

# The Structure of Methylene

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Methylene is of interest because it is (1) the smallest polyatomic free radical with a low-lying triplet state; (2) the parent carbene; (3) small enough to be studied by fairly sophisticated *ab initio* calculations and thus provide an important benchmark in our assessment of the reliability of computationally determined structures.

For many years the structure of methylene was the exclusive domain of the theoretician,<sup>1</sup> starting in 1932 with Mulliken's qualitative speculations<sup>2</sup> and culminating with the recent surge of extensive *ab initio* studies.<sup>1,3-15</sup> Experimental work, though late in coming, has been profound in its consequences. In 1961 Herzberg<sup>16a</sup> published his classic study of the electronic spectra of both singlet and triplet CH<sub>2</sub>, followed in 1966 by a more detailed study with Johns<sup>16b,17</sup> of the singlet state. The period 1970-1972 was dominated by the spectacular announcement by two groups of spectroscopists that the elusive esr spectrum of methylene had finally been observed.<sup>18-23</sup>

The purpose of this Account is to describe the role the various *ab initio* calculations have played in shaping our current understanding of the structure of methylene. My emphasis on *ab initio* calculations should not be interpreted as a reflection of my assessment of the significance of semiempirical studies. I believe that, if it were not for the chemical insight and variety of experience acquired by trying to understand CH<sub>2</sub> in a semiempirical vein, the *ab initio* calculations reported in the recent literature would not be sufficiently well understood for their proponents to claim parity with experiment in the reliability of their predictions.

## Nature of the Problem

Some insight into the problems associated with the structure of methylene may be gained from the following very qualitative arguments.

If CH<sub>2</sub> were linear we would expect the *in situ* carbon atom to be sp hybridized. Allotting two electrons to the carbon 1s orbital and two to each C-H bond leaves two remaining to be distributed among the unhybridized carbon p<sub>π</sub> orbitals. Allotting these electrons consistent with the Pauli principle and elementary valence theory<sup>24</sup> results in the anticipated energy ordered-state sequence  $^3\Sigma_g^- < ^1\Delta_g < ^1\Sigma_g^-$ . A schematic representation of the electron distribution in these states is shown in Figure 1. As we bend

the molecule, the orbital perpendicular to the molecular plane retains its atomic p character while the one in plane ( $\sigma$ ) begins to acquire s character and consequently an increased stability. Note that this stability is acquired at the expense of the C-H bonds; the hybridization, and therefore the bond energy, changes in concert with the increased s character of the in-plane ( $\sigma$ ) orbital.<sup>25</sup> In Figure 1 we display the correlation between the states of  $D_{\infty h}$  (linear) and  $C_{2v}$  symmetry (bent). The angle  $\phi$  equals  $\pi/4$  in the linear molecule and tends toward 0 with decreasing bond angle. The behavior of the  $^3B_1$  energy as the HCH angle is closed depends on whether the increased H-H repulsion and decreased C-H bond energy offset the increased stabilization of the  $\sigma$  orbital. If so, the molecule will assume a linear equilibrium geometry; if not, a bent conformation will obtain. Note that the  $^1A_1$  component of the  $^1\Delta_g$  state has two electrons in the  $\sigma$  orbital and since the electron repulsion of a  $\sigma$ -p electron pair is comparable to a  $\sigma$ - $\sigma$  pair, a bent  $^3B_1$  state suggests a strongly bent  $^1A_1$ . Indeed the  $^1A_1$  state may be so stabilized

(1) See the historical review by J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, **91**, 807 (1969), or J. F. Harrison in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1971.

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(11) C. F. Bender, H. F. Schaefer, D. R. Franceschetti, and L. C. Allen, *J. Amer. Chem. Soc.*, **94**, 6888 (1972).

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(18) R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *J. Chem. Phys.*, **53**, 1280 (1970).

(19) E. Wasserman, W. A. Yager, and V. J. Kuck, *Chem. Phys. Lett.*, **7**, 409 (1970).

(20) E. Wasserman, V. J. Kuck, R. S. Hutton, and W. A. Yager, *J. Amer. Chem. Soc.*, **92**, 7491 (1970).

(21) R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *J. Chem. Phys.*, **54**, 3223 (1971).

(22) E. Wasserman, V. J. Kuck, R. S. Hutton, E. D. Anderson, and W. A. Yager, *J. Chem. Phys.*, **54**, 4120 (1971).

(23) E. Wasserman, R. S. Hutton, C. J. Kuck, and W. A. Yager, *J. Chem. Phys.*, **55**, 2593 (1971).

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(25) This  $\sigma_p$  notation was introduced by R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).

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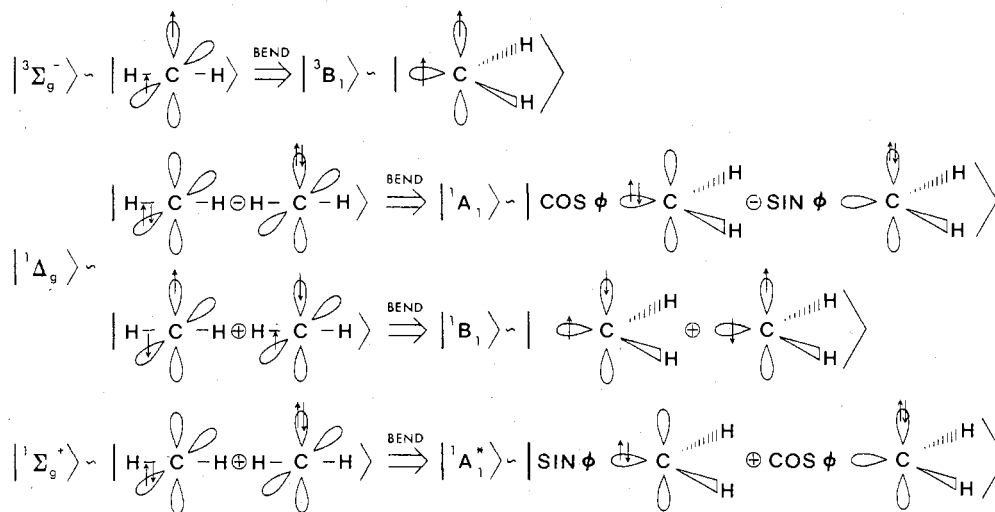


Figure 1. Schematic representation of the orbital occupancy in the low-lying states of methylene.

Table I  
Observed  $D$  and  $E$  Parameters of Various Isotopes of  $^3B_1$  Methylene as a Function of Solvent<sup>a</sup>

Molecule	Xenon			Octafluorocyclobutane (OFCB) <sup>e</sup>			SF <sub>6</sub> <sup>e</sup>			
	$D_{\text{obsd}}$	$D_n$	$E_{\text{obsd}}$	$E_n$	$D_{\text{obsd}}$	$D_n$	$E_{\text{obsd}}$	$D_{\text{obsd}}$	$D_n$	$E_{\text{obsd}}$
CH <sub>2</sub>	0.6881 <sup>b</sup>	0.93 <sup>b</sup>	0.00346 <sup>b</sup>	0.074	0.6430	0.075	0.0137	0.6122	0.744	0.0206
CHD	0.69 <sup>c</sup>		0.003							
CD <sub>2</sub>	0.7443 <sup>d</sup>	0.93 <sup>d</sup>	0.00640 <sup>d</sup>	0.074	0.6814	0.0775	0.0170	0.6505	0.744	0.0237

<sup>a</sup> All entries are in cm<sup>-1</sup>. <sup>b</sup> Reference 19. <sup>c</sup> Reference 18. <sup>d</sup> Reference 20. <sup>e</sup> Reference 23.

upon bending as to overtake the  $^3B_1$  and assume the role of ground state. The problem then is to deduce/infer/determine the geometry, multiplicity, and relative energies of the low-lying states of CH<sub>2</sub>.

### Summary of Experimental Information

Most of the experimental information we have regarding the electronic structure of methylene has been obtained from electronic spectroscopy, electron spin resonance, and photochemistry.

To date, electronic spectroscopy<sup>16,17</sup> has been concerned with the observation and interpretation of the visible and ultraviolet bands. The visible bands have been assigned to the  $^1A_1 \leftarrow ^1B_1$  transition and analysis produces a fairly reliable geometry for the  $^1A_1$  state ( $R = 1.11 \text{ \AA}$ ,  $\theta = 102.4^\circ$ ), but a far more uncertain geometry for the  $^1B_1$  state ( $R = 1.05 \text{ \AA}$ ,  $\theta = 140 \pm 15^\circ$ ). The bond length of the  $^1B_1$  state was obtained from the rotational structure by assuming a linear molecule, while the vibrational structure was best interpreted in terms of a quasi-linear molecule with a bond angle of  $140^\circ$ . The limited structure of the ultraviolet bands admits a linear ( $^3\Sigma_g^- \leftarrow ^3\Sigma_u^-$ ) or a bent ( $^3B_1 \leftarrow ^3A_2$ ) interpretation. The bent interpretation ( $\theta(^3B_1) = 136^\circ$ ;  $\theta(^3A_2) = 125^\circ$ ) is preferred because of the resulting agreement with both the first-principles calculations and the interpretation of the epr spectra. In addition, the pressure dependence of the intensity of the observed bands suggests that the  $^3B_1$  has a lower energy than the  $^1A_1$ .

The observation<sup>18-20</sup> of a stable epr signal attributable to CH<sub>2</sub> strongly implies a triplet ground state,

while the characterization of the spectrum in terms of a non-zero  $E$  parameter suggests that this state is nonlinear. The observed  $D$  and  $E$  parameters for various isotopes in three matrices are collected in Table I. ( $D_n$  and  $E_n$  refer to the parameters corrected for motional averaging.) The large solvent effect of  $D_n$  in going from OFCB and SF<sub>6</sub> to xenon is attributed to enhanced external spin-orbit effects<sup>23</sup> which one might expect in a high  $Z$  solvent. If we accept this and discard the xenon result the average of the remaining two  $D_n$ 's is  $0.76 \pm 0.02 \text{ cm}^{-1}$  and is taken as more characteristic of free methylene. This is in substantial agreement with Wasserman's<sup>26a</sup> previous estimate of  $0.69\text{--}0.72 \text{ cm}^{-1}$  obtained by extrapolating from observed  $D$ 's of related compounds. Detailed analysis<sup>19,20</sup> by Wasserman, *et al.*, of the xenon data results in an  $E/D$  ratio corresponding to an HCH angle of  $136 \pm 5^\circ$ .

Additional geometric information obtained from various interpretations<sup>21,22,26b</sup> of the <sup>13</sup>C hyperfine spectra suggests an HCH angle between  $126$  and  $137^\circ$ . Current interpretations of the epr experiments provide no bond length information.

There have been three published studies in which the singlet-triplet separation in CH<sub>2</sub> was estimated. The first, by Halberstadt and McNesby,<sup>27</sup> is based on the  $3130\text{-\AA}$  photolysis of ketene (CH<sub>2</sub>CO) in the

(26) (a) E. Wasserman, L. Barash, and W. A. Yager, *J. Amer. Chem. Soc.*, **87**, 4974 (1965). (b) An unpublished interpretation by J. F. Harrison of the <sup>13</sup>C experiments reported in ref 12 and 22 suggests an HCH angle between  $126$  and  $135^\circ$ .

(27) M. L. Halberstadt and J. R. McNesby, *J. Amer. Chem. Soc.*, **89**, 4317 (1967).

Table II  
*Ab Initio* Studies of the Electronic Structure of Methylene

Ref	Geometry and energy												Energy differences, kcal/mol	Comments	
	<sup>3</sup> B <sub>1</sub>				<sup>1</sup> A <sub>1</sub>				<sup>1</sup> B <sub>1</sub>						
	R, au	θ	E, au	R, au	θ	E, au	R, au	θ	E, au	R, au	θ	E, au			
15	2.1	134	-39.07539	2.1	102.5	-39.06070								9.2	s,p,d + polarization, gaussian lobe basis; configuration interaction (independent electron pair approximation)
14	2.07	132	-39.0319												s,p,d + polarization, gaussian lobe basis; configuration interaction; iterative natural orbital basis; configuration interaction (first-order wave function)
13	2.056	134	-39.0121												s,p,d + polarization, gaussian lobe basis; configuration interaction (first-order wave function)
11				2.126	101	-38.9898								14.0	s,p gaussian basis; configuration interaction (first-order wave function)
5		133	-38.983												
7				2.315	104	-38.9472	2.060	144	-38.9114					22.2	44.4
12	2.1	~135	-38.9598	2.1	~105	-38.9414	2.1	~135	-38.8998					11.5	43.8
4	2.034	135	-38.93161	2.084	105	-38.8885	2.019	150	-38.8525					27.0	49.5
10	2.0	130	-38.9248	2.0	100	-38.8930	2.0	140	-38.8595					21.0	40.9
1	2.0	138	-38.915	2.0	108	-38.864	2.0	148	-38.833					19.4	51.3
6	2.0	133	-38.9080	2.1	102	-38.8690	2.1	180	-38.8454					14.8	39.2
3	2.11	129	-38.904	2.21	90	-38.865	2.11	132	-38.808					35.7	60.1
9	2.02	132	-38.8696	2.079	105	-38.8103								37.0	
8	2.02	130	-38.838	2.08	105	-38.784	2.00	151	-38.765					11.9	45.7

STO (4,31G), self-consistent field

s,p gaussian; self-consistent field

presence of methane and propane and entails an estimate of the rate of dissociation of activated ethylene formed by the insertion of singlet  $\text{CH}_2$  into the C-H bond of methane. The data are analyzed using the RRKM theory<sup>28</sup> and the assumption that the singlet  $\text{CH}_2$  involved in the insertions is fully relaxed before reaction. An estimate of 2.5 kcal/mol is obtained.

The second study, by Carr, Eder, and Topor,<sup>29</sup> is based on an estimate of the ratio of singlet to triplet  $\text{CH}_2$  produced in the 3500-Å photolysis of ketene. In an earlier study,<sup>30</sup> Eder and Carr photolyzed a mixture of ketene and *cis*-2-butene, the first pass being without and the second with 10% added  $\text{O}_2$ . The photolysis was allowed to proceed to 5% conversion of  $\text{CH}_2\text{CO}$ ; the amount of product in each pass was determined and found to be different. If one assumes that the added molecular oxygen has no effect on the primary photochemical process, completely suppresses  $^3\text{CH}_2$  products, and does not reduce the yield of  $^1\text{CH}_2$  products,<sup>31</sup> this difference in product yield is a direct measure of the amount of  $^3\text{CH}_2$  produced. In this way one estimates that at 3500 Å (81.5 kcal/mol) approximately  $13 \pm 2\%$  of the  $\text{CH}_2$  produced is in a singlet state.

Carr, Eder, and Topor<sup>29</sup> then estimate the  $\Delta H_f^\circ$  of



to be  $81 \pm 1$  kcal/mol, making  $^3\text{CH}_2$  just energetically favorable at 3500 Å. These authors then assume that the fraction  $R$  of singlet relative to triplet  $\text{CH}_2$  produced at 3500 Å is governed by a Boltzmann factor so that  $R = e^{\Delta E/RT}$ ;  $\Delta E = E_S - E_T > 0$ , and taking  $R = 0.10$  with  $T = 298$  results in  $\Delta E = 1.3$  kcal/mol. It is then suggested that the exact  $\Delta E$  lies between 1 and 2 kcal/mol.

The third study is by Frey,<sup>32</sup> who points out that the low reactivity of triplet methylene relative to singlet methylene, coupled with the ease of collisional interconversion of singlet and triplet, would preclude the observation of triplet products if the singlet-triplet separation was as small as the two preceding estimates. By analyzing the singlet-triplet ratio in the 2700-Å photolysis of ketene, he estimates a singlet-triplet separation of approximately 8 kcal/mol.

### First Principles Calculations

The first principles approaches are conveniently considered in two stages. First one attempts to predict the geometry of  $\text{CH}_2$  in its various states by minimizing the total energy and secondly one uses the wave functions obtained to calculate the parameter used to characterize the model employed to interpret the epr experiments.

The predictions of the initial stage of the first principles approach are summarized in Table II. As significant as the technical characteristics of the various calculations are, we will not dwell on them, but will concentrate on the results. However, as an aid in

(28) See, for example, P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions," Wiley-Interscience, New York, N. Y., 1972.

(29) R. W. Carr, Jr., T. W. Eder, and M. G. Topor, *J. Chem. Phys.*, **53**, 4716 (1970).

(30) T. W. Eder and R. W. Carr Jr., *J. Phys. Chem.*, **73**, 2074 (1969).

(31) Reference 30 cites experimental data which may be interpreted as supporting these assumptions.

(32) H. M. Frey, *J. Chem. Soc., Chem. Commun.*, **18**, 1024 (1972).

assessing the relative quality of a calculation, its position in the table has been determined by the computed energy of the  $^3\text{B}_1$  state, the lowest energy being the first listed and the highest the last. Equally important as the total energy, for our purposes, is the balance of the calculation, *i.e.*, the extent to which the various excited states have been subjected to the same level of approximation as the ground state; this is very difficult to determine.

Note that: (1) every calculation predicts the  $^3\text{B}_1$  angle to be between 129 and 138°, with the preferred angle close to 133°. In addition, a very small barrier to linearity is predicted, being only 4 kcal/mol in the "best" calculation listed; (2) where several states have been studied, the  $^3\text{B}_1$  is always lowest; (3) the first excited state is predicted to be the  $^1\text{A}_1$  state, with a bond angle between 90 and 109°, with the more recent calculations clustering around 105°; (4) the second excited state is predicted to be of  $^1\text{B}_1$  symmetry, with a bond angle between 132 and 180°, with the more recent calculations favoring 140°. This state also has a very shallow barrier to linearity.

While most calculations are consistent in predicting the relative order of the singlet and triplet states, as well as their geometries, no such unified prediction holds for the magnitude of the singlet-triplet energy separation. In Figure 2 I plot this separation ( $E(^1\text{A}_1) - E(^3\text{B}_1)$ ) as a function of publication date, the number associated with each point identifying the reference. Clearly, as the quality or completeness of the calculation improves, the singlet-triplet separation decreases.

We have further divided these plotted points into three groups according to the separation predicted, and note that all calculations within a group have employed atomic basis sets of comparable quality, group I being a fairly minimal sp basis, group II a double-zeta sp basis, while group III boasts double zeta + polarization functions. While the calculations in group III can be improved, it is not likely that the magnitude of the energy lowering in future calculations will be comparable to that obtained in going from group II to group III. Indeed, if it is even half as much, the singlet-triplet separation would not go below 7 kcal/mol.

The reason why improving the total energy results in a continuously decreasing singlet-triplet separation is both interesting and suggestive. From the representation given in Figure 1 we see that in going from the  $^3\text{B}_1$  to the  $^1\text{A}_1$  we pair two electrons in, primarily, the  $\sigma$  orbital and increase the correlation energy. However, in going from the  $^3\text{B}_1$  to the  $^1\text{B}_1$  state we neither break nor form any electron pairs, we merely change the spin coupling in the essentially nonbonding  $\sigma\text{p}$  pair. This implies that the correlation energy change in going from  $^3\text{B}_1$  to  $^1\text{B}_1$  should be small and the corresponding energy separation faithfully represented in an orbital model. To the extent that the invariance of the  $^3\text{B}_1$ - $^1\text{B}_1$  energy separations to the level of the calculation is a manifestation of this expectation, Figure 3 substantiates this inference. This plot suggests very strongly that the  $^3\text{B}_1$ - $^1\text{B}_1$  separation is between 40 and 45 kcal/mol.

We then interpret the effect of an improved calculation as a preferential lowering of the  $^1\text{A}_1$  state relative to the  $^3\text{B}_1$  state because of a better representa-

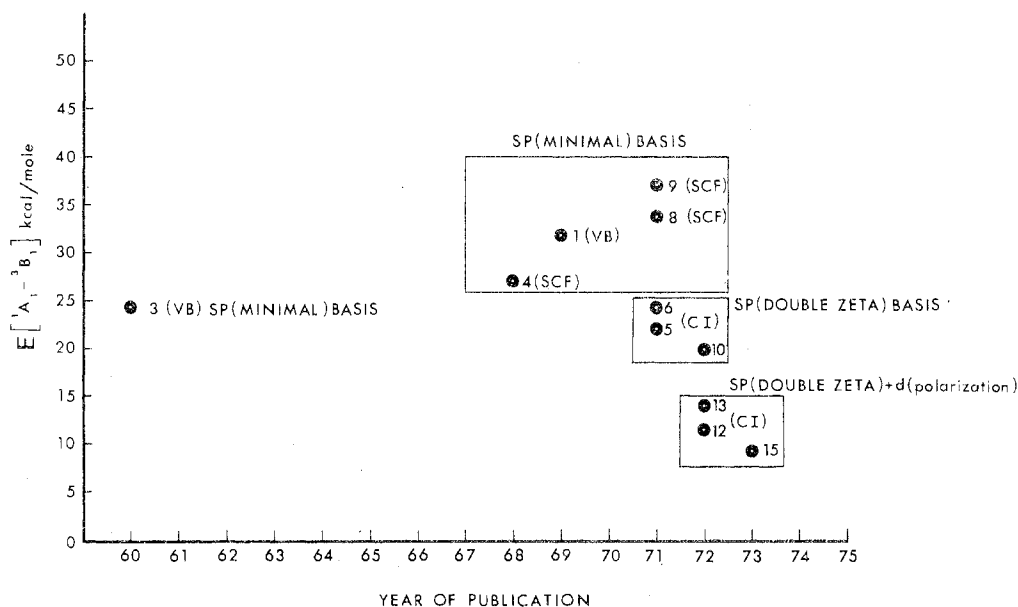


Figure 2.  ${}^1A_1-{}^3B_1$  energy separation as a function of basis set, calculation technique and year of publication.

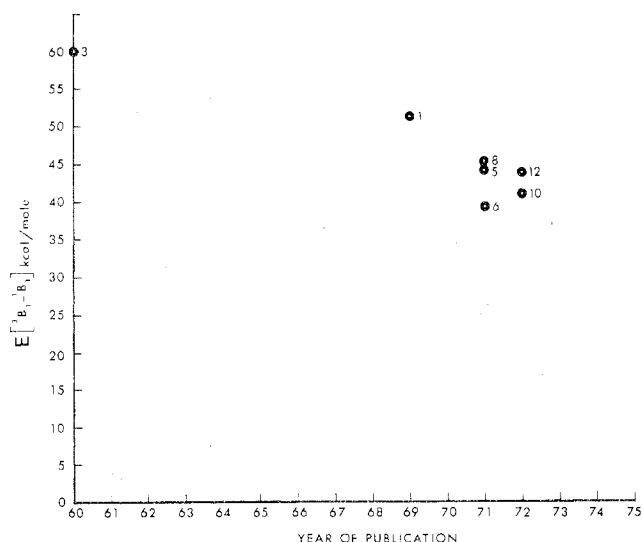


Figure 3.  ${}^3B_1-{}^1B_1$  energy separation for several calculations vs. year of publication.

tion of the correlation energy of the  ${}^1A_1$  state. This then implies that further improvements will result in a lower singlet-triplet splitting.

To estimate this separation we note the constraint  $E({}^1B_1 \leftarrow {}^3B_1) = E({}^1B_1 \leftarrow {}^1A_1) + E({}^1A_1 \leftarrow {}^3B_1) = 42.5$  kcal/mol; where on the basis of the above discussion we have accepted 42.5 kcal/mol as a fairly realistic estimate of  $E({}^1B_1 \leftarrow {}^3B_1)$ . Using the suggested<sup>16b</sup>  $E({}^1B_1 \leftarrow {}^1A_1)$  of 20 kcal/mol we have  $E({}^1A_1 \leftarrow {}^3B_1) = 22$  kcal/mol, much larger than the preceding arguments will allow. A possible explanation has been suggested by Hay,<sup>12</sup> *et al.*, who note that the lowest observed transition in the red bands of  $\text{CH}_2$  is 30.8 kcal/mol, which is assigned by Herzberg and Johns<sup>16b</sup> to  ${}^1B_1(060) \leftarrow {}^1A_1(000)$ . The suggested 0-0 energy of 20 kcal/mol is obtained by an extrapolation based on the frequency shift going from  ${}^{12}\text{CH}_2$  to  ${}^{13}\text{CH}_2$  and assumes the excited state is linear and the bending mode  $\nu_2$  harmonic. While Herzberg and Johns allow that these assumptions introduce an uncertainty of  $\pm 2$  in the vibrational quantum number  $\nu_2$  so that the observed 30.8 kcal/mol transition en-

ergy might refer to the (080) or (040) level of the  ${}^1B_1$  state, Hay, *et al.*, suggest that the (theoretically) extremely anharmonic  ${}^1B_1$  surface might render the assignment technique totally invalid and that the observed transition is really the 0-0 band. If this is so and we estimate the zero point energies of 0.04 eV for the  ${}^1B_1$  and 0.08 eV for the  ${}^1A_1$ , we have  $E({}^1B_1 \leftarrow {}^1A_1) = 31.8$  kcal/mol and therefore  $E({}^1A_1 \leftarrow {}^3B_1) = 9.7$  kcal/mol. This singlet-triplet separation is both consistent with our extrapolation and in remarkable agreement with the most recent (best) theoretical estimate of 9.3 kcal/mol by Staemmler<sup>15</sup> and the 8-kcal/mol experimental estimate of Frey.<sup>32</sup>

In the second stage of the first principles approach,  $D$  and  $E$  parameters are computed as a function of geometry and compared with those extracted from the experimental spectra.

The problem of obtaining  $D$  and  $E$  theoretically for  $\text{CH}_2$  consists of two independent parts, *i.e.*, the spin-dipole-spin-dipole (first order in perturbation theory) and the spin-orbit (second order in perturbation theory) contribution.

$$D_n = D_n^{ss} + D_n^{so}$$

$$E_n = E_n^{ss} + E_n^{so}$$

The spin-dipole contribution is the less difficult of the two since it involves only the ground-state triplet wave function; we will discuss this first.<sup>33,34</sup>

In Figure 4 we display  $D_n^{ss}$  and  $E_n^{ss}$  as function of the bond angle as calculated by several investigators.<sup>14,35-37</sup> In constructing curve 1, Higuchi<sup>35</sup> assumed that the unpaired electrons in  $\text{CH}_2$  are resident in orbitals representable as

$$|\sigma\rangle = \sqrt{\frac{1 + \cos \phi}{1 - \cos \phi}} |2s\rangle - \sqrt{\frac{-2 \cos \phi}{1 - \cos \phi}} |2p_x\rangle$$

(33) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1965.

(34) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967.

(35) J. Higuchi, *J. Chem. Phys.*, **38**, 1237 (1963).

(36) J. F. Harrison, *J. Chem. Phys.*, **54**, 5413 (1971).

(37) J. F. Harrison and R. C. Liedtke, *J. Chem. Phys.*, **58**, 3106 (1973).

and

$$|P\rangle = |2P_y\rangle$$

*i.e.*, pure carbon hybrid orbitals with  $2\phi$  as the angle between bond hybrids. Note if we interpret  $2\phi$  as  $\theta$ , the bond angle, we are assuming perfect orbital following, *i.e.*, the bond hybrids lie along the lines connecting the carbon and hydrogen nuclei. Higuchi used the 2s and 2p orbitals obtained by Löwdin<sup>38</sup> for the  $^1D$  state of atomic carbon, constructed  $|\sigma\rangle$  and  $|\rho\sigma\rangle$ , and evaluated  $D_n^{ss}$  and  $E_n^{ss}$ . Since, however, there is no theoretical equilibrium geometry, one cannot say *a priori* which  $D_n^{ss}$  and  $E_n^{ss}$  this model would give.

The remaining curves are the results of more recent *ab initio* calculations.<sup>14,36,37</sup> The energy as a function of bond angle predicted by the wave function used to construct these curves is also displayed in Figure 4. Note that, despite the very large energy difference, all functions predict the triplet equilibrium angle to be 132–133°. The  $D_n^{ss}$  and  $E_n^{ss}$  parameters corresponding to this angle are indicated in the appropriate curve. Interestingly all of these wave functions share the distinction of being constructed in a lobe function basis.<sup>39</sup>

We note some of the more general characteristics of these functions: calculation 2<sup>36</sup> is a minimal CI representation using orbitals derived for the lowest  $^1A_1$  state of  $CH_2$  (this is an attempt to generate a  $3a_1$  and  $1b_1$  orbital which would approximate those obtained from an open-shell calculation on the  $^3B_1$  state); calculation 3<sup>37</sup> is an improvement on 2 obtained by including 100 energy-ordered configurations in a configuration interaction (CI) calculation. Curves 4 and 5<sup>14</sup> form a pair—the former representing an SCF study of the  $^3B_1$ , the latter a thorough CI study containing about 200 energy-selected configurations constructed with the SCF open-shell orbitals. In comparing calculations 2 and 3 with 4 and 5 we note from Figure 4 that at the equilibrium angle the difference between the pairs is essentially present at the SCF level as the CI correction to 2 (0.012  $cm^{-1}$ ) is comparable to the CI correction to 4 (0.020  $cm^{-1}$ ). Presumably the difference at the SCF level (0.05  $cm^{-1}$ ) is due to the more flexible basis used in 4.

In Table III I collect the various estimates of the spin-orbit contribution to  $D$ . The earliest of these, by Glarum,<sup>40</sup> uses SCF orbitals and energies given by Padgett and Krauss<sup>41</sup> and approximates the spin-orbit interaction by an effective one-electron operator. The second attempt, by Fogel and Hameka,<sup>42</sup> also employed SCF orbitals and energies, but these authors used the correct microscopic spin-orbit operator. The third study, by Hall and Hameka,<sup>43</sup> extended the Fogel and Hameka work to bent geometries.

The fourth and most recent study, by Langhoff,<sup>44</sup> is also the most complete. The excited states included in the second-order perturbation sum were  $1,^3A_2$

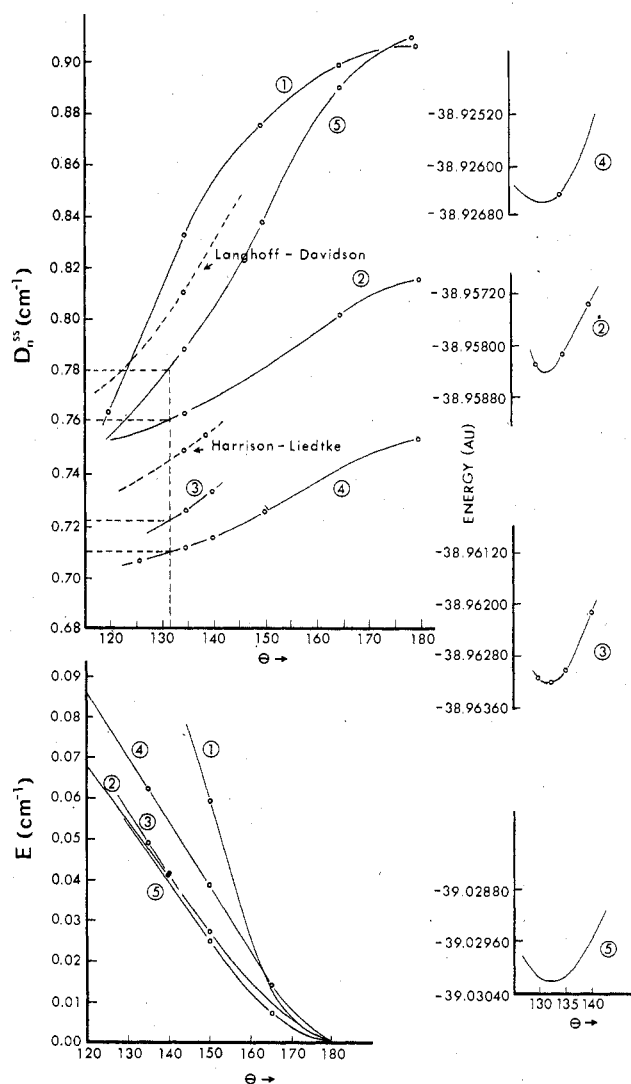


Figure 4. Zero-field splitting parameters and total molecular energy as a function of bond angle.

Table III  
Spin-Orbit Contributions to the Methylene  $D$  Parameter

$\theta$	$D_n^{so}, cm^{-1}$				
	Glarum <sup>a</sup>	Fogel and Hameka <sup>b</sup>	Hall and Hameka <sup>c</sup>	Langhoff <sup>d</sup>	
90			0.009	-0.011	
120	0.091		0.143	0.054	
135			0.075	0.066	0.023
150	0.027		0.073	0.082	
180	0.027	0.1128		0.113	0.0245

<sup>a</sup> Reference 40. <sup>b</sup> Reference 42. <sup>c</sup> Reference 43 (the two columns correspond to two choices for the required excitation energies). <sup>d</sup> Reference 44.

and  $1,^3B_2$  as well as the two lowest states of  $^1A_1$  symmetry. These states as well as the ground  $^3B_1$  state were represented by large configuration interaction wave functions. The correct spin-orbit operator was used, and all integrals were evaluated. Langhoff's results imply that the spin-orbit contribution to  $D$  is smaller than had been expected and is fairly constant over a wide range of bond angles. In addition he shows that the spin-orbit contribution to  $E$  is negligible for  $CH_2$ .

In Figure 4 we show the result of adding  $D_n^{so} =$

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(43) W. R. Hall and H. F. Hameka, *J. Chem. Phys.*, **58**, 226 (1973).

(44) S. R. Langhoff, personal communication.

0.023  $\text{cm}^{-1}$  to the previously described  $D_n^{\text{ss}}$  curves. When appended by this spin-orbit contribution, the Harrison-Liedtke<sup>37</sup> curve predicts  $D = 0.745 \text{ cm}^{-1}$  at the computed equilibrium angle of  $133^\circ$ , while that of Langhoff and Davidson<sup>14</sup> predicts  $D = 0.807 \text{ cm}^{-1}$  at this same angle. While both estimates are in reasonable agreement with the experimental number,<sup>23</sup>  $0.76 \pm 0.02 \text{ cm}^{-1}$ , it is somewhat disconcerting that the more complete theoretical study of Langhoff and Davidson is outside of the experimental range. Indeed, if we ask what HCH angle the theoretical curves would predict, given the experimental  $D$ , we see that the Harrison-Liedtke curve is consistent with a range of angles from  $145$  to  $135^\circ$  while the Langhoff-Davidson calculation suggests an angle less than  $125^\circ$ . However, given the complexity of both the experimental interpretation and theoretical calculations, mutual agreement, even at the  $\pm 5\%$  level, must be regarded as a satisfying accomplishment.

### Concluding Remarks

While theory and experiment concur on many of

the characteristics of  $\text{CH}_2$ , a few loose ends remain. Most notable is the energy of the  ${}^1\text{B}_1 \leftarrow {}^1\text{A}_1$  0-0 transition. Experiment places this at 20 kcal/mol while a larger separation, perhaps 33 kcal/mol, is suggested theoretically. Also, while an analysis of the spectrum arising from the  ${}^3\text{A}_2 \leftarrow {}^3\text{B}_1$  transition fixes the angle of the  ${}^3\text{B}_1$  state at  $136^\circ$ , it also demands that the  ${}^3\text{A}_2$  state be strongly bent with a bond angle of  $125^\circ$ . The nature of this  ${}^3\text{A}_2$  state has not been characterized theoretically.<sup>45</sup>

That  $\text{CH}_2$  was predicted<sup>3</sup> to be a bent triplet by *ab initio* calculations at least 10 years before it was experimentally substantiated<sup>17,19,20</sup> speaks to both the difficulty of doing the experiments and the reliability of current computational techniques and suggests that similar calculations can play a significant, if not major, role in elucidating the electronic structure of other reactive intermediates.<sup>46</sup>

(45) This problem is being studied in our laboratory by Mr. David Werette.

(46) J. F. Harrison and C. W. Eakers, *J. Amer. Chem. Soc.*, **95**, 3467 (1973).

## Applications of Qualitative Molecular Orbital Theory

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Much information of chemical interest can be obtained from molecular orbital (MO) theory without resort to any calculations at all. Considerations of symmetry properties, nodal surfaces, and atomic orbital (AO) overlaps in MO's have been used quite fruitfully in recent years by Woodward and Hoffmann<sup>1</sup> to elucidate mechanisms of chemical reactions. In this Account I will use similar arguments to predict, understand, or at least rationalize the shapes, *i.e.*, the gross geometrical features, of small polyatomic molecules in both ground and excited states. In some cases these considerations lead naturally to discussions of other properties such as hydrogen bonding, barriers to inversion and rotation, and hydrogen bridging.

In most introductory chemistry textbooks, molecular shapes are explained by an electrostatic model of repulsions among lone pairs and bonding pairs of valence electrons. This valence-shell electron-pair repulsion (VSEPR) model has been summarized at various stages in its development by Sidgwick and

Powell,<sup>2</sup> Gillespie and Nyholm,<sup>3</sup> and Bartell.<sup>4</sup> It has recently been extended by Wolfe<sup>5</sup> to rationalize rotational conformations about single bonds. Schnuelle and Parr<sup>6</sup> have discussed a related qualitative model of molecular shapes based on ideas from crystal field theory.

Molecular orbital theory offers an alternative qualitative model for explaining or rationalizing molecular shapes. It began with the work of Mulliken<sup>7</sup> in the 1930's and '40's. It blossomed in the 1950's when Walsh<sup>8</sup> published a series of papers containing qualitative or empirically deduced MO correlation diagrams showing how orbital energies change with changes in molecular shape. Recent years have seen an increase in interest in MO-based models for molecular shapes. Gavin<sup>9</sup> has discussed some of the qualitative aspects of extended Hückel MO calcula-

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