

What Parameters Determine N–N and O–O Coupling Constants (${}^2hJ_{X-X}$) Across X–H⁺–X Hydrogen Bonds?

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Equation of motion coupled-cluster calculations (EOM-CCSD) have been performed to obtain ${}^{15}\text{N}$ – ${}^{15}\text{N}$ and ${}^{17}\text{O}$ – ${}^{17}\text{O}$ coupling constants (${}^2hJ_{X-X}$) across N–H⁺–N and O–H⁺–O hydrogen bonds in a series of protonated dimers. ${}^2hJ_{X-X}$ values are dominated by the Fermi-contact term and are distance dependent. Large coupling constants are associated with symmetric hydrogen bonds, short hydrogen bond distances, and low electron densities on the hydrogen-bonded proton, and are not related to the binding energies of these complexes. The magnitudes of coupling constants do not appear to be related to the nature of the covalent bonding of the hydrogen-bonded nitrogen and oxygen atoms, although this bonding indirectly determines the coupling constant by determining the N–N or O–O distance. Complexes with sp^2 -hybridized oxygens are more sensitive to the trans or cis orientation of the hydrogen-bonded pairs than are the corresponding nitrogen complexes. One-bond coupling constants (${}^1hJ_{X-H}$) are greater than two-bond couplings (${}^2hJ_{X-X}$) in complexes with symmetric hydrogen-bonds, but ${}^1J_{N-H}$ is greater than ${}^2hJ_{N-N}$ which is greater than ${}^1hJ_{N-H}$ for nonsymmetric hydrogen bonds. When reduced coupling constants are used for comparison, ${}^2hK_{X-X}$ is always greater than ${}^1K_{X-H}$, which is greater than ${}^1hK_{X-H}$.

Introduction

In recent years there has been significant excitement about NMR coupling constants across X–H–Y hydrogen bonds.^{1–15} This interest is related to the potential usefulness of coupling constants for structure determination, particularly in biological systems. We have developed in this laboratory the equation-of-motion coupled-cluster singles and doubles technique (EOM-CCSD)^{16–19} for computing NMR spin–spin coupling constants. With this technique and an appropriate basis set, computed coupling constants have been shown to be in agreement with available experimental data and to have predictive value. In five recent papers, we have evaluated coupling constants in hydrogen-bonded systems. The first system consists of the clusters F[−](HF)_{*n*} for *n* = 1–4,¹¹ for which good experimental values are available.² Contrary to recent SOS-DFT results,² we obtained values of ${}^2hJ_{F-F}$ that, without any rescaling, are in agreement with experimental data. We have also investigated sets of prototypical cationic, neutral, and anionic complexes containing N–H–N, N–H–O, and O–H–O hydrogen bonds, and confirmed the dominance of the Fermi-contact term for determining ${}^2hJ_{X-Y}$, and the distance dependence of this term.¹² The third study focused on the complex ClH:NH₃, and related Cl–N coupling constants and proton chemical shifts of the hydrogen-bonded proton to equilibrium structures and anharmonic proton-stretching vibrational frequencies in external electric fields.¹³ We have also investigated four-bond couplings [${}^4hJ({}^{31}\text{P}–{}^{31}\text{P})$] across an N–H⁺–N hydrogen bond in a model system [H₃P–(H)N⋯H⁺⋯N(H)–PH₃], and computed ${}^4hJ({}^{31}\text{P}–{}^{31}\text{P})$ coupling constants in agreement with experimentally measured values.¹⁴ Finally, in a very recent study we have investigated the influence of the bonding at the nitrogens on computed N–N coupling

constants across traditional, linear N–H⋯N hydrogen bonds in neutral complexes.¹⁵

In the present paper, our aim is to examine relationships between the computed values of two-bond ${}^{15}\text{N}$ – ${}^{15}\text{N}$ and ${}^{17}\text{O}$ – ${}^{17}\text{O}$ coupling constants (${}^2hJ_{N-N}$ and ${}^2hJ_{O-O}$) and other parameters that are useful descriptors for hydrogen-bonded complexes. We will address the following questions.

1. To what extent are binding energies of hydrogen-bonded complexes related to the magnitude of ${}^2hJ_{X-X}$?
2. Do structural parameters (hydrogen bond distances and the relative orientation of the hydrogen-bonded molecules) correlate with the magnitudes of coupling constants?
3. To what extent does the nature of the covalent bonds formed by O and N atoms in O–H⁺–O and N–H⁺–N hydrogen bonds influence coupling constants?

Because the magnitude of coupling constants across hydrogen bonds is relatively small in neutral hydrogen-bonded complexes, we have focused this investigation on cationic complexes, which exhibit much larger coupling constants.¹² In some cases, we have imposed symmetry restrictions on the structures of these complexes. These restrictions are useful not only for doing the calculations, but also for removing small structural differences among closely related complexes. The complexes investigated in this study are protonated dimers of H₂O, H₂CO, CO, HNO, and HPO with O–H⁺–O hydrogen bonds; and protonated dimers of NH₃, N₂, HCN, HNO, and HPNH with N–H⁺–N hydrogen bonds. Because oxygen nuclei that are magnetically active have quadrupole moments, spin–spin coupling constants have not been measured experimentally for these atoms. The computed values reported here are therefore predictive.

Methods

The structures of the complexes O₂H₅⁺, H₂CO–H⁺–OCH₂, CO–H⁺–OC, HNO–H⁺–ONH, HPO–H⁺–OPH, N₂H₇⁺,

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TABLE 1: O–O Distances (Å) and Coupling Constants in Complexes with O–H⁺–O Hydrogen Bonds

| complex | sym ^a | O–O | PSO ^b | DSO ^b | FC ^b | SD ^b | ^{2h} J _{O–O} ^b |
|---|--------------------------------|-------|------------------|------------------|-----------------|-----------------|---|
| O ₂ H ₅ ⁺ ^c | C ₂ * ^c | 2.385 | −0.6 | 0.0 | 39.9 | 0.2 | 39.5 |
| CO–H ⁺ –OC | D _{∞h} * ^c | 2.393 | −0.2 | 0.0 | 42.9 | 0.1 | 42.8 |
| H ₂ CO–H ⁺ –OCH ₂ | C _{2h} * ^c | 2.409 | −0.3 | 0.0 | 19.3 | 0.5 | 19.5 |
| | C _{2v} | 2.394 | −0.4 | 0.0 | 26.9 | 0.2 | 26.7 |
| | D _{2h} | 2.351 | | | 63.1 | | 63.1 |
| H ₂ CO–H ⁺ –OCH ₂ ^d | C _{2v} | 2.409 | | | 21.0 | | 21.0 |
| | D _{2h} | 2.409 | | | 59.2 | | 59.2 |
| | D _{2d} | 2.409 | | | 59.0 | | 59.0 |
| HNO–H ⁺ –ONH | C _{2h} * ^c | 2.448 | −0.1 | 0.0 | 13.7 | 0.8 | 14.4 |
| | C _{2v} | 2.449 | −0.4 | 0.0 | 16.8 | 0.6 | 17.0 |
| | C _{2h} ^e | 2.448 | | | 55.5 | | 55.5 |
| HPO–H ⁺ –OPH | C _{2h} * ^c | 2.400 | −0.4 | 0.0 | 23.2 | 0.3 | 23.1 |
| | C _{2v} | 2.388 | | | 30.5 | | 30.5 |

^a The symmetry constraint placed on the structure during optimization. Complexes designated with an asterisk are equilibrium structures on the potential surfaces. ^b Total coupling constant ^{2h}J_{O–O} and its components (paramagnetic spin–orbit, PSO; diamagnetic spin–orbit, DSO; Fermi-contact, FC; and spin-dipole, SD), given in Hz. ^c Data taken from ref 12. ^d Calculations on these complexes were done at the optimized O–O distance in the equilibrium C_{2h} structure. ^e The O–O distance in this complex was set equal to the distance in the C_{2h} complex, and the N–O–H⁺–O–N atoms are collinear.

NN–H⁺–NN, HCN–H⁺–NCH, O(H)N–H⁺–N(H)O, and HP(H)N–H⁺–N(H)PH were optimized at second-order many-body perturbation theory [MBPT(2) = MP2]^{20–23} with the 6-31+G(d,p) basis set^{24–27} under the symmetry constraints indicated in Tables 1 and 2. Harmonic vibrational frequencies were computed to identify those complexes that are equilibrium structures (no imaginary frequencies). The coupling constants ^{2h}J_{X–X} were obtained from equation-of-motion coupled cluster singles and doubles (EOM-CCSD) calculations using the configuration interaction (CI-like) approximation,^{16–19} a level of theory that produces quantitatively accurate coupling constants when compared to experimentally measured values. These calculations were carried out using the Ahlrichs²⁸ qzp basis set on non-hydrogen atoms and qz2p on phosphorus and the hydrogen-bonded proton, and the Dunning cc-pVDZ basis set on other hydrogens.^{29,30} The effect of replacing the qz2p basis set on non-hydrogen-bonded hydrogens by the cc-pVDZ basis set was tested on the equilibrium C_{2h} structure of H₂CO–H⁺–OCH₂, in which case the computed value of the Fermi-contact term was unchanged. Gaussian 98³¹ had been used previously to optimize the structures of these ions. All of the NMR calculations were carried out using the ACES II program³² on the SGI Origin computer at the Ohio Supercomputer Center.

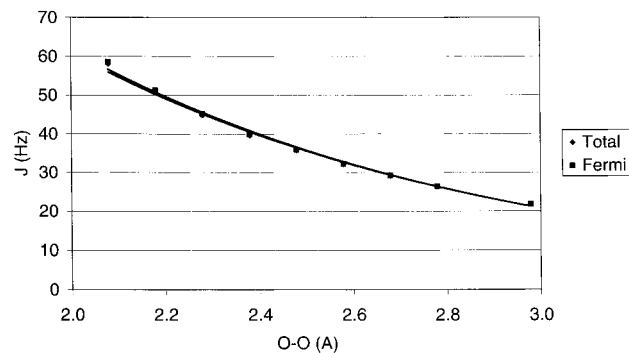
Results and Discussion

Complexes with O–H⁺–O Hydrogen Bonds. The complexes O₂H₅⁺ (protonated water dimer, C₂), CO–H⁺–OC (protonated carbon monoxide dimer, D_{∞h}), H₂CO–H⁺–OCH₂ (protonated formaldehyde dimer, C_{2h}), HNO–H⁺–ONH (C_{2h}), and HPO–H⁺–OPH (C_{2h}) are equilibrium structures on their respective potential surfaces, each having a symmetrical proton-shared O–H⁺–O hydrogen bond. As evident from Table 1, these complexes have very short O–O distances, which range from 2.385 Å in O₂H₅⁺ to 2.448 Å in HNO–H⁺–ONH. The complexes with C_{2h} symmetry will be referred to subsequently as “trans” structures, since in these complexes the monomer units are trans with respect to the hydrogen-bonding O–O line. The corresponding “cis” complexes of C_{2v} symmetry have also been optimized, and data for these are reported in Table 1. The O–O distances in the cis isomers are within 0.01 Å of the O–O distances in the corresponding trans isomers, and the hydro-

TABLE 2: N–N Distances (Å) and Coupling Constants (Hz) in Complexes with N–H⁺–N hydrogen bonds

| complex | sym ^a | N–N | PSO | DSO | FC | SD | ^{2h} J _{N–N} |
|--|--------------------------------|--------------------|------|-----|------|-----|--------------------------------|
| N ₂ H ₇ ⁺ | C _{3v} * ^c | 2.705 ^b | −0.1 | 0.0 | 12.9 | 0.1 | 12.9 |
| | D _{3d} | 2.597 | −0.1 | 0.0 | 17.2 | 0.1 | 17.2 |
| HCN–H ⁺ –NCH ^c | D _{∞h} * ^c | 2.521 | 0.0 | 0.0 | 32.5 | 0.1 | 32.6 |
| NN–H ⁺ –NN | D _{∞h} * ^c | 2.550 | 0.0 | 0.0 | 28.5 | 0.0 | 28.5 |
| O(H)N–H ⁺ –N(H)O | C _s * ^c | 2.674 ^d | | | 19.4 | | 19.4 |
| | C _{2h} | 2.600 | −0.1 | 0.0 | 25.4 | 0.1 | 25.4 |
| | C _{2v} | 2.592 | −0.2 | 0.0 | 25.8 | 0.1 | 25.7 |
| HP(H)N–H ⁺ –N(H)PH | C _{2h} | 2.572 | | | 22.1 | | 22.1 |
| | C _{2v} | 2.564 | | | 23.3 | | 23.3 |

^a The symmetry constraint placed on the structure during optimization. Complexes designated with an asterisk are equilibrium structures on the potential surfaces. ^b The shorter N–H distance is 1.113 Å. ^c Data taken from ref 12. ^d The shorter N–H distance is 1.135 Å.

**Figure 1.** Fermi-contact contribution to *J* and total *J* for O₂H₅⁺ plotted against the O–O distance.

gen bond is essentially linear, although the hydrogen-bonded proton lies near but usually not exactly on the O–O line. An H₂CO–H⁺–OCH₂ complex having D_{2h} symmetry has also been optimized and found to have the shortest O–O distance of 2.351 Å.

The paramagnetic spin–orbit (PSO), diamagnetic spin–orbit (DSO), Fermi-contact (FC), and spin-dipole (SD) contributions to the coupling constant *J*, and total *J* (^{2h}J_{O–O}), are reported in Table 1. As noted previously,¹² the coupling constant *J* is dominated by the Fermi-contact term, which is always more than an order of magnitude larger than any other term. The dominance of the Fermi-contact term is again evident from Table 1. All terms which contribute to total *J* have not been evaluated for some of the complexes listed in Tables 1 and 2. For these, total *J* will be approximated by the Fermi-contact term.

A comparison of the coupling constants for the equilibrium structures of all complexes with O–H⁺–O hydrogen bonds shows that O₂H₅⁺ and CO–H⁺–OC have the largest ^{2h}J_{O–O} values, 39.5 and 42.8 Hz, respectively. This is an interesting observation in itself, particularly when it is noted that the hybridization of O in these two complexes is sp³ and sp, respectively. The O–O coupling constants in the equilibrium structures of the remaining three complexes which have sp²-hybridized oxygens are significantly less at 19.5, 14.4, and 23.1 Hz. Plots of the Fermi-contact term and total *J* as a function of distance for O₂H₅⁺ are essentially superimposable, as shown in Figure 1. ^{2h}J_{O–O} for CO–H⁺–OC lies close to the curves shown in this plot, which means that the distance dependence of ^{2h}J_{O–O} for O₂H₅⁺ and CO–H⁺–OC are similar. In contrast, coupling constants for the equilibrium structures of complexes that have C_{2h} symmetry lie significantly below these curves. For example, the computed coupling constant for H₂CO–H⁺–OCH₂ would correspond to an O–O distance of about 3.0 Å in

TABLE 3: Hydrogen Bond Distances (X–X, Å), Binding Energies (ΔE_e , kcal/mol), and the Spin–Spin Coupling Constant (${}^2hJ_{X-X}$, Hz) for Equilibrium Structures

| complex | sym | X–X | ΔE_e^a | ${}^2hJ_{X-X}$ |
|-------------------|----------------|-------|----------------|----------------|
| $O_2H_5^+$ | C_2 | 2.385 | –35.9 | 39.5 |
| $CO-H^+-OC$ | $D_{\infty h}$ | 2.393 | –20.6 | 42.8 |
| $H_2CO-H^+-OCH_2$ | C_{2h} | 2.409 | –32.3 | 19.5 |
| $HNO-H^+-ONH$ | C_{2h} | 2.448 | –30.1 | 14.4 |
| $HPO-H^+-OPH$ | C_{2h} | 2.400 | –31.4 | 23.1 |
| $N_2H_7^+$ | C_{3v} | 2.705 | –27.6 | 12.9 |
| $HCN-H^+-NCH$ | $D_{\infty h}$ | 2.521 | –30.6 | 32.6 |
| $NN-H^+-NN$ | $D_{\infty h}$ | 2.550 | –17.7 | 28.5 |
| $O(H)N-H^+-N(H)O$ | C_s | 2.674 | –21.2 | 19.4 |

^a The binding energy (ΔE_e) is the electronic energy for the reaction $B + BH^+ \rightarrow B_2H^+$.

Figure 1. Moreover, for complexes with sp^2 -hybridized oxygens, the less stable “cis” C_{2v} isomers have the larger O–O coupling constants of 26.7, 17.0, and 30.5 Hz, respectively. That is, the nonequilibrium C_{2v} structures have larger coupling constants than the corresponding equilibrium structures of C_{2h} symmetry. This demonstrates that the magnitude of the coupling constant across a hydrogen bond does not in general correlate with the stability of the complex. The absence of a correlation between binding energy and proton NMR chemical shift of the hydrogen-bonded proton had been observed previously.³³

A closer examination of the complexes $CO-H^+-OC$ and $O_2H_5^+$ suggests that there is cylindrical and pseudo-cylindrical symmetry about the hydrogen-bonding O–O axis. In an effort to impose similar symmetry onto the complexes with sp^2 -hybridized oxygens, we have optimized a structure of $H_2CO-H^+-OCH_2$ with D_{2h} symmetry, which has a linear C–O–H⁺–O–C arrangement. This complex has a very short O–O distance of 2.351 Å, and a very large O–O coupling constant of 63.1 Hz. To illustrate that this large increase is not simply a result of the shorter O–O distance, we have computed O–O coupling constants for $H_2CO-H^+-OCH_2$ isomers of C_{2h} , C_{2v} , D_{2h} , and D_{2d} symmetries, fixing the O–O distance at 2.409 Å, the value in the equilibrium C_{2h} structure. The values of the O–O coupling constants, given in Table 1, are 19.5, 21.0, 59.2, and 59.0 Hz, respectively. Thus, the largest coupling constants are found in the structures having the linear C–O–H⁺–O–C arrangement, despite the fact that these isomers have an unfavorable orientation of carbonyl groups for hydrogen bonding, and are significantly less stable than the C_{2h} and C_{2v} isomers. (The optimized D_{2h} structure is 20 kcal/mol less stable than the equilibrium C_{2h} structure, which has a binding energy of –32.3 kcal/mol, as reported in Table 3.) The hydrogen-bonded proton has a lower electron density, that is, it is more positively charged, and the O–O distance is shorter in the optimized D_{2h} complex than in the C_{2h} and C_{2v} isomers. The linear arrangement of atoms which yields the large coupling constants for D_{2h} and D_{2d} $H_2CO-H^+-OCH_2$ has a similar effect in $HNO-H^+-ONH$. An isomer of this complex with C_{2h} symmetry but with a linear N–O–H⁺–O–N arrangement at the C_{2h} equilibrium O–O distance of 2.448 Å has an O–O coupling constant of 55.5 Hz, significantly larger than the values of 14.4 and 17.0 Hz for the trans and cis isomers, respectively.

Are O–O spin–spin coupling constants sensitive to the nature of the covalent bonds formed by the hydrogen-bonded oxygens? A comparison of the complexes $H_2CO-H^+-OCH_2$, $HNO-H^+-ONH$, and $HPO-H^+-OPH$ does show significant differences in coupling constants. When nitrogen atoms are bonded to the oxygens in $HNO-H^+-ONH$, the coupling constants for the trans and cis isomers are 14.4 and 17.0 Hz, respectively. The coupling constants increase when carbons are bonded to

the oxygens in $H_2CO-H^+-OCH_2$, with ${}^2hJ_{O-O}$ values for the trans and cis isomers of 19.5 and 26.7 Hz, respectively. The largest O–O coupling constants are found when phosphorus atoms are bonded to the oxygens in $HPO-H^+-OPH$, in which case ${}^2hJ_{O-O}$ values are 23.1 and 30.5 Hz for the trans and cis isomers, respectively. It is important to note once again that this order is not determined by the relative binding energies of these complexes, as evident from Table 3. Once again, the order of increasing ${}^2hJ_{O-O}$ is the order of decreasing O–O distance in these complexes. To the extent that the bonding at the proton-donor and proton-acceptor atoms determines the equilibrium structures of these complexes and therefore the hydrogen bond O–O distance, the bonding at the oxygens does influence the coupling constant. In addition, ${}^2hJ_{O-O}$ is also sensitive to the orientation of the hydrogen-bonded molecules with respect to the O–O line.

Complexes with N–H⁺–N Hydrogen Bonds. The complexes $N_2H_7^+$ (protonated ammonia dimer, C_{3v}), $HCN-H^+-NCH$ (protonated hydrogen cyanide dimer, $D_{\infty h}$), $NN-H^+-NN$ (protonated nitrogen dimer, $D_{\infty h}$), and $O(H)N-H^+-N(H)O$ (C_s) are equilibrium structures on their respective potential energy surfaces. Neither the optimized C_{2h} nor the C_{2v} structure of $HP(H)N-H^+-N(H)PH$ is an equilibrium structure, but these have been included for comparative purposes. The complexes $HCN-H^+-NCH$ and $NN-H^+-NN$ have equilibrium structures with short, symmetrical, proton-shared hydrogen bonds. The other two complexes, $N_2H_7^+$ and $O(H)N-H^+-N(H)O$, are stabilized by proton-shared hydrogen bonds,^{13,34} but the proton is not symmetrically bonded to the two nitrogen atoms.

The absence of a symmetrical proton-shared hydrogen bond in the equilibrium structures of $N_2H_7^+$ and $O(H)N-H^+-N(H)O$ leads to longer N–N distances, greater electron densities on the hydrogen-bonded proton, and smaller N–N coupling constants relative to the corresponding isomers that are stabilized by symmetric hydrogen bonds. Thus, the C_{3v} structure of $N_2H_7^+$ has an N–N coupling constant of 12.9 Hz, compared to 17.2 Hz in the D_{3d} isomer. Similarly, ${}^2hJ_{N-N}$ in the C_s isomer of $O(H)N-H^+-N(H)O$ is 19.4 Hz, less than the values of 25.4 and 25.7 Hz in isomers with C_{2h} and C_{2v} symmetry, respectively.

The equilibrium structures of the complexes $N_2H_7^+$ (C_{3v}), $O(H)N-H^+-N(H)O$ (C_s), $NN-H^+-NN$ ($D_{\infty h}$), and $HCN-H^+-NCH$ ($D_{\infty h}$) have coupling constants of 12.9, 19.4, 28.5, and 32.6 Hz, respectively. Once again, increasing coupling constant correlates with decreasing N–N distance, and not with binding energy, as evident from Table 3. Moreover, the relatively large difference between ${}^2hJ_{O-O}$ for cis and trans isomers in complexes with O–H⁺–O hydrogen bonds is not found for complexes with N–H⁺–N hydrogen bonds. Thus, for $O(H)N-H^+-N(H)O$, the N–N coupling constants for the trans and cis isomers are 25.4 and 25.7 Hz, respectively, and for $HP(H)N-H^+-N(H)PH$, they are 22.1 and 23.3 Hz, respectively. These observations for complexes with N–H⁺–N hydrogen bonds are consistent with observations made in ref 15, which demonstrated that ${}^2hJ_{N-N}$ for five neutral complexes with traditional linear N–H \cdots N hydrogen bonds but with different proton-donor and proton-acceptor molecules varied smoothly with N–N distance, and could be fitted by a single curve.

X–X and X–H Coupling Constants: J versus K . In a recent paper it was noted that X–Y coupling constants in X–H–Y hydrogen bonds can be larger than X–H and Y–H coupling constants, contrary to chemical intuition.⁴ This relationship is not found in these cationic complexes with symmetric

TABLE 4. X–H Coupling Constants ($^1J_{X-H}$ and $^2J_{X-H}$, Hz) in X–H⁺–X Hydrogen Bonds

| complex | sym | PSO | DSO | FC | SD | total <i>J</i> |
|--|-------------------------------------|------|------|--------------------|------|--------------------|
| O ₂ H ₅ ⁺ | <i>C</i> ₂ | 0.6 | –0.6 | –47.5 | 0.0 | –47.5 |
| CO–H ⁺ –OC | <i>D</i> _{∞h} | 1.0 | –0.7 | –68.0 | –0.5 | –68.2 |
| H ₂ CO–H ⁺ –OCH ₂ | <i>C</i> _{2h} | 1.1 | –0.6 | –27.7 | –0.6 | –27.8 |
| HNO–H ⁺ –ONH | <i>C</i> _{2h} | 1.4 | –0.6 | –23.0 | –2.1 | –24.3 |
| HPO–H ⁺ –OPH | <i>C</i> _{2h} | 2.0 | –0.8 | –31.6 | –0.6 | –31.0 |
| N ₂ H ₇ ⁺ | <i>C</i> _{3v} ^a | –0.4 | –0.2 | –60.5 | –0.1 | –61.2 ^a |
| | | 0.5 | –0.4 | –0.1 | –0.3 | –0.3 ^a |
| | <i>D</i> _{3d} | 0.4 | –0.3 | –26.6 | –0.2 | –26.6 |
| HCN–H ⁺ –NCH | <i>D</i> _{∞h} | 0.7 | –0.4 | –56.6 | –0.6 | –56.9 |
| NN–H ⁺ –NN | <i>D</i> _{∞h} | 0.5 | –0.4 | –57.0 | –0.6 | –57.5 |
| O(H)N–H ⁺ –N(H)O | <i>C</i> _s ^a | | | –82.4 ^a | | –82.4 |
| | | | | –4.3 ^a | | –4.3 |
| | <i>C</i> _{2h} | –0.6 | –0.4 | –39.0 | –1.5 | –41.5 |

^a For complexes with nonsymmetric N_a–H⁺–N_b hydrogen bonds, the N_a–H distance is shorter than N_b–H. The first line is $^1J_{N-H}$ for N_a–H; the second line is $^1J_{N-H}$ for N_b–H.

hydrogen bonds. Table 4 lists the one-bond coupling constants for the equilibrium structures of all complexes investigated in this paper. All of the complexes with O–H⁺–O hydrogen bonds have equilibrium structures with symmetrically bonded protons. For these, the absolute value of the one-bond coupling constant ($^1J_{O-H}$, which is always negative) is greater than the two-bond coupling constant ($^2J_{O-O}$). Similarly, for those complexes with symmetric N–H⁺–N hydrogen bonds, the absolute value of $^1J_{N-H}$ is always greater than $^2J_{N-N}$. However, for complexes with nonsymmetrical N_a–H⁺–N_b hydrogen bonds [N₂H₇⁺ (*C*_{3v}) and O(H)N–H⁺–N(H)O (*C*_s), with the N_a–H distance shorter than N_b–H], the one-bond coupling constant $^1J(N_a-H)$ is significantly greater than $^2J(N_a-N_b)$, but $^2J(N_a-N_b)$ is greater than $^1J(N_b-H)$.

It should be recognized, however, that although it is the coupling constant *J* that is measured experimentally, J_{X-Y} is equal to

$$J_{X-Y} = \gamma_X \gamma_Y h K_{X-Y} / 4\pi^2$$

where K_{X-Y} is the reduced indirect spin–spin coupling constant involving nuclei X and Y and γ_X and γ_Y are the nuclear magnetic moments.³⁵ The reduced coupling constant K_{X-Y} is independent of the magnitude of the nuclear magnetic moments and is therefore more appropriate for comparing coupling constants involving different nuclei. Table 5 reports reduced X–X and X–H coupling constants for the equilibrium structures of all complexes investigated in this study. The reduced N–N and O–O coupling constants ($^2hK_{X-X}$) across the hydrogen bond are always greater than the N–H or O–H coupling constant $^1hK_{X-H}$ despite the fact that N–N and O–O distances are longer than N–H and O–H distances, and irrespective of whether the hydrogen bond is symmetric or not. In the equilibrium structures of N₂H₇⁺ (*C*_{3v}) and O(H)N–H⁺–N(H)O (*C*_s) in which the proton is not symmetrically bonded, $^2hK_{N-N}$ is significantly greater than $^1K_{N-H}$ which is greater than $^1hK_{N-H}$.

Conclusions

The EOM-CCSD method has been used to compute spin–spin coupling constants across O–H⁺–O and N–H⁺–N hydrogen bonds in cationic complexes. The results of these calculations support the following statements.

1. $^2hJ_{X-X}$ coupling constants across O–H⁺–O and N–H⁺–N hydrogen bonds are dominated by the Fermi-contact term, which is distance dependent. Large coupling constants are associated

TABLE 5: $^2hK_{X-X}$, $^1K_{X-H}$, and $^1hK_{X-H}$ (N/A² m³) for Equilibrium Structures^a

| complex | sym | X–Y | | | | | total <i>K</i> |
|--|------------------------|-------|------|-----|-------|-----|--------------------|
| | | (Å) | PSO | DSO | FC | SD | |
| O ₂ H ₅ ⁺ | <i>C</i> ₂ | 2.385 | –2.7 | 0.0 | 180.6 | 0.9 | 178.8 |
| | | | –0.4 | 0.4 | 29.2 | 0.0 | 29.2 |
| CO–H ⁺ –OC | <i>D</i> _{∞h} | 2.393 | –0.9 | 0.0 | 194.2 | 0.5 | 193.8 |
| | | | –0.6 | 0.4 | 41.7 | 0.3 | 41.8 |
| H ₂ CO–H ⁺ –OCH ₂ | <i>C</i> _{2h} | 2.409 | –1.4 | 0.0 | 87.4 | 2.3 | 88.3 |
| | | | –0.7 | 0.4 | 17.0 | 0.4 | 17.1 |
| HNO–H ⁺ –ONH | <i>C</i> _{2h} | 2.448 | –0.5 | 0.0 | 62.0 | 3.6 | 65.1 |
| | | | –0.9 | 0.4 | 14.1 | 1.3 | 14.9 |
| HPO–H ⁺ –OPH | <i>C</i> _{2h} | 2.400 | –1.8 | 0.0 | 105.0 | 1.4 | 104.6 |
| | | | –1.2 | 0.5 | 19.4 | 0.4 | 19.1 |
| N ₂ H ₇ ⁺ | <i>C</i> _{3v} | 2.705 | –0.8 | 0.0 | 104.5 | 0.8 | 104.5 ^b |
| | | | +0.3 | 0.2 | 49.7 | 0.1 | 50.3 ^b |
| | | | –0.4 | 0.3 | 0.1 | 0.2 | 0.2 ^b |
| HCN–H ⁺ –NCH | <i>D</i> _{∞h} | 2.521 | 0.0 | 0.0 | 263.3 | 0.8 | 264.1 |
| | | | –0.6 | 0.3 | 46.5 | 0.5 | 46.7 |
| NN–H ⁺ –NN | <i>D</i> _{∞h} | 2.550 | 0.0 | 0.0 | 230.9 | 0.0 | 230.9 |
| | | | –0.4 | 0.3 | 46.8 | 0.5 | 47.2 |
| O(H)N–H ⁺ –N(H)O | <i>C</i> _s | 2.674 | | | 157.2 | | 157.2 ^b |
| | | | | | 67.7 | | 67.7 ^b |
| | | | | | 3.5 | | 3.5 ^b |

^a Values given should be multiplied by 10¹⁹. The first entry for each complex is $^2hK_{X-X}$. The second entry for complexes with symmetric hydrogen bonds is $^1hK_{N-H}$. ^b For complexes with nonsymmetric N_a–H⁺–N_b hydrogen bonds, the first entry is $^2hK_{N-N}$, the second is $^1K_{N-H}$, and the third is $^1hK_{N-H}$. See footnote *a* of Table 4.

with symmetric hydrogen bonds, short O–O and N–N distances, and low electron densities on the hydrogen-bonded proton.

2. The magnitude of the coupling constant across a hydrogen bond is not related to the binding energy of the complex.

3. In complexes with O–H⁺–O hydrogen bonds, it appears that coupling constants are not simply related to the hybridization of the oxygen atom. Although the bonding at the oxygens indirectly determines the coupling constant by determining the equilibrium O–O distance, others factors must also influence *J*. For example, for complexes with sp²-hybridized oxygens, $^2hJ_{O-O}$ is (a) greater in the cis structure than in the equilibrium trans structure, and (b) highest in complexes in which A–O–H⁺–O–A are arranged linearly, with A the non-hydrogen atom bonded to O.

4. In complexes with N–H⁺–N hydrogen bonds, N–N coupling constants are determined by the nature of the hydrogen bond and the N–N distance. $^2hJ_{N-N}$ values in complexes with sp²-hybridized nitrogens appear to be much less sensitive to the relative orientation of the hydrogen-bonded molecules (trans or cis) with respect to the N–N axis than $^2hJ_{O-O}$.

5. X–H coupling constants ($^1hJ_{X-H}$) in complexes with symmetric O–H⁺–O and N–H⁺–N hydrogen bonds have absolute values which are larger than X–X coupling constants ($^2hJ_{X-X}$). In complexes having unsymmetrical hydrogen bonds N_a–H⁺–N_b, with the N_a–H distance shorter than N_b–H, the absolute value of $^1J(N_a-H)$ is significantly greater than $^2hJ(N_a-N_b)$, which is greater than $^1hJ(N_b-H)$. When comparisons are made using reduced coupling constants, $^2hK_{X-X}$ is greater than $^1K_{X-H}$ which is greater than $^1hK_{X-H}$.

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