Ab Initio Investigation of the Vibronic Structure of the C_2H Spectrum: Calculation of the Hyperfine Coupling Constants for the Three Lowest-Lying Electronic States[1]

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The hyperfine coupling constants (isotropic hfcc and four Cartesian components of the anisotropic tensor) are calculated for all three atoms of C_2H in its three lowest-lying electronic states at various molecular geometries by means of the ab initio configuration interaction (MRD-CI) method. The off-diagonal electronic matrix elements involving the two species of the A' symmetry are also computed. A diabatic transformation is performed leading to simple geometrical dependences of the hyperfine coupling constants. © 1991 Academic Press, Inc.

INTRODUCTION

With this paper and the following one we complete our ab initio study of the spectrum of the ethynyl radical (*1–5*). In the preceding papers of this series we presented the adiabatic potential surfaces for the three lowest-lying states, $1\,^2A'$, $2\,^2A'$, and $1\,^2A''$ (*1*), the method for an ab initio treatment of the vibronic coupling involving these three electronic states (*2, 3*), the computed vibronic energies and transition probabilities for various isotopomers of ethynyl (*3, 4*), and a study of the spin–orbit interaction in the vibronic states (*5*). The present paper and that following (*6*) deal with the hyperfine effects in C_2H.

This work is motivated by the fact that the determination of the hyperfine coupling constants (hfcc) has played an important role in identifying the ethynyl radical in interstellar space and in the laboratory (see, for example, references cited in Refs. (*1, 6*)), and that, to our knowledge, no high-quality ab initio calculations of these quantities have been published so far.

The magnetic hyperfine interaction results from the interaction of the nuclear spin I and the spin S of the electron. It can be divided into the dipole–dipole (anisotropic) part and the Fermi contact (isotropic) term; the latter possesses no classical analogue and arises from the interaction of I with the magnetic field produced at the nucleus

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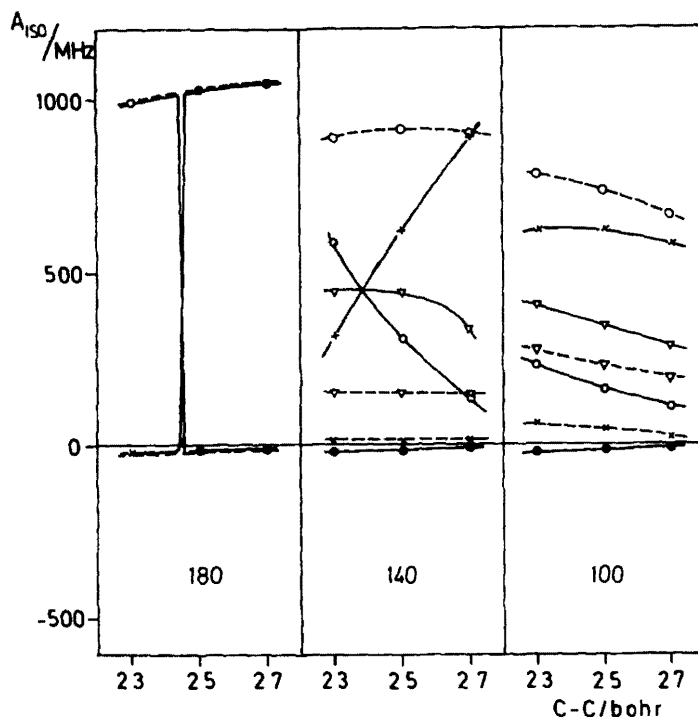
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FIG. 1. C–C bond length dependence of the isotropic hyperfine coupling constant for the terminal carbon atom (^{13}C) in C_2H, calculated at the valence bond angles of 180°, 140°, and 100°. C–H = 2.0 Bohr. Full lines: adiabatic electronic matrix elements; dashed lines: diabatic elements of the isotropic hfcc. (O) $\langle 1A'|A_{iso}|1A'\rangle$, $\langle \Sigma|A_{iso}|\Sigma\rangle$; (×) $\langle 2A'|A_{iso}|2A'\rangle$, $\langle \Pi^+|A_{iso}|\Pi^+\rangle$; (●) $\langle A''|A_{iso}|A''\rangle = \langle \Pi^-|A_{iso}|\Pi^-\rangle$; (∇) $\langle 1A'|A_{iso}|2A'\rangle$, $\langle \Sigma|A_{iso}|\Pi^+\rangle$.

by the spin of the unpaired electrons. The isotropic hyperfine coupling constant, A_{iso}, being the proportionality factor between the scalar product $I \cdot S$ and the corresponding part of the Hamiltonian, is given for the atom N by

$$A_{iso}^{N} = \frac{8}{3} \pi g_N g \beta_N \beta_e \frac{1}{S_z} \left\langle \Psi \left| \sum_{k=1}^{n} \delta(r_{kN}) S_{zk} \right| \Psi \right\rangle, \tag{1}$$

where β_N, g_N are the nuclear magneton and nuclear g factors, respectively. The term g is the g value for the electrons in the free radical, while β_e is the Bohr magneton. In the present work a value of 2.0 is used for g. S_z denotes the projection of the spin momentum onto the molecule-fixed z axis. The sum on the right-hand side of Eq. (1) runs over all electrons of the molecule, r_{kN} represents the distance of the ith electron from the nucleus N, and S_{zk} is the z component of the spin of the electron k. Ψ represents in principle the total molecular wavefunction. If A_{iso} is assumed to represent only the electronic part of the hyperfine coupling matrix element, Ψ is replaced in Eq. (1) by the electronic wavefunction(s).
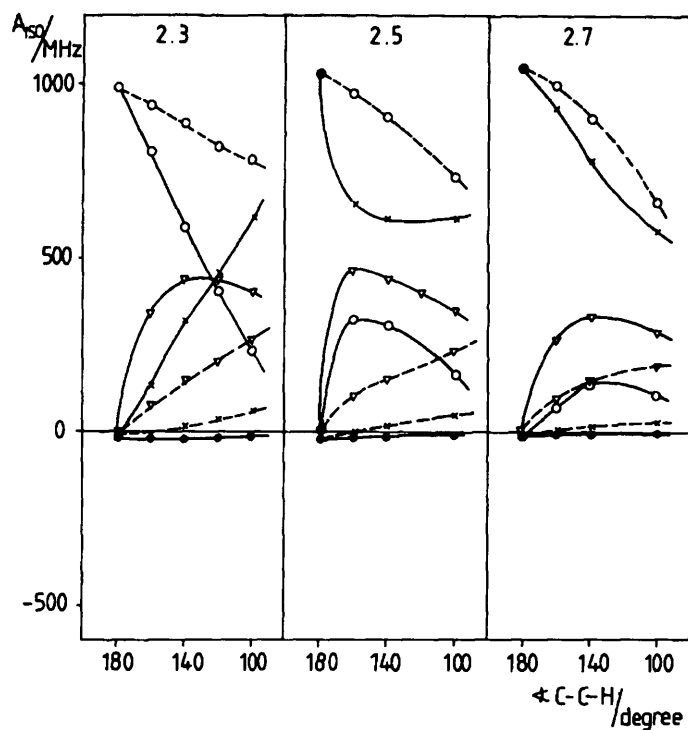
FIG. 2. Bond angle dependence of the isotropic hfcc for the terminal carbon atom (^{13}C) in C_2H calculated at the C–C bond length of 2.3, 2.5, and 2.7 Bohr and the C–H bond length kept fixed at 2.0 Bohr. For notation see Fig. 1.
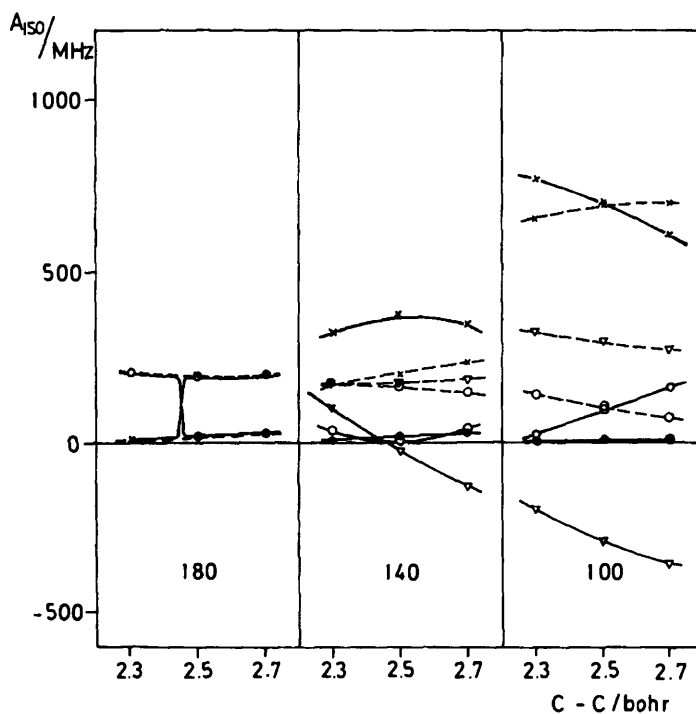

FIG. 3. C–C bond length dependence of the isotropic hfcc for the middle ^{13}C atom at the bond angle of 180°, 140°, and 100°. For notation see Fig. 1.
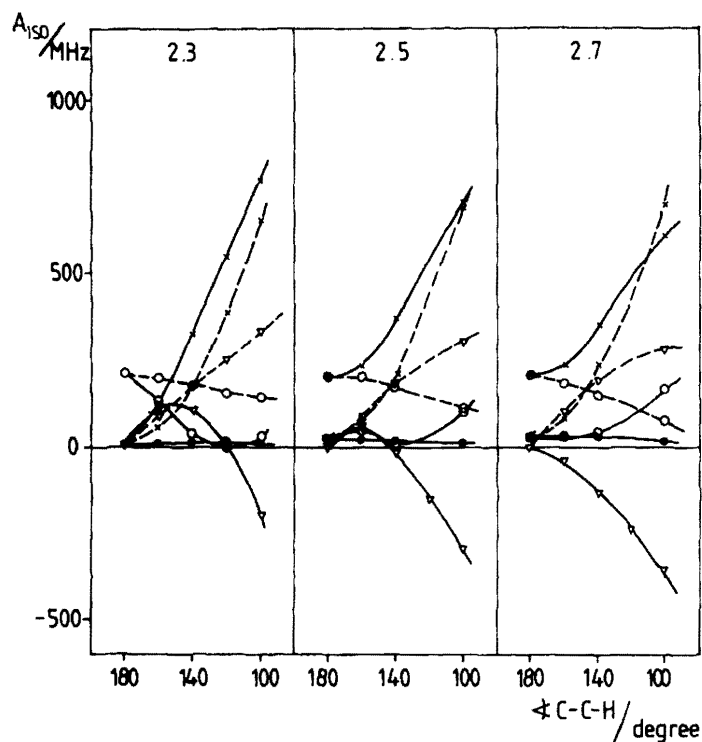
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FIG. 4. Bond angle dependence of the isotropic hfcc for the middle ^{13}C atom calculated at the C–C bond lengths of 2.3, 2.5, and 2.7 Bohr and the C–H distance of 2.0 Bohr. For notation see Fig. 1.
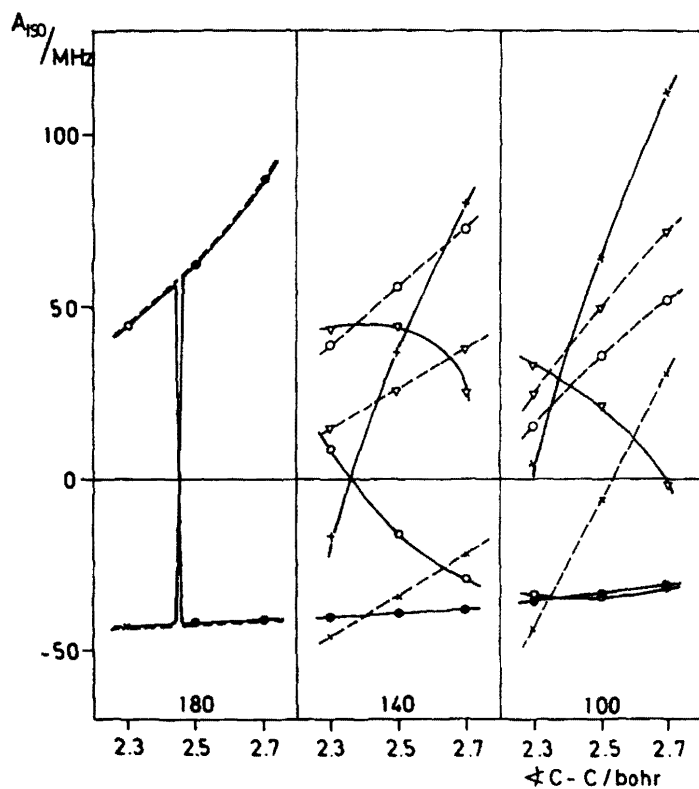

FIG. 5. C–C bond length dependence of the isotropic hfcc for the hydrogen atom (^{1}H) calculated at the bond angle values of 180°, 140°, and 100° and the C–H distance kept fixed at 2.0 Bohr. For notation see Fig. 1.
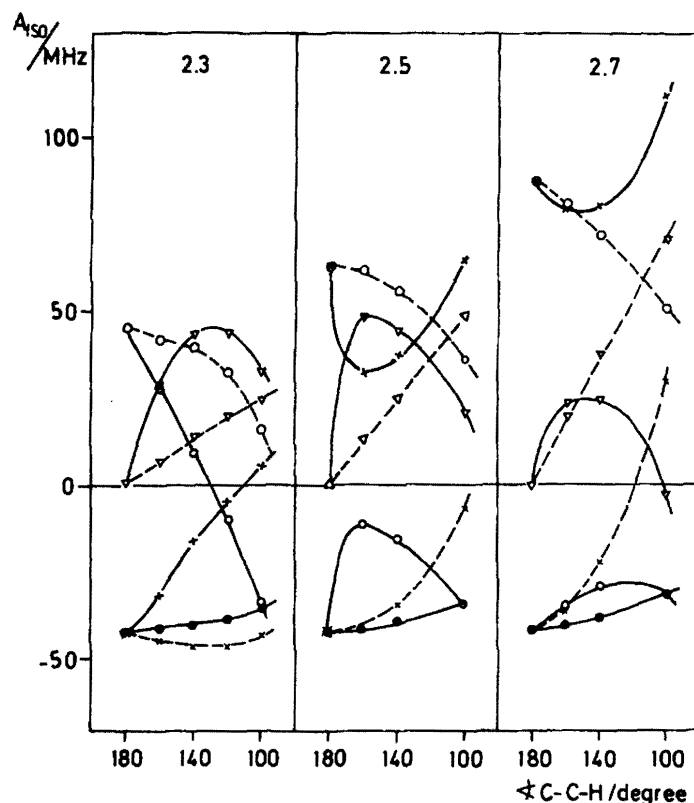
FIG. 6. Bond angle dependence of A_{iso} for the hydrogen atom in C_2H calculated at the C–C bond lengths of 2.3, 2.5, and 2.7 Bohr. For notation see Fig. 1.

The anisotropic part of the hf operator for the atom N is represented by a tensor whose Cartesian components with respect to a molecule-fixed frame are given by

$$A_{ij}^N = g_N g \beta_N \beta_e \frac{1}{S_z} \langle \Psi | \sum_{k=1}^{n} \left(\frac{3ij - r^2 \delta_{ij}}{r^5} \right)_{kN} S_{zk} | \Psi \rangle \qquad (2)$$

with $i, j = x, y, z$. Because the ethynyl radical is linear in its equilibrium geometry, the hfcc's are generally given in the Frosh–Foley notation. The relations between the Cartesian and the latter representation of the A_{ij} components are given elsewhere (6, 7).

Because of the significant coupling of the three lowest-lying electronic states of C_2H found earlier, a reliable rovibronic wavefunction for this system can only be represented by a linear combination involving the electronic wavefunctions for all three states. Thus besides the usual diagonal electronic matrix elements appearing already in the framework of the Born–Oppenheimer approximation, in the present work off-diagonal elements of the type
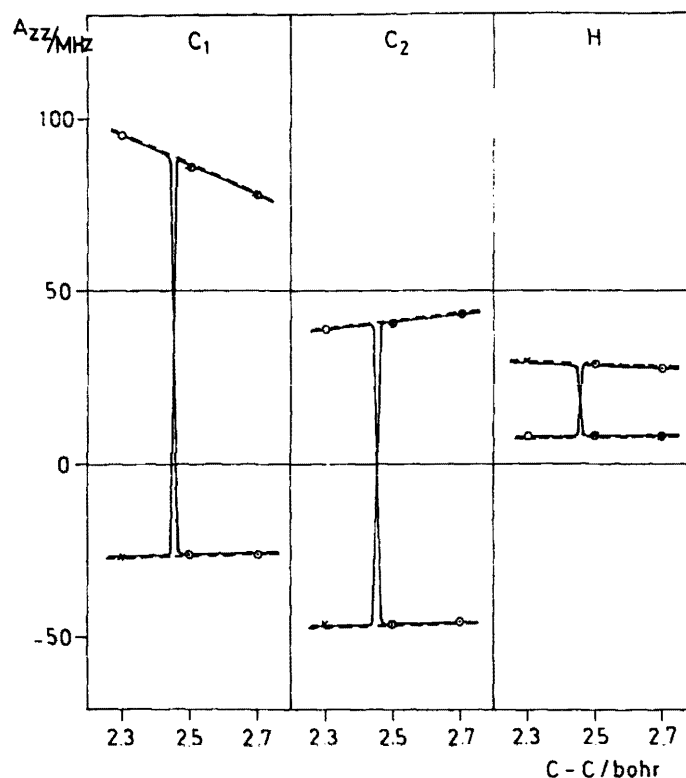
FIG. 7. C–C bond length dependence of the zz component of the anisotropic hfcc for the terminal ($^{13}C_1$), middle carbon atom ($^{13}C_2$), and the hydrogen atom (^1H) calculated at the linear molecular geometry and the C–H bond length kept fixed at 2.0 Bohr. For notation see Fig. 1.

$$A_{iso}^N = \frac{8}{3}\,\pi g_N g \beta_N \beta_e \frac{1}{S_z} \left\langle 1A' \middle| \sum_{k=1}^{n} \delta(r_{kN}) S_{zk} \middle| 2A' \right\rangle \tag{3}$$

and the analogous expression for the dipole–dipole part are also calculated. In the following paper (6) the results of an averaging of the isotropic and anisotropic parts of the hf operator over vibronic wavefunctions are presented.

TECHNICAL DETAILS

The same AO basis as that used for the computation of the potential energy surfaces, the electronic transition moments, and the matrix elements of the spin–orbit operator (1–5) is employed in the present work for the computation of the contribution of the hfcc's. It consists of 72 contracted Gaussians involving d functions centered at the carbon atoms, one s and one p bond function placed in the middle of the C–H bond, and one s function in the midpoint of the C–H bond. All calculations are performed
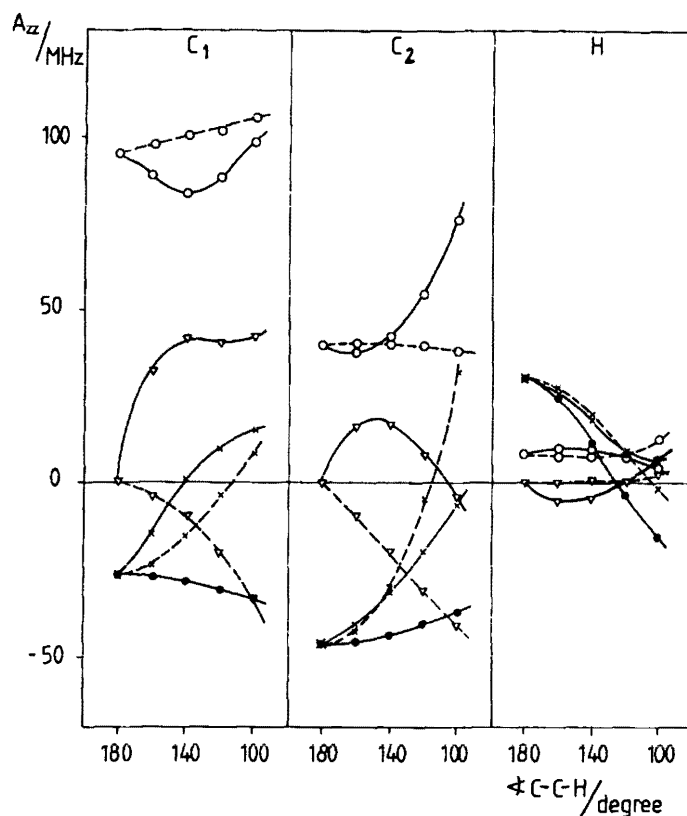
FIG. 8. Angular dependence of the A_{zz} electronic matrix element of the anisotropic hf tensor calculated at the C–C distance of 2.3 Bohr and C–H = 2.0 Bohr. For notation see Figs. 1 and 7.

in the C_s point group, but in contrast to the previous work none of the MOs generated by the SCF procedure are kept in core or discarded in the CI calculations. The standard MRD-CI method involving use of the natural orbitals, configuration selection (threshold $T = 5$ μH), energy extrapolation (8), as well as estimation of the higher-order excitations by a Davidson-type perturbative formula (9) is employed. The calculations are performed at the C–H distance kept fixed at 2.0 Bohr and at the C–C bond lengths of 2.3, 2.5, and 2.7 Bohr, combined with the bond angle values of 180°, 160°, 140°, 120°, and 100°. Taking into account excitations from the 1s core leads to larger CI spaces than previously consisting of singly and doubly excited configurations with respect to 20 reference configurations for both the A' and A'' symmetry. The dimensions of the MRD-CI space are 3 699 144 SAFs for A' and 2 575 083 for A'', and slightly larger dimensions of the secular equations are actually solved (up to 13 000) than before, but accounting for part of the 1s correlation energy leads to an essentially parallel lowering of the potential surfaces by about 0.035–0.039 hartree with respect to the energies published in the first paper of this series (1).
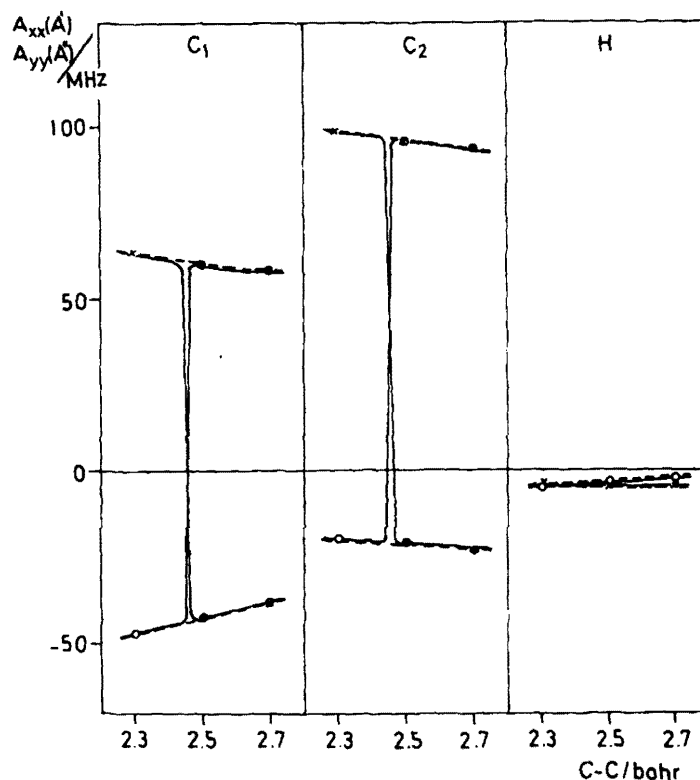
FIG. 9. C–C bond length dependence of $A_{xx}(A'/\Sigma, \Pi^+)$, $A_{yy}(A''/\Pi^-)$ for C₂H at the linear molecular geometry. For notation see Figs. 1 and 7.

RESULTS

Selected results of the calculation on the electronic matrix elements for the isotropic hfcc and the Cartesian components of the anisotropic tensor for the ¹³C, ¹³C, and ¹H atoms in the C–C–H molecule are presented in Figs. 1–14. C_1 denotes the terminal and C_2 the middle carbon atom. The molecule is assumed to lie in the yz plane with the z axis along the C–C bond. A_{xx} matrix element for the Π^+ and A_{yy} for Π^- (and vice versa) having the same value at the linear geometry are always given in the same figure (Figs. 9–12). When a comparison of the results of the present work with the corresponding experimental findings is made it should be kept in mind that we do not employ the main hfcc tensor axis system (10) but the approximate main axis system of the tensor of inertia. Figures 1–14 show the C–C bond length and the bond angle dependences of the diagonal matrix elements for all three electronic states considered, as well as the off-diagonal elements involving both species of A' symmetry. As already noted in the previous papers (1–5) in which the electronic transition moments between electronic states and the electronic matrix elements of L_z as well as the spin–orbit operators are published, the straight forward computed C–C distance—
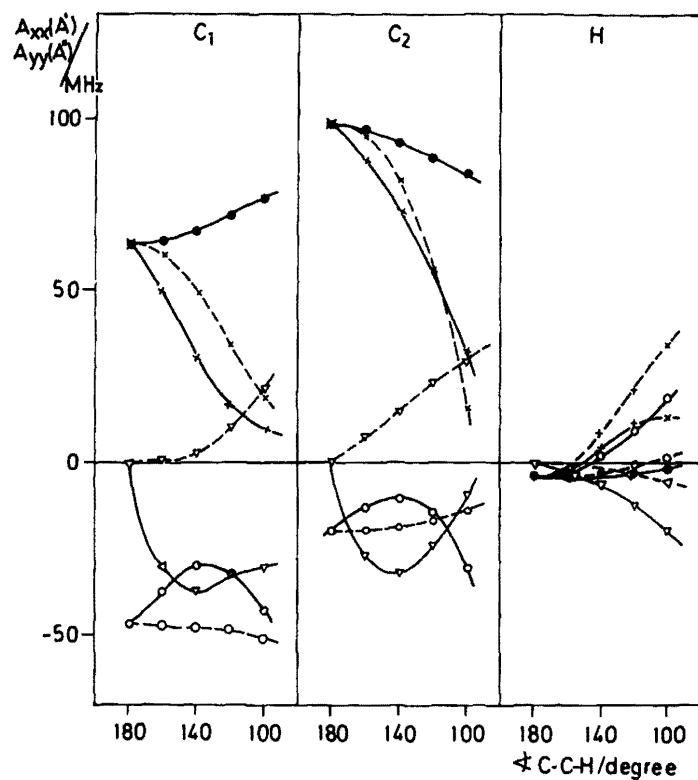
FIG. 10. Angular dependence of $A_{xx}(A'/\Sigma, \Pi^+)$, $A_{yy}(A''/\Pi^-)$ at C–C = 2.3 Bohr and C–H = 2.0 Bohr For notation see Figs. 1 and 7.
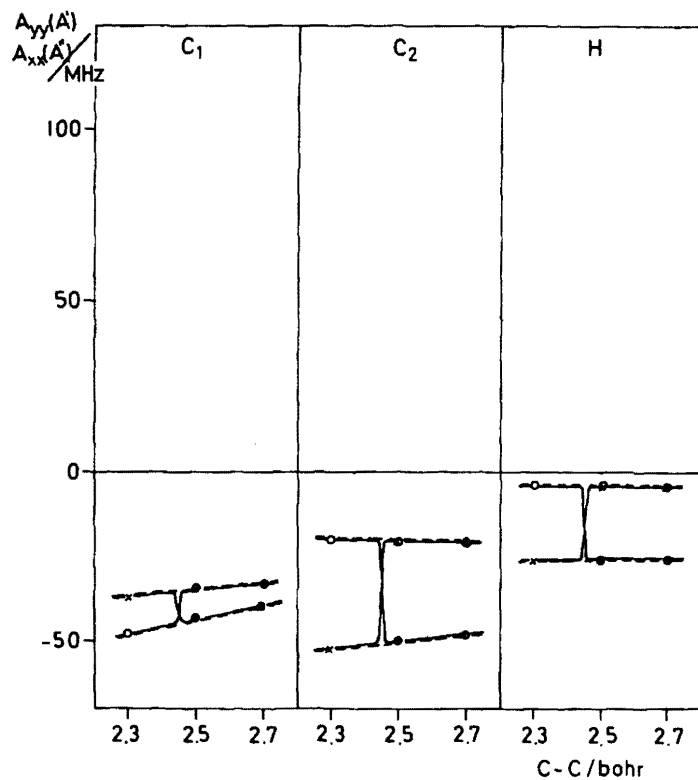

FIG. 11. C–C bond length dependence of $A_{yy}(A'/\Sigma, \Pi^+)$, $A_{xx}(A''/\Pi^-)$ calculated at the linear molecular geometry. For explanation see Figs. 1 and 7.
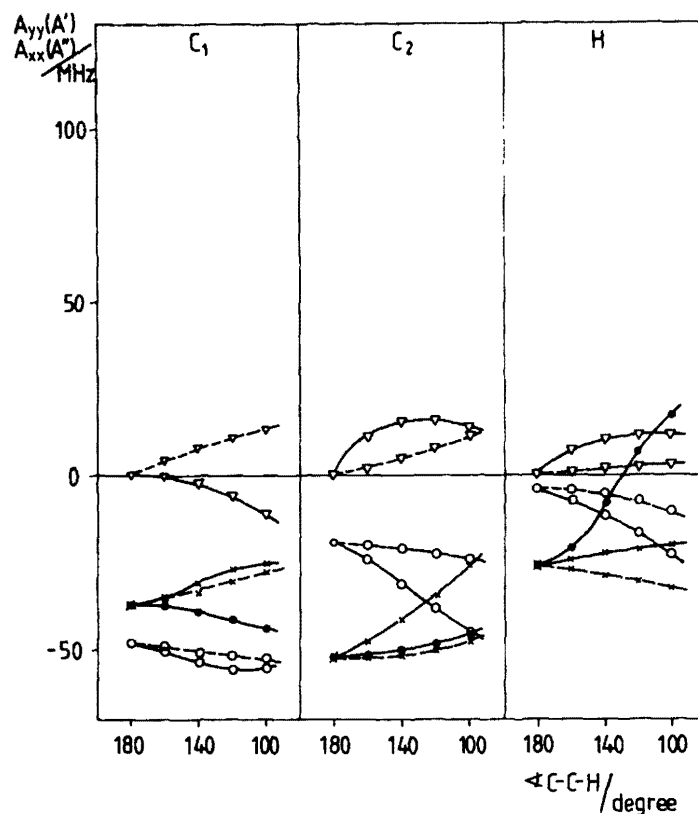
FIG. 12. Bond angle dependence of $A_{yy}(A'/\Sigma, \Pi^+)$, $A_{xx}(A''/\Pi^-)$ calculated at C-C = 2.3 Bohr and C-H = 2.0 Bohr. For notation see Figs. 1 and 7.

and bond angle dependences—are in many instances complicated, reflecting strong coupling between the adiabatic electronic states of the A' symmetry. Thus, as mentioned above, a diabatic transformation of the electronic basis is performed (Eq. (1) of Ref. (2)) in the following manner:

$$|\Sigma\rangle = |1A'\rangle\cos\gamma - |2A'\rangle\sin\gamma$$

$$|\Pi^+\rangle = |1A'\rangle\sin\gamma + |2A'\rangle\cos\gamma$$

$$(|\Pi^-\rangle = |1A''\rangle). \qquad (4)$$

This transformation results in the geometry dependences of the hyperfine-operator matrix elements shown by dashed lines in Figs. 1–14. The values for the transformation angle γ are chosen to be those presented in Figs. 9 and 10 of Ref. (2). It should be noted that these angles might differ slightly from those which would be obtained by applying the approach described in detail in Ref. (2) to the wavefunctions calculated in the present work because of a somewhat different CI treatment (all electrons are
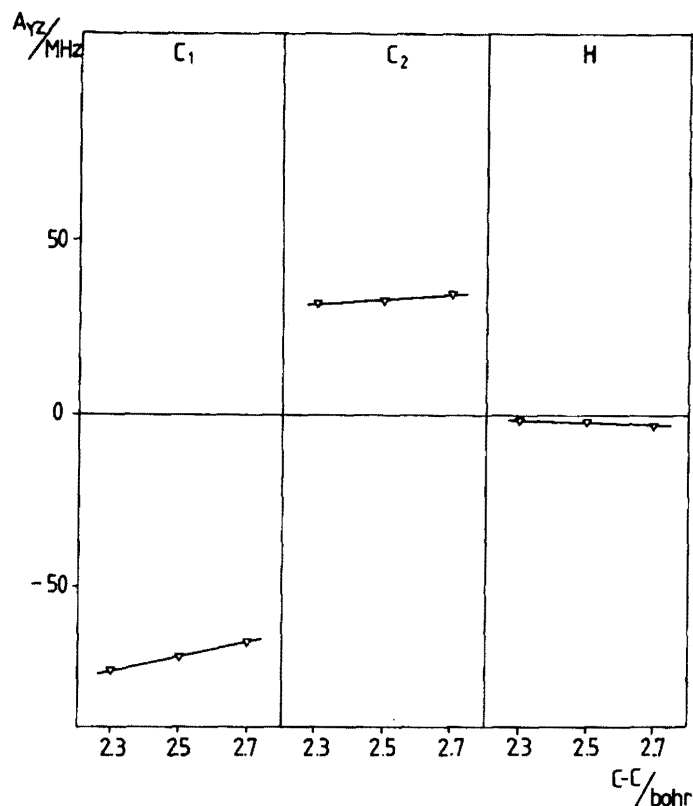
FIG. 13. C–C bond length dependence of the off-diagonal electronic matrix element for A_{yz} computed at the linear nuclear arrangement in C_2H. For notation see Figs. 1 and 7.

correlated in the present CI calculations). We use the transformation angle from Ref. (2) because we want to employ the potential surfaces computed in Ref. (1) for a larger number of geometries as well as the corresponding vibronic wavefunctions (2–4) for the calculations of the vibronically averaged values of the hyperfine part of the Hamiltonian. The accuracy of these computations is not affected by this choice because the transformation to the diabatic electronic wavefunctions represents only a change of the basis and leads to the same numerical values, provided the corresponding transformation of the matrix elements in the vibronic secular problem is properly performed.

The matrix elements of the hfcc's expressed in the diabatic basis show much simpler geometrical dependences than their adiabatic counterparts, just as has been observed for the other properties presented in Refs. (2, 3, 5). The most striking difference consists in the very similar bond angle dependences of the diabatic hfcc's for different values of the C–C bond lengths; this is in contrast to the situation in which they are given in the adiabatic electronic basis. The diagonal (with respect to the electronic basis) diabatic matrix elements of the components of the hyperfine part of the Hamiltonian retain much more of the Σ/Π electronic character at bent nuclear confor-
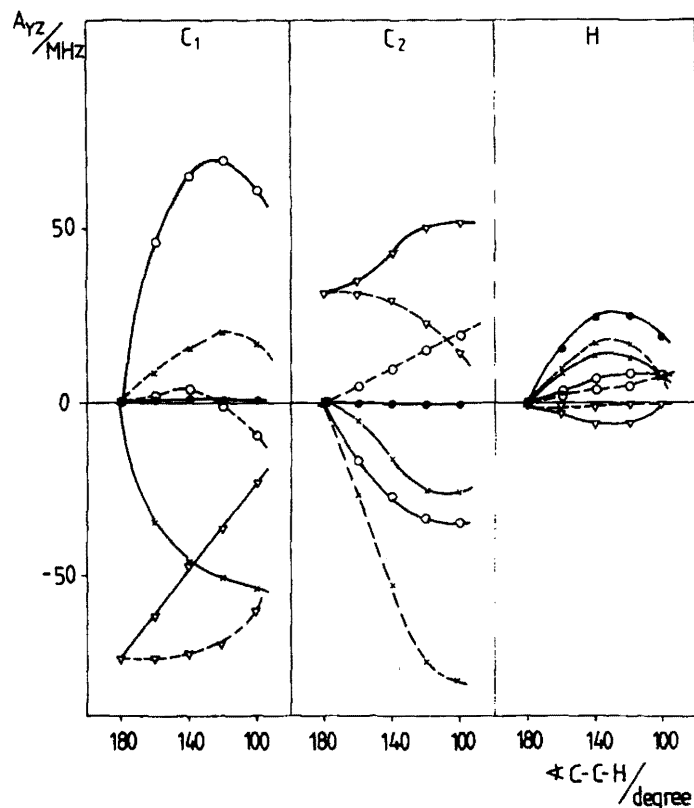
FIG. 14. Angular dependence of A_{yz} computed at C-C = 2.3 Bohr and C-H = 2.0 Bohr. For notation see Figs. 1 and 7.

mations than their adiabatic counterparts do. It should be noted that the off-diagonal matrix elements (with respect to both diabatic electronic species of the A symmetry) of A_{iso} and A_{xx}, A_{yy}, A_{zz} have nonvanishing values at nonlinear geometries reflecting the fact that the diabatic transformation cannot produce pure Σ and Π character electronic species when the molecule is bent.[3]

The values for the matrix elements of the isotropic hfcc and the components of the dipole–dipole tensor calculated at the linear molecular geometry and the C–C bond length of 2.3 Bohr (ground state equilibrium geometry of C₂H) are collected in Table I. For comparison the experimentally derived results for the lowest-lying vibronic state are also shown. The theoretical results are presented in terms of the diabatic matrix elements which have at the linear geometry the same values as the corresponding adiabatic matrix elements of course: for the C–C distance of 2.3 Bohr the 1 A' adiabatic state correlates with the Σ diabatic species, and the 2A' state with Π^+; at C–C = 2.5 and 2.7 Bohr the situation is opposite. The off-diagonal electronic elements for the

[3] The nonvanishing of the off-diagonal elements is partly caused by the use of the transformation angle values generated in other calculations (see discussion above).

TABLE I

Values (in MHz) for hfcc's of C_2H Calculated at Linear Nuclear Arrangement with the C–H Distance
Kept Fixed at 2.0 Bohr for C–C = 2.3, 2.5, and 2.7 Bohr

		¹³C₁			¹³C₂			¹H		
	C–C	2.3	2.5	2.7	2.3	2.5	2.7	2.3	2.5	2.7
A_{∞}	Σ	993	1030	1047	211	198	204	44.6	62.8	87.8
		902*			156*			44*		
	Π*	-23.5	-16.5	-9.96	11.6	22.8	31.2	-43.1	-42.5	-41.6
A_{π}	Σ	95.0	86.1	77.8	39.4	41.0	43.4	8.30	8.06	8.58
		78ᵇ			34ᵇ			8ᵇ		
	Π*	-26.5	-25.5	-25.2	-46.4	-46.4	-46.3	30.0	28.9	28.1
$A_{\perp}$	Σ	-48.1	-43.3	-39.6	-19.4	-20.3	-20.9	-4.07	-3.93	-4.14
	Π*	-37.1	-34.4	-33.0	-52.4	-50.1	-48.3	-26.1	-25.8	-25.6
$A_{\parallel}$	Σ	-46.9	-42.7	-38.2	-20.0	-20.7	-22.5	-4.23	-4.13	-4.44
	Π*	63.6	59.9	58.2	98.8	96.5	94.6	-4.01	-3.11	-2.51
A_{yz}	ΣΠ*	-74.2	-69.9	-65.9	31.6	32.4	34.6	-1.51	-2.17	-2.86

Note. The following abbreviations are used: $\Sigma \equiv \langle \Sigma | A | \Sigma \rangle$, $\Pi^{\pm} \equiv \langle \Pi^{\pm} | A | \Pi^{\pm} \rangle$, $\Sigma\Pi^{+} \equiv \langle \Sigma | A | \Pi^{+} \rangle$; $A_{\perp} \equiv A_{xx}(A')A_{yy}(A'')$; $A_{\parallel} \equiv A_{yy}(A'), A_{xx}(A'')$. $\Sigma\Pi^{+}$ is only different from zero for A_{yz}.
* Reference (4).
ᵇ Reference (4) (multiplied by 2).

isotropic hfcc and the diagonal (with respect to the Cartesian axes) components of the anisotropic tensor, A_{zz}, A_{xx}, and A_{yy}, vanish at the linear geometry. It should be noted that the off-diagonal electronic element of the yz component of the anisotropic tensor has a significant value at the linear nuclear arrangement. The matrix elements for the nontotally symmetric components, A_{xz} and A_{xy}, connecting the electronic species of A' and A'' symmetry with each other, are not calculated in the present work.

In general the results for hfcc's calculated in the present study slightly overestimate the values derived from experimentally observed spectra. This is apparently in contrast to our experience with other σ radicals (12, 13). The differences between the theoretical and experimentally derived results might, at least partially, be caused by the insufficiency of the AO basis employed and the use of a truncated CI wavefunction (11). On the other hand, the results derived from experimental data do not represent pure electronic matrix elements but rather the rovibrationally averaged values. The latter problem is studied in the following paper (6).

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