Theor Chem Account (2008) 119:29–34
DOI 10.1007/s00214-006-0182-5

REGULAR ARTICLE

The change of the proton magnetic shielding in red- and blue-shifted linear hydrogen-bonded complexes

Sean A. C. McDowell · A. David Buckingham

Received: 26 July 2006 / Accepted: 27 September 2006 / Published online: 7 December 2006

Abstract The change in the proton magnetic shielding constant of FH and FArH on the formation of the vibrationally red-shifted FH. . .Rg and blue-shifted FArH. . . Rg (Rg = Ne, Ar) complexes was determined by GIAO ab initio computations at various levels of theory. The blue-shifted FArH. . . N_2 and red-shifted FArH. . . P_2 complexes were also studied. The characteristic downfield shift of the isotropic proton magnetic resonance in red-shifted hydrogen-bonded complexes is smaller in the blue-shifted complexes. In FArH. . .Ne and FArH. . . N_2 the proton NMR actually shifts to higher fields on complexation. These results are rationalized by considering the changes in the magnetic and electric contributions to the proton shielding in FH and FArH.

1 Introduction

Hydrogen bonding between molecules can lead to observable changes in the properties of the interacting species. For example, it is normal to obtain a large red shift (decrease) of the A–H stretching frequency of the proton donor in H-bonded complexes A–H. . .B, where the base B is a proton acceptor, and a downfield shift of the proton magnetic resonance ranging up to about 5 ppm when the A–H molecule goes from the gas to liquid phase [1–3].

Other characteristic features of hydrogen bonding include the elongation of the A–H bond due to the attraction of the proton to the electron-rich region of B and an increase in the IR intensity of the A–H stretch [1,4]. However, it has become evident that sometimes the A–H stretching frequency *increases* on complexation (a blue shift). There is now a growing body of experimental and theoretical evidence for this unusual behaviour in which three features of conventional hydrogen bonds (elongation, red shift and IR intensity increase) are reversed in blue-shifting hydrogen bonds, mainly for hydrogen-bonded C–H bonds [5, references therein, 6] and metastable complexes containing inert gas molecules of general formula XRgH (Rg = inert gas atom, X = electronegative fragment) [7–9]. Although there is no widely accepted explanation for the blue-shifting behaviour, it appears to be due to the electrostatic interaction between the proton donor and proton acceptor along with the short-range overlap repulsion (see, for example, Refs. [10–12]).

Since the blue-shifted H-bonded complexes have features that are markedly different from those of the usual red-shifted complexes, it is of interest to investigate whether these differences also apply to the changes in the proton magnetic shielding on complex formation. In this paper, we report on computations of the isotropic and anisotropic components of the proton NMR shielding tensor for the linear FArH. . .Ne, FArH. . .Ar and FArH. . . N_2 complexes. Recent computations on the five linear complexes ClH. . .Y (Y = N_2, CO, OC, BF, FB) show that the two blue-shifting complexes ClH. . .OC and ClH. . .FB have substantially smaller downfield shifts on complexation [13]. The above FArH species

---

S. A. C. McDowell (✉) · A. David Buckingham
Department of Chemistry, University of Cambridge,
Lensfield Road, Cambridge CB2 1EW, UK
e-mail: sacm1@cam.ac.uk

Present Address:
S. A. C. McDowell
Department of Biological and Chemical Sciences,
University of the West Indies, Cave Hill Campus,
Bridgetown, Barbados

Table 1 MP2/6-311++G(2d,2p) optimized distances (in Å), interaction energies ΔE (in kJ mol^{-1}, uncorrected for zero-point energy) and harmonic vibrational frequency shifts (in cm^{-1}) for FH…Rg, FArH… Rg (Rg = Ne, Ar), FArH…N$_2$ and FArH…P$_2$ complexes

Species	r(A–H)	r(F–A)	R(H…B)	Δr(A–H)	ΔE	$\Delta\omega$(A–H)
FH…Ne	0.9179		2.2982	0.0001	−2.6	+2
FH…Ar	0.9186		2.5840	0.0008	−2.8	−18
FArH…Ne	1.3246	1.9995	2.6803	−0.0014	−1.5	+25
FArH…Ar	1.3214	2.0043	2.7526	−0.0046	−2.1	+59
FArH…N$_2$	1.3140	2.0286	2.1641	−0.0120	−8.1	+153
FArH…P$_2$	1.3362	2.0389	2.3370	0.0102	−9.9	−116

The frequency shift $\Delta\omega$ is defined as $\omega_{\text{complex}} - \omega_{\text{monomer}}$. The atom denoted A represents the atom to which the H atom is directly bonded in the proton donor and the atom denoted B represents the atom of the partner molecule to which the H atom is hydrogen bonded. The interaction energies are computed at the CCSD(T)/6-311++G(2d,2p) level of theory using the MP2/6-311++G(2d,2p) optimized geometries

exhibit a blue shift of the Ar–H vibrational stretching frequency (see Table 1) and a blue shift in FArH…N$_2$ has been observed in low-temperature matrix isolation experiments [7]. These results are consistent with computational studies, which also show that the Ar–H bond length contracts on complexation [7–9]. Similar computations for the red-shifting complexes FH…Ar and FArH…P$_2$ (as well as for FH…Ne which in the linear configuration exhibits a small blue shift) were also performed for comparison. The NMR computations were performed using the GIAO (gauge-including atomic orbitals) method [14–16] implemented in the Gaussian 03 suite of programs [17].

2 Basic theory and model

The nuclear shielding tensor $\boldsymbol{\sigma}^{(\mathrm{I})}$ for the nucleus I can be calculated as the second derivative of the energy W with respect to the external magnetic field $\mathbf{B}$ and the magnetic moment $\boldsymbol{\mu}^{(\mathrm{I})}$ of the nucleus:

$$W = W_0 \;-\; \mu_\alpha^{(\mathrm{I})}\left(\delta_{\alpha\beta} \;-\; \sigma_{\alpha\beta}^{(\mathrm{I})}\right)\mathrm{B}_\beta \tag{1}$$

The gauge-origin dependence problem in the calculation of magnetic properties (arising from the approximate wavefunctions and finite basis sets used in the calculations) is overcome by using the GIAO method [14–16].

The proton shielding tensor in weakly bound H-bonded complexes A–H…B is modelled as [18,19]:

$$\sigma_{\alpha\beta}^{(\mathrm{H})} = \sigma_{\alpha\beta}^{(\mathrm{H})(0)} + \sigma_{\alpha\beta}^{(\mathrm{H})(\mathrm{el})} + \sigma_{\alpha\beta}^{(\mathrm{H})(\mathrm{mag})} \tag{2}$$

where $\sigma_{\alpha\beta}^{(\mathrm{H})(0)}$ is the shielding tensor in the isolated A–H molecule, $\sigma_{\alpha\beta}^{(\mathrm{H})(\mathrm{el})}$ is the change in the tensor due to the non-uniform electric field, including those due to high-frequency fluctuations, arising from molecule B and $\sigma_{\alpha\beta}^{(\mathrm{H})(\mathrm{mag})}$ is the change due to the magnetization induced in molecule B. Hence, the change in the proton shielding tensor of A–H on complexation, $\delta\sigma_{\alpha\beta}^{(\mathrm{H})} = \sigma_{\alpha\beta}^{(\mathrm{H})} - \sigma_{\alpha\beta}^{(\mathrm{H})(0)}$, is

$$\delta\sigma_{\alpha\beta}^{(\mathrm{H})} = \sigma_{\alpha\beta}^{(\mathrm{H})(\mathrm{el})} + \sigma_{\alpha\beta}^{(\mathrm{H})(\mathrm{mag})} \tag{3}$$

$\delta\sigma_{\alpha\beta}^{(\mathrm{H})}$ can be evaluated by taking the difference between the ab initio values for the proton shielding tensors for A–H…B and isolated A–H, while $\sigma_{\alpha\beta}^{(\mathrm{H})(\mathrm{mag})}$ can be estimated by computing the magnetizability, $\boldsymbol{\xi}$, of B. If the magnetization of B can be represented as $\boldsymbol{\xi}$ times the magnetic field then, in the long-range limit [2] that neglects contributions from higher induced magnetic multipole moments (i.e. magnetic quadrupoles, octopoles, etc.) [20]

$$\sigma_{\alpha\beta}^{(\mathrm{H})(\mathrm{mag})} = -(\mu_0/4\pi)T_{\alpha\gamma}\xi_{\gamma\beta} \tag{4}$$

where μ_0 is the permeability of a vacuum ($\mu_0/4\pi = 10^{-7}\,\mathrm{JA^{-2}m^{-1}}$) and $T_{\alpha\gamma} = (3R_\alpha R_\gamma - R^2\delta_{\alpha\gamma})/R^5$. R is the distance from an origin in B to the H nucleus; if B = Rg, the natural choice of origin is the nucleus of the Rg atom in the complex, while if B is either N$_2$ or P$_2$, then the origin is at the centre of the bond in the diatomic molecule. For the diatomic molecules, there are two independent components of the magnetizability, $\xi_\parallel$ and $\xi_\perp$, so that for the linear A–H…B complex lying on the z axis from A→B the proton magnetic shielding is given by [2]

$$\sigma_{zz}^{(\mathrm{H})(\mathrm{mag})} = -(\mu_0/4\pi)(2\xi_\parallel/R^3) \tag{5}$$

$$\sigma_{xx}^{(\mathrm{H})(\mathrm{mag})} = \sigma_{yy}^{(\mathrm{H})(\mathrm{mag})} = (\mu_0/4\pi)(\xi_\perp/R^3), \tag{6}$$

The isotropic shielding is $\sigma^{\mathrm{iso}} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$ and the shielding anisotropy $\Delta\sigma = 3(\sigma_{zz} - \sigma^{\mathrm{iso}})/2 = \sigma_{zz} - \sigma_{xx}$ for linear systems. In previous work, the term $\sigma_{\alpha\beta}^{(\mathrm{H})(\mathrm{el})}$ was evaluated by expressing it as a Taylor series expansion in the electric field and field gradient [18,19]. However, in this study we evaluate it as a difference through Eq. (3). The values of $\sigma_{\alpha\beta}^{(\mathrm{H})(\mathrm{mag})}$ and $\sigma_{\alpha\beta}^{(\mathrm{H})(\mathrm{el})}$ that are obtained are useful in interpreting the change in the proton shielding tensor for red- and blue-shifted complexes and any significant differences can be assessed and rationalized using this approach.

3 Computational method

All ab initio calculations were performed using the Gaussian 03 suite of programs [17]. The complexes and the monomers were optimized to linear structures and the harmonic vibrational frequencies were computed at the MP2/6-311++G(2d,2p) level of theory; the bond length changes and frequency shifts were determined as the differences between the complex and monomer properties. The interaction energies for the complexes were determined at the CCSD(T)/6-311++G(2d,2p) level. The results for FH…Rg, FArH…Rg (Rg = Ne, Ar), FArH…N_2 and FArH…P_2 are in Table 1.

The monomer and complex geometries are fixed at their MP2/6-311++G(2d,2p) optimized values for the computation of the magnetic properties. The GIAO atomic and molecular magnetizabilities were computed at SCF and B3LYP using the large 6-311++G(3df,3pd) basis set, while the GIAO nuclear shielding tensors were calculated at the SCF, B3LYP and MP2 levels of theory using 6-311++G(2d,2p) and 6-311++G(3df,3pd) basis sets. There have been previous computations of nuclear shielding tensors using the GIAO formalism (see, for example, [21, 22, references therein]) and it has been noted previously that the LDA, BLYP and B3LYP functionals have a tendency to predict shielding tensors which are significantly too deshielded [22, references therein, 23]. Consequently, it is of interest to assess the performance of the B3LYP functional relative to SCF and MP2. Table 2 shows the magnetizabilities computed for Ne, Ar, N_2 and P_2. In Table 3 the proton magnetic shielding constants $(\sigma_{xx}, \sigma_{zz}, \sigma^{\text{iso}}, \Delta\sigma)$ of the FH…Rg and FArH…Rg complexes are com-

Table 2 B3LYP/6-311++G(3df,3pd) GIAO magnetizabilities for Ne, Ar, N_2 and P_2

Property	Ne	Ar	N_2	P_2
ξ_{xx} / a.u.	−1.621 (−1.567)	−4.370 (−4.342)	−1.838 (−1.832)	−3.687 (−4.091)
ξ_{zz} / a.u.	−1.621 (−1.567)	−4.370 (−4.342)	−3.870 (−3.899)	−9.860 (−10.10)
ξ^{iso} / a.u.	−1.621 (−1.567)	−4.370 (−4.342)	−2.515 (−2.521)	−5.745 (−6.093)

The parallel (ξ_{zz}), perpendicular (ξ_{xx}) and isotropic magnetizabilities (ξ^{iso}) were computed at the MP2/6-311++G(2d,2p) optimized geometries. SCF/6-311++G(3df,3pd) magnetizabilities are shown in parentheses. 1 a.u. = 7.891×10^{-29} JT^{-2}

Table 3 MP2/6-311++G(2d,2p) and MP2/6-311++G(3df,3pd) GIAO proton magnetic shielding (in ppm) for the linear optimized structures of FH…Rg and FArH…Rg (Rg = Ne, Ar) computed at the MP2/6-311++G(2d,2p) optimized geometries

Property	FH	FH…Ne	FH…Ar	FArH	FArH…Ne	FArH…Ar
(a) 6-311++G(2d,2p)						
$\sigma_{xx}^{(\text{H})}$	21.7391	20.5633	19.5004	13.7557	13.1517	12.0606
$\sigma_{zz}^{(\text{H})}$	44.1967	46.2809	48.1319	41.5221	42.8904	44.9786
$\sigma^{\text{iso}(\text{H})}$	29.2250	29.1359	29.0442	23.0111	23.0646	23.0333
$\Delta\sigma^{(\text{H})}$	22.4576	25.7176	28.6315	27.7664	29.7386	32.9179
$\delta\sigma_{xx}^{(\text{H})}$		−1.176	−2.239		−0.604	−1.695
$\delta\sigma_{zz}^{(\text{H})}$		2.084	3.935		1.368	3.456
$\delta\sigma^{\text{iso}(\text{H})}$		−0.089	−0.181		0.054	0.022
$\delta(\Delta\sigma^{(\text{H})})$		3.260	6.174		1.972	5.152
(b) 6-311++G(3df,3pd)						
$\sigma_{xx}^{(\text{H})}$	21.0030	19.7509	18.6510	13.2760	12.6650	11.5002
$\sigma_{zz}^{(\text{H})}$	44.1924	46.2796	48.1226	41.3897	42.7486	44.8336
$\sigma^{\text{iso}(\text{H})}$	28.7328	28.5938	28.4749	22.6472	22.6929	22.6113
$\Delta\sigma^{(\text{H})}$	23.1894	26.5287	29.4716	28.1137	30.0836	33.3334
$\delta\sigma_{xx}^{(\text{H})}$		−1.252	−2.352		−0.611	−1.776
$\delta\sigma_{zz}^{(\text{H})}$		2.087	3.930		1.359	3.444
$\delta\sigma^{\text{iso}(\text{H})}$		−0.139	−0.258		0.046	−0.036
$\delta(\Delta\sigma^{(\text{H})})$		3.339	6.282		1.970	5.219

The changes in the shielding from the free FH (FArH) molecule values on complexation are also given. The *xx* and *zz* components of the shielding tensor, the isotropic shielding and the shielding anisotropy are shown

Table 4 MP2/6-311++G(2d,2p) and MP2/6-311++G(3df,3pd) GIAO proton magnetic shielding (in ppm) for the linear optimized structures of FArH. . . N_2 and FArH. . . P_2 computed at the MP2/6-311++G(2d,2p) optimized geometries

Property	FArH. . . N_2	FArH. . . P_2
(a) MP2/6-311++G(2d,2p)		
$\sigma_{xx}^{(H)}$	12.0707	9.7412
$\sigma_{zz}^{(H)}$	45.5622	47.5354
$\sigma^{\text{iso(H)}}$	23.2345	22.3392
$\Delta\sigma^{(H)}$	33.4915	37.7942
$\delta\sigma_{xx}^{(H)}$	−1.685	−4.014
$\delta\sigma_{zz}(H)$	4.040	6.013
$\delta\sigma^{\text{iso(H)}}$	0.223	−0.672
$\delta(\Delta\sigma^{(H)})$	5.725	10.028
(a) MP2/6-311++G(3df,3pd)		
$\sigma_{xx}^{(H)}$	11.4684	9.4260
$\sigma_{zz}^{(H)}$	45.4146	47.3711
$\sigma^{\text{iso(H)}}$	22.7838	22.0744
$\Delta\sigma^{(H)}$	33.9462	37.9451
$\delta\sigma_{xx}^{(H)}$	−1.808	−3.850
$\delta\sigma_{zz}^{(H)}$	4.025	5.981
$\delta\sigma^{\text{iso(H)}}$	0.137	−0.573
$\delta(\Delta\sigma^{(H)})$	5.348	9.831

The changes in the shielding from the free FArH molecule values on complexation are also given. The *xx* and *zz* components of the shielding, the isotropic shielding and the shielding anisotropy are shown

pared, while in Table 4 a similar comparison is made for FArH. . . N_2 and FArH. . . P_2.

In Table 5, the change in the isotropic ($\delta\sigma^{\text{iso}}$) and the anisotropic ($\delta\Delta\sigma$) shielding are compared for the SCF, B3LYP and MP2 methods using the 6-311++G(3df,3pd) basis set, while in Table 6, the electric and magnetic components of the proton shielding tensors at the MP2/6-311++G(3df,3pd) level for all of the complexes are compared in order to assess their relative contributions to the changes in the isotropic shielding ($\delta\sigma^{\text{iso}}$).

Table 5 Comparison of the change in the proton isotropic shielding ($\delta\sigma^{\text{iso}}$) and the proton anisotropic shielding ($\delta(\Delta\sigma)$) for FH. . .Rg, FArH. . .Rg (Rg = Ne, Ar), FArH. . . N_2 and FArH. . . P_2 computed at the SCF, B3LYP and MP2 levels of theory using the 6-311++G(3df,3pd) basis set

Property	SCF	B3LYP	MP2
$\delta\sigma^{\text{iso}}$ {FH . . . Ne}	−0.153	−0.152	−0.139
$\delta\sigma^{\text{iso}}$ {FH . . . Ar}	−0.323	−0.306	−0.258
$\delta\sigma^{\text{iso}}$ {FArH . . . Ne}	0.005	0.015	0.046
$\delta\sigma^{\text{iso}}$ {FArH . . . Ar}	−0.162	−0.109	−0.036
$\delta\sigma^{\text{iso}}$ {FArH . . . N_2}	−0.148	0.235	0.137
$\delta\sigma^{\text{iso}}$ {FArH . . . P_2}	−1.068	−0.273	−0.573
$\delta(\Delta\sigma)$ {FH . . . Ne}	3.264	3.383	3.339
$\delta(\Delta\sigma)$ {FH . . . Ar}	6.319	6.371	6.282
$\delta(\Delta\sigma)$ {FArH . . . Ne}	1.976	2.034	1.970
$\delta(\Delta\sigma)$ {FArH . . . Ar}	5.370	5.358	5.219
$\delta(\Delta\sigma)$ {FArH . . . N_2}	6.291	5.833	5.348
$\delta(\Delta\sigma)$ {FArH . . . P_2}	10.373	9.480	9.831

4 Discussion

The data given in Table 1 are useful in characterising the red- and blue-shifted complexes. In the red-shifted complexes (FH. . .Ar, FArH. . . P_2), the A–H bond is elongated while in the blue-shifted complexes (FArH. . .Rg, FArH. . . N_2), the A–H bond is compressed. This is typical. The FH. . .Ne species is an exception since a small elongation of the F–H bond is obtained even though the F–H vibrational stretch is shifted upwards by 2 cm^{-1}; this species represents the threshold between red-and blue-shifting behaviour and we should take into consideration the small structural and vibrational changes when assessing the changes in the FH magnetic properties on complexation.

The more strongly bound species (FArH. . . N_2 and FArH. . . P_2) also show the larger structural and vibrational changes. The interaction energies are in the order FArH . . . P_2 > FArH . . . N_2 > FH . . . Ar > FH . . . Ne > FArH . . . Ar > FArH . . . Ne. Table 2 compares the magnitudes of the magnetizabilities of the proton acceptor molecules; SCF and B3LYP values are in reasonable agreement. ξ(Ar) is almost three times larger than ξ(Ne). The magnetizability components of P_2 are larger (in magnitude) than those of N_2, with the isotropic magnetizability of P_2 being more than twice as large as the corresponding value for N_2.

Table 3 compares the MP2 magnetic properties of the FH. . .Rg and FArH. . .Rg complexes with fair agreement between the two different basis sets. The change in the sign of $\delta\sigma^{\text{iso}}$ for FArH. . .Ar with basis set prompted us to assess the basis set superposition error (BSSE) on $\delta\sigma^{\text{iso}}$ so that we could have confidence in the results with the larger basis set. Counterpoise correction to $\delta\sigma^{\text{iso}}$ using the 6-311++G(2d,2p) basis set for FArH. . .Ar (and FArH. . .Ne, for comparison) gave an estimate of −0.061 ppm (0.035 ppm), which has the same sign as and is in qualitative agreement with the value of −0.036 ppm (0.046 ppm) obtained with the 6-311++G(3df,3pd) basis set. There is a decrease in $\sigma_{xx}^{(H)}$ and an increase in $\sigma_{zz}^{(H)}$ which results in an increased shielding anisotropy ($\Delta\sigma$) on complexation, ranging in magnitude from 3.3 ppm (for FH. . .Ne) to 6.3 (for FH. . .Ar). Complexation leads to a reduction in σ^{iso} at 6-311++G(3df,3pd), except for FArH. . .Ne, where an *increase* in σ^{iso} is obtained. What is notable here is the *relative* magnitude of these changes in the isotropic shielding. The red-shifted FH…Ar has the largest decrease in $\sigma^{\mathrm{iso(H)}}$ of 0.258 ppm compared with the blue-shifted FArH…Ne and FArH…Ar complexes, which show, respectively, an increase of 0.046 ppm and a decrease of 0.036 ppm. The small blue shift of 2 cm^{-1} for FH…Ne correlates with a change of $\sigma^{\mathrm{iso(H)}}$ of −0.139 ppm.

The relationship between the sign of the frequency shift (red or blue) and the change in the proton isotropic shielding is more striking when FArH…N_2 and FArH…P_2 are compared, as shown in Table 4. As is the case for the FH…Rg and FArH…Rg complexes, $\delta\sigma_{xx}^{\mathrm{(H)}}$ is negative while $\delta\sigma_{zz}^{\mathrm{(H)}}$ is positive, with larger changes obtained for the more strongly bound FArH…P_2 complex. However, for these two species $\delta\sigma^{\mathrm{iso}}$ has *opposite* signs. The strongly red-shifted FArH…P_2 shows the typical downfield shift of the isotropic proton shielding (by −0.573 ppm at MP2/6-311++G(3df,3pd)) while the strongly blue-shifted FArH…N_2 shows an upfield shift of the proton isotropic shielding (by 0.137 ppm). The shielding anisotropy in *both* complexes is increased (by as much as 9.8 ppm for FArH…P_2) but this is not anomalous.

Table 5 shows good agreement between SCF, B3LYP and MP2 for the change in the anisotropic proton shielding. However, the B3LYP and MP2 values for the isotropic proton shielding are only in qualitative agreement. For example, the MP2 value for $\delta\sigma^{\mathrm{iso}}$ of FArH…P_2 (−0.573 ppm) is more than twice the B3LYP value (−0.273 ppm), while $\delta\sigma^{\mathrm{iso}}$ at MP2 for FArH…N_2 (0.137 ppm) is only 0.6 of the B3LYP value (0.235 ppm). The SCF values for $\delta\sigma^{\mathrm{iso}}$ seem to be unreliable for the FArH complexes. For example, compared with the B3LYP and MP2 results, it is too small for FArH…Ne, too large for FArH…Ar and FArH…P_2, and has the wrong sign for FArH…N_2.

In order to rationalize the contrasting results for the change in isotropic proton shielding, $\delta\sigma^{\mathrm{iso}}$ was partitioned into its electric ($\delta\sigma^{\mathrm{iso(el)}}$) and magnetic ($\delta\sigma^{\mathrm{iso(mag)}}$) components; the results for the six complexes are in Table 6.

We consider the FH…Rg and FArH…Rg complexes together since the proton acceptor is spherically symmetric. For these species the magnetic contribution to the proton isotropic shielding is zero, even if higher induced magnetic moments are considered [20], so that the relative magnitude of the proton isotropic shielding is determined by the effect of the electric field originating from the Rg atom. This electric field arises from the multipole moments induced in the Rg atom by the polar FH and FArH molecules and from the rapidly oscillating field due to the fluctuating electronic coordinates in Rg that give rise to dispersion interactions. For FH…Ne and FH…Ar, $\sigma_{xx}^{\mathrm{(H)(el)}}$, $\sigma_{yy}^{\mathrm{(H)(el)}}$ and $\sigma_{zz}^{\mathrm{(H)(el)}}$ are negative and taken together yield a reduction in the isotropic proton shielding (characteristic of red-shifted complexes). However, the $\sigma_{xx}^{\mathrm{(H)(el)}} (= \sigma_{yy}^{\mathrm{(H)(el)}})$ component is positive for FArH…Ne and negative for FArH…Ar, but $\sigma_{zz}^{\mathrm{(H)(el)}}$ is positive for both species, leading to a reduced isotropic downfield shift in FArH…Ar and a small isotropic *upfield* shift in FArH…Ne of the proton resonance.

For FArH…N_2 and FArH…P_2, the magnetic component of the proton isotropic shielding is no longer zero. The $\sigma_{xx}^{\mathrm{(H)(mag)}} (= \sigma_{yy}^{\mathrm{(H)(mag)}})$ term is negative and substantially smaller than the positive $\sigma_{zz}^{\mathrm{(H)(mag)}}$ term in both complexes, leading to a net increase in σ^{iso} (due to the magnetization of the proton acceptor) by 0.531 ppm in FArH…N_2 and 0.901 ppm in FArH…P_2. The magnitudes of $\sigma_{xx}^{\mathrm{(H)(mag)}}$ and $\sigma_{zz}^{\mathrm{(H)(mag)}}$ for FArH…P_2 are larger than the corresponding values for FArH…N_2 by 0.1 and 1.3 ppm, respectively. The $\sigma_{xx}^{\mathrm{(H)(el)}} (= \sigma_{yy}^{\mathrm{(H)(el)}})$ and the $\sigma_{zz}^{\mathrm{(H)(el)}}$ terms are opposite in sign in both complexes but by contrast with the magnetic terms, lead

Table 6 Comparison of the electric ($\sigma_{zz}^{\mathrm{H(el)}}$) and magnetic ($\sigma_{zz}^{\mathrm{H(mag)}}$) components of the proton shielding tensors, and the change in the proton isotropic shielding ($\delta\sigma^{\mathrm{iso}}$) for FH…Rg, FArH…Rg (Rg = Ne, Ar), FArH…N_2 and FArH…P_2 complexes (in ppm) computed at the MP2/6-311++G(3df,3pd) level of theory. $\sigma^{\mathrm{iso}} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$ and $\delta\sigma^{\mathrm{iso}} = \sigma^{\mathrm{iso(el)}} + \sigma^{\mathrm{iso(mag)}}$. The magnetic components were computed using the B3LYP/6-311++G(3df,3pd) magnetizabilities

Property	FH…Ne	FH…Ar	FArH…Ne	FArH…Ar	FArH…N_2	FArH…P_2
$\sigma_{xx}^{\mathrm{H(el)}}$	−0.198	−0.353	0.053	−0.123	−1.088	−3.044
$\sigma_{zz}^{\mathrm{H(el)}}$	−0.021	−0.067	0.030	0.138	0.993	1.667
$\sigma_{xx}^{\mathrm{H(mag)}}$	−1.054	−1.999	−0.664	−1.653	−0.720	−0.806
$\sigma_{zz}^{\mathrm{H(mag)}}$	2.108	3.997	1.329	3.306	3.032	4.314
$\sigma^{\mathrm{iso(el)}}$	−0.139	−0.258	0.046	−0.036	−0.394	−1.474
$\sigma^{\mathrm{iso(mag)}}$	0.0	0.0	0.0	0.0	0.531	0.901
$\delta\sigma^{\mathrm{iso}}$	−0.139	−0.258	0.046	−0.036	0.137	−0.573

to a reduction in σ^{iso} by 0.394 ppm in FArH…N_2 and 1.474 ppm in FArH…P_2. The relative differences between the individual shielding tensor components (electric and magnetic) for these two complexes are useful in rationalizing why the net shift in σ^{iso} is positive for FArH…N_2 and negative for FArH…P_2. The electric terms are due to the effects of the static and fluctuating electric field originating from the proton acceptor; the fluctuating field gives rise to a long-range dispersion-force-type interaction which will be more significant for the larger P_2 molecule. However, the dominant magnetic contributions in both complexes ($\sigma_{zz}^{(\mathrm{H})(\mathrm{mag})}$) are positive in sign. Hence, the relatively smaller negative electric contribution in FArH…N_2 combined with the larger positive magnetic contribution leads to a *positive* proton isotropic shielding for this blue-shifted complex, while the relatively larger electric contribution in FArH…P_2 leads to a *negative* proton isotropic shielding for this red-shifted complex.

In conclusion, it seems that another manifestation of the difference between red- and blue-shifted hydrogen-bonded complexes may be the relative magnitude, and in some cases the sign, of the change in the proton isotropic shielding tensor for these complexes. The blue-shifted complexes seem to be either shifted upfield or shifted downfield to a lesser extent than red-shifted complexes for which a downfield shift is typical. It will be interesting to learn if this phenomenon is more widespread.

Acknowledgements The authors wish to acknowledge the financial support of the Engineering and Physical Sciences Research Council (EPSRC) through a Visiting Fellowship (EP/C517792) for SACM to the University of Cambridge. One of us (ADB) would like to express his pleasure in contributing to this special issue in honour of his former research student Philip Stephens.

References

1. Pimentel GC, McLellan AL (1960) The hydrogen bond. Freeman, San Francisco
2. Pople JA, Schneider WG, Bernstein HJ (1959) High-resolution nuclear magnetic resonance. McGraw-Hill, New York
3. Pullman B (ed) (1981) Intermolecular forces: the Jerusalem symposia on quantum chemistry and biochemistry. D. Reidel, Dordrecht
4. Scheiner S (1997) Hydrogen bonding. Oxford University Press, New York
5. Hobza P, Havlas Z (2002) Theor Chem Acc 108:325
6. Pohle W, Gauger DR, Bohl M, Mrazkova E, Hobza P (2004) Biopolymers 74:27
7. Lignell A, Khriachtchev L, Pettersson M, Rasanen M (2003) J Chem Phys 118:11120
8. McDowell SAC (2003) J Chem Phys 119:3711
9. McDowell SAC (2003) Phys Chem Chem Phys 5:808
10. Hermansson K (2002) J Phys Chem A 106:4695
11. Li X, Liu L, Schlegel HB (2002) J Am Chem Soc 124:9639
12. McDowell SAC, Buckingham AD (2005) J Am Chem Soc 127:15515
13. McDowell SAC, Buckingham AD (2006) Mol Phys 104:2527
14. London F (1937) J Phys Radium 8:397
15. Ditchfield R (1974) Mol Phys 27:789
16. Wolinski K, Hinton JF, Pulay P (1990) J Am Chem Soc 112:8251
17. Gaussian 03, Revision A.7, Frisch MJ et al (2003) Gaussian, Inc., Pittsburgh
18. Buckingham AD, Tantirungrotechai Y (1999) Mol Phys 96:1217
19. Buckingham AD, Tantirungrotechai Y (1999) Mol Phys 96:1225
20. Buckingham AD, Stiles PJ (1972) Mol Phys 24:99
21. Rauhut G, Puyear S, Wolinski K, Pulay P (1996) J Phys Chem 100:6310
22. Keal TW, Tozer DJ, Helgaker T (2004) Chem Phys Lett 391:374
23. Wilson PJ, Amos RD, Handy NC (1999) Mol Phys 97:757