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Finite Perturbation–Configuration Interaction Calculations of Nuclear Spin–Spin Coupling Constants for Some Monosubstituted Methanes

A. Laaksonen and J. Kowalewski*

Contribution from the Department of Physical Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden. *Received January 28, 1981*

Abstract: Nonempirical finite perturbation calculations at the Hartree–Fock and configuration interaction levels of approximation are presented for the Fermi contact contribution to all nuclear spin–spin coupling constants in ethane, aminomethane, methanol, and fluoromethane. For CH_3CH_3, CH_3NH_2, and CH_3OH, calculations of all the coupling constants have been performed for staggered and eclipsed conformations. In some cases, a more detailed analysis of conformational dependencies also has been carried out. All known experimental trends are successfully reproduced. For some of the coupling constants the agreement with experiment is quantitative. The correlation effects are found to be extremely important, of the order of 50% or more, for geminal (two–bond) coupling constants. For one-bond and three-bond coupling constants, the correlation effects are, with few exceptions, somewhat less important. The role of noncontact terms is discussed with reference to previously published data.

1. Introduction

Nuclear spin–spin coupling constants have for a long time been an invaluable source of information about the nature of bonding, stereochemistry in solution, etc. The theoretical foundations for many such applications have recently been reviewed.[1] However, quantitatively relevant nonempirical calculations for polyatomic molecules have started appearing first quite recently. Some authors have dealt with proton–proton and proton–heavy atom coupling constants in the first-row hyrides[2,3] and their second-row counterparts.[4,5] Some papers have also described calculations for molecules containing two first-row atoms. Ditchfield and Synder[6] have reported coupled Hartree–Fock (CHF) calculations of coupling constants in fluoromethane. Lazzeretti[7] has published a similar investigation (using, however, a much larger basis set) for methanol. Laaksonen and co-workers[8] have investigated the vicinal proton–proton coupling constants in ethane as a function of the dihedral HCCH angle. Here we report a systematic study of all possible nuclear spin–spin coupling constants in the series ethane–aminomethane–methanol–fluoromethane. When appropriate, comparisons are also made with the simple first-row hydrides. In the case of ethane, aminomethane, and methanol, we also report an extensive investigation of the conformational dependencies of various coupling constants. We limit our interest to the Fermi contact term, since most of the trends of interest appear to arise from this contribution. The computational approach is very similar to that used in earlier work from this laboratory[3,5,8] and is described briefly in section 2 of the paper. The results are presented and discussed in section 3, and concluding remarks are made in section 4.

2. Computational Details

In the finite perturbation–configuration interaction (FP–CI) method, presented earlier,[3] the calculation of the Fermi contact contribution to nuclear spin–spin coupling constants involves finding the derivatives of total energy with respect to the magnetic moments of the coupled nuclei. The second derivative is evaluated using the method of finite differences. The calculations of the total energy for a given set of magnetic moments are carried out in two steps. In the first step, an unrestricted Hartree–Fock (UHF) calculation is performed with the Fermi contact interaction explicitly included in the Fock operator. The coupling constant calculated at this level of approximation is in principle equivalent to the infinitesimal coupled Hartree–Fock (CHF) result. In the second step, the UHF orbitals are used to generate a CI expansion and to obtain the correlation energy. The primitive Gaussian basis set in this study is 9s5p on the heavy atoms—contracted to 4s2p; for hydrogen 4s is contracted to 2s (double ζ). The exponents and coefficients are taken from van Duijneveldt.[9] In calculating the correlation effects, the same philosophy is followed as in our previous work[8] on vicinal coupling constants in ethane. The correlation energy is estimated using second-order perturbation theory, denoted as "SECORD" in this work. However, this type of approximation tends to overestimate the correlation contribution to coupling constants.[3,5] In those cases where the correlation effects seem to play an important role in describing a trend in coupling constants for the whole series of molecules, the full configuration interaction (CI) calculations, including all single and double replacements of the valence shell MOs in the UHF determinant, are also reported. The scaling of the SECORD values, suggested previously,[8] has been tried in the case of vicinal H–H couplings for aminomethane, but it has not worked completely satisfactorily. All the calculations in this study have been performed using the program system MOLECULE.[10-12] The experimental equilibrium geometries are taken from Fink and Allen[13] for ethane and aminomethane, from Boyd and Thompson[14] for methane, and from Venkateswarlu and Gordy[15] for methanol. For fluoromethane, we have adopted the standard geometrical model.[16] In calculations for all conformations other than staggered, the rotation around the central CX bond is the only geometry change made.

3. Results and Discussion

A. Directly Bonded Atoms. Table I contains the Fermi contact contributions to the one-bond coupling constants between the

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Table I. Reduced One-Bond Coupling Constants ^1K(C-X) in Some Substituted Methanes CH_3XY (in 10^{19} m^{-2} kg s^{-2} A^{-2})[d]

X	Y	CHF	SECORD	CI	CHF + SECORD	CHF + CI	exptl
C	H_3	79.7	−45.3	−36.5	34.4	43.2	45.6[a]
N	H_2	37.9	−38.9	−27.1	−1.0	10.8	14.7[b]
O	H	−47.7	−15.2	−8.8	−62.9	−56.5	
F		−114.0	14.9	12.4	−99.1	−101.6	−57.0[c]

[a] Reference 17. [b] Reference 18. [c] Reference 19. [d] To convert *K* to *J* (in Hz), multiply by 0.759 for X = ^{13}C, −0.306 for *X* = ^{15}N, −0.409 for X = ^{17}O, and 2.84 for X = ^{19}F.

Table II. Calculated Contributions to the Reduced One-Bond Coupling Constants ^1K(X–H) in Some Selected Compounds RXY (in 10^{19} m^{-2} kg s^{-2} A^{-2})[j]

				contact				
R	*X*	*Y*	confor- mation	CHF	CHF + SECORD	CHF + CI	noncontact CHF	exptl
H	C	H_3		49.9	36.3	38.5	0.4[a]	41[d]
H	N	H_2		48.5	35.2	37.8	2.2[a]	36[e]
H	O	H		24.9	18.3	19.8	7.9[a]	48[f]
CH_3	C	H_3	stagg	52.3	36.9	39.8	0.3[b]	41.4[g]
CH_3	C	H_3	eclip	52.1	36.5			
CH_3	N	H_2	stagg	53.1	38.3	41.7	not available	53.7[h]
CH_3	N	H_2	eclip	50.9	36.1			
CH_3	O	H	stagg	27.6	19.4	21.5	6.0[c]	52+/−7[i]
CH_3	O	H	eclip	28.1	19.7			

[a] Reference 2. [b] Reference 21 and 22. [c] Reference 7. [d] Reference 23. [e] Reference 24. [f] Reference 25. [g] Reference 17. [h] Reference 18. [i] Reference 26. [j] To convert *K* to *J* (in Hz) multiply by 3.02 for X = ^{13}C, −1.22 for X = ^{15}N, and −1.63 for X = ^{17}O.

methyl carbon and the heavy atom in the substituent group. The compounds are arranged after the increasing electronegativity of the substituents. For a meaningful comparison, the signs and the magnitudes of the magnetogyric ratios have been left out by using the values of the reduced coupling constants. The relation between the reduced coupling constant *K*(A–B) and the ordinary coupling constant *J*(A–B) is:

$$K(\text{A–B}) = J(\text{A–B})\frac{4\pi^2}{\gamma_A\gamma_B h} \qquad (1)$$

where γ_A and γ_B are the magnetogyric ratios of the A and B nuclei. The data for ethane, aminomethane, and methanol are for the staggered conformation. The corresponding values for the eclipsed conformation do not differ by more than 1% from the results presented in the Table I. Typically the coupled Hartree–Fock method tends to overestimate the magnitudes of the calculated coupling constants. This can be observed in Table I as well as in all the following tables in this study. The values of ^1K(C–X) at the Hartree–Fock level are approximately twice as large as their experimental counterparts.[17–19]

Fortunately, the calculation of the electron correlation effects damps this tendency markedly. There is a clear trend in the values of one-bond C–X coupling constants. Actually, they follow linearly the values of the electronegativities, E_{XY}: 2.55, 3.00, 3.50, and 4.00 when XY = $-CH_3$, $-NH_2$, –OH and –F.[20] It is also very interesting to notice the peculiar behavior of the correlation effects themselves. They seem to have a trend of their own, which makes the correlation contribution to ^1K(C–X) in CH_3OH and CH_3F relatively less important than in CH_3CH_3 and CH_3NH_2. This phenomenon has been observed previously in the case of one-bond coupling constants in the second-row hydrides, i.e., SiH_4, PH_3, H_2S, and HCl.[5] There is still another trend in Table I. The agreement with experimental data gradually gets worse as we go from ethane toward fluoromethane. This is due to two facts. First, comparing again with the calculated one-bond coupling constants in the simple hydrides, we see that the basis set sensitivity increases markedly in the direction from CH_4 and SiH_4 to HF and HCl.[2–5] The calculations in the series of methyl-substituted first-row hydrides may be expected to follow a similar trend for changes in the same direction. Second, one has to include the noncontact mechanisms in performing calculations of this type of couplings. Today, it is generally known, on the basis of several papers,[2,4–7,21,22] that one has to be very careful in neglecting these terms, if a reasonably good qualitative description is desired. In fact, as was evidenced in the calculations of nuclear spin–spin coupling constants for the first- and second-row hydrides XH_n,[2,4] the significance of the noncontact terms increses very rapidly as X becomes more electronegative. This also seems to be true for ^1K(C–X) in the substituted methanes in Table I, although to a somewhat lesser degree. For ^1K(C–F) in CH_3F, Ditchfield and Synder[6] have reported Fermi contact (FC), orbital (OB), and spin dipolar (SD) terms of −38.9, 8.4, and 5.1 10^{19} m^{-2} kg s^{-2} A^{-2} using the self-consistent perturbation theory (SCPT) at the ab ibitio level. For ^1K(C–O) in methanol, Lazzeretti[7] gives values of −25.2, 4.0, 4.7 10^{19} m^{-2} kg s^{-2} A^{-2}, respectively, using the coupled Hartree–Fock method. Lee and Schulman estimate the orbital and spin dipolar terms in ethane as 0.2[21] and 0.8 10^{19} m^{-2} kg s^{-2} A^{-2}, respectively.[22] Following the simple idea that the nonspherical charge distribution around the coupled nuclei enhances the noncontact terms,[5] the share of the noncontact terms seems to increase as the series moves toward the more electronegative substituent atom and the molecular shape becomes more linear.

In Table II, the reduced one-bond X–H coupling constants in both first-row hydrides and their methyl-substituted counterparts, calculated using the double ζ basis set, are gathered. Also some available noncontact terms, calculated by other authors using the CHF method, have been included. There is a great similarity between the upper and the lower section of Table II. The only difference is simply the increase of about 10% caused by the methyl substitution of the first-row hydrides. It is therefore tempting to extrapolate some of the observations regarding the role of the basis set size and of the orbital and the spin-dipolar terms. Characteristic for methane was the dual insensitivity with respect to the basis set size and the small share of the noncontact contributions. This can be assumed to hold even for the directly

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Table III. Calculated Fermi Contact Contributions to One-Bond C-H Couplings in Some Substituted Methanes (in Hz)

system	CHF	CHF + SECORD	exptl
CH_4	150.7	109.6	125.0[a]
CH_3CH_3[d]	157.9	111.4	124.9[b]
CH_3NH_2[d]	161.7	116.2	133.0[a]
CH_3OH[d]	169.5	121.4	141.0[a]
CH_3F	177.8	128.2	149.1[c]

[a] Reference 23. [b] Reference 17. [c] Reference 19. [d] Average coupling constant for staggered conformation.

bonded carbon–proton coupling in ethane. Good agreement between the calculated, 40.1 (CHF + CI + other mechanisms[21,22]), and the observed values, $41.4\ 10^{19}\ m^{-2}\ kg\ s^{-2}\ A^{-2}$,[17] strengthens this claim. When the methyl group is changed to more electronegative group (NH_2 or OH), the basis set sensitivity of ^1K(X–H) again increases dramatically. In the large basis set calculation for methanol, Lazzeretti[7] has obtained ^1K(O–H) (FC) that is a factor about 2.5 times larger than ours. Also the significance of the other mechanisms increases (cf. Table II). Both these features can be included in our discussion above of the nonsphericity of charge distributions around the coupled nuclei. In other words, the use of a limited basis set and the Fermi contact term alone can still satisfactorily describe nuclear spin–spin couplings where the electron charge is evenly distributed around the coupled nuclei, provided, of course, that the electron correlation effects have been taken into account. Finally, the nonsensitivity of the calculated ^1K(X–H) to the choice of conformation should be noted.

Before leaving the discussion of the behavior of ^1K(X–C) and ^1K(X–H) as a function of X, it may be of some interest to compare the trends displayed by the two types of coupling constants. While the X–C coupling constants vary dramatically along the series X = C, N, O, F, the corresponding X–H couplings, in either the simple hydrides or their methyl derivatives, only vary very little. The trend in ^1K(X–C) has been explained by Gutowsky and co-workers[27,28] in terms of the core polarization mechanism. One explanation of the fact that ^1K(H–F) in hydrogen fluoride has the same sign and a magnitude similar to K(H–C) in methane is the substantial ionic character in the HF bond.[27,28] Our data give no direct information on these mechanisms, but the difference in the two experimental trends is clearly reproduced.

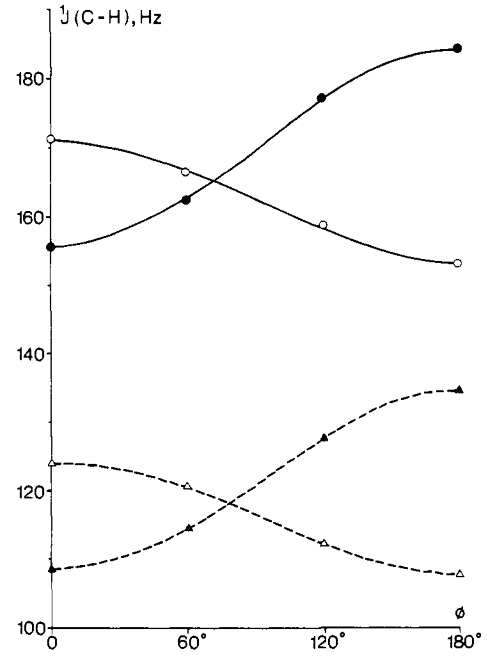

Figure 1. The dependence of ^1J(C–H) in aminomethane and methanol on the rotation around the CX bond. The dihedral angle ϕ is defined as the HCN–lone pair for aminomethane (○, CHF; △, CHF + SECORD) and as HCOH in methanol (●, CHF; ▲, CHF + SECORD). The solid and dashed lines correspond to plots of eq 2 with parameters of Table IX.

Table IV. Calculated Fermi Contact Contributions to ^2J(H–H) Values in Some Substituted Methanes (in Hz)

system	CHF	CHF + SECORD	exptl
CH_4	−31.2	−17.2	−12.4[a]
CH_3CH_3[c]	−30.9	−15.7	
CH_3NH_2[c]	−28.4	−14.4	
CH_3OH[c]	−28.4	−14.2	−10.8[b]
CH_3F	−27.8	−13.9	−9.6[b]

[a] Reference 35. [b] Reference 36. [c] Average coupling constant for staggered conformation.

Several workers[29,30] have been successful in calculating one-bond C–H couplings in simple hydrocarbons and their substituted derivatives. In Table III the corresponding ^1J(C–H) values obtained in this study are presented. For ethane, aminomethane, and methanol, the average coupling constant in the staggered conformation is quoted. The agreement with the experimental values is good. The linear dependence on the electronegativities, observed in experiments,[19,24] is reproduced both at the Hartree–Fock level and after taking into account the electron correlation contributions. The second-order perturbation method (SECORD) overestimates the magnitude of the correlation contribution.[3,8] The more accurate CI calculation should therefore give values which lie somewhere between the CHF and CHF + SECORD values in Table III. This is also the case. Full CI calculations have been performed for ^1J(C–H) in methane (120.1 Hz), staggered ethane (121.0 Hz), and fluoromethane (136.6 Hz). It should be noted that only the contact terms are quoted in Table III. The role of the other mechanisms is of minor importance in ^1J(C–H) couplings. The orbital and spin-dipolar terms are calculated to be 1.6 and −0.4 Hz, respectively, in methane,[2] 1.2 and −0.2 Hz in ethane,[21,22] and 0.4 and −0.4 Hz in fluoromethane.[6] One reason for not applying the expensive CI calculation to aminomethane and methanol is that in these cases the ^1J(C–H) couplings show a marked angular dependence during a rotation around the C–X bond. The calculation of the one-bond C–H coupling constants in these two molecules requires a calculation of the average coupling constant for the three C–H bonds in the methyl group. In staggered and eclipsed rotamers the number of calculations reduces to two. The angular dependence curves for ^1J(C–H) in aminomethane and methanol are shown in Figure 1. We can note that the angular dependence curves for methanol and aminomethane, calculated by Aminova and Samitov[31] using extended Hückel theory, show a different behavioral pattern.

B. Two Bond Couplings. Three types of geminal couplings can be found in a compound CH_3XY: the coupling between methyl protons, the coupling between carbon and the proton in the substituent group, and finally the coupling between the heavy atom in the substituent group and the methyl proton. The general trends in the geminal proton–proton couplings in the methyl group—but not the absolute values—have been quite easy to handle with different theoretical tools. As early as 1965, Pople and Bothner-By[32] successfully summarized the geometrical and substituent effects with four well-known rules using simple MO theory. More recently, the rules have been further supported by FPT INDO calculations.[33] Nonempirical double perturbation theory calculations of ^2J(H–H), using the minimal STO basis set in the series ethane–aminomethane–methanol–fluoromethane have also been reported by Barbier et al.[34]

Our results are quoted in Table IV. For ethane, aminomethane,

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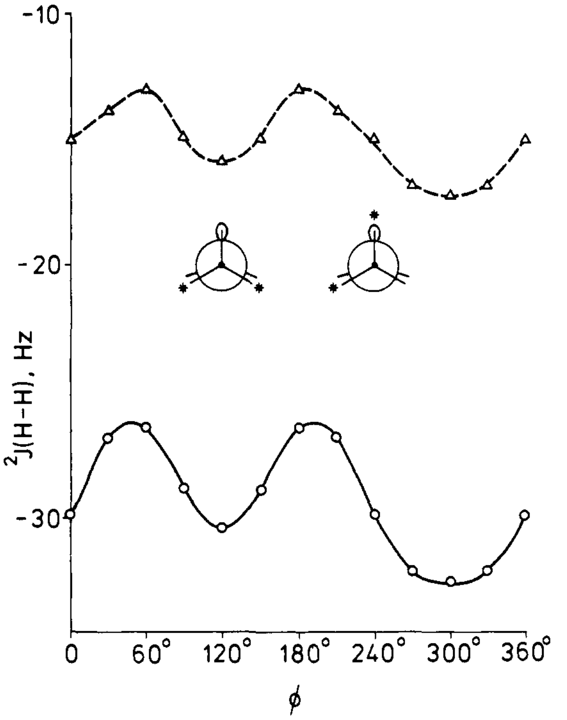

Figure 2. The dependence of ^2J(H–H) in aminomethane on the dihedral HCN-lone pair angle (○, CHF; △, CHF + SECORD). Two of the conformations are defined in the figure.

and methanol, the average coupling constants for the staggered conformation are given. The values obtained in the Hartree–Fock calculation are approximately 2.5–3.0 times larger than the experimental values[35-38] in the whole series and are reduced by 40–50% upon including correlation effects. The coupling constants in Table IV follow the trend of ^2J(H–H) increasing (in the algebraic sense) with the increasing substituent electronegativity. However, the calculated differences in the series CH_3CH_3, CH_3NH_2, CH_3OH, CH_3F are smaller than the experimental ones. The double ζ basis set is not sufficient to give a good description of ^2J(H–H) couplings. Even the results for methane, for which this small basis set has been flexible enough to give a rather accurate value for ^1J(C–H) couplings, can be improved considerably. For ^2J(H–H) in this molecule we have previously reported[3] the CHF value of −24.2 Hz derived using the $\langle 5,3,1/3,1 \rangle$ basis set. Guest et al.[2] obtain −25.4 Hz with their largest basis set. The coupled Hartree–Fock calculations of the noncontact terms using large basis sets have been reported for methane[2] and methanol.[7] Both calculations yield a total noncontact contribution of about 3 Hz. The calculations by Lee and Schulman, who used a basis set similar to that applied here, have for ethane given a value for ^2J(H–H) (OB) of about 1 Hz[21] and ^2J(H–H) (SD) of about 0.5 Hz.[22]

The geminal proton coupling constants in ethane, aminoethane, and methanol are dependent on the rotation around the C–X bond. When the individual ^2J(H–H) coupling in methanol and aminomethane is followed during one rotation around the C–X bond, an asymmetric curve with respect to 180° is obtained; cf. Figures 2 and 3. It is interesting to note that the electron correlation tends to decrease the angular dependence of ^2J(H–H). In the case of methanol, the shape and the periodicity of the curve shown in Figure 3 superposes with the corresponding FPT INDO curve obtained by Maciel et al.[33] For aminomethane, however, there is a clear disagreement between Figure 2 and the angular variation curve for ^2J(H–H), reported by Wasylishen and Schaefer[37] who also used the FPT INDO approach. The angular dependence of ^2J(H–H) in aminomethane and methanol has also been studied by Aminova and Samitov[31] using the extended Hückel theory.

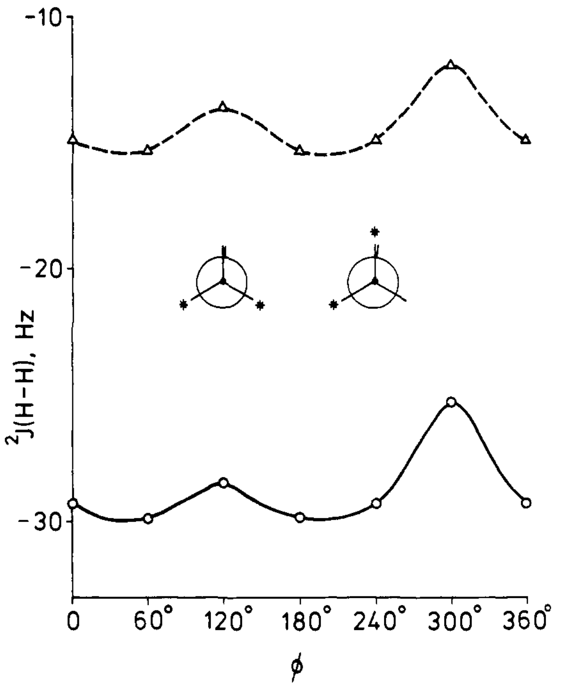

Figure 3. The dependence of ^2J(H–H) in methanol on the dihedral HCOH angle (○, CHF; △, CHF + SECORD). Two of the conformations are defined in the figure.

Table V. Calculated Fermi Contact Contributions to ^2J(C–H) Coupling Constants in Some Substituted Methanes CH_nXY (in Hz)

X	*Y*	conformation	CHF	SECORD	CHF + SECORD	exptl
C	H_3	stagg	−16.4	10.8	−5.6	−4.5[a]
C	H_3	eclip	−17.2	11.3	−5.9	
N	H_2	stagg	−10.4	7.7	−2.7	
N	H_2	eclip	−11.2	8.2	−3.0	
O	H	stagg	−8.4	7.0	−1.6	
O	H	eclip	−9.0	7.4	−1.6	

[a] Reference 17.

In aminomethane, there is one additional geminal proton–proton coupling, that in the NH_2 group. This coupling constant is calculated to be about −22 Hz at the CHF level and about −9 Hz at the CHF + SECORD level. It is found to be quite insensitive to the conformation changes, which may be due to the high symmetry of the methyl group opposing the NH_2 moiety. In ammonia, which provides the best comparison for this coupling, the proton–proton coupling constant is calculated as −21.6 Hz (CHF) and −12.2 Hz (FP-CI) using the double ζ basis set. Clearly, the effect of the methyl substituent on ^2J(H–H) in the NH_2 group is small. The ^2J(H–H) coupling constant in the amino group in aminomethane has also been calculated by Wasylishen and Schaefer,[37] who report −6.6 Hz for the staggered and −7.1 Hz for the eclipsed conformation, using the FPT INDO method. To our knowledge, no experimental data for this coupling constant are available.

The angular dependence is small even in the two-bond C–H couplings (cf. Table V). Analogous with the case of ^1J(X–H) and ^2J(H–H) couplings in the NH_2 group in aminomethane, the coupling path can also here be projected on the highly symmetric background of a methyl group. The values follow nicely the trend of electronegativity. The electron correlation effects are very large, and in the case of aminomethane and methanol they almost cancel the CHF values. The values obtained for methanol in Table V can be compared to the values obtained by Lazzeretti,[7] which are for staggered conformation: −8.3, 0.7, and 0.0 Hz for the FC, OB, and SD terms, respectively. For the eclipsed conformation, the corresponding values are −8.6, 0.6, and 0.1 Hz.

The two-bond X–H coupling constants mirror the same distinctive trend in the CHF values and correlation corrections, as

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Table VI. Calculated Fermi Contact Contributions to ^2K(X-H) Coupling Constants in Some CH_3XY Compounds (in 10^{19} m^{-2} kg s^{-2} A^{-2})[e]

X	Y	CHF	SECORD	CHF + SECORD	exptl
C	H_3	−5.6	3.6	−2.0	−1.4[a]
N	H_2	−1.7	2.7	1.0	0.8[b]
O	H	4.1	0.5	4.6	4.7[c]
F		6.5	−1.4	5.1	4.1[d]

[a] Reference 17. [b] Reference 18. [c] Reference 40. (measured for methyl formate). [d] Reference 19. [e] To converst *K* to *J* (in Hz) multiply by the conversion factors given in the footnote of Table II for X = ^{13}C, ^{15}N, and ^{17}O and the factor of 11.30 for X = ^{19}F.

Table VII. *A*, *B*, and *C* Parameters in Eq 2 Obtained by Least-Squares Fitting of ^3J(H-H) in Ethane and Methanol Calculated at Different Levels of Approximations

method	molecule	*A*	*B*	*C*	calculated (J-av) stagg	calculated (J-av) eclip	exptl av
CHF	CH_3CH_3[a]	10.7	−1.4	7.4	10.5	10.8	8.0[c]
	CH_3OH	7.2	−3.6	7.4	6.9	7.2	5.0[d]
	CH_3OH[b]	8.4	−5.3	7.0	8.4	8.3	
CHF + SECORD	CH_3CH_3	6.3	−1.0	5.9	6.3	6.3	
	CH_3OH	5.9	−1.0	7.5	5.3	6.2	
CHF + CI	CH_3CH_3	6.9	−1.0	6.1	7.0	6.9	

[a] Reference 8. [b] Reference 7. [c] Reference 17. [d] Reference 26.

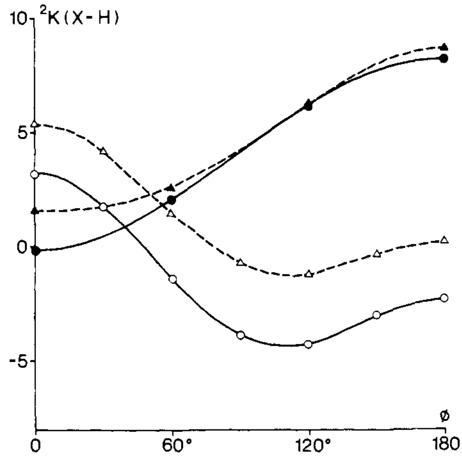

Figure 4. The dependence of ^2K(X-H) in aminomethane (X = N) and methanol (X = O) on the rotation around the CX bond. The dihedral angle ϕ is defined as HCN-lone pair in aminomethane (○, CHF; △, CHF + SECORD) and as HCOH in methanol (●, CHF; ▲, CHF + SECORD). The solid and dashed lines correspond to plots of eq 2 with parameters of Table IX.

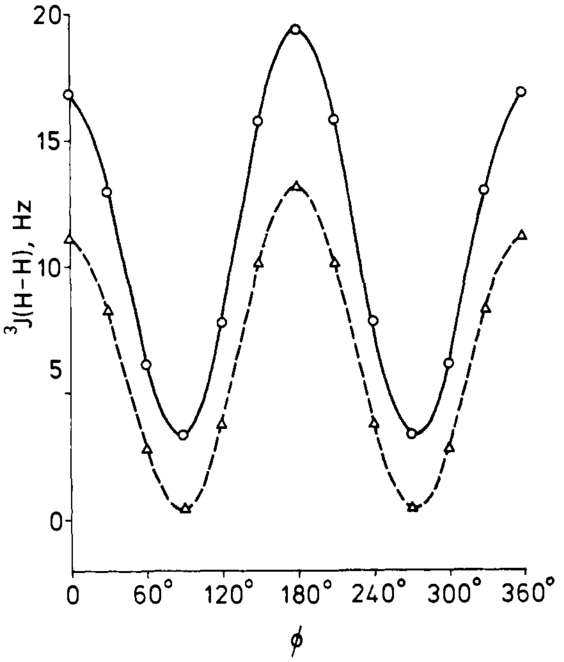

Figure 5. The dependence of ^3J(H-H) in ethane on the dihedral HCCH angle (○, CHF; △; CHF + SECORD). The lines correspond to plots of eq 2 with the parameters of Table VII.

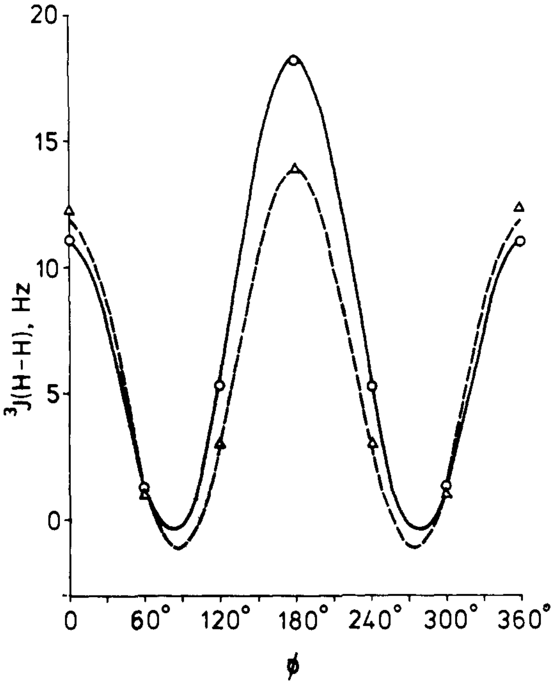

Figure 6. The dependence of ^3J(H-H) in methanol on the dihedral HCOH angle (○, CHF; △, CHF + SECORD). The lines correspond to plots of eq 2 with the parameters of Table VII.

was evidenced by the one-bond C-X couplings in Table I, although with opposite signs. In Table VI, the reduced geminal X-H couplings are given. In the case of ethane, aminomethane, and methanol, the average values for staggered conformation are reported. The angular dependencies of ^2K(X-H) in methanol and aminomethane are shown in Figure 4. No experimental value for ^2K(O-H) in methanol has been reported in literature. However, for the sake of comparison, in Table VI we provide the values for ^2K(O-H) measured in methyl formate.[40] For CH_3OH Lazzeretti[7] reports the calculated values of 3.0 10^{19} m^{-2} kg s^{-2} A^{-2} for the contact term and 0.66 for the noncontact contributions. ^2K(N-H) in aminoethane has also been calculated by Wasylishen and Schaefer[39] and Aminova and Samitov.[31]

C. Vicinal Coupling Constants. We turn now to the vicinal (three-bond) proton-proton coupling constants. The prediction of the conformational dependence of such a coupling constant in ethane probably constitutes the most successful application of the early theoretical methods.[39] The modified Karplus equation[40] is:

$$^3J(\text{H-H}) = A + B\cos\phi + C\cos 2\phi \qquad (2)$$

In an earlier communication, we found that eq 2 is an excellent representation of our coupled Hartree-Fock and finite perturbation configuration interaction calculations for ethane.[8] The dependence of the vicinal coupling constants in ethane, aminomethane, and methanol on the dihedral HCXH angle is displayed in Figures 5, 6, and 7. We see in these that the presence of the electronegative oxygen or nitrogen atom in the coupling path does not

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(39) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11.
(40) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.

Table VIII. Parameters of Eq 3 for Individual ^3J(H-H) in Aminomethane Obtained by Least-Squares Fitting of Various Calculated Data

	standard			correction				max		min	
	A	B	C	D	E	F	G	θ	J	θ	J
CHF	4.8	5.2	8.8	5.5	0.1	−0.4	0.4	4.7	19.0	93.7	−0.5
CHF + SECORD	5.0	2.1	6.4	0.9	0.2	0.1	0.0	1.6	13.6	266.5	−1.1
FPT INDO[a]	7.5	−3.9	7.1	0.1	−0.1	1.0	0.0	184.8	18.8	86.1	−0.4
simple LCAO-MO[b]	3.0	−2.4	2.6	−0.2	0.9	−0.2	0.5	169.0	8.2	284.1	−0.4

[a] Reference 44. [b] Reference 31.

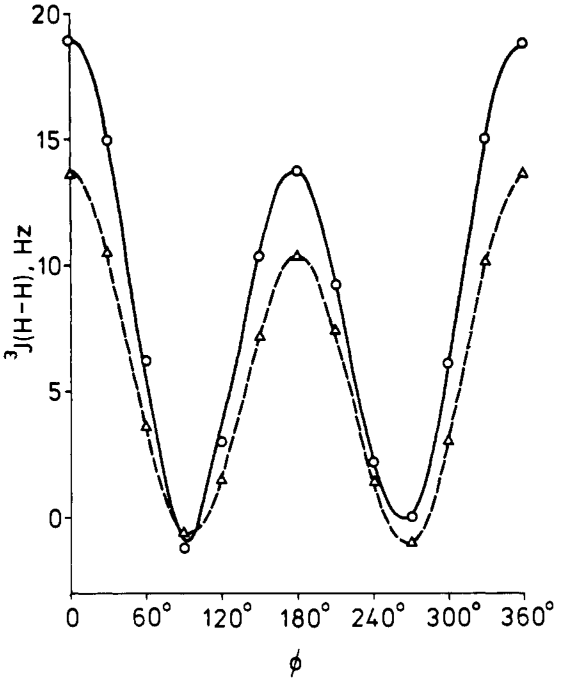

Figure 7. The dependence of ^3J(H–H) in aminomethane on the dihedral HCNH angle (○, CHF; △, CHF + SECORD). The lines correspond to plots of eq 3 with parameters of Table VIII.

have any dramatic effect on the coupling constant. Also, the role of correlation is here clearly less important than for the geminal couplings.

The curve plotting ^3J(H-H) vs. the dihedral angle for methanol (Figure 6) can also be described with eq 2, with the parameters A, B, and C givein in Table VII. Similar curves, symmetric around 180°, have been obtained earlier in semiempirical calculations for ethane[29,41-43] and methanol.[31,42] For methanol, an accurate coupled Hartree–Fock calculation, including the noncontact terms, has also been reported by Lazzeretti[7] for staggered and eclipsed conformations. He has found that the Fermi contact contribution is clearly dominant. Lee and Schulman have also reported calculations of the orbital[21] and spin-dipolar[22] contributions to the vicinal coupling constant in ethane.

The plot of ^3J(H-H) vs. the dihedral HCNH angle in aminomethane shows a distinct asymmetry around 180°. Such asymmetric deviations from the Karplus relation have been predicted earlier, both for substituted ethanes[20,43] and for aminomethane,[31,44] on the basis of semiempirical studies. Pachler[20] has suggested that the symmetry could be described analytically by adding sin ϕ and sin 2ϕ terms to the Karplus relation. We have chosen the following function involving two additional terms:

$$^3J(\text{H-H}) = A + B\cos\phi + C\cos 2\phi + D\sin\phi/2 + E\sin\phi + F\sin 2\phi + G\sin 3\phi \quad (3)$$

In Table VIII, we present the parameters A–G obtained by least-squares fitting of our data to eq 3. The table also contains results of the fitting of the data obtained by Gopinathan and Narasimhan[44] using the FPT INDO method, and of Aminova and Samitov,[31] who used the extended Hückel theory. In considering our results, it is interesting to note that the correlation effects decrease the importance of the sine terms, i.e., render the curve more symmetric. The sine terms are also small in the semiempirical calculations. Further we can note in Table VIII and in Figure 7 that the ab initio curves show a global maximum in the vicinity of 0°, while the semiempirical calculations predict a global maximum in the vicinity of 180°. The average calculated ^3J(H-H) is 8.7, 5.7, and 6.0 Hz at the CHF, CHF + SECORD, and CHF + CI level of approximation, respectively. To our knowledge, no experimental data for this coupling constant are available.

Table IX. A, B, and C Parameters in Eq 2 Obtained by Least-Squares Fitting of Calculated ^1J(C-H) and ^2K(X-H) in Aminomethane and Methanol

				calcd J_{av}	
	A	B	C	stagg	eclip
		^1J(C-H) CHF			
CH_3NH_2	163.8	−5.9	−1.7	161.0	165.9
CH_3OH	169.8	14.2	0.2	169.5	170.0
		CHF + SECORD			
CH_2NH_2	117.7	−6.0	−1.5	117.7	119.9
CH_3OH	121.2	13.0	0.4	121.5	121.4
		^2K(X-H) CHF			
CH_3NH_2	−1.7	2.8	2.2	−1.6	−1.7
CH_3OH	4.2	−4.2	−0.1	4.1	4.2
		CHF + SECORD			
CH_3NH_2	1.0	2.6	1.8	1.1	1.0
CH_3OH	4.7	−3.6	0.5	4.6	4.7

[a] The angle is defined as H–C–X–H.

Two further comments are appropriate regarding the form of eq 2. First, we note that both cos ϕ and cos 2ϕ functions have a property that the sum of their values at three arbitrary angles 120° apart is equal to zero. Thus, if the methyl group is assumed to have the property of undistorded threefold symmetry, the constant A in eq 2 should be equal to the average ^3J(H-H) for any conformation of ethane or methanol. In Table VII, we have also included the average vicinal coupling constants obtained by direct calculation for the eclipsed and staggered conformations of methanol and ethane. Second, we would like to report the observation that two of the couplings transmitted through the "subpath" to the full HCXH coupling path and involving the methyl proton, i.e., ^1J(C-H) and ^2J(X-H), can also be described faithfully by eq 2. The corresponding A, B, and C parameters for aminomethane and methanol are given in Table IX (the parameters for the two-bond coupling constant refer to the reduced coupling constant). The amplitude of the angle-dependent terms is essentially zero for ethane and rises rapidly with the increasing electronegativity of the atom X for both types of coupling constants, in analogy with the case of ^3J(H-H) in ethane and methanol.

4. Conclusions

The nonempirical calculations using the finite perturbation configuration interaction method and a basis set of double ζ quality

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(41) Maciel, G. E.; McIver, J. W.; Ostlund, N. S.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4497.

(42) Govil, G. *Indian J. Chem.* **1971**, *9*, 824.

(43) Gopinathan, M. S.; Narasimhan, P. T. *Mol. Phys.* **1971**, *21*, 1141.

(44) Gopinathan, M. S.; Narasimhan, P. T. *Mol. Phys.* **1971**, *22*, 473.

are capable of reproducing all known trends for all nuclear spin-spin coupling constants in the series ethane-aminomethane-methanol-fluoromethane. For some of the coupling constants, primarily ^1J(C-H) and ^3J(H-H), the absolute values of the calculations are also very close to experimental values. Geminal coupling constants are a more difficult case. The one-bond coupling constants between the atom X (C, N, O, F) and the methyl carbon become increasingly more difficult to describe as the electronegativity of X increases. This is also true for the one-bond couplings between X and the proton, in analogy with earlier observations in simple hydrides.

The inclusion of correlation effects is of varying importance for different types of coupling constants. If we use the ratio Q(SECORD) = $-J$(SECORD)/J(CHF) as the measure of the importance of the correlation effects, and limit our interest to the average values of coupling constants for the staggered conformation, we can note two types of behavior. First, we have the coupling constants for which Q(SECORD) is always positive and roughly constant in the series of molecules. These are, ordered by decreasing Q(SECORD), given in parentheses: ^2J(C-H) (74%), ^2J(H-H) (48%), ^3J(H-H) (37%), ^1K(X-H) (29%), and ^1J(C-H) (28%). For these cases, we can also note that Q(CI) = $-J$(CI)/J(CHF), when available, is similar to Q(SECORD) though somewhat smaller. The second type of behavior is observed for ^1K(X-C) and ^2K(X-H). Considering these coupling constants to be a function of X, we find that the CHF values and the correlation corrections have trends of their own: both change sign somewhere along the series X = C-F, but the positions of the sign change do not coincide. Consequently, Q(SECORD) and Q(CI) vary strongly throughout the series of substituted methanes and become negative for both couplings in methanol, where the correlation contributions thus enhance the CHF results.

Several of the coupling constants show a strong dependence on conformation. Inclusion of the correlation corrections always has a moderating effect on this dependence. The modified Karplus relation, eq 2, is an excellent representation of the dihedral angle dependence of ^3J(H-H) along the HCXH path in ethane and methanol. In the case of aminomethane and methanol, the angular dependence of coupling constants along the subpaths to the HCXH path, originating at the methyl proton, i.e., ^1J(C-H) and ^2K(X-H), can also be described by eq 2. It would undoubtedly be interesting to see whether this observation could be confirmed experimentally for suitable rigid compounds.

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Ion-Molecule Radiative Association Reactions. A Statistical Phase Space Theory Model

Lewis M. Bass, Paul R. Kemper, Vincent G. Anicich, and Michael T. Bowers*

Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. Received November 20, 1980

Abstract: A general model is presented for the application of statistical reaction rate theory to ion-molecule association reactions. A detailed mechanism which accounts for both collisional and radiative transitions is invoked and the formal solution of the resulting mathematical equations is discussed. A simplified working model is then developed and applied to the reaction $CH_3^+ + HCN \rightarrow CH_3{\cdot}HCN^+$. The theoretical predictions are compared with new experimental data reported here as well as that of McEwan et al. and Schiff and Bohme. The model is then used to provide the foundation for a critical discussion of previous work on ion-molecule association reactions.

I. Introduction

The importance of ion-molecule reactions in the chemistry of interstellar clouds has been firmly established.[1] Measurement of a significant number of rate constants for reactions of species of interstellar importance has been accomplished. These rate constants, usually measured at 300 K, have been very useful in modeling interstellar molecular abundances.[1] There remain, however, some serious gaps in information, particularly regarding synthesis of some of the larger species that have been observed. This manuscript addresses this point, particularly the role of radiative association and how this process can be modeled by using statistical rate theory.

McEwan et al.[2] have recently reported the results of an ICR (ion-cyclotron resonance) spectrometry study of reaction I.1 in the presence of He bath gas in the pressure range from 1×10^{-6} to 2×10^{-2} torr. They concluded that the observed reaction proceeds via two distinct pathways

$$CH_3^+ + HCN \xrightarrow{k_{obsd}^{(2)}} CH_3{\cdot}HCN^+ \qquad (I.1)$$

$$CH_3^+ + HCN \xrightarrow{k_{RA}^{(2)}} CH_3{\cdot}HCN^+ + h\nu \qquad (I.2)$$

$$CH_3^+ + HCN + He \xrightarrow{k^{(3)}} CH_3{\cdot}HCN^+ + He \qquad (I.3)$$

where $k_{RA}^{(2)}$ is the bimolecular rate constant for radiative association and $k^{(3)}$ is the rate constant for three-body association. The results were interpreted in terms of the mechanism given in eq I.4a-c,

$$A^+ + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (AB^+)^* \qquad (I.4a)$$

$$M + (AB^+)^* \xrightarrow{\beta k_c} AB^+ + M \qquad (I.4b)$$

$$(AB^+)^* \xrightarrow{k_r} AB^+ + h\nu \qquad (I.4c)$$

where A ≡ CH_3, B ≡ HCN, M = He, and the rate constants k_f, k_b, k_c, and k_r correspond to formation of the complex, back-dissociation of the complex, collisions of the complex with bath

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