

## Ab Initio Investigation of the Vibronic Structure of the C<sub>2</sub>H Spectrum: Computation of the Vibronically Averaged Values for the Hyperfine Coupling Constants<sup>1</sup>

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The vibronically averaged values for the hyperfine coupling constants in the  $X^2\Sigma-A^2\Pi$  system of the ethynyl radical are computed by means of the ab initio method calculations. The results point at the importance of taking into account the coupling of all three electronic states in question ( $1^2A'$ ,  $2^2A'$ , and  $1^2A''$ ) for a reliable explanation of the available experimental findings. The mean values of the hfcc's for  $K = 0$  and 1 levels in  $^{13}\text{C}_2\text{H}$  and  $^{13}\text{C}_2\text{D}$  in the energy range up to  $6000\text{ cm}^{-1}$  are predicted. © 1991 Academic Press, Inc.

### INTRODUCTION

With the present paper we conclude our ab initio study of the  $A^2\Pi-X^2\Sigma$  spectrum of ethynyl (1-6). We report the mean values for the isotropic hyperfine constant (hfcc) and for the  $A_{zz}$  component of the anisotropic hyperfine tensor in the vibronic states of various isotopomers of C<sub>2</sub>H as obtained from our calculations. Thereby we employ the vibronic wavefunctions computed by means of the approach described in detail in Ref. (3) and the electronic matrix elements for hfcc's published in the preceding paper (6). The aim of this work is to reproduce and explain the results of numerous experimental studies undertaken especially in the last few years (7-18), and to make predictions which might be useful for future investigations.

### CALCULATION OF VIBRONICALLY AVERAGED hfcc's

The rovibronic wavefunction suitable to represent a vibronic state arising from coupling of the three electronic states ( $1^2A'$ ,  $2^2A'$ , and  $1^2A''$ ), the stretching and bending vibrations, as well as the rotation around the  $z$  axis, corresponding to the smallest moment of inertia, can be written in the form (3)

<sup>1</sup> This is Part VII of the ab initio studies related to C<sub>2</sub>H.

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$$\begin{aligned}
\Psi^p &= [\psi_{[s,\rho,\phi]}^{\Sigma} \sum_k \xi_k^{\Sigma}(s) \sum_i c_{pki}^{\Sigma} \chi_i^K(\rho) + \psi_{[s,\rho,\phi]}^{\Pi_1} \sum_k \xi_k^{\Pi}(s) \sum_i c_{pki}^{\Pi_1} \chi_i^{K-1}(\rho) \\
&\quad + \psi_{[s,\rho,\phi]}^{\Pi_2} \sum_k \xi_k^{\Pi}(s) \sum_i c_{pki}^{\Pi_2} \chi_i^{K+1}(\rho)] e^{iK\phi} \\
&\equiv \left\{ \sum_k [\psi_{[s,\rho,\phi]}^{\Sigma} \xi_k^{\Sigma}(s) f_{pk}^K(\rho) + \psi_{[s,\rho,\phi]}^{\Pi_1} \xi_k^{\Pi}(s) f_{pk}^{K-1}(\rho) \right. \\
&\quad \left. + \psi_{[s,\rho,\phi]}^{\Pi_2} \xi_k^{\Pi}(s) f_{pk}^{K+1}(\rho)] \right\} e^{iK\phi}. \tag{1}
\end{aligned}$$

In Eq. (1)  $\psi^{\Sigma}$ ,  $\psi^{\Pi_1}$ , and  $\psi^{\Pi_2}$  represent electronic basis functions related to the eigenfunctions of the electronic Hamiltonian  $\psi^{1A'}$ ,  $\psi^{2A'}$ , and  $\psi^{A''}$  computed in the framework of the Born–Oppenheimer approximation by

$$\begin{aligned}
\psi^{\Sigma} &= \psi^{1A'} \cos \gamma - \psi^{2A'} \sin \gamma \\
\psi^{\Pi_1} &= \frac{1}{\sqrt{2}} (\psi^{\Pi^+} + \psi^{\Pi^-}) = \frac{1}{\sqrt{2}} (\psi^{1A'} \sin \gamma + \psi^{2A'} \cos \gamma + \psi^{A''}) \\
\psi^{\Pi_2} &= \frac{1}{\sqrt{2}} (\psi^{\Pi^+} - \psi^{\Pi^-}) = \frac{1}{\sqrt{2}} (\psi^{1A'} \sin \gamma + \psi^{2A'} \cos \gamma - \psi^{A''}), \tag{2}
\end{aligned}$$

where  $\gamma$  is the angle by means of which the adiabatic electron functions  $\psi^{1A'}$  and  $\psi^{2A'}$  are transformed into their diabatic counterparts  $\psi^{\Sigma}$  and  $\psi^{\Pi^+}$  ( $\psi^{A''} \equiv \psi^{\Pi^-}$ );  $\psi^{\Pi_1}$  and  $\psi^{\Pi_2}$  represent “linear” electronic basis functions suitable for a treatment of the usual Renner–Teller effect within a  $\Pi$  electronic state. The electronic functions are assumed to depend on the C–C stretching coordinate  $s$ , the bending coordinate  $\rho$  ( $\rho \equiv \pi$ -bond angle), and the angle  $\phi$  conjugate to the projection of the total angular momentum on the  $z$  axis.  $\xi$  are the C–C stretching functions assumed to have different forms in the  $\Sigma$  and  $\Pi$  electronic states but to be identical for both components of the  $\Pi$  state,  $\Pi^+$  and  $\Pi^-$ . The function  $f$  represents the  $\rho$ -dependent part of the bending wavefunction expanded into a basis consisting of the eigenfunctions  $\chi_i$  of a suitable two-dimensional harmonic oscillator; the expansion coefficients are denoted by  $c_{pki}$  and are determined variationally.  $K$  is the quantum number corresponding to the  $z$  component of the total angular momentum (excluding spin). Writing the rovibronic wavefunction in the form of Eq. (1) we assume that the remaining degrees of freedom (C–H stretching and the rotations around the  $x$  and  $y$  axes) can be separated out (3).

The average value of a quantity  $A$  (in the present work the isotopic hfcc or the components of the dipole–dipole hf tensor) in the rovibronic state  $p$  is given by

$$A^p = \int \Psi^{*p} A \Psi^p d\tau, \tag{3}$$

where the integration is performed over all degrees of freedom. The integration over the electronic coordinates leads to the electronic matrix elements

$$\begin{aligned}
A^{\Sigma\Sigma} &= \int \psi^{\Sigma*} A \psi^{\Sigma} d\tau_e \equiv A^{\Sigma} \\
A^{\Pi_1\Pi_1} &= \frac{1}{2} \left( \int \psi^{\Pi_1*} A \psi^{\Pi_1} d\tau_e + \int \psi^{\Pi_2*} A \psi^{\Pi_2} d\tau_e \right) \equiv A^{\Pi_1\Pi_2} \equiv A^{\Pi} \\
A^{\Sigma\Pi_1} &= \frac{1}{\sqrt{2}} \int \psi^{\Sigma*} A \psi^{\Pi_1} d\tau_e \equiv A^{\Sigma\Pi_2} \equiv A^{\Sigma\Pi} \\
A^{\Pi_1\Pi_2} &= \frac{1}{2} \left( \int \psi^{\Pi_1*} A \psi^{\Pi_1} d\tau_e - \int \psi^{\Pi_2*} A \psi^{\Pi_2} d\tau_e \right) \equiv A^{\Pi_{12}} \quad (4)
\end{aligned}$$

expressed in Eq. (4) in terms of the diabatic electronic wavefunctions. The matrix elements  $A^{\alpha\beta}$  ( $\alpha = \Sigma, \Pi^+,$  or  $\Pi^-$ ) are the functions of both the vibrational coordinates considered,  $s$  and  $\rho$ . In the previous paper (6) it was shown that in a good approximation they can be represented as products of two functions, each one depending on only one of the coordinates

$$A^{\alpha\beta}(s, \rho) = U^{\alpha\beta}(s) V^{\alpha\beta}(\rho). \quad (5)$$

Thus the expression (3) can be written

$$\begin{aligned}
A^p &= \sum_k \sum_l \int \xi_k^{\Sigma} U^{\Sigma\Sigma}(s) \xi_l^{\Sigma} ds \int f_{pk}^K V^{\Sigma\Sigma}(\rho) f_{pl}^K \rho d\rho \\
&+ \sum_k \sum_l \int \xi_k^{\Pi} U^{\Pi\Pi}(s) \xi_l^{\Pi} ds \int f_{pk}^{K-1} V^{\Pi\Pi}(\rho) f_{pl}^{K-1} \rho d\rho \\
&+ \sum_k \sum_l \int \xi_k^{\Pi} U^{\Pi\Pi}(s) \xi_l^{\Pi} ds \int f_{pk}^{K+1} V^{\Pi\Pi}(\rho) f_{pl}^{K+1} \rho d\rho \\
&+ 2 \sum_k \sum_l \int \xi_k^{\Sigma} U^{\Sigma\Pi}(s) \xi_l^{\Pi} ds \int f_{pk}^K(\rho) V^{\Sigma\Pi}(\rho) f_{pl}^{K-1} \rho d\rho \\
&+ 2 \sum_k \sum_l \int \xi_k^{\Sigma} U^{\Sigma\Pi}(s) \xi_l^{\Pi} ds \int f_{pk}^K(\rho) V^{\Sigma\Pi}(\rho) f_{pl}^{\Sigma\Pi} f_{pl}^{K+1} \rho d\rho \\
&+ 2 \sum_k \sum_l \int \xi_k^{\Pi} U^{\Pi\Pi}(s) \xi_l^{\Pi} ds \int f_{pk}^{K-1}(\rho) V^{\Pi\Pi}(\rho) f_{pl}^{K+1} \rho d\rho. \quad (6)
\end{aligned}$$

In the present treatment the functions  $U^{\alpha\beta}(s)$  are represented by polynomial series in  $s$ , and  $V^{\alpha\beta}(\rho)$  by polynomials in  $\rho$ ,  $V^{\Sigma\Pi}(\rho)$  containing odd and all other  $V^{\alpha\beta}(\rho)$  quantities containing even terms.

In order to prevent any possible confusion when the results of the present study are compared with the experimental findings let us make a brief summary of various ways in which the hfcc's are usually defined in the literature. The part of the Hamiltonian describing the hyperfine interaction of an unpaired electron with the angular momentum  $L$  and spin  $S$ , and the nucleus  $N$  with spin  $T_N$  is given (19) by

$$H_{\text{hf}}^{\text{N}} = g_{\text{N}}g_{\text{e}}\beta_{\text{N}}\beta_{\text{e}} \left\{ \frac{\mathbf{L} \cdot \mathbf{I}_{\text{N}}}{r_{\text{N}}^3} + \frac{3(\mathbf{S} \cdot \mathbf{r}_{\text{N}})(\mathbf{r}_{\text{N}} \cdot \mathbf{I}_{\text{N}}) - r_{\text{N}}^2 \mathbf{S} \cdot \mathbf{I}_{\text{N}}}{r_{\text{N}}^5} + \frac{8\pi}{3} \delta(r_{\text{N}}) \mathbf{S} \cdot \mathbf{I}_{\text{N}} \right\}, \quad (7)$$

where  $g_{\text{N}}$  and  $g_{\text{e}}$  are the nuclear and electronic  $g$  factor, respectively,  $\beta_{\text{N}}$  is the nuclear and  $\beta_{\text{e}}$  the Bohr magneton.  $\mathbf{r}_{\text{N}}$  is the radius vector of the unpaired electron with respect to the nucleus N. The first term on the right-hand side of Eq. (7) represents the interaction between the electronic orbital momentum and nuclear spin and the last two terms represent the dipole-dipole and the Fermi contact interaction between electronic and nuclear spin (19). If the hf interaction is taken into account by the first-order perturbation theory the effects are commonly interpreted in terms of a phenomenological Hamiltonian which usually contains only momentum operators together with the numerical parameters serving as "coupling constants" (20). For a linear molecule (7) can be reduced to (21)

$$H_{\text{hf}}^{\text{N}} = a^{\text{N}}L_zS_z + b^{\text{N}}\mathbf{I}_{\text{N}} \cdot \mathbf{S} + c^{\text{N}}I_zS_z. \quad (8)$$

In the present paper we do not consider the first (usually small) term on the right-hand side of Eq. (8). The coefficients  $b$  and  $c$  are given by (19, 21)

$$b^{\text{N}} = \frac{8}{3} \pi g_{\text{N}}g_{\text{e}}\beta_{\text{N}}\beta_{\text{e}} \frac{1}{S} \left\langle \Psi \left| \left( \delta r_{\text{N}} - \frac{3 \cos^2 \alpha_{\text{N}} - 1}{2r_{\text{N}}^3} \right) S_z \right| \Psi \right\rangle \quad (9a)$$

$$c^{\text{N}} = 3g_{\text{N}}g_{\text{e}}\beta_{\text{N}}\beta_{\text{e}} \frac{1}{S} \left\langle \Psi \left| \left( \frac{3 \cos^2 \alpha_{\text{N}} - 1}{2r_{\text{N}}^3} \right) S_z \right| \Psi \right\rangle, \quad (9b)$$

where  $\alpha_{\text{N}}$  is the angle between  $\mathbf{r}_{\text{N}}$  and the molecular axis and  $\Psi$  is, generally, the total molecular wavefunction. The operator  $S_z$  points out that the coefficients  $b$  and  $c$  depend on the spin density, and the factor  $1/S$  arises from the normalization of the spin density (20). Thus  $b$  and  $c$  are related to  $A_{\text{iso}}$  and  $A_{zz}$  calculated in the present work (Eqs. (1) and (2) of Ref. (6)) by

$$b^{\text{N}} = A_{\text{iso}}^{\text{N}} - \frac{A_{zz}^{\text{N}}}{2} \quad (10a)$$

$$c^{\text{N}} = \frac{3A_{zz}^{\text{N}}}{2}. \quad (10b)$$

Another form of the  $H_{\text{hf}}$  operator for linear molecules, commonly used in the ESR literature, is (19)

$$H_{\text{hf}} = \bar{\mathbf{T}} \mathbf{T} \underline{\mathcal{S}}, \quad (11)$$

where  $\bar{\mathbf{T}}$  and  $\underline{\mathcal{S}}$  are the vector array of Cartesian nuclear spin components and the vector column of the electronic spin components, respectively (both of them acting on a model spin space), and  $\mathbf{T}$  is the tensor involving the hyperfine coupling coefficients. For linear molecules (where the  $z$  axis is assumed to coincide with the nuclear axis)  $\mathbf{T}$  is a diagonal tensor; furthermore, in  $\Sigma$  electronic states the equality  $T_{xx} = T_{yy} \equiv T_{\perp}$  holds and thus  $\mathbf{T}$  becomes

$$\mathbf{T} = \begin{pmatrix} T_{\perp} & 0 & 0 \\ 0 & T_{\perp} & 0 \\ 0 & 0 & T_{\parallel} \end{pmatrix} \quad (12)$$

with  $T_{\perp}$  denoting the  $zz$  component. Thus in this case (11) can be written in the form

$$H_{\text{hf}} = T_{\parallel} S_z I_z + T_{\perp} (I_x S_x + I_y S_y). \quad (13)$$

Comparison of (13) with (8) yields

$$T_{\parallel}^{\text{N}} = b + c \quad (14a)$$

$$T_{\perp}^{\text{N}} = b. \quad (14b)$$

The tensor (12) can be decomposed into its isotropic<sup>3</sup> and anisotropic parts,

$$\mathbf{T} = A_{\text{iso}} \mathbf{I} + \mathbf{A}_{\text{dip}}, \quad (15)$$

where  $\mathbf{I}$  is the unit tensor and  $\mathbf{A}_{\text{dip}}$  is a traceless tensor

$$\mathbf{A}_{\text{dip}} = \begin{pmatrix} -A_{\text{dip}} & 0 & 0 \\ 0 & -A_{\text{dip}} & 0 \\ 0 & 0 & 2A_{\text{dip}} \end{pmatrix} \quad (16)$$

the elements of which are related to the quantities defined above by

$$A_{\text{dip}}^{\text{N}} = \frac{T_{\parallel}^{\text{N}} - T_{\perp}^{\text{N}}}{3} = \frac{c}{3} = \frac{A_{zz}}{2}. \quad (17)$$

For bent molecular geometries  $\mathbf{A}_{\text{dip}}$  has no longer diagonal form and  $T_{xx} \neq T_{yy}$ . In those cases various choices of the Cartesian coordinate axes are possible having as a consequence different forms of the  $\mathbf{A}_{\text{dip}}$  elements. The information which can be obtained from the gas phase measurements is limited to the (diagonal) components of the  $A_{\text{dip}}$  tensor related to its principle axes, connecting the rotational states of an assumed symmetric top with  $\Delta K = 0, \pm 2$ . In our previous paper (6) we have presented the results of computation of the electronically averaged values for  $A_{\text{iso}}$  and all components of  $\mathbf{A}_{\text{dip}}$  with respect to the Cartesian system whose  $z$  axis is always along the C-C bond. Thus our coordinate system coincides only at the linear geometry with the principal axes of  $\mathbf{A}_{\text{dip}}$ .

## RESULTS AND DISCUSSION

In this paper we present the results of calculations of the rovibronically averaged values for the isotropic hfcc,  $A_{\text{iso}}$ , and for the quantity  $A_{\text{dip}}$  related by Eq. (17) to the  $zz$  component of the dipole-dipole tensor, being derived from the observed spectra in the experimental studies cited. In Tables I-III are the results computed for the two lowest-lying vibronic states in  $\text{C}_2\text{H}$ , (000)  $K = 0$  and (010)  $K = 1$  compared with the corresponding experimental findings.<sup>4</sup> Generally, a good agreement between two sets

<sup>3</sup>  $A_{\text{iso}}$  is in the literature often denoted by  $b_{\text{F}}$  (22).

<sup>4</sup> The ab initio values are given with five decimal units in order to show the predicted isotope effects.

TABLE I

Comparison of Mean Values for the Isotropic hfcc in the Lowest  $K = 0$  and  $K = 1$  Vibronic Levels of Various Isotopomers of Ethynyl Calculated in the Present Study with the Corresponding Experimentally Derived Data

		$\langle A_{iso} \rangle / \text{MHz}$					
		$C_1$		$C_2$		H	
$v_1 v_2 v_3$		th	exp	th	exp	th	exp
$^{12}\text{C}^{12}\text{CH}$	000					39.260	43.30 <sup>b*</sup> 44.51 <sup>c*</sup> 44.91 <sup>d*</sup> 44.511 <sup>e</sup>
	010					31.838	35.37 <sup>f</sup>
$^{12}\text{C}^{13}\text{CH}$	000			153.01	177.9 <sup>g</sup>	39.271	55.5 <sup>h</sup>
	010			118.14		31.879	
$^{13}\text{C}^{12}\text{CH}$	000	881.47	939.0 <sup>i</sup>			39.224	49.4 <sup>j</sup>
	010	790.50				31.800	
$^{13}\text{C}^{13}\text{CH}$	000	881.53	902 <sup>k</sup>	152.78	156 <sup>l</sup>	39.231	44 <sup>m</sup>
	010	790.87		117.88		31.835	
$^{12}\text{C}^{12}\text{CD}$	000					6.2029	7.159 <sup>n</sup> 6.88 <sup>o*</sup>
	010					5.2085	
$^{12}\text{C}^{13}\text{CD}$	000			159.02		6.2075	
	010			127.33		5.2193	
$^{13}\text{C}^{12}\text{CD}$	000	895.47				6.1960	
	010	814.88				5.2009	
$^{13}\text{C}^{13}\text{CD}$	000	895.91		158.80		6.2011	
	010	815.81		127.10		5.2123	

Note. The values with an asterisk are recalculated by means of Eq. (10a) from the originally published experimental results for *b*. Theoretical results are given with five significant figures to show the expected isotope shift.

<sup>a</sup> Reference (8).

<sup>b</sup> Reference (9).

<sup>c</sup> Reference (10).

<sup>d</sup> Reference (13).

<sup>e</sup> Reference (14).

<sup>f</sup> Reference (15).

<sup>g</sup> Reference (12).

<sup>h</sup> Reference (17).

<sup>i</sup> Reference (18).

of results can be seen;<sup>5</sup> particularly, the vibronic averaging in most instances considerably reduces the discrepancies between the computed hfcc's and their experimental counterparts (see also Table I of Ref. (6)). Moreover, the remaining discrepancies

<sup>5</sup> It should be noted that the number of significant figures for experimentally derived hfcc values is generally smaller than that given in Tables I and II; in some instances the ab initio results are within the estimated error limits quoted in experimental studies cited. Note that the results published in Ref. (18) for  $^{12}\text{C}^{13}\text{CH}$  and  $^{13}\text{C}^{12}\text{CH}$  deviate much more than expected from those found in other experimental works for  $^{12}\text{C}^{12}\text{CH}$  and  $^{13}\text{C}^{13}\text{CH}$ .

TABLE II

Comparison of the Theoretical Vibronically Averaged Values for  $1/2A_{zz}$  with the Corresponding Experimental Findings Given Generally in Terms of the Parameter  $c$  (see Eq. (10b))

		$1/2\langle A_{zz} \rangle / \text{MHz}$					
		$C_1$		$C_2$		H	
$\nu_1\nu_2\nu_3$		th	exp	th	exp	th	exp
$^{12}\text{C}^{12}\text{CH}$	000					4.4264	4.077 <sup>a</sup> 4.110 <sup>f</sup> 3.977 <sup>a</sup> 4.0847 <sup>b</sup>
	010					4.6437	4.413 <sup>b</sup>
$^{12}\text{C}^{13}\text{CH}$	000			19.351	16.3 <sup>i</sup>	4.4278	4.0 <sup>i</sup>
	010			19.288		4.6454	
$^{13}\text{C}^{12}\text{CH}$	000	42.600	44.0 <sup>i</sup>			4.4288	4.0 <sup>i</sup>
	010	41.044				4.6463	
$^{13}\text{C}^{13}\text{CH}$	000	42.591	39 <sup>a</sup>	19.346	17 <sup>a</sup>	4.4305	4 <sup>a</sup>
	010	41.037		19.282		4.6482	
$^{12}\text{C}^{12}\text{CD}$	000					0.67760	0.712 <sup>a</sup> 0.530 <sup>f</sup>
	010					0.71108	
$^{12}\text{C}^{13}\text{CD}$	000			19.259		0.67773	
	010			19.129		0.71125	
$^{13}\text{C}^{12}\text{CD}$	000	42.717				0.67808	
	010	41.268				0.71163	
$^{13}\text{C}^{13}\text{CD}$	000	42.715		19.252		0.67818	
	010	41.269		19.121		0.71177	

Note. For notation see Table I.

between the ab initio results for  $A_{\text{iso}}$  and their experimentally derived counterparts, after the integration over the vibronic wavefunctions has been performed, are in accord with the experience with similar systems (24, 25): It has been found, namely, that the computed values for  $A_{\text{iso}}$  normally underestimate those obtained experimentally, which should be looked upon as a consequence of difficulties in describing the correlation effects. The differences in the relative errors for various nuclei can be explained in terms of the structure of the electronic wavefunction for the  $1^2A'$  ( $\Sigma$ ) state which dominates the electronic part of the total wavefunction for the lowest-lying vibronic levels. In this state the singly occupied orbital represents a binding  $\sigma$  orbital between two carbon atoms, localized predominantly at the terminal nucleus ( $C_1$ ). This results in a large value for  $A_{\text{iso}}$  of  $C_1$  and a relatively good description already at the SCF level of sophistication. The absolute values for  $A_{\text{iso}}$  become smaller and the relative errors (due to increasing importance of a proper description of the electronic correlation) larger by going toward the  $C_2$  and partially the H nucleus.

The above statements demonstrate clearly that the vibronic coupling produces significant effects even in the lowest vibrational states. Let us illustrate this in two examples.

TABLE III

Mean Values of the  $A_{iso}$  for All  $K = 0$  and  $K = 1$  Vibronic Levels of  $^{13}C^{13}CH$  with  $\nu_1$  (C-H Stretch) = 0 up to  $6000\text{ cm}^{-1}$

K = 0				K = 1							
$\nu_2$	$\nu_3$	$\tilde{\nu}/\text{cm}^{-1}$	$\langle A_{iso} \rangle / \text{MHz}$			$\nu_2$	$\nu_3$	$\tilde{\nu}/\text{cm}^{-1}$	$\langle A_{iso} \rangle / \text{MHz}$		
			$^{13}C_1$	$^{13}C_2$	H				$^{13}C_1$	$^{13}C_2$	H
0	0	0	882	153	39.2	1	0	332	791	118	31.8
2	0	714	761	111	28.9	3	0	1105	716	98	24.8
4	0	1513	693	95	22.3	5	0	1934	665	89	19.5
0	1	1814	808	143	34.1	1	1	2077	704	117	24.6
6	0	2362	648	90	17.4	7	0	2793	628	93	15.6
2	1	2488	728	129	26.3	3	1	2849	636	105	17.1
8	0	3218	628	104	15.4	0 <sup>0</sup>	0	3550	263	71	-17.4
4	1	3288	635	104	15.8	5	1	3640	602	115	13.1
0	2	3563	701	143	24.7	9	0	3734	601	94	11.6
1 <sup>-</sup>	0	3838	-18.3	20.9	-42.0	1	2	3954	430	98	0.3
6	1	4058	594	117	12.0	2 <sup>-</sup>	0	4379	120	50	-29.6
10	0	4190	590	96	9.9	7	1	4485	570	121	9.7
2	2	4273	697	153	24.1	11	0	4648	549	92	5.8
3 <sup>-</sup>	0	4829	-18.2	20.9	-41.5	3	2	4738	536	125	9.0
8	1	4900	586	150	11.7	0 <sup>0</sup>	1	5150	178	71	-25.8
1 <sup>+</sup>	0	4945	518	124	4.5	4 <sup>-</sup>	0	5328	439	124	-1.2
12	0	5122	543	92	3.5	9	1	5370	233	68	-20.4
4	2	5265	604	154	14.5	5	2	5465	431	116	-2.5
1 <sup>-</sup>	1	5454	-17.8	22.0	-42.0	13	0	5600	528	95	1.2
0	3	5506	382	135	-3.7	1	3	5713	467	131	2.4
10	1	5785	523	144	4.9	2 <sup>-</sup>	1	5994	67	48	-34.6
5 <sup>-</sup>	0	5875	-17.9	20.9	-41.1						
6	2	5943	559	147	8.5						

Note.  $C_1$  is the terminal and  $C_2$  the middle C atom. The vibronic term values are also indicated. Superscripts 0, -, and + of  $\nu_2$  (bending) quantum numbers denote the "unique" level and the levels belonging (predominantly) to the  $\Pi^-$  and  $\Pi^+$  potential surfaces. No superscript: vibronic levels of predominantly  $\Sigma$  electronic character.

Cochran *et al.* (7) stated in their paper that the ratio of the splittings of the lines in the ESR spectra of  $C_2H$  and  $C_2D$  attributed to the hyperfine structure of the hydrogen isotopes is 6.33, differing significantly from the theoretical value of 6.51. The authors concluded that "the mechanism which produces the observed hyperfine splitting in ethylene is rather complicated, and at present we cannot explain this isotope effect." The result of the present study (6.32, Table I) is in quantitative agreement with that



TABLE IV  
Vibronically Averaged Values for  $A_{\text{iso}}$  in  $^{13}\text{C}^{13}\text{CD}$  Calculated in the Present Study

K = 0			K = 1								
$v_2$	$v_3$	$\tilde{\nu}/\text{cm}^{-1}$	$\langle A_{\text{iso}} \rangle / \text{MHz}$			$v_2$	$v_3$	$\tilde{\nu}/\text{cm}^{-1}$	$\langle A_{\text{iso}} \rangle / \text{MHz}$		
			$^{13}\text{C}_1$	$^{13}\text{C}_2$	D				$^{13}\text{C}_1$	$^{13}\text{C}_2$	D
0	0	0	896	159	6.20	1	0	252	816	127	5.21
2	0	543	786	118	4.78	3	0	838	744	105	4.22
4	0	1148	721	100	3.88	5	0	1464	694	93	3.48
0	1	1702	825	148	5.47	1	1	1900	739	124	4.28
6	0	1790	678	92	3.20	7	0	2123	658	88	2.88
2	1	2206	750	131	4.40	3	1	2474	686	116	3.49
8	0	2461	645	88	2.63	9	0	2806	629	87	2.34
4	1	2788	685	120	3.41	5	1	3088	636	112	2.69
10	0	3154	618	87	2.11	0 <sup>0</sup>	0	3430	466	106	0.27
0	2	3334	702	139	3.77	11	0	3507	605	87	1.84
6	1	3425	659	123	2.97	1	2	3688	356	77	-1.17
1 <sup>-</sup>	0	3741	-18.3	21.0	-6.48	7	1	3770	522	109	1.06
12	0	3861	646	118	2.71	2 <sup>-</sup>	0	4082	361	90	-1.06
2	2	3862	646	118	2.68	13	0	4221	582	88	1.32
8	1	4084	613	121	2.19	3	2	4267	277	75	-2.19
4	2	4415	641	152	2.87	9	1	4433	591	123	1.83
3 <sup>-</sup>	0	4498	-18.2	20.9	-6.40	5	2	4745	552	136	1.67
14	0	4579	573	90	1.09	4 <sup>-</sup>	0	4935	121	48	-4.52
10	1	4747	503	113	0.54	15	0	4941	544	90	0.60
1 <sup>*</sup>	0	4825	539	141	1.15	0 <sup>0</sup>	1	4975	272	85	-2.55
6	2	5061	629	160	2.71	11	1	5122	551	123	1.10
0	3	5220	383	119	-0.46	1	3	5250	336	106	-1.55
1 <sup>-</sup>	1	5282	-17.8	22.0	-6.48	7	2	5416	556	153	1.63
5 <sup>-</sup>	0	5293	-18.1	20.9	-6.35	2 <sup>-</sup>	1	5654	209	78	-3.33
16	0	5300	553	93	0.55	17	0	5663	534	94	0.17
12	1	5483	569	134	1.25	6 <sup>-</sup>	0	5693	42	44	-5.45
2	3	5538	646	168	3.06	2 <sup>*</sup>	0	5761	247	85	-2.88
8	2	5749	594	170	2.12	13	1	5854	518	140	0.60
						3	3	5987	434	144	0.21

Note. For notation see Table III.

finding and moreover offers its simple explanation: In  $\text{C}_2\text{D}$  the ground vibronic level lies somewhat lower than in  $\text{C}_2\text{H}$  and consequently possesses a slightly smaller "percentage" of the  $\Pi$  electronic character than the corresponding  $\text{C}_2\text{H}$  level (see Tables

TABLE V  
Vibronically Averaged Values for  $1/2A_{zz}$  in  $^{13}\text{C}^{13}\text{CH}$

		K = 0					K = 1		
$v_2$	$v_3$	$1/2\langle A_{zz} \rangle / \text{MHz}$			$v_2$	$v_3$	$1/2\langle A_{zz} \rangle / \text{MHz}$		
		$^{13}\text{C}_1$	$^{13}\text{C}_2$	$^1\text{H}$			$^{13}\text{C}_1$	$^{13}\text{C}_2$	$^1\text{H}$
0	0	42.6	19.3	4.43	1	0	41.0	19.3	4.65
2	0	41.3	20.1	4.48	3	0	41.1	20.6	4.49
4	0	41.4	21.3	4.32	5	0	41.4	21.8	4.26
0	1	39.5	17.6	4.91	1	1	36.6	16.6	5.29
6	0	41.6	22.3	4.18	7	0	40.0	21.2	4.43
2	1	39.5	19.1	4.64	3	1	38.4	19.5	4.72
8	0	39.3	20.7	4.51	0 <sup>0</sup>	0	7.5	-6.1	9.78
4	1	41.3	22.4	4.16	5	1	35.8	17.6	5.04
0	2	34.2	14.2	5.69	9	0	42.2	23.8	4.03
1 <sup>-</sup>	0	-13.8	-23.0	11.41	1	2	19.1	3.2	7.47
6	1	37.9	20.0	4.63	2 <sup>-</sup>	0	-3.0	-13.9	9.19
10	0	42.6	24.4	3.97	7	1	37.0	19.6	4.73
2	2	38.6	18.9	4.64	11	0	40.7	23.2	4.24
3 <sup>-</sup>	0	-14.1	-22.6	9.08	3	2	30.9	13.6	5.36
8	1	33.2	15.3	5.42	0 <sup>0</sup>	1	-0.6	-13.0	11.09
1 <sup>*</sup>	0	32.0	15.0	5.69	4 <sup>-</sup>	0	23.7	8.4	5.66
12	0	42.9	25.5	4.01	9	1	10.1	-2.0	6.48
4	2	32.0	13.5	5.83	5	2	23.6	8.0	6.12
1 <sup>-</sup>	1	-13.8	-23.0	11.41	13	0	42.7	25.6	4.05
0	3	13.4	-2.2	9.00	1	3	24.0	7.9	6.41
10	1	35.1	18.6	4.95	2 <sup>-</sup>	1	-7.4	-17.5	9.69
5 <sup>-</sup>	0	-14.3	-22.3	7.12					
6	2	35.3	17.7	5.09					

Note. For notation see Table III.

I and V of Ref. (4)). Since the electronic matrix element of the isotropic hfcc for the  $\Sigma$  electronic state has, according to our calculations, the value of  $\approx 45$  MHz at the linear molecular geometry, and since furthermore that for the  $\Pi$  state  $\approx -43$  MHz, it follows that the vibronically averaged value for the isotropic hfcc in  $\text{C}_2\text{D}$  should slightly increase relative to that in  $\text{C}_2\text{H}$ .

Woodward *et al.* (17) found that in the (010)  $K = 1$  vibronic state of  $\text{C}_2\text{H}$  "the dipole-dipole parameter  $c$  is 7% larger than in the ground state, but the Fermi contact parameter,  $b_F$  is 21% smaller, possibly reflecting the effect of vibronic mixing on the unpaired electron." The present study predicts almost exactly the same decrease of the  $b_F$  value by going from the (000) to (010) vibronic level (Table I) and a very

TABLE VI  
Vibronical Mean Values for  $1/2A_{zz}$  in  $^{13}\text{C}^{13}\text{CD}$

		K = 0					K = 1		
$v_2$	$v_3$	$1/2\langle A_{zz} \rangle / \text{MHz}$			$v_2$	$v_3$	$1/2\langle A_{zz} \rangle / \text{MHz}$		
		$^{13}\text{C}_1$	$^{13}\text{C}_2$	D			$^{13}\text{C}_1$	$^{13}\text{C}_2$	D
0	0	42.7	19.3	0.678	1	0	41.3	19.1	0.712
2	0	41.3	19.7	0.696	3	0	41.0	20.0	0.695
4	0	41.2	20.6	0.679	5	0	41.2	21.1	0.669
0	1	39.7	17.6	0.752	1	1	37.4	16.8	0.801
6	0	41.5	21.7	0.653	7	0	41.7	22.2	0.642
2	1	39.2	18.4	0.736	3	1	37.7	18.0	0.764
8	0	42.0	22.8	0.628	9	0	42.2	23.3	0.617
4	1	38.7	19.1	0.722	5	1	37.5	18.7	0.744
10	0	42.6	23.9	0.605	0 <sup>0</sup>	0	18.7	2.2	1.260
0	2	33.9	13.9	0.891	11	0	42.9	24.4	0.596
6	1	39.1	20.0	0.694	1	2	16.5	1.6	1.274
1 <sup>-</sup>	0	-13.8	-23.1	1.841	7	1	28.6	11.5	0.931
12	0	39.6	20.6	0.697	2 <sup>-</sup>	0	13.9	-0.7	1.182
2	2	40.0	20.9	0.684	13	0	43.6	25.5	0.579
8	1	39.4	21.2	0.670	3	2	9.2	-4.3	1.306
4	2	34.6	15.8	0.814	9	1	38.3	20.4	0.677
3 <sup>-</sup>	0	-14.0	-22.8	1.538	5	2	30.5	13.2	0.834
14	0	44.1	26.2	0.569	4 <sup>-</sup>	0	-3.4	-14.2	1.307
10	1	31.6	14.8	0.892	15	0	42.3	24.9	0.599
1 <sup>+</sup>	0	27.2	9.6	1.020	0 <sup>0</sup>	1	5.9	-7.7	1.527
6	2	32.7	14.1	0.868	11	1	38.3	21.1	0.680
0	0	16.5	9.7	1.308	1	3	13.3	-1.2	1.348
1 <sup>-</sup>	1	-13.8	-23.1	1.841	7	2	30.8	13.4	0.853
5 <sup>-</sup>	0	-14.2	-22.5	1.280	2 <sup>-</sup>	1	3.2	-9.1	1.360
16	0	44.9	27.5	0.557	17	0	44.4	27.3	0.571
12	1	40.6	23.2	0.626	6 <sup>-</sup>	0	-10.3	-20.0	1.385
2	3	31.3	12.4	0.915	2 <sup>+</sup>	0	10.9	-1.9	1.138
8	2	36.5	18.7	0.722	13	1	35.1	18.5	0.717
					3	3	17.3	1.2	1.207

Note. For notation see Table III.

similar ( $\approx 5\%$ ) increase of  $c$  (Table II), both of these effects being easily explainable in terms of a significantly stronger admixture of the II electronic state in the (010) vibronic state (Table I of Ref. (4)) and of the values for the isotropic hfcc and the  $A_{zz}$  component of the dipole-dipole tensor (Table I, Figs. 6 and 8 of Ref. (6)).

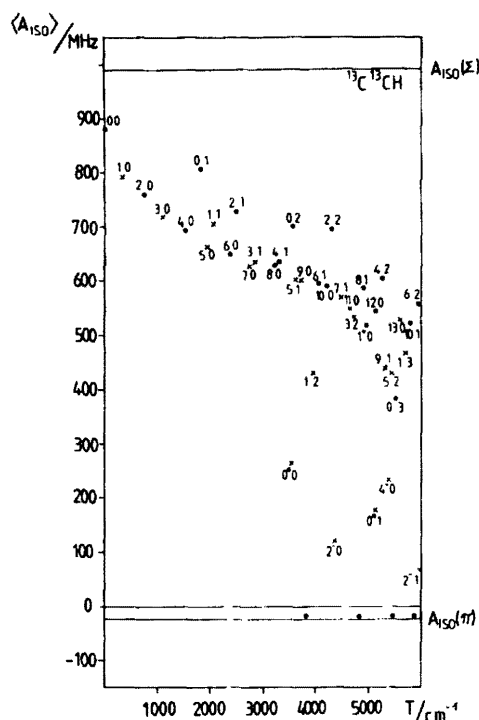


FIG. 1. Vibronically averaged values for  $A_{iso}$  for the terminal C atom in  $^{13}\text{C}^{13}\text{CH}$  calculated in the present work. (●)  $K = 0$ , (×)  $K = 1$  vibronic states. Notation:  $v_2v_1$ ;  $v_1$  is always equal zero. Superscripts 0, -, and + denote the unique vibronic level and the levels corresponding (predominantly) to the  $\Pi^-$  and  $\Pi^+$  electronic states, respectively. Horizontal lines denoted by  $A_{iso}(\Sigma/\Pi)$  correspond to the values for the electronic matrix element of the isotropic hfcc calculated for the pure  $\Sigma$  and  $\Pi$  states at the linear geometry and the C-C distance for 2.3 Bohr.

Tables III-VI give the vibronically averaged values of the isotropic hfcc and the quantity  $1/2A_{zz}$  for all  $K = 0$  and  $K = 1$  levels of  $^{13}\text{C}^{13}\text{CH}$  and  $^{13}\text{C}^{13}\text{CD}$  in the energy range up to  $6000 \text{ cm}^{-1}$  calculated in the present study.<sup>6</sup> We do not present the results for the other isotopomers because of relatively small differences arising by substitution of  $^{12}\text{C}$  by  $^{13}\text{C}$  (see Table I). Figures 1-3 graphically present the results for the isotropic hfcc for all three atoms in  $^{13}\text{C}^{13}\text{CH}$ . In spite of the fact that the present theoretical results very reliably reproduce and explain the experimental findings for the lowest-lying vibronic levels, their predictive power (at least in the quantitative sense) concerning the higher levels should not be overestimated. As discussed in detail in Refs. (3-5), the accuracy of the calculations for the vibronic levels lying in the region where the  $\Sigma$  and  $\Pi$  electronic states are strongly coupled with one another (particularly in the neighborhood of the minimum of the  $\Pi$  potential surface) is restricted by the

<sup>6</sup> The results for the levels with  $v_1 \neq 0$  are not presented because C-H stretching is assumed to be decoupled from other degrees of freedom (3).

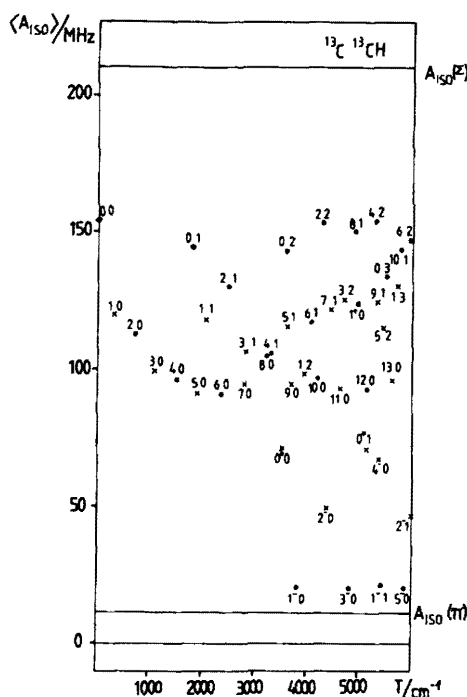


FIG. 2. Vibronically averaged values for  $A_{150}$  for the middle C atom in  $^{13}\text{C}^{13}\text{CH}$ . For notation see Fig. 1.

inability of the pure ab initio treatment to ensure a quantitatively reliable description of the local perturbations between the levels belonging in the zeroth-order approximation (no vibronic coupling) to different potential surfaces. This is caused primarily by a very probable underestimation of the electronic energy difference between the  $\Pi$  and  $\Sigma$  states by  $\cong 270 \text{ cm}^{-1}$  (3). Furthermore, as already mentioned the Cartesian components of the anisotropic part of the hff tensor are related to the coordinate system whose  $z$  axis lies always along the C-C bond, i.e., to the frame corresponding neither to the principal axes of inertia system (for bent molecular geometries) nor to the principal hff tensor axes system—this might contribute somewhat to the discrepancies between the theoretical and experimental (if they are related, as usually, to the principal  $\mathbf{A}_{\text{dip}}$  axis system) results, for higher vibronic levels.

In general, the variations of the mean values for the hfcc's from one vibronic level to another can be looked upon as superposition of three effects: (i) geometry (particularly C-C stretching and bending) dependence of the electronic matrix elements of the hfcc's; (ii) presence of the nondiagonal electronic matrix elements  $\langle \Sigma | A | \Pi^+ \rangle$ ; and (iii)  $\Sigma$ - $\Pi$  electronic admixture in the vibronic levels. We find that the main source for inaccuracies in the calculation of the vibrationally averaged mean values is the effect (iii). This is in accord with our experience in computing of the vibronic transition moments (3, 4) and the spin-orbit splittings of the vibronic levels (5).

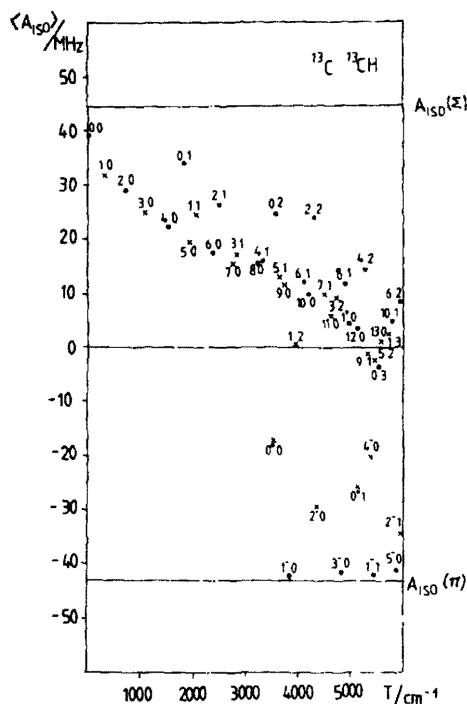


FIG. 3. Vibronical mean values of  $A_{150}$  for the hydrogen atom in  $^{13}\text{C}^{13}\text{CH}$ . For notation see Fig. 1.

#### CONCLUSION

In the present paper we show that a pure ab initio treatment is capable of reproducing reliably and explaining the experimental findings concerning the hyperfine effects in the long wavelength region of the  $\text{C}_2\text{H}$  spectrum, at least those formulated in terms of the values for the hfcc's. The importance of averaging over the vibronic wavefunction for achieving a quantitative agreement with the experimental data is also demonstrated. By the same token it is seen that it is not justified to evaluate the accuracy of ab initio calculated electronic mean values for the hyperfine parameters solely on the basis of the discrepancies between these quantities and the corresponding experimental data, in particular if a significant coupling of electronic states is present as in  $\text{C}_2\text{H}$ .

As a general conclusion concerning this series of papers devoted to the explanation and prediction of the features of the  $\text{C}_2\text{H}$  spectrum we want to stress a few important points.

The key step in the vibronic treatment undertaken is the transformation of the adiabatic electronic wavefunctions into their diabatic counterparts. Through this simple "rotation" of the basis several important goals are simultaneously achieved:

— The cumbersome nonadiabatic matrix elements of the  $\partial/\partial\rho$  and  $\partial^2/\partial\rho^2$  type are avoided or at least their influences minimized. This means a significant saving in computer time which would otherwise be required for their computation at various nuclear arrangements.

— The geometry dependence of the potentials as well as of a number of molecular properties (electronic transition moments, spin-orbit and hyperfine matrix elements, etc.) is greatly simplified. This offers the possibility of several approximations which substantially simplify the vibronic treatment.

— A number of effects can be elucidated easily in terms of the diabatic quantities.

Of course the attraction of the diabatic transformations is substantially determined by the ease with which the transformation matrix (in the present case the transformation angle for the two-state problem) can be obtained. Fortunately it is possible to find ways to construct it simply and reliably without any additional calculations over those serving to generate the electronic energies and wavefunctions and elementary molecular properties (e.g., electronic transition moments) (2).

We hope that in this series of papers we have shown that *ab initio* calculations by themselves are capable of reproducing reliably not only the global structure of the electronic spectra of small molecules, but are also able to predict a number of details caused by subtle interactions between various states. It is also seen, however, that the accuracy of the theoretical results for energy levels is generally lower than that normally achieved in high-resolution measurements. This is particularly apparent for effects which depend strongly on local perturbations being extremely sensitive to the relative position of energy levels; this means that very small errors in the calculated potential surface may cause an energy shift large enough so that local perturbations are not operative any more. In principle, the overall accuracy of the *ab initio* results could be improved by a more elaborate theoretical treatment; this would include a larger AO basis and a more complete CI, use of the entire three-dimensional potential surface as well as the explicit consideration of the rotation-vibration coupling, etc. Even if such a type of calculation were possible to date for a three-state problem as the present system treated, it would require probably an order of magnitude more computational expenditure. At the present time we do not feel that such effort would be justified by the expected higher numerical accuracy of results. Certainly one major advantage of the theoretical treatment is that it was able to explain the source of the various irregularities observed in the measured spectrum, to show the interactions between various states, and to point out the mechanisms operative for the appearance of the low-energy levels of the ethynyl radical.

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