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### Authors

Dupuis, M.

Wendoloski, J.J.

### Publication Date

1982-09-01

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September 1982

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THEORETICAL STUDY OF THE VINYL RADICAL:  
STRUCTURE AND VIBRATIONAL ANALYSIS

M. Dupuis<sup>+</sup> and J. J. Wendoloski<sup>++</sup>

National Resource for Computation in Chemistry  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, California 94720

<sup>+</sup>Present address: Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

<sup>++</sup>Present Address: E. I. duPont de Nemours & Company, Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898

\*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098 and by the National Science Foundation under Grant No. CHE-7721305.

THEORETICAL STUDY OF THE VINYL RADICAL:  
STRUCTURE AND VIBRATIONAL ANALYSIS

M. Dupuis and J. J. Wendoloski

National Resource for Computation in Chemistry  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, California 94720Abstract

Generalized Valence Bond (GVB) calculations, using Pople's 6-31G\*\* basis set, are presented for the structure and vibrational frequencies of the vinyl radical. It is found that the  $\alpha$ CH bond to the radical center has a length of 1.085Å, shorter than the other CH bonds (~ 1.092Å). The C=C bond length in the vinyl radical is 1.332Å, shorter than the same bond in ethylene (1.345Å). The angle between the CC and  $\alpha$ CH bonds is 134.2°, and the barrier to inversion of the radical center is 8.9 kcal/mol. In addition the dipole moment derivatives have been calculated. The data predict that the out of plane bending motion of the hydrogen atoms is responsible for a very intense band of the IR spectrum at  $\nu=918\text{ cm}^{-1}$ .

## I. Introduction

Previous theoretical studies of acyclic alkyl radicals<sup>1,2</sup> have shown that a consistent analysis of the structure and dynamics of radicals is obtained from the calculations and the infrared spectra generated in low temperature matrices.<sup>3</sup> A common feature of the structure of these radicals is that bonds  $\beta$  to the radical center and eclipsed by the half filled p-orbital of the radical center are longer than the corresponding bonds normally encountered in alkanes. Furthermore, the CH stretches associated with the radical center are in the region where ethylene type CH stretches are found. The bonds  $\alpha$  to the radical center are shorter than normal CH and CC bonds. In this paper we report a theoretical investigation of the structure of the vinyl radical, the simplest radical originating from an unsaturated hydrocarbon. In light of the ethylenic character of the radical center of the ethyl radical, we expect the vinyl radical to acquire an acetylenic character. However, while the change in hybridization from  $sp^3$  to  $sp^2$  of the carbon atom at the radical center of ethyl is facile, the  $sp^2$  to  $sp$  change in the vinyl radical is expected to require more energy since the extent of rehybridization is higher in this case.

The structure of the vinyl radical has been investigated by Electron Spin Resonance (ESR) techniques.<sup>4</sup> ESR data suggest that the radical center is non-linear, and that the unpaired electron resides in an orbital very close to a  $sp^2$  hybrid orbital. A lower limit of 2 kcal/mol was estimated for the barrier height to inversion of the radical center. Theoretical studies of the vinyl radical include the spin density calculation by Chipman,<sup>5</sup> and the hydrogen migration study by Harding.<sup>6</sup>

The structure of molecular species can be efficiently determined using the analytically calculated energy gradient to minimize the energy with respect to all geometrical degrees of freedom simultaneously.<sup>7</sup> Force constant matrices and dipole moment derivatives are obtained from numerical differences of the energy gradient<sup>7</sup> and dipole moments. This paper is organized as follows: the wavefunction calculations are described in Section II; the structure of the vinyl radical is discussed in Section III; the vibrational spectra of the vinyl radical and some deuterium substituted analogues are presented in Section IV, and the dipole moment derivatives data in Section V.

## II. Computational Method

Most of our previous<sup>1,2</sup> work on hydrocarbons and radicals was based on closed-shell spin restricted Hartree-Fock (HF) wavefunctions,<sup>8</sup> and on spin unrestricted (UHF) wavefunctions.<sup>9</sup> The independent particle HF model is reliable for molecules in their ground state and near their equilibrium structure. UHF wavefunctions are not pure eigenstates of  $S^2$ . The amount of contamination from higher spin states is shown in the calculated expectation value of  $S^2$ . In all the calculations previously reported  $S^2$  was found to be  $\sim 0.76$  compared to the exact value of 0.75, indicating that the UHF wavefunctions were nearly pure doublets. A comparison of the UHF structure of the ethyl radical with the spin restricted open-shell<sup>10</sup> structure confirmed the idea that the UHF formalism was adequate for all these previously studied radical species.

The inadequacy of the UHF formalism is most evident for open-shell species which contain multiple bonds. The expectation value of  $S^2$  can be in error by a very large amount ( $S^2 \sim 1$  or more compared to exact 0.75 for doublets). It is then clear that accurate calculations of the structure of the vinyl radical requires the spin restricted formalism.

Better quantitative accuracy than provided by the HF model is obtained by describing electron correlation effects. The Generalized Valence Bond<sup>10</sup> (GVB) model in the perfect pairing approximation is one way to introduce correlation effects. In this model each bond of the molecule is described by two electronic configurations each involving a bonding orbital and its antibonding counterpart. This model accounts for significant correlation effects and is reliable for many molecules near their equilibrium structure. The form of the GVB wavefunction for the vinyl radical is shown in Eq. 1.

$$\psi = a \left[ 1s_{C_1}^2 \times 1s_{C_2}^2 \times (\sigma_{C_1C_2}^2 + \sigma_{C_1C_2}^{*2}) \times (\sigma_{C_1H_1}^2 + \sigma_{C_1H_1}^{*2}) \times (\sigma_{C_1H_2}^2 + \sigma_{C_1H_2}^{*2}) \times (\sigma_{C_2H_3}^2 + \sigma_{C_2H_3}^{*2}) \times (\pi_{C_1C_2}^2 + \pi_{C_1C_2}^{*2}) \times \sigma_{\text{unpaired}}^1 \right] \quad (1)$$

A wavefunction of this form is known to give bond lengths and stretching frequencies in better agreement with experiment than HF computed values.

Double zeta (DZ) quality basis sets, such as the standard "split valence" 4-31G basis<sup>11</sup> are required for reliable structure predictions. A comparison of the 4-31G basis with larger basis sets including polarization functions showed that the 4-31G basis provides a qualitatively

correct description of the studied radical species. In addition the 4-31G basis is found computationally efficient for large molecular species. In the present study however we chose the larger 6-31G basis<sup>11</sup> augmented by one set of d polarization functions on each carbon atom ( $\alpha_C = 0.8$ ), and one set of p polarization functions on each hydrogen atom ( $\alpha_H = 1.0$ ). This basis set, standardly denoted 6-31G\*\* is expected to provide quantitative accuracy for the structure, frequencies and dipole moment derivatives of the vinyl radical.

### III. Ethylene, Acetylene, and Vinyl Radical

The HF(6-31G\*\*) and GVB(6-31G\*\*) optimized structures of ethylene, acetylene, and the vinyl radical are given in Table I, along with the experimental structures of ethylene and acetylene. A common feature of the computed HF(6-31G\*\*) structures is their shorter bond lengths compared to experiment. The GVB(6-31G\*\*) calculated bond lengths however are consistently longer than the experimental ones. The lengthened bonds are, of course, due to electron correlation effects accounted for in the GVB wavefunction. In general the GVB(6-31G\*\*) results are in better agreement with experiment than the HF(6-31G\*\*) results. This finding is expected to hold for the two structures of the vinyl radical shown in Table 1.

The lowest energy conformation of the vinyl radical has  $C_s$  symmetry and a non-linear radical center. The angle between the CC bond and the  $\alpha$ CH bond is  $134.2^\circ$ , which is  $12.6^\circ$  larger than the CCH angle in ethylene. The CC bond length is  $1.332\text{\AA}$ , shorter than the CC bond length in ethylene ( $1.345\text{\AA}$ ). The CC bond shortening compared to ethylene, computed in the



vinyl radical (0.013Å) is not as dramatic as that observed in the ethyl radical (0.030Å). In addition for ethyl a lengthening of the  $\beta$ CH bonds, and a shortening of the  $\alpha$ CH bonds was observed. For vinyl a similar situation occurs, as can be seen in Table I. The  $\alpha$ CH bond length (1.085Å) is shorter than the CH bond lengths in ethylene (1.092Å), while the  $\beta$ CH bond lengths (1.093Å and 1.095Å) are longer than the CH bond lengths in ethylene. The orientation of the unpaired electron orbital is more favorable for hyperconjugative interaction with the hydrogen  $H_2$  in the "trans" position to the radical half filled orbital than with the cis hydrogen  $H_1$ . Therefore, the trans  $C_1H_2$  bond length is longer than cis  $C_1H_1$ . In the ethyl radical the  $\alpha$ CH bond length were found to be nearly identical to CH bond lengths in ethylene. For the vinyl radical the  $\alpha$ CH bond length (1.085Å) is shorter than the CH bond length in ethylene (1.092Å), but longer than the CH bond length in acetylene (1.070Å). Thus, the geometrical parameters of the vinyl radical suggest that the radical center tends to acquire acetylenic character. However, because of the extent of rehybridization that takes place, the differences between ethylene and vinyl are not as dramatic as those between ethane and ethyl. Further indication of the rehybridization energy in vinyl is given by the barrier to inversion of the radical center for which the  $C_{2v}$  symmetry structure with a linear radical center is the transition state. The optimized  $C_{2v}$  structure is also given in Table 1. The unpaired electron resides in an in-plane orbital which interacts with the CH bonds of the  $CH_2$  group, resulting in lengthened CH bonds (1.096Å). The CC bond is further shortened to 1.322Å, a value still far from the CC

bond length in acetylene (1.210Å). The  $\alpha$ CH bond length is now much shorter (1.070Å)—close to the CH bond length in acetylene. The energy of the  $C_{2v}$  structure is 8.9 kcal/mole above the lowest  $C_s$  symmetry structure. The bending potential for inversion of the  $\alpha$ CH bond is shown in Fig. 1, as a function of the bending angle  $\gamma = \angle (C_1C_2H_3)$ . On the potential curve, point A represents the  $C_s$  symmetry structure, point B in the  $C_{2v}$  symmetry transition state. The two points are connected through the dashed line. Point C corresponds to a structure in which all the geometrical parameters have their point A value, except for the bending angle  $\gamma$ , which is  $0^\circ$ . Point C is only 0.18 kcal/mol above point B.

#### IV. Vibrational Spectra of Ethylene, Acetylene, and the Vinyl Radical

In Table 2 we present the observed frequencies, the harmonic contribution to the observed frequencies, and the calculated harmonic frequencies of ethylene, and acetylene, along with the calculated harmonic frequencies of the vinyl radical. The harmonic frequencies calculated for various deuterium substituted vinyl analogues are given in Table 3.

Until recently Pulay's force method for the calculation of the force constant matrix has been applied only to HF wavefunction. It was found for HF wavefunction that the calculated frequencies were 10% to 15% larger than the observed frequencies. In this work we have used GVB wavefunctions which account for some important electron correlation effects. We can see in Table 2 that the agreement between the calculated GVB(6-31G\*\*) frequencies and the experimental frequencies is better:

the average error between the calculated harmonic frequencies and the observed frequencies is less than 2.5% for CH stretches, less than 6.5% for CC stretches and always less than 7.5% for ethylene and acetylene. It is reasonable to expect the same level of accuracy for the vinyl radical.

In the previous section we analyzed the features of the vinyl radical implied by the calculated equilibrium structure. In particular we noted the ethylenic character of the CH bonds, and that  $\alpha$ CH bonds are shortest ones. The frequency of the  $\alpha$ CH stretching ( $3265\text{ cm}^{-1}$ ) mode is found slightly higher than any CH stretching frequency of ethylene (between  $3086\text{ cm}^{-1}$  and  $3179\text{ cm}^{-1}$ ), but it is lower than the same mode frequencies of acetylene ( $3356\text{ cm}^{-1}$  and  $3452\text{ cm}^{-1}$ ). The CC bond in the vinyl radical is slightly shorter than in ethylene, but much longer than in acetylene. The CC stretching frequency of the vinyl radical ( $1670\text{ cm}^{-1}$ ) is, surprisingly, lower than the same mode frequency in ethylene ( $1735\text{ cm}^{-1}$ ). The presence of the radical center results in a smaller repulsive interaction of the CH bonds upon CC vibrations in the vinyl radical than in ethylene, and thus the vibrational potential is "softer." While the symmetric bending mode frequency of vinyl ( $1444\text{ cm}^{-1}$ ) lies between the same mode frequencies of ethylene ( $1539\text{ cm}^{-1}$  and  $1403\text{ cm}^{-1}$ ) there is a small shift of the asymmetric bending mode frequencies, due to the radical center. The  $\text{CH}_2$  asymmetric bending mode couple with the in plane  $\alpha$ CH bending mode to give rise to the  $1185\text{ cm}^{-1}$  and  $827\text{ cm}^{-1}$  frequency modes. The  $\alpha$ CH bending motion contributes more to the  $827\text{ cm}^{-1}$  mode, the  $\text{CH}_2$  asymmetric bending motion more to the  $1185\text{ cm}^{-1}$ . The comparable

frequencies in ethylene are  $1302\text{ cm}^{-1}$  and  $863\text{ cm}^{-1}$ . Similarly the out-of-plane motions of the hydrogen atoms in vinyl give rise to two modes with frequencies  $918\text{ cm}^{-1}$  and  $783\text{ cm}^{-1}$  to be compared with the torsion and out-of-plane frequencies of ethylene:  $1065\text{ cm}^{-1}$ ,  $926\text{ cm}^{-1}$ , and  $871\text{ cm}^{-1}$ .

To summarize, there is very little difference between the spectra of ethylene and the vinyl radical. Except for the  $\text{CH}_2$  asymmetric bending ( $1302\text{ cm}^{-1}$ ), and torsional ( $1065\text{ cm}^{-1}$ ) frequencies of ethylene replaced by the asymmetric bending frequency at  $1185\text{ cm}^{-1}$  in the vinyl radical, all the other modes have very similar frequencies. The vinyl radical spectrum is closer to the ethylene spectrum than to the acetylene spectrum.

#### V. Dipole Moment Derivatives of Ethylene, Acetylene, and the Vinyl Radical

The integrated intensity  $A_k$  of a vibrational band  $k$  in the infrared spectrum is proportional to the square of  $\partial_{\mu}/\partial Q_k$ , the derivative of the dipole moment with respect to the normal coordinate  $Q_k$ . Using the ab initio calculated normal modes of vibration at the equilibrium geometry, we have computed the dipole moment derivatives for ethylene, acetylene, and the vinyl radical.

The infrared active vibrational modes of ethylene are schematically represented in Fig. 2. The HF(6-31G\*\*) and GVB(6-31G\*\*) calculated dipole moment derivatives, along with the experimental values are reported in Table 4. Both set of calculated values are in semiquantitative agreement with the experimental data. It is somewhat surprising

that the HF results are of comparable quality since the GVB wavefunction takes into account some electron correlation effects. Improved agreement with the experimental value could be obtained with a more extended basis set and a more correlated CI wavefunction. In any case from these results we expect the calculated dipole moment derivatives of the vinyl radical to constitute a semiquantitative prediction of the infrared intensities of the vinyl radical.

A schematic representation of the normal modes of vibration of the vinyl radical are shown in Fig. 3. The arrows showing the atomic displacement define a positive direction of the normal modes, when the cartesian coordinate system of Fig. 4 is used. The permanent dipole moment of the vinyl radical calculated with the GVB (6-31G\*\*) wavefunction is 0.576 Debyes. The calculated dipole moment derivatives are given in Table 5. The out of plane bend ( $\nu = 918 \text{ cm}^{-1}$ ) in which all three hydrogen atoms vibrate on the same side of the molecular plane is the mode with the largest dipole moment derivatives  $1.16 \text{ (D/\AA) amu}^{-1/2}$ . This mode is analogous to the out of plane bend  $B_{1u}$  (calculated  $\nu = 871 \text{ cm}^{-1}$ ) which has the largest dipole derivative in ethylene. The next largest dipole derivatives are due to the  $\text{CH}_2$  asymmetric stretch  $0.56 \text{ (D/\AA) amu}^{-1/2}$  with  $\nu = 3192 \text{ cm}^{-1}$ , the asymmetric bends  $0.48$  and  $0.39 \text{ (D/\AA) amu}^{-1/2}$  with  $\nu = 827 \text{ cm}^{-1}$  and  $1185 \text{ cm}^{-1}$  respectively, and the  $\text{CH}_2$  symmetric stretch  $0.42 \text{ (D/\AA) amu}^{-1/2}$  with  $\nu = 3116 \text{ cm}^{-1}$ .

## VI. Conclusions

We used ab initio GVB(6-31G\*\*) wavefunction to characterize the structure of the vinyl radical, by comparison with ethylene and acetylene. The vinyl radical has an  $\alpha$ CH bond and  $\alpha$ CC bond which are only slightly shorter than CH and CC bonds in ethylene. The radical center may be described as  $sp^2$  hybrid with the angle between the  $\alpha$ CH and CC bond equal to  $134.2^\circ$ . The barrier to inversion of the radical center is calculated to be 8.9 kcal/mol. The dipole moment derivatives suggest a very intense IR band for the out of plane bending motion of the hydrogen atoms at  $\nu = 918 \text{ cm}^{-1}$ .

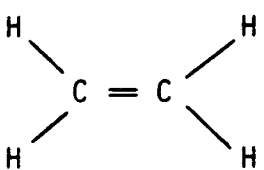

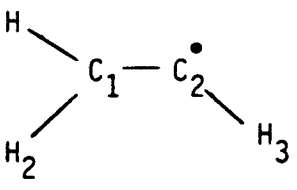
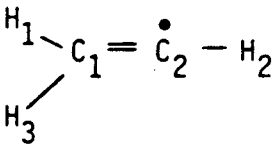
## Acknowledgment

The authors gratefully acknowledge many stimulating discussions with Dr. J. Pacansky (IBM Research Laboratory). This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098 and by the National Science Foundation under Grant No. CHE-7721305.

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Table 1 HF (6-31G\*\*) and GVB (6-31G\*) Optimized Structures of Ethylene, Acetylene, and the Vinyl Radical<sup>a</sup>

	Exp.	HF	GVB
			
Energy	-	-78.038841	-78.136504
R(CC)	1.337	1.317	1.345
R(CH)	1.086	1.076	1.092
<(CCH)	121.3°	122.0°	121.6°
			
Energy	-	-76.821807	-76.903525
R(CC)	1.205	1.186	1.210
R(CH)	1.059	1.056	1.070
			
Energy	-	-77.386914	-77.465265
R(C <sub>1</sub> C <sub>2</sub> )	-	1.303	1.332
R(C <sub>1</sub> H <sub>1</sub> )	-	1.077	1.093
R(C <sub>1</sub> H <sub>2</sub> )	-	1.080	1.095
R(C <sub>2</sub> H <sub>3</sub> )	-	1.073	1.085
<(H <sub>1</sub> C <sub>1</sub> C <sub>2</sub> )	-	121.5°	121.2°
<(H <sub>2</sub> C <sub>1</sub> C <sub>2</sub> )	-	121.9°	121.5°
<(H <sub>3</sub> C <sub>2</sub> C <sub>1</sub> )	-	135.3°	134.2°
			
Energy	-	-	-77.451098
R(C <sub>1</sub> C <sub>2</sub> )	-	-	1.322
R(C <sub>1</sub> H <sub>1</sub> )	-	-	1.096
R(C <sub>1</sub> H <sub>2</sub> )	-	-	1.096
R(C <sub>2</sub> H <sub>3</sub> )	-	-	1.070
<(H <sub>1</sub> C <sub>1</sub> C <sub>2</sub> )	-	-	121.8°
<(H <sub>2</sub> C <sub>1</sub> C <sub>2</sub> )	-	-	121.8°
<(H <sub>3</sub> C <sub>2</sub> C <sub>1</sub> )	-	-	180.0°

a. Energies in atomic units, bond length in angstroms.



Table 2 Vibrational Frequencies (cm<sup>-1</sup>) of Ethylene, Acetylene, and the Vinyl Radical

<u>Molecule</u>	<u>Mode</u>	<u>v (obs.) Anharmonic</u>	<u>v (obs.) Harmonic</u>	<u>v (obs.) GVB (6-31G**) </u>
C <sub>2</sub> H <sub>4</sub>	CH <sub>2</sub> stretch	3106 <sup>a</sup>	3234	3179
	CH <sub>2</sub> stretch	3103	3232	3156
	CH <sub>2</sub> stretch	3026	3153	3111
	CH <sub>2</sub> stretch	2989	3147	3086
	CC stretch	1623	1655	1735
	Sym. bend	1444	1473	1539
	Sym. bend	1342	1370	1403
	Asym. bend	1236	1245	1302
	Torsion	1023	1044	1065
	Out of plane bend	949	959	926
	Out of plane bend	943	969	871
	Asym. bend	826	843	863
C <sub>2</sub> H <sub>2</sub>	CH stretch	3374 <sup>b</sup>	3496	3452
	CH stretch	3282	3419	3356
	CC stretch	1974	1992	2089
	Linear bend	730	764	714 <sup>c</sup>
	Linear bend	613	625	648 <sup>c</sup>
C <sub>2</sub> H <sub>3</sub>	αCH stretch	-	-	3265
	CH <sub>2</sub> stretch	-	-	3192
	CH <sub>2</sub> stretch	-	-	3116
	CC stretch	-	-	1670
	CH <sub>2</sub> sym. bend	-	-	1444
	CH <sub>2</sub> asym. bend + αCH bend	-	-	1185
	Out of plane bend	-	-	918
	CH <sub>2</sub> asym. bend + αCH bend	-	-	827
Out of plane bend	-	-	783	

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 b. I. Suzuki and J. Overend, *Spectrochim. Acta.* **A25**, 977 (1969).  
 c. GVB(4-31G) frequency.

Table 3 Vibrational Frequencies ( $\text{cm}^{-1}$ ) of the Vinyl Radical  
and Deuterium Substituted Analogues

	<u>CH<sub>2</sub>=CH</u>	<u>CH<sub>2</sub>=CD</u>	<u>CD<sub>2</sub>=CH</u>	<u>CD<sub>2</sub>=CD</u>
$\alpha$ CH stretch	3265	2424	3265	2431
CH <sub>2</sub> stretch	3192	3193	2377	2377
CH <sub>2</sub> stretch	3116	3118	2281	2271
CC stretch	1670	1650	1593	1565
CH <sub>2</sub> sym. bend	1444	1433	1064	1075
CH <sub>2</sub> asym. bend + $\alpha$ CH bend	1185	1118	1101	961
CH <sub>2</sub> out of plane bend + CH out of plane bend	918	886	791	699
CH <sub>2</sub> asym. bend - $\alpha$ CH bend	827	670	697	597
CH <sub>2</sub> out of plane bend - CH out of plane bend	783	671	677	612

Table 4 Dipole Moment Derivatives  $\partial\mu/\partial s$  of Ethylene and Acetylene<sup>a</sup>

<u>Molecule</u>	<u>Mode</u>	<u>Exp.</u>	<u>Calc.</u>	
			<u>RHF(6-31G**)</u>	<u>GVB(6-31G**)</u>
Ethylene	B <sub>1u</sub> bend	1.926 <sup>b</sup>	2.200	1.849
	B <sub>2u</sub> stretch	0.766	0.920	0.928
	B <sub>2u</sub> bend	0.042	0.084	0.020
	B <sub>3u</sub> stretch	0.606	0.732	0.732
	B <sub>3u</sub> bend	0.285	0.252	0.159
Acetylene	Stretch	1.228 <sup>c</sup>	1.400	1.183
	Bend	1.482	1.474	1.432 <sup>d</sup>

- a. Units are (D/Å) amu<sup>-1/2</sup>. Internal coordinates are as defined in G. Jalsorszky and P. Pulay, J. Mol. Struct. 26, 277 (1975) and references therein.
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- d. GVB(4-31G) value.

Table 5. Dipole Moment Derivatives  $\partial\mu/\partial s$  of the Vinyl Radical.<sup>a</sup>

	$\nu(\text{cm}^{-1})$	$\frac{\partial\mu_x}{\partial Q}$	$\frac{\partial\mu_y}{\partial Q}$	$\frac{\partial\mu_z}{\partial Q}$	$\frac{\partial\mu}{\partial Q}$
$\alpha\text{CH}$ stretch	3265	-0.21	0.07	0.	0.22
$\text{CH}_2$ asym. stretch	3192	0.02	-0.56	0.	0.56
$\text{CH}_2$ sym. stretch	3116	0.41	0.10	0.	0.42
CC stretch	1670	-0.08	0.04	0.	0.09
$\text{CH}_2$ sym. bend	1444	0.27	0.06	0.	0.27
$\text{CH}_2$ bend + $\alpha\text{CH}$ bend	1185	-0.37	-0.12	0.	0.39
Out of plane bend	918	0.	0.	-1.16	1.16
$\text{CH}_2$ bend + $\alpha\text{CH}$ bend	827	0.46	0.13	0.	0.48
Out of plane bend	783	0.	0.	-0.11	0.11

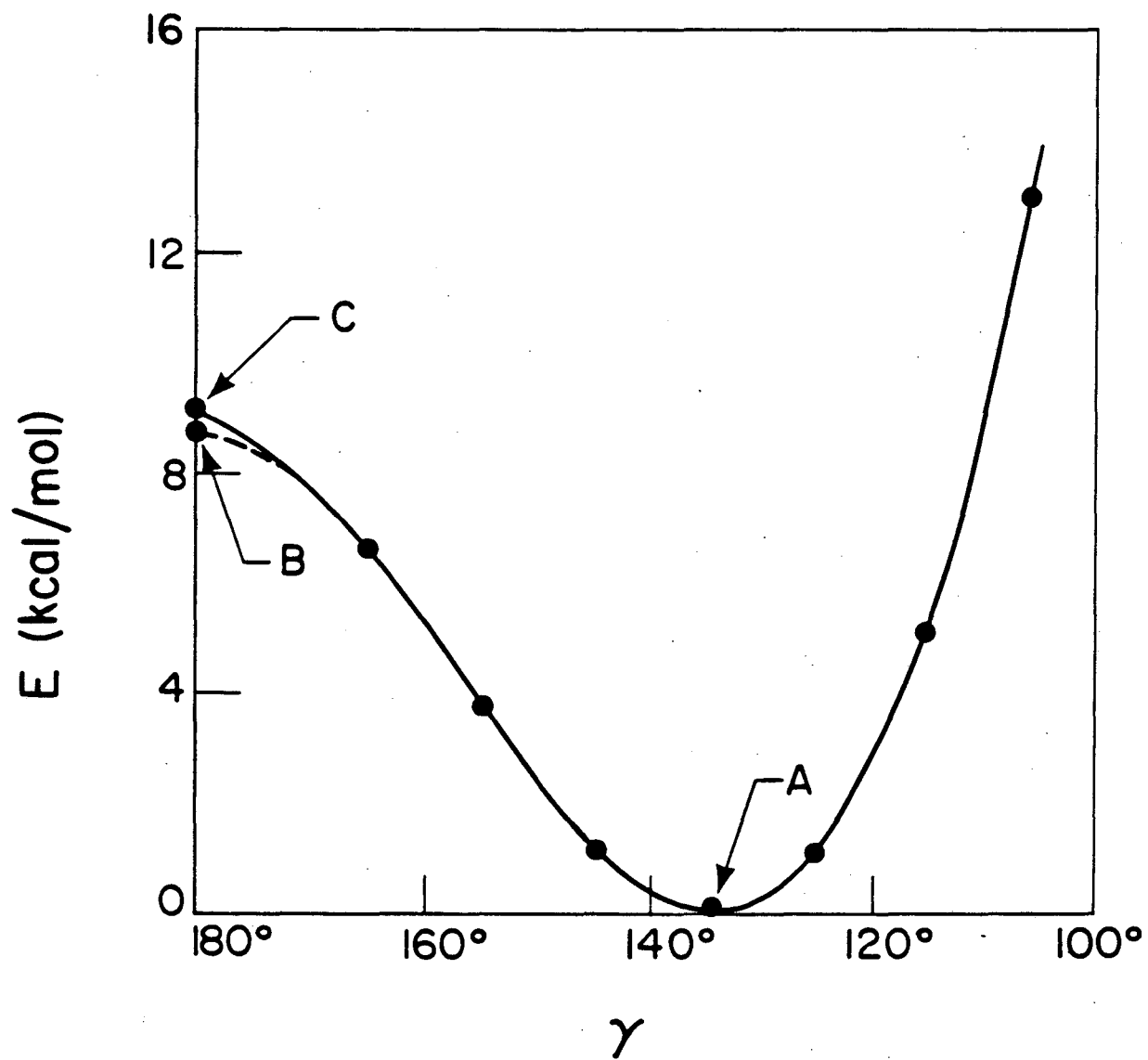
a. Units are D/Å)  $\text{amu}^{-1/2}$  permanent dipole in the coordinate system of Fig. 4 =  $\mu_x = -0.233\text{D}$ ;  $\mu_y = -0.531\text{D}$ ;  $\mu = 0.576\text{D}$ .

Figure Captions

- Figure I Bending Potential of the Inversion Motion of the  $\alpha$ CH Bond of the Vinyl Radical.
- Figure II Infrared Archive Vibrational Modes of Ethylene.
- Figure III Normal Modes of the Vinyl Radical.
- Figure IV Coordinate System for Dipole Moment Derivatives Calculation of the Vinyl Radical.

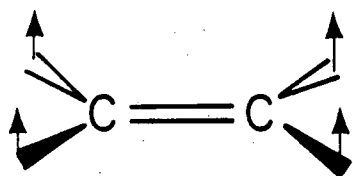
Table Captions

- Table I HF(6-31G\*\*) and GVB(6-31G\*\*) Optimized Structures of Ethylene, Acetylene, and the Vinyl Radical.
- Table II Vibrational Frequencies ( $\text{cm}^{-1}$ ) of Ethylene, Acetylene, and the Vinyl Radical.
- Table III Vibrational Frequencies ( $\text{cm}^{-1}$ ) of the Vinyl Radical and Deuterium Substituted Analogues.
- Table IV Dipole Moment Derivatives  $\partial\mu/\partial s$  of Ethylene and Acetylene.
- Table V Dipole Moment Derivatives  $\partial\mu/\partial Q$  of the Vinyl Radical.

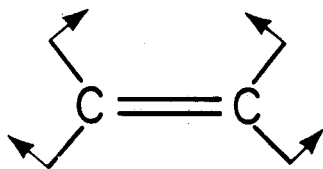


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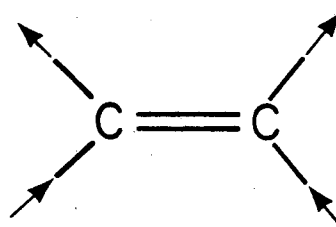
Fig. 1



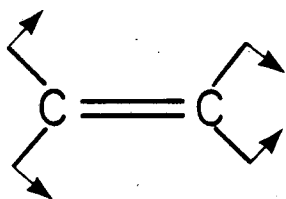
$B_{1u}$  bend ( $871\text{ cm}^{-1}$ )



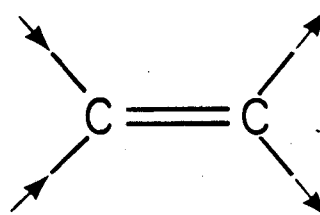
$B_{2u}$  bend ( $863\text{ cm}^{-1}$ )



$B_{2u}$  stretch ( $3234\text{ cm}^{-1}$ )



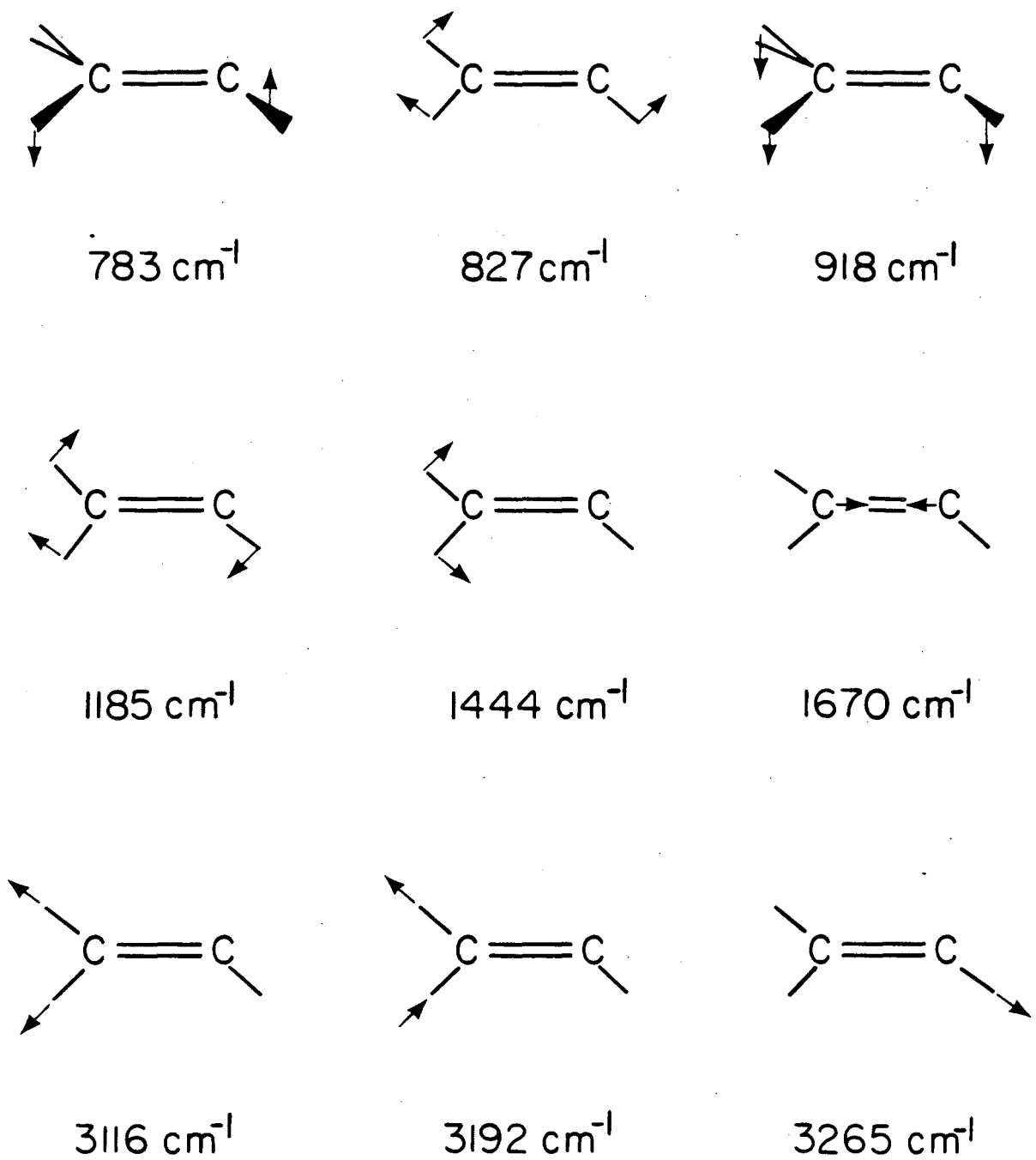
$B_{3u}$  bend ( $1539\text{ cm}^{-1}$ )



$B_{3u}$  stretch ( $3086\text{ cm}^{-1}$ )

XBL 826-1408

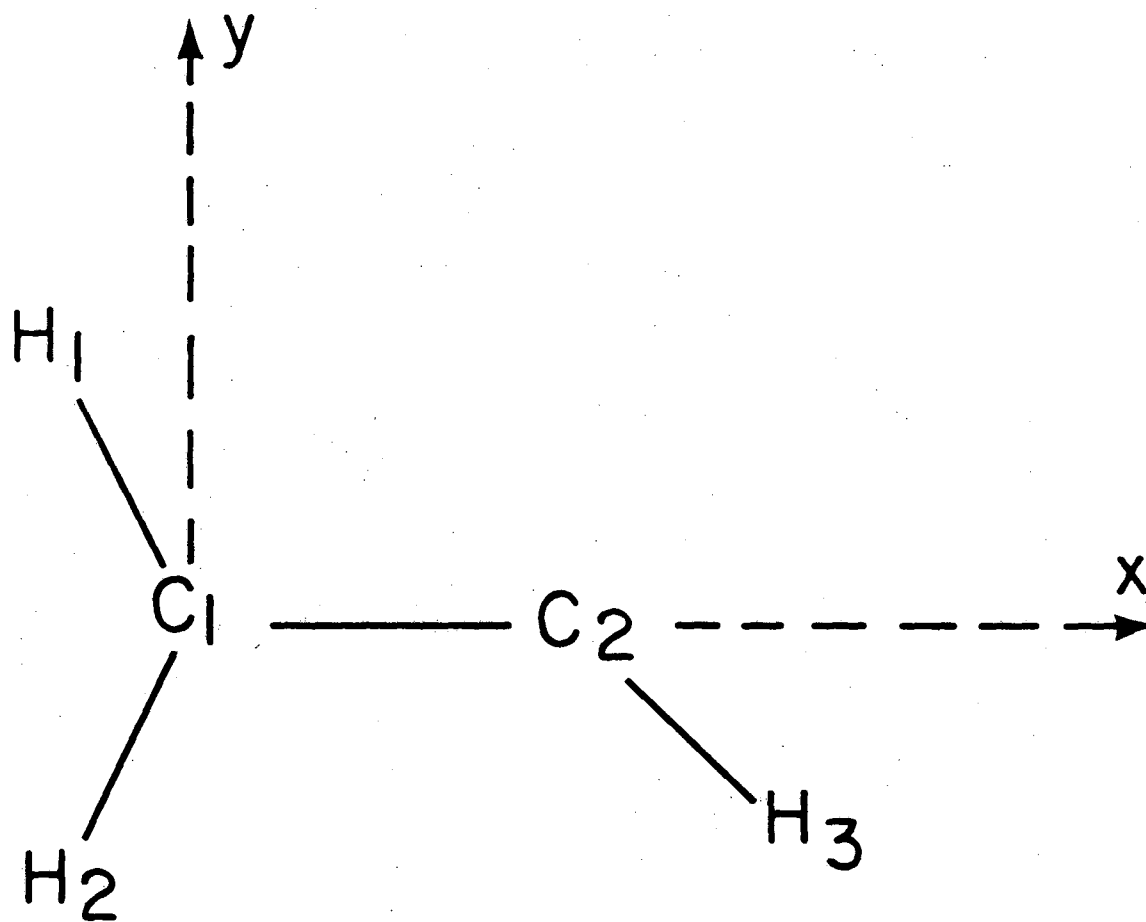
Fig. 2



XBL 826-1409

Fig. 3





XBL 826-1402

Fig. 4

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TECHNICAL INFORMATION DEPARTMENT  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720