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ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY A · APRIL 2004

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Received: January 29, 2004

One-bond X–Y spin–spin coupling constants ($^1J_{X-Y}$) for 18 H_mX-YH_n molecules, with X and Y = ^{13}C , ^{15}N , and ^{31}P , have been computed using the equation-of-motion coupled-cluster singles and doubles method. The molecules investigated include all possible combinations of these three elements bonded with single, double, and triple bonds. The computed coupling constants are in good agreement with experiment over a range that extends from –250 to +200 Hz. With only two exceptions, the sign of the Fermi-contact (FC) term is the same as the sign of $^1J_{X-Y}$, but the FC term may or may not be a good quantitative estimate of $^1J_{X-Y}$. When reduced spin–spin coupling constants ($^1K_{X-Y}$) are used for comparing coupling constants involving different atoms, a linear relationship is observed between $^1K_{X-N}$ and $^1K_{X-P}$. The signs of $^1J_{X-Y}$ for approximately half of the molecules included in this study are exceptions to the Dirac vector model. The recently proposed NMR triplet wave function model has been used to provide insight into the variation of the signs of these one-bond spin–spin coupling constants.

Introduction

The coupling constant between a pair of atoms X and Y is an important molecular property measured by means of classical NMR experiments. Although such measurements have been made for a large number of molecules, interpreting the experimental data is often a challenging task. First, experimental coupling constants (J_{X-Y}) are often measured in relatively complex molecules, thereby making it difficult to assess how specific factors influence J_{X-Y} and lead to the variations observed experimentally. Second, coupling constants for some smaller symmetrical compounds cannot be directly measured since the technique of isotopic substitution cannot be employed if the substituted isotope does not have a nuclear spin (e.g., substituting ^{14}N for ^{15}N). Finally, the Dirac vector model,¹ which has led to the generalization that one-bond coupling constants are positive, two-bond negative, three-bond positive, and so on, is often violated.

In this paper, we present the results of a systematic study of X–Y coupling constants ($^1J_{X-Y}$) in molecules H_mX-YH_n , for X and Y = ^{13}C , ^{15}N , and ^{31}P . The molecules investigated are illustrated in Chart 1 and include all possible combinations of these three elements bonded with single, double, and triple bonds. We will compare our computed results with experimental data and transform $^1J_{X-Y}$ to the corresponding reduced coupling constants $^1K_{X-Y}$ to compare coupling constants involving different atoms. We will also examine the signs of the one-bond coupling constants, particularly the Fermi-contact (FC) terms, using our newly formulated NMR triplet wave function model (NMRTWM)² that relates the sign of J to the phases of

the wave functions for excited triplet states and the resulting alignments of nuclear magnetic moments.

Methods

The structures of molecules having only C and N atoms for X and Y were fully optimized by second-order Møller–Plesset perturbation theory (MP2)^{3–6} using the 6-31+G(d,p) basis set.^{7–10} Molecules containing P were also optimized at MP2 but with the larger and more flexible Dunning aug-cc-pVTZ basis.^{11–13} These levels of theory usually produce molecular geometries in agreement with experimental geometries. Harmonic vibrational frequencies were computed to verify that the optimized structures are equilibrium structures on their potential surfaces.

One-bond spin–spin coupling constants ($^1J_{X-Y}$) were computed using equation-of-motion coupled-cluster theory (EOM-CCSD) in the CI-like approximation^{14–17} with the Ahlrichs¹⁸ qz2p basis set on H and P, and qzp on C and N. All electrons were included in the EOM-CCSD calculations. This level of theory has been shown to give good agreement between computed and experimental 2-, 3-, and 4-bond ^{19}F – ^{19}F spin–spin coupling constants in small molecules, which is notable given the difficulty of computing F–F coupling.¹⁹ Recently, Gauss and co-workers have extended the CCSD formalism for computing spin–spin coupling constants to CCSD(T), CCSDT, and CC3.^{20,21} However, these levels of theory are not feasible for the molecules investigated in this work, nor have their performance and reliability been established. The total CCSD spin–spin coupling constants for the molecules investigated in this study have been evaluated as a sum of four terms: the paramagnetic spin–orbit (PSO); diamagnetic spin–orbit (DSO); FC; and spin-dipole (SD). To facilitate comparisons of coupling constants between different nuclei, values of $^1J_{X-Y}$ have been converted to reduced coupling constants, $^1K_{X-Y}$.²²

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CHART 1

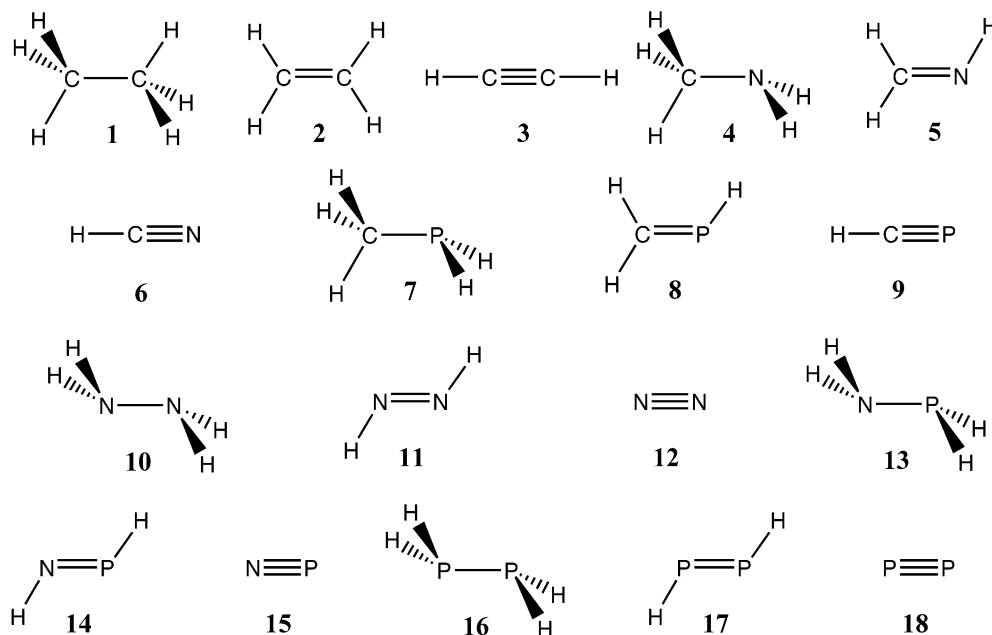


TABLE 1: Computed X–Y Distances (Å), One-Bond X–Y Coupling Constants ($^1J_{X-Y}$) and Components of $^1J_{X-Y}$ (Hz), and Reduced Coupling Constants ($^1K_{X-Y}$, $\text{N A}^{-2} \text{ m}^{-3} \times 10^{19}$)

molecule	$R(X-Y)$	PSO	DSO	FC	SD	$^1J_{X-Y}$	$^1K_{X-Y}$
ethane (1)	1.525	0.2	0.1	34.6	1.0	35.9	47.3
ethylene (2)	1.339	−8.9	0.1	77.7	2.6	71.5	94.1
acetylene (3) ^a	1.221	6.2	0.0	178.9	8.2	193.2	254.3
methylamine (4)	1.465	−0.5	0.0	−4.5	−0.7	−5.7	18.6
methanimine (5)	1.284	8.2	0.0	−8.7	−1.3	−1.8	5.9
hydrogen cyanide (6) ^b	1.179	0.2	0.0	−7.9	−4.9	−12.6	41.1
methyl phosphine (7)	1.858	1.3	0.1	−7.1	6.5	0.8	0.7
methylene phosphine (8)	1.674	−54.8	0.0	15.7	12.4	−26.7	−21.8
methylidene phosphine (9) ^c	1.560	9.8	0.0	5.9	39.5	55.2	45.1
hydrazine (10)	1.434	1.1	0.0	−8.0	0.7	−6.2	−50.2
<i>E</i> -diazene (11)	1.265	−11.6	0.0	−5.7	−0.5	−17.8	−144.2
dinitrogen (12)	1.131	−4.3	0.0	−4.0	2.6	−5.7	−46.2
phosphinous amide (13)	1.720	2.0	0.0	45.2	−2.6	44.6	−90.4
<i>E</i> -phosphinimine (14)	1.601	61.5	0.0	27.0	−1.6	86.9	−176.1
phosphorous nitride (15)	1.529	40.5	0.0	55.7	−20.9	75.3	−152.6
diphosphine (16)	2.221	4.4	0.1	−178.3	40.0	−133.8	−67.8
<i>E</i> -diphosphene (17)	2.042	−379.0	0.0	−129.3	44.9	−463.4	−234.9
molecular phosphorus (18)	1.927	−238.2	0.0	−288.9	141.3	−385.8	−195.6

^a Ethyne. ^b Hydrocyanic acid. ^c Phosphaethyne.

Within the CCSD ansatz, values of T2 amplitudes greater than 0.1 are interpreted as a warning that a single-reference wave function may not be sufficient for a CCSD calculation.²³ For some molecules included in this study, particularly those with double bonds, T2 amplitudes of this magnitude were observed. However, the largest T2 amplitudes are less than 0.15, and there is no indication that the larger amplitudes are associated with pathological behavior of the computed results. Structure optimizations were carried out using the Gaussian 98 suite of programs,²⁴ and coupling constants were computed using ACES II.²⁵ All calculations were performed on the Cray SV1 or the Itanium 2 Cluster at the Ohio Supercomputer Center.

Results and Discussion

$^1J_{X-Y}$ and Its Components. Table 1 reports the optimized distances, the coupling constants ($^1J_{X-Y}$) and their components, and the reduced coupling constants ($^1K_{X-Y}$) for the 18 molecules investigated in this study. The following observations can be made from Table 1.

1. For a given set of three molecules for which X and Y are fixed, the X–Y distance decreases in the order single bond > double bond > triple bond. However, with only one exception (X = Y = C), the values of neither the FC terms nor $^1J_{X-Y}$ increase as the bond distance decreases. Although this may initially appear to be a surprising result, particularly in view of the well-known distance dependence of $^{2h}J_{X-Y}$ for X–H...Y hydrogen bonds,^{26–31} it is a consequence of the absence of an explicit distance-dependent term in the FC operator.³²

2. For fixed X and Y, the PSO term has its largest absolute value when the X–Y bond is a double bond. For molecules with double bonds, the PSO term is negative, except for methanimine (5) and *E*-phosphinimine (14). The largest PSO term is computed for *E*-diphosphene (17). The DSO term is essentially zero for all molecules.

3. As expected from the Dirac vector model, the FC terms are positive for molecules with C–C bonds and negative for C–N bonds (taking into account the magnetogyric ratio of ^{15}N). However, the signs of the FC terms are negative for N–N

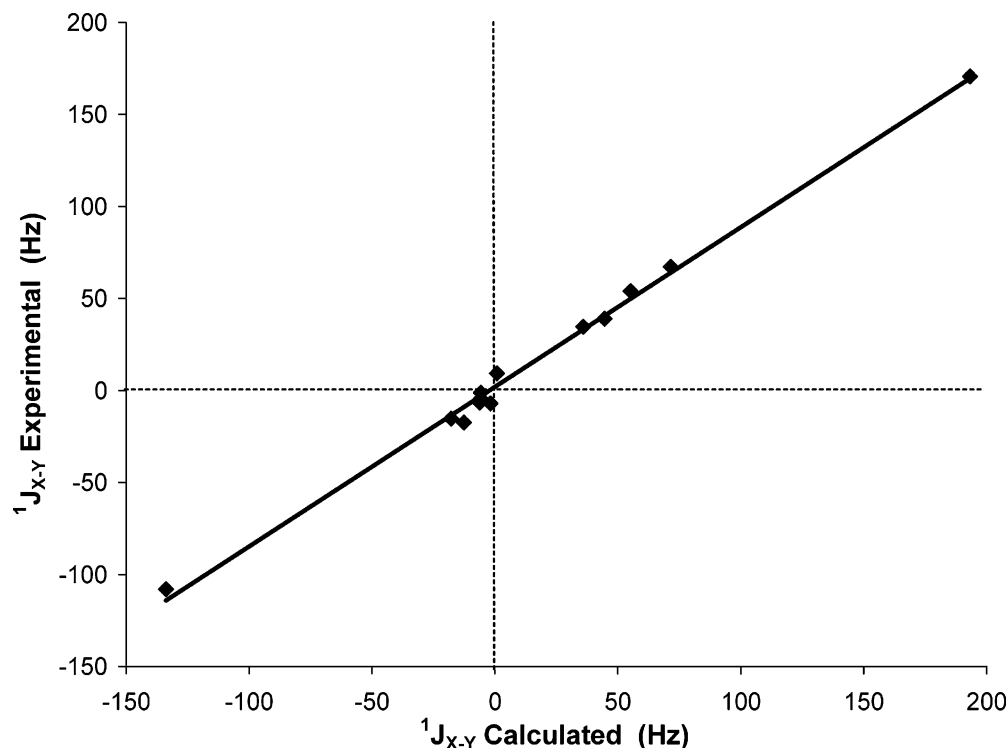


Figure 1. Experimental vs computed one-bond spin–spin coupling constants ($^1J_{X-Y}$) for molecules H_mX-YH_n with X and Y = ^{13}C , ^{15}N , and ^{31}P .

TABLE 2: Computed and Experimental Coupling Constants ($^1J_{X-Y}$, Hz) for Molecules H_mX-YH_n

computed		experimental		
molecule	$^1J_{X-Y}$	molecule	$^1J_{X-Y}$	ref
ethane (1)	35.9	(1)	34.6	33a
ethylene (2)	71.5	(2)	67.2	33b
acetylene (3)	193.2	(3)	170.6	33b
methylamine (4)	-5.7	(4)	-4.5	34a
methanimine (5)	-1.8	$\text{C}_6\text{H}_5-\text{CH}=\text{NCH}_3$	-7.1	33c
hydrogen cyanide (6)	-12.6	$\text{CH}_3-\text{C}\equiv\text{N}^a$	-17.5	33c
methyl phosphine (7)	0.8	(7)	9.3	35a
methylene phosphine (8)	-26.7			
methylidene phosphine (9)	55.2	(9)	54.0	34b
hydrazine (10)	-6.2	$\text{C}_6\text{H}_5-\text{NH}-\text{NH}_2$	-6.7	34c
<i>E</i> -diazene (11)	-17.8	$\text{Ar}-\text{N}=\text{N}-\text{Ar}'$	-15.4	36a
dinitrogen (12)	-5.7	(12)	-1.3	34c
phosphinous amide (13)	44.6	$(\text{CH}_3)_2\text{N}-\text{P}(\text{CH}_3)_2$	39.0	36b
<i>E</i> -phosphinimine (14)	86.9			
phosphorus nitride (15)	75.3			
diphosphine (16)	-133.8	(16)	-108.0	35b
<i>E</i> -diphosphene (17)	-463.4	$\text{Ar}-\text{P}=\text{P}-\text{Ar}'$	-574.0	34d
molecular phosphorus (18)	-385.8			

^a The computed $^{13}\text{C}-^{15}\text{N}$ coupling constant for CH_3CN (acetonitrile) is -12.3 Hz.

and P–P couplings when they would be predicted to be positive and positive for N–P couplings when predicted to be negative. The FC term is negative for the molecule with a C–P single bond but positive for the molecules with C–P double and triple bonds. The variations in the signs of the FC terms for these molecules will be discussed in detail below.

4. With the exception of molecules (7) and (8) which have C–P single and double bonds, respectively, the sign of the FC term is the same as the sign of $^1J_{X-Y}$. However, the FC term may or may not be a good estimate of $^1J_{X-Y}$.

5. The SD term may make a large or small contribution to $^1J_{X-Y}$, depending on the specific molecule.

Computed vs Experimental Data. Computed and experimental $^1J_{X-Y}$ values are reported in Table 2. Experimental data for some of these molecules are not available, so data taken

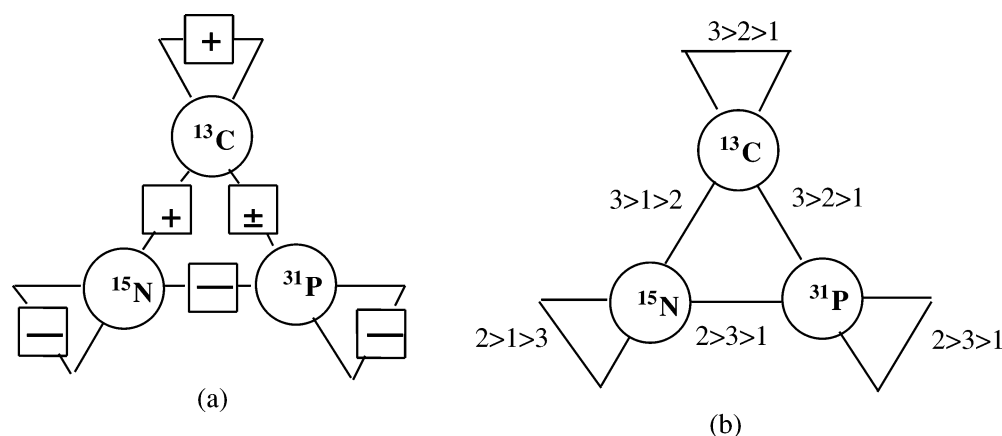
from their derivatives were used instead, as indicated in Table 2.^{33–36} A plot of the experimental vs the calculated coupling constants is presented in Figure 1. Molecule **17** has been omitted from this plot since the calculations were done for $\text{H}-\text{P}=\text{P}-\text{H}$, whereas the experimental data are for $\text{Ar}-\text{P}=\text{P}-\text{Ar}'$, where Ar and Ar' are aromatic substituents. These groups have strong electronic effects that would be expected to alter significantly the electron densities at the two P atoms relative to $\text{H}-\text{P}=\text{P}-\text{H}$, thereby giving rise to the large discrepancy between the computed (-463.4 Hz) and experimental (-574.0 Hz) values. The computed value underestimates the (absolute value) of $^1J_{\text{P}-\text{P}}$ by 19%. It is interesting to note that for *E*-diazene (**11**), for which a similar molecule is used for comparison, the difference between computed and experimental $^1J_{\text{N}-\text{N}}$ values is much smaller (-17.8 vs -15.4 Hz), due in part to the relatively small value of the coupling constant. However, the absolute value of the computed coupling constant overestimates the experimental value by 16%.

With molecule **17** omitted, the equation of the line shown in Figure 1 is

$$^1J_{X-Y}(\text{exp}) = (0.88 \pm 0.02)^1J_{X-Y}(\text{calcd}) \quad (1)$$

with $n = 13$ and $r^2 = 0.993$. Excluding **17**, the largest differences between computed and experimental coupling constants are found for acetylene (**3**), in which case the computed value of 193 Hz overestimates the experimental value of 171 Hz, and diphosphine (**16**), in which case the computed value of -134 Hz overestimates (in an absolute sense) the experimental value of -108 Hz. Nevertheless, given the range of coupling constants (approximately -250 to +200 Hz), the agreement between theory and experiment is quite good. Moreover, it should be noted that the calculations have been performed at computed gas-phase equilibrium geometries, whereas the experiments were done on molecules in solution at their ground-state geometries. These differences could lead to some discrepancies between computed and experimental

CHART 2



values, although it is not expected that these discrepancies would be large. Although the calculations were carried out at equilibrium geometries, the computed results should be viewed as applying to molecules in their ground vibrational state.

$^1K_{X-Y}$. Table 1 also reports the reduced coupling constants ($^1K_{X-Y}$), which should be used when comparing coupling constants involving different X and Y atoms.²² Chart 2 illustrates relationships among the signs of these reduced coupling constants (Chart 2a) and among their values and the nature of the bond (single, double, triple) between X and Y (Chart 2b). As summarized in Chart 2b, for C–C and C–P coupling, the absolute values of the reduced coupling constants decrease in the order triple bond > double bond > single bond. For N–N coupling, the order is double > single > triple, but for N–P and P–P bonds, the order is double > triple > single. The order for C–N coupling is triple > single > double. Correlations between the reduced coupling constants are found only for $^1K_{X-N}$ and $^1K_{X-P}$. For the pairs of molecules **4/7**, **5/8**, **6/9**, **10/13**, **11/14**, and **15/18**, a linear relationship

$$^1K_{X-P} = (1.17 \pm 0.07)^1K_{X-N} - (19 \pm 6) \quad (2)$$

exists, with $n = 6$, and $r^2 = 0.987$. Previously, Wrackmeyer³⁷ compared nitriles (related to **6**) and phosphalkynes (related to **9**) and observed a linear relationship between $^1J_{C-N}$ and $^1J_{C-P}$ for molecules with C–N and C–P triple bonds. From this comparison, he predicted that the sign of $^1J_{C-P}$ for $^{13}\text{C}\equiv^{31}\text{P}$ should be positive. His prediction agrees with our value of +55.2 Hz for compound **9**, $\text{H}-\text{C}\equiv\text{P}$. Relationships such as that shown in eq 2 could play an important role in estimating coupling constants that cannot be unambiguously measured experimentally, and could lead to a better understanding of factors that influence coupling constants when molecules appear to exhibit anomalous behavior.

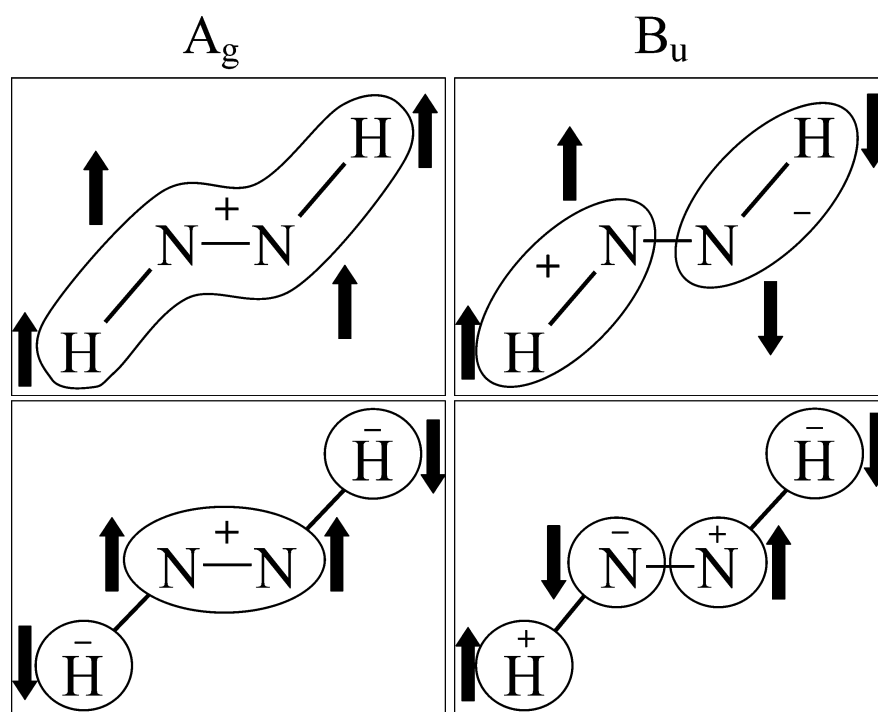
NMRTWM and the Signs of the Reduced FC Term and $^1K_{X-Y}$. All of the signs of $^1K_{X-Y}$ would be expected to be positive from the Dirac vector model,¹ but Chart 2a illustrates that this is not the case. Why is this? In a recent paper, a model (NMRTWM)² for the sign of J (more specifically, the sign of the FC term) was presented which arose from consideration of the relationship between J_{X-Y} and the second derivative of the energy with respect to the nuclear magnetic moments of X and Y and the sum-over-states expression for computing the FC term. According to NMRTWM, the orientation of nuclear magnetic moments responds to the phases of the wave functions for the excited triplet states that couple to the ground state. As a result, the sign of the contribution to the FC term for a pair of atoms from a given triplet state is determined by the nodal

properties of the wave function, which determines the relative orientation of the magnetic moments of the pair. If a pair of nuclei have a parallel alignment in a given triplet state, then the sign of the contribution is negative. If the nuclei are aligned in an antiparallel fashion, then the sign is positive.³⁸ It should be apparent, therefore, that the overall sign of the FC term results from a sum of contributions from excited triplet states that couple to the ground state. Thus, for the molecules $\text{H}_m\text{X}-\text{YH}_n$, the sign of the FC term is determined by whether states with or without a node intersecting the X–Y bond (σ -type states with s electron densities on X and Y) dominate. Because the molecules included in this study span a number of different point groups, we will use $\text{H}-\text{N}=\text{N}-\text{H}$, which belongs to point group C_{2h} , to illustrate the model, focusing on the nodal patterns involving the N–N bond.

For molecules with C_{2h} symmetry, only excited triplet states with A_g or B_u symmetry can interact with the ground state through the FC coupling operator. The wave functions for these states do not have a nodal plane containing the X–Y bond, that is, they are σ -type states with s electron densities on X and Y. Chart 3 shows the possible nodal patterns of lower-energy wave functions for 3A_g and 3B_u states. If a 3A_g state has no nodes, then the magnetic moments of all nuclei have a parallel alignment, and the FC term for each pair is negative. The number of states of this type is expected to be relatively small. Wave functions for 3A_g states may also have two nodes, intersecting the two N–H bonds. However, once again there is no node between the two N atoms, so the contributions to the N–N FC term from states of this type are negative. In contrast, wave functions for 3B_u states may have an odd number of nodes, and in both cases, there is one node that bisects the N–N bond. As a result, the magnetic moments of the two N nuclei have an antiparallel alignment, and the contributions to the FC term from these states are positive. It is apparent that the resultant sign of the FC term will be determined by whether states of 3A_g or 3B_u symmetry dominate. For ease of discussing the signs of the FC terms for the molecules investigated in this study, we will not discuss all of the possible nodal patterns of wave functions for states which contribute to $^1J_{X-Y}$ but, rather, will focus on whether the states that dominate have a node that intersects the X–Y bond.

The FC terms will be discussed in terms of “reduced” FC terms, so that the signs of the FC terms for molecules with a single N atom (**4**, **5**, **6**, **13**, **14**, **15**) given in Table 1 should be reversed. If this is done, then the signs of the reduced FC terms are the same as the signs of the reduced coupling constants ($^1K_{X-Y}$) except for molecules **7** and **8**, which have C–P single

CHART 3



and double bonds. The signs of the reduced FC terms can then be readily discussed with reference to Chart 2a. The first set of molecules (**1**, **2**, **3**) with C–C bonds have no lone pairs of electrons. The sign of the reduced FC term is positive in each case, which indicates that triplet states that have a node bisecting the C–C bond must dominate. In contrast, molecules with N–N, N–P, and P–P bonds (molecules **10–18**) have one pair of nonbonding (“lone-pair”) electrons on each atom, and the signs of the reduced coupling constants are negative. For these molecules, it is the triplet states that do not have nodes intersecting the N–N, N–P, and P–P bonds that dominate. Molecules **4–9** with C–N and C–P bonds have only one atom (N or P) with a lone pair of electrons. The molecules with C–N bonds (**4–6**) have reduced FC terms that are positive, indicating that triplet states with a nodal plane intersecting the C–N bond dominate. Thus, the behavior of the reduced FC terms for molecules with C–N bonds is the same as that for molecules with C–C bonds. The signs of the reduced FC terms change in the group of molecules with C–P bonds (**7–9**), implying that the type of triplet state that dominates also changes within this series. The molecules $H_2C=PH$ (**8**) and $HC\equiv P$ (**9**) have positive reduced FC terms, as do molecules **1–6**, whereas H_3C-PH_2 (**7**) has a negative reduced FC term like molecules **10–18**. Although NMRTWM is not in general a predictive theory at this point, it does provide insight into the variation of the signs of coupling constants. It is our hope that continued application of NMRTWM will lead to a better understanding of the factors that determine whether triplet states with or without nodes between a pair of atoms dominate.

Conclusions

EOM-CCSD calculations have been carried out to investigate one-bond spin–spin coupling constants ($^1J_{X-Y}$) for 18 molecules H_mX-YH_n , with X and Y = ^{13}C , ^{15}N , and ^{31}P , in which the X–Y bond may be a single, double, or triple bond. The computed coupling constants are in quite good agreement with experimental data. With only two exceptions, the signs of the FC terms are the same as the signs of the total spin–spin

coupling constants, although the FC term may or may not be a good quantitative estimate of $^1J_{X-Y}$. The signs of the FC terms have been analyzed using NMRTWM. This model provides insight into the dependence of the signs of the FC terms on the nodal properties of wave functions for excited triplet states and the resulting alignment of nuclear magnetic moments, the nature of the atoms X and Y and their bonding, which influences whether states with or without nodes intersecting the X–Y bond dominate, and the presence of lone pairs of electrons on X and/or Y, which also appears to be a factor in determining whether states with or without nodes intersecting the X–Y bond are the dominate states.

Acknowledgment. The support of the work by the National Science Foundation through NSF Grant CHE-9873815 and by the Ohio Supercomputer Center is gratefully acknowledged. Thanks are also due to the Spanish DGI/MCYT (Project No. BQU2000-0906).

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