen bond
strength, ranging from less than 10 ppm for weakly hydrogen
bonded systems to over 20 for the strongest hydrogen bonds.
Qualitative agreement with this trend was obtained in ab initio
calculations [10].

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quadrupole coupling constants over a range of $r_{\text{OO}}$ values from
243.7 pm to effectively infinity (the isolated O–H group in
calcium hydroxide); their data show that $\text{eq}_{\text{V}_{zz}}$ decreases from
approximately 275 kHz at infinite $r_{\text{OO}}$ to around 50 kHz for the
shortest hydrogen bonds. Unfortunately, ab initio calculations
based on the equilibrium structure, even with high-level
corrections for electron correlation, do not accurately reproduce
the experimental data; this has greatly hindered theoretical
interpretation, but has made analysis of correlations [8,11]
between experimental measurables all the more important.

The failure so far to quantitatively interpret NMR data means
that while we can use chemical shifts and deuteron coupling
constants to obtain relative strengths of hydrogen bonds, we
cannot yet use their magnitudes to gauge the form of the potential.
Three years ago [12], therefore, we proposed that the temperature
dependence of the deuterium quadrupole coupling constant
might be more informative than its absolute magnitude. We noted
that two compounds with very strong hydrogen bonds—sodium
deuterium bis-4-nitrophenolate dihydrate [13] and the enolated
tautomer of 4-cyano-2,2,6,6-tetramethyl-3,5-heptanediione show
large anomalous temperature coefficients; in both cases, the
deuterium electric quadrupole coupling constant increases with
temperature—whereas the commonly encountered thermal
averaging mechanisms tend cause $\text{eq}_{\text{V}_{zz}}$ to decrease with
temperature. Miyakubo and Nakamura [14] and previously
Kalsbeek et al. [15] had reported similar phenomena for other
strongly hydrogen bonded deuterons. We proposed that the root
of the phenomenon required two conditions to be fulfilled; a
vibrational first excited state with a much larger $\text{eq}_{\text{V}_{zz}}$ than the
ground state, and a first vibrational frequency in the range
100–700 cm$^{-1}$, making the first excited state thermally
accessible around and below room temperature. We have since
reported similar large positive temperature coefficients for the
deuteron $\text{eq}_{\text{V}_{zz}}$ and the proton chemical shift in the strongly
O–H⋯N system 4-methylpyridine pentachlorophenate; the
group of Lluch had previously proposed [16] that temperature
dependent proton chemical shifts might be a diagnostic feature of
low-barrier hydrogen bonds. In the present work, we report a
survey of quadrupole coupling constants in 10 strongly hydrogen
bonded compounds, and advance a quantitative explanation for
the observed temperature coefficients.

2. Theory

Electronic structure calculations were carried out using the
program GAMESS, using a 6-311G**(3df, 3pd) basis set, with
the B3LYP density functional, integrated over a $128 \times 32 \times 16$
grid, and using a polarizable continuum model for the dielectric
with $\varepsilon = \varepsilon_{\infty} = 5.0$ and a nominal solvent radius of 200 pm. The
hydroxyl hydrate structure (H–O–H$^\cdot$) was used as a
model, as in previous work [12]. After optimization of the
structure in $C_{2h}$ symmetry, energies and electric field gradients
were calculated over a $41 \times 41$ grid of points spaced by 40 pm
about median values of $r_{\text{OO}} = 245.3$ pm and $r_{\text{OH}}$ (hydrogen
displacement from the center of the system) = 0. The energies
were fit to a full polynomial of order 6 in $r_{\text{OO}}$ multiplied by an
even polynomial of order 10 in $r_{\text{OH}}$; this fit gave a maximum
residual of less than 0.2 mHartree. The two-dimensional linear
Schrödinger equation was then solved variationally, using a
basis set of 36 two-dimensional harmonic oscillator wavefunctions,
with independent variational optimization of the
harmonic oscillator force constants. Energies and wavefunctions
were computed for the ground state and the first excited
states along the $r_{\text{OH}}$ and $r_{\text{OO}}$ coordinates, the expectation value
of the electric field gradient tensor computed for each of these
states, a Boltzmann-weighted average performed, and then the
EFG tensor diagonalized, with the quadrupole coupling
constant calculated as previously described [12].

3. Methods

3.1. Sample preparation

Detailed preparative methods for the deuterated derivatives
are as follows. Nitromalonamide (I) was prepared by nitration
of malonamide with fuming red nitric acid by the classic
procedure of Ratz [17] and recrystallized from
methoxyethanol. To synthesize nitromalonamide-$d_5$, the undeuterated material was dissolved in dimethylsulfone, and precipitated by addition of $D_2O$; the powder was about 95% deuterated by NMR. Bis(pyridinebetaine) hydrochloride monohydrate ($II$) was prepared by adding chloroacetic acid to pyridine and stirring overnight at room temperature [18]. The white crystals were collected and dissolved in methanol. By adding diethylether dropwise, $II$ was precipitated. $II-d_3$ was made by exchanging $II$ with an excess of $CH_3OD$. Urea phosphate-$d_7$ ($III$) was obtained by combining equimolar quantities of orthophosphoric acid and urea in $D_2O$, and allowing the material to crystallize by slow evaporation. Sodium deuterium bis-4-nitrophenolate dideuterate ($IV-d_5$) was obtained from a saturated solution containing a 2:1 molar ratio of 4-nitrophenol and sodium hydroxide in $D_2O$. After crystallization, it was dried in vacuo and transferred to a sealed tube for NMR measurements. Benzoylacetone ($V$) and dibenzoylmethane ($VI$) were purchased from Aldrich, and crystallized from $C_2H_5OD$ solution to yield $V-d_1$ and $VI-d_1$. Potassium hydrogen maleate ($VII$) was made by neutralizing a suspension of maleic acid in water with 1 equiv. of potassium hydroxide, and crystallizing from alcohol/water. The product was recrystallized from $C_2H_5OD/D_2O$ to give $VII-d_1$.

The structures of compounds $I$–$VII$ are shown in Fig. 1.

3.2. NMR

Deuterium spectra of $IV-d_5$ were acquired at 46.77011 MHz with a home-built spectrometer and probe, over a 213–333 K temperature range, using a standard solid echo pulse sequence, with a $\pi/2$ pulse of 2 $\mu$s and inter-pulse delays of 50 $\mu$s. At each temperature, two spectra were collected; one with a short relaxation delay (typically 50 ms–5 s, depending on temperature); and a second with a long delay (typically 60 s). Simulations of the deuteron powder spectra, shown below the experimental spectra, were carried out using the MXQET program. Spectra of $V-d_1$ and $VI-d_1$ were obtained on the same instrument, with a 3 $\mu$s $\pi/2$ pulse and an interpulse delay $\tau$ of 80 $\mu$s.

The singularities in the spectra were extracted by inspection, and the quadrupole coupling constant and asymmetry parameter $\eta$ obtained using standard formulas. Spin lattice...
relaxation times $T_1$, were determined by a three parameter fit to data from an inversion recovery quadrupole echo pulse sequence. Because these relaxation times were often very long (see below) recovery delays of 200 s were used between transients.

Variable temperature $^1$H and $^2$H NMR MAS spectra for compounds I, II and III were obtained on a Bruker Avance NMR spectrometer operating at 14 T, using a simple one-pulse sequence. $\pi/2$ pulses were $4 \mu$s for proton and $3 \mu$s for deuterons, respectively. Both isotopes were referenced to the isotropic frequencies of residual protons and of deuterons in solid dimethylsulfone-$d_6$, whose chemical shift was assumed to lie 2.4 ppm downfield from TMS. MAS sideband intensities were fit to computed patterns using $eqV_{zz}$ and $\eta$ as adjustable parameters, using a computer program based on the formulas derived by Herzfeld and Berger [19].

4. Results

Spectra of IV-$d_5$, obtained at 273 K as described above, with relaxation delays of 50 ms and 60 s are shown in Fig. 2(a) and (b), respectively. Because the phenolic deuteron had a long relaxation time, roughly independent of temperature, the spectra obtained at short relaxation times contained only signals from the four water deuterons (Fig. 2(a)), while the long-relaxation delay spectra had contributions from both water and phenolic deuterons (Fig. 2(b)); subtraction of the two spectra gave spectra from the phenolic deuterons alone (Fig. 2(c)). The value of the quadrupole coupling constant and asymmetry parameter obtained are consistent with the MAS sideband patterns previously measured by Wolf et al. [20] (those authors did not extract quantitative quadrupolar coupling parameters from their spectra).

Room temperature static quadrupole-echo $^2$H spectra of benzoylaceton-$d_1$ (V-$d_1$) and dibenzoylmethane-$d_1$ (VI-$d_1$) are shown in Fig. 3(a) and (b), respectively; both these and Fig. 2(c) are typical of the large-$\eta$ deuterium Pake doublets obtained from strongly hydrogen-bonded deuterons.

Fig. 4 shows $^1$H and $^2$H 14 T MAS spectra of the residual protons and the deuterons of nitromalonamide-$d_5$ (I-$d_5$). The proton spectrum shows one sharp peak around 18.5 ppm, which we assign to the O–H···O proton, and two complex multiplets between 7 and 11 ppm which are assigned to the four amide protons. A signal around 2.5 ppm arises from residual DMSO. Fine structure in the amide doublets arises from the slight non-degeneracy of the shifts, and also from the residual dipolar interaction between $^1$H and the quadrupolar $^{14}$N nucleus, which

![Fig. 2. $^1$H NMR spectra of sodium deuterium bis-4-nitrophenolate dideuterate, obtained (a) with a short recycle delay of 50 ms (b) a long recycle delay of 60 s (c) difference. Simulations (asterisked) are shown under the experimental spectra.](image1)

![Fig. 3. $^2$H solid-state NMR spectra of (a) benzoylaceton-$d_1$ (b) dibenzoylmethane-$d_1$.](image2)
is not fully removed by MAS. The deuterium spectrum (Fig. 3(b)) is somewhat more poorly resolved, but the O–D⋯O proton and the two amide peaks are clearly visible (inset), and therefore full MAS sideband patterns can be determined for each; these allow reconstruction of the deuterium eqVzz and η.

Fig. 5 shows the 2H 14T MAS spectra of the deuterons of bis(pyridinebetaine) hydrochloride monohydrate-d3 (II-d3). In this relatively simple spectrum only two sets of MAS sideband patterns are resolved, from the O–D⋯O and the water of hydration respectively. The D2O signal has the η=1 sideband envelope characteristic of a flipping water molecule; the considerable asymmetry of the O–D⋯O sideband envelope is indicative of a large chemical shielding anisotropy.

Fig. 6 shows 1H and 2H 14T MAS spectra of the residual protons and the deuterons of urea phosphoric acid-d7 (III-d7). The proton spectrum shows the expected sharp peak around 21 ppm for the O–H⋯O proton, a pair of resonances between 13 and 15 ppm arising from the other two P–O–H protons, and two complex multiplets between 8 and 12 ppm which are assigned to the four amide protons. The signal around 4.7 ppm arises from the liquid HDO contaminant; magic-angle spinning rotational sidebands are asterisked. The deuterium spectrum (Fig. 5(b)) is more cluttered than the comparable spectrum of I-d5, but the O–D⋯O signal is still clearly resolved (inset).

In every case, quadrupole coupling constants were extracted either from the singularities of the static patterns, or by fitting the sideband envelopes; these are plotted as a function of temperature in Fig. 7, along with previously [6] obtained data for 3-cyano-2,4-pentanedione-d1 (VIII-d1). The temperature dependences were fit to quadratic functions, and the first derivative of the dependence of the quadrupole coupling constant with temperature at 250 K extracted; these temperature derivatives are compiled, along with the extracted...
deuterium quadrupole coupling constants and proton chemical shifts, where available, in Table 2 and plotted in Fig. 8 versus the O···O distance, given in Table 1 with the relevant reference, along with some values obtained from the literature. In this plot, we chose to separate systems where the hydrogen bond forms part of a six-membered ring, where the hydrogen bond is substantially non-linear, from those where the hydrogen bond is linear or nearly linear.

5. Discussion

The experimental temperature coefficients presented in Fig. 8 contend persuasively to be diagnostic of short strong hydrogen bonds. Clearly, such large, counter-intuitive coefficients indicate a thermally accessible vibrational excited state with a larger $\varepsilon_{zz}$ than the ground state. While the unsophisticated model we presented previously [12] provides a plausible qualitative explanation for the temperature coefficients, it is clear from the computed values of the coefficients, shown as a hatched line in Fig. 8, that the simple one-dimensional potential does not quantitatively reproduce experimental data. Having examine a plethora of possible explanations for this discrepancy (use of Gaussian rather than Slater type orbitals, insufficient attention to electron correlation, interactions with lattice vibrations) we settled on two primary sources. One is neglect of the dielectric: symmetrical hydrogen bonds are necessarily non-polar along the hydrogen bond axis, while displacement of the hydrogen to either side creates a component of the molecular dipole along this axis. Such a dipole interacts with a polarizable medium, lowering the energy and thus relatively stabilizing off-center hydrogens. While these effects are more significant in other systems (particularly where displacement of the hydrogen creates a zwitterion), even in symmetric systems they tend to deepen double-well potentials.

A more significant effect still is the coupling between the hydrogen displacement mode and the longitudinal hydrogen bond O···O mode itself. The latter, in effect, creates the potential in which the hydrogen atoms vibrate. It is typically highly anharmonic and of higher symmetry than the hydrogen atom displacement, and therefore couples with both the vibrational ground and excited states of the hydrogen displacement mode. Because of the anharmonicity, the first excited vibrational state of $\psi_{OO}$ necessarily has an effective

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**Table 1**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Label</th>
<th>$r_{OO}$ (pm)</th>
<th>$r_{OH}$ (pm)</th>
<th>$r_{H-O}$ (pm)</th>
<th>$T$ (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitromalonamide</td>
<td>I</td>
<td>239.1</td>
<td>114.0</td>
<td>130.8</td>
<td>15</td>
<td>[21]</td>
</tr>
<tr>
<td>Bis(pyridine betaine) hydrochloride monohydrate</td>
<td>II</td>
<td>243.6</td>
<td>–</td>
<td>–</td>
<td>300</td>
<td>[22]</td>
</tr>
<tr>
<td>Urea phosphate</td>
<td>III</td>
<td>242.2</td>
<td>115.8</td>
<td>126.7</td>
<td>15</td>
<td>[23]</td>
</tr>
<tr>
<td>Sodium hydrogen bis-4-nitrophenolate dihydrate</td>
<td>IV</td>
<td>246.5</td>
<td>123.2</td>
<td>123.2</td>
<td>20</td>
<td>[24]</td>
</tr>
<tr>
<td>Benzoylacetone</td>
<td>V</td>
<td>249.9</td>
<td>124.5</td>
<td>132.9</td>
<td>20</td>
<td>[25]</td>
</tr>
<tr>
<td>Dibenzoylmethane</td>
<td>VI</td>
<td>245–246</td>
<td>–</td>
<td>–</td>
<td>5</td>
<td>[26,27]</td>
</tr>
<tr>
<td>Potassium hydrogen maleate</td>
<td>VII</td>
<td>242.7</td>
<td>121.5</td>
<td>121.5</td>
<td>5</td>
<td>[28]</td>
</tr>
<tr>
<td>4-Cyano-2,2,6,6-tetramethyl-3,5-heptanediene</td>
<td>VIII</td>
<td>239.3</td>
<td>121.6</td>
<td>122.0</td>
<td>20</td>
<td>[6]</td>
</tr>
</tbody>
</table>
average \( r_{OO} \) value significantly larger than the ground state, and therefore has a lower energy. Coupling of these modes together, therefore, lowers the first vibrational excited state energy, thus reducing the vibrational splitting and making the first vibrational state more thermally accessible. The effect is twofold; first, the maximum temperature coefficient is shifted to shorter \( r_{OO} \) distances; and second, the ground and particularly the first excited state quadrupole coupling constant acquire increased contributions from instantaneous configurations with larger \( r_{OO} \) values, thence increasing the thermal equilibrium value of eq\( V_{zz} \). The effect on the temperature coefficient is dramatically illustrated in Fig. 8, where the solid line depicts \( \delta (eq_{V_{zz}}) / \delta T \), computed assuming a reasonable solid-state dielectric and coupling between the two aforementioned modes. The computed curve now matches the maximum value of \( r_{OO} \) almost exactly, albeit the temperature coefficients are still approximately a factor of 2 smaller. As can be seen in Fig. 9, we also get a grossly improved agreement between the absolute magnitude of eq\( V_{zz} \) and experimental data. The points in Fig. 9 correspond to experimental values of eq\( V_{zz} \) tabulated by Berglund and Vaughan [8], supplemented with our values for compounds I–VIII. The lines are computed from the one-dimensional vacuum calculations (hatched) and the two-dimensional coupled, polarizable continuum model (solid). Clearly, the latter model agrees far better with the data, particularly considering the experimental data contain a considerable diversity of O–H···O systems, and asymmetrical as well as symmetrical hydrogen bonds (Table 2).

The major remaining discrepancy between experiment and theory lies in the magnitude of the experimental temperature coefficients. The origin of this discrepancy is likely our failure to include the effects of thermal expansion of the \( r_{OO} \) distance itself. Since thermal expansion of intermolecularly hydrogen-bonded crystals often leads to a significant increase in \( r_{OO} \), and since the quadrupole coupling constant depends strongly on \( r_{OO} \), we expect that this effect will augment the effect of thermal excitation of the vibrationally exited states top increase the positive dependence of eq\( V_{zz} \) on temperature. Preliminary calculations on IV, where the \( r_{OO} \) dependence on temperature has been measured crystallographically, seem to support this conjecture.

The four non-linear hydrogen bonds studied fall on a slightly different curve, and maximum temperature coefficients are obtained for somewhat smaller \( r_{OO} \) distances. It is likely that this is simply due to the non-linear nature of the minimum of the potential along the O···O direction; we have not yet completed calculations for such systems.

The significant interaction between O···O and O–H modes in these systems to some extent invalidates the discussion of what constitutes a ‘low-barrier hydrogen bond’, since the hydrogen wavefunction is no longer considered to be moving in a one-dimensional potential. It is better, perhaps, to look at the shape of the wavefunction itself. We find that |\( \psi_{IJ} \)| has

### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>( r_{OO} ) (pm)</th>
<th>( \delta(eq_{V_{zz}})/\delta T ) (kHz/K)</th>
<th>eq( V_{zz} ) kHz, 300 K</th>
<th>( \delta_{OHH} ) ppm, 300 K</th>
<th>( ^1H ) NMR, Ref.</th>
<th>( ^2H ) NMR, Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea phosphate (<strong>III</strong>)</td>
<td>242.2</td>
<td>0.027</td>
<td>71</td>
<td>20.9</td>
<td>This work</td>
<td>This work</td>
</tr>
<tr>
<td>Potassium hydrogen maleate (<strong>VII</strong>)</td>
<td>242.7</td>
<td>0.079</td>
<td>55</td>
<td>21.0</td>
<td>[29]</td>
<td>This work</td>
</tr>
<tr>
<td>Bis(pyridine betaine) hydrochloride monohydrate (<strong>II</strong>)</td>
<td>243.6</td>
<td>0.062</td>
<td>59</td>
<td>–</td>
<td>This work</td>
<td>This work</td>
</tr>
<tr>
<td>Potassium hydrogen succinate</td>
<td>244.1</td>
<td>0.062</td>
<td>53</td>
<td>–</td>
<td>[15]</td>
<td>[15]</td>
</tr>
<tr>
<td>Methylammonium hydrogen succinate monohydrate</td>
<td>244.5</td>
<td>0.075</td>
<td>59</td>
<td>–</td>
<td>This work</td>
<td>This work</td>
</tr>
<tr>
<td>KH acetylene dicarboxylate</td>
<td>244.5</td>
<td>0.078</td>
<td>60.5</td>
<td>–</td>
<td>[14]</td>
<td>[14]</td>
</tr>
<tr>
<td>RbH acetylene dicarboxylate</td>
<td>244.9</td>
<td>0.079</td>
<td>66</td>
<td>–</td>
<td>[14]</td>
<td>[14]</td>
</tr>
<tr>
<td>Sodium hydrogen bis-4-nitrophenolate dihydrate (<strong>IV</strong>)</td>
<td>246.5</td>
<td>0.112</td>
<td>87</td>
<td>–</td>
<td>This work</td>
<td>This work</td>
</tr>
<tr>
<td>Sodium hydrogen malonate</td>
<td>255.5</td>
<td>–0.034</td>
<td>165.5</td>
<td>–</td>
<td>[15]</td>
<td>[15]</td>
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<tr>
<td>KHCO\textsubscript{3}</td>
<td>260.7</td>
<td>–0.02</td>
<td>154.5</td>
<td>–</td>
<td>[14]</td>
<td>[14]</td>
</tr>
<tr>
<td>Nitromalonamide (<strong>I</strong>)</td>
<td>238.4</td>
<td>0.069</td>
<td>69</td>
<td>18.5</td>
<td>This work</td>
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<tr>
<td>4-Cyano-2,2,6,6-tetramethyl-3,5-heptanedione (<strong>VIII</strong>)</td>
<td>239.3</td>
<td>0.110</td>
<td>77</td>
<td>19.0</td>
<td>[6]</td>
<td>[6]</td>
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<tr>
<td>Dibenzoylethylene (<strong>VI</strong>)</td>
<td>245.5</td>
<td>–0.020</td>
<td>104</td>
<td>18.1</td>
<td>[9]</td>
<td>This work</td>
</tr>
<tr>
<td>Benzoyleacetone (<strong>V</strong>)</td>
<td>248.9</td>
<td>–0.018</td>
<td>111</td>
<td>16.2</td>
<td>[9]</td>
<td>This work</td>
</tr>
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</table>

Linear systems are given above non-linear systems.
a single maximum below 245 pm and a double maximum above this value, and thus for \( r_{\text{OO}} \) values under 245 pm linear O–H···O systems are best described by a model of a centered proton rather than a proton equally distributed between two wells. These systems still have significant deuterium temperature coefficients, albeit below the maximum observed.

In conclusion, with proper consideration of the medium dielectric and of the coupling between coupled hydrogen bond modes, we can get good agreement between computed and experimental NMR temperature coefficients, and these coefficients are both on theoretical and experimental grounds believed to be diagnostic of hydrogen bonds which are transitional between low-barrier double well and true single well systems.

Acknowledgements

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References