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GEOMETRY AND SINGLET–TRIPLET ENERGY GAP IN METHYLENE: A CRITICAL REVIEW OF EXPERIMENTAL AND THEORETICAL DETERMINATIONS†

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Abstract—The experimental and theoretical attempts to determine the equilibrium bond angle in the $^3B_1$ ground state and the $^1A_1$–$^3B_1$ energy gap between the lowest two states of the methylene molecule are reviewed. Misinterpretations of experimental data and inadequate theoretical treatments have caused discrepancies in both these quantities. The errors in the experimental and theoretical determinations are discussed. The best experimental and theoretical values now available are seen to be in substantial agreement.

I. INTRODUCTION

A study of the various experimental and theoretical determinations of the properties of the methylene molecule provides an interesting case history for the interaction between theory and experiment and for the problems which can be encountered in the interpretation of both experimental and theoretical results. It provides examples of the effects of incorrect conclusions on the interpretation of subsequent work and of the stimulating effects of controversy in promoting further research. And ultimately, it also demonstrates how the synergistic interplay between theory and experiment contributes to the resolution of the discrepancies.

This review focuses primarily on the various determinations of the energy difference between the lowest singlet and triplet states of methylene. It also includes a short discussion of the equilibrium bond angle in the triplet ground state of this molecule. For both of these properties, the initial interpretations of spectroscopic measurements could not be reconciled with other data, either experimental or theoretical, and eventually had to be modified. But because of the highly convincing nature of the measurements and their analyses, these interpretations strongly affected the assumptions and conclusions of at least some subsequent experimental and theoretical studies.

Methylene is, of course, the parent carbene, and its properties are relevant for the understanding of many organic reaction mechanisms.[1–5] Since several excellent reviews on methylene are available,[6–9] we shall not cover the early work in detail, but concentrate on some key papers and on the most recent work. The bond angle of triplet methylene will be discussed briefly in the next section, and the rest of this review will focus on the singlet–triplet energy gap.

II. THE BOND ANGLE IN TRIPLET METHYLENE

The determination of the HCH equilibrium bond angle in the triplet ground state of methylene provided one of the early successes of *ab initio* quantum chemical calculations, and contributed to a re-interpretation of the spectroscopic data.[10–13]

The electronic spectra of methylene have been studied extensively by Herzberg *et al.*[10–13] The triplet absorbs in the vacuum UV, beginning at 141.6 nm and extending in a Rydberg series to an ionization limit at 10.396 eV. The analysis of this absorption presents some problems. The structure of the 141.6 nm band of CD_2 is consistent with a linear molecule $\Sigma_u^- \leftarrow \Sigma_g^-$ transition. It is also consistent with a $K' = 0 \leftarrow K'' = 0$ subband of a bent molecule, but in that case other subbands would also be expected, and these are not observed; however, if predissociation were involved, it could cause extensive broadening of the other subbands and their effective disappearance from the spectrum. On the other hand, if the molecule is assumed to be linear, then there is a small discrepancy in the bond lengths determined from the B values (related to the moments of inertia) of the CD_2 and CHD ground states. Herzberg and co-workers adopted the linear interpretation in their early papers,[10–12] though they conceded that a bent structure with a bond angle as low as 140° was possible.

Early *ab initio* calculations of the electronic structure of methylene by Padgett and Krauss[14] and by Foster and Boys[15] predicted a bent equilibrium structure for the triplet state (120° and 129°, respectively), but were not taken very seriously at the time, in the face of the accepted interpretation of the spectroscopic data. In fact, several subsequent analyses and semiempirical treatments concurred with the linear structure,[16–21] while other theoretical studies simply assumed it (see Ref. 9 for additional refs). There were some exceptions, including a very early semiempirical treatment by Niira and Oohata[22] (who obtained an angle of about 140°), as well as CNDO and INDO calculations by Pople and co-workers[23,24] (141° and 132°, respectively). Harrison and Allen,[25] in *ab initio* valence bond calculations, obtained an angle of 138°, but concluded that since the bending potential curve was rather flat, the results could still be consistent with the linear or nearly linear structure deduced by Herzberg. Bender and Schaefer[26] were the first to insist, on the basis of extensive *ab initio* configuration interaction calculations which produced an angle of 135°, that ground-state methylene must indeed be bent.

This assertion soon got support from the results of low-temperature electron paramagnetic resonance

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studies of triplet methylene trapped in xenon matrices by Bernheim *et al.*[27] and by Wasserman *et al.*[28,29] Both these studies determined the zero-field splitting parameters D and E, and obtained a nonzero value of E, indicating a nonlinear structure. Bernheim *et al.* initially interpreted their result as indicating that methylene is "slightly bent", but Wasserman *et al.*, on the basis of measurements on CHD and CD_2, as well as CH_2, determined a bond angle of 136°, in good agreement with the theoretical predictions. While the structure of methylene in the solid matrix could conceivably be different from its gas phase structure, the accumulating evidence and theoretical results led Herzberg and Johns[13] to reinterpret the VUV spectrum in terms of a bent structure, with a bond angle of about 136°. Additional support for this interpretation came from measurements[30,31] of ^{13}C hyperfine interactions in xenon-trapped CD_2, and from many subsequent theoretical calculations. The most extensive theoretical calculations (to be discussed below) produce bond angles between 132° and 133°, while the latest spectroscopic data has been analyzed by Bunker and Jensen[32] to give an angle of $133.84 \pm 0.05°$. The likeliest explanation for the lack of higher-K subbands in the VUV spectrum is still Herzberg's original predissociation broadening conjecture.[11,13]

While the equilibrium geometry of ground-state methylene is undoubtedly bent, it should be noted that the barrier to linearity is quite small, and the molecule is properly described as quasilinear. Bunker and Jensen[32] obtained a value of 1940 ± 80 cm^{-1} ($= 5.55 \pm 0.23$ kcal/mol) for the barrier, with only two vibrational levels (v = 0, 1) below the barrier (see below, Fig. 2).

III. EXPERIMENTAL DETERMINATIONS OF THE SINGLET-TRIPLET ENERGY GAP

The principal experimental determinations of the singlet–triplet energy difference in methylene are summarized in Table 1. Most of these experiments are photochemical, involving *in situ* preparation of methylene by the photolysis of a precursor (ketene, diazomethane, diazirine, etc.), followed by detection of the reaction products with various hydrocarbons[33–41,43–45] or detection of the singlet by laser-induced fluorescence.[46–48] Two are more direct spectroscopic measurements,[42,50] and it was the surprising result of one of these, the laser photodetachment photoelectron spectroscopy of CH_2^- by Lineberger and co-workers,[42] which stimulated much of the subsequent theoretical and experimental work trying to resolve the discrepancy with previous results. At present the singlet–triplet gap can be considered to have been determined with considerable accuracy in the laser magnetic resonance spectroscopy measurements of perturbations and direct transitions between the singlet and triplet manifolds by McKellar *et al.*[50] Remaining to be fully resolved are the reasons for certain characteristics of the photodetachment results which led to their misinterpretation, as discussed further below.

The various experiments can also be classified

Table 1. Experimental determinations of the singlet–triplet energy gap in methylene

Year	Authors	Ref.	Method[a]	T_0 (kcal/mol)[b]
1967	Halberstadt and McNesby	33	RRKM(Ph)	~2.5
1968	Rowland, McKnight and Lee	34	RRKM(Ph)	9
1970	Carr, Eder and Topor	35	Eq(Ph)	1–2
1971	Hase, Phillips and Simons	36	Th(Ph)	~9
1972	Frey	37	Eq(Ph)	~8
1975	Frey and Kennedy	38	Eq(Ph)	9.1
	Kelley and Hase	39	Th(Ph)	9
	Simons *et al.*	40	RRKM(Ph)	9 ± 3
1976	Simons and Curry	41	Th(Ph)	8.3 ± 1.0
	Lineberger and co-workers	42	Sp(PES)	19.5 ± 0.7
	Lahmani	43	Eq(Ph)	7.5 ± 0.7
1977	Frey and Kennedy	44	Eq(Ph)	8.7 ± 0.8
	Hase and Kelley	45	Th(Ph)	(~20)
1978	Lengel and Zare	46	Th(Ph, LIF)	$\leqslant 8.1 \pm 0.8$
	Welge and co-workers	47, 48[c]	Th(Ph, LIF)	$\leqslant 9.8 \pm 1.5$
1982	Lee and co-workers	49	KE(Ph)	8.5 ± 0.7
1983	McKeller *et al.*	50	Sp(LMR)	9.05 ± 0.06

[a] Key for methods:
RRKM = determination of excess energy of singlet methylene by RRKM analysis of reaction product decomposition;
Eq = determination of equilibrium concentration of singlet and triplet methylene;
Th = determination of photolysis energy thresholds for singlet and triplet methylene (or for singlet only);
Sp = spectroscopic experiment;
KE = recoil kinetic energy measurement of photolysis fragments;
Ph = photochemical experiment;
PES = photoelectron spectroscopy;
LIF = laser induced fluorescence;
LMR = laser magnetic resonance spectroscopy.

[b] Energy difference ($^1E_0 - {}^3E_0$) between the ground vibrational levels of the singlet and triplet states.

[c] Reference 47 obtained $T_0 = 6.3 \pm 0.8$ kcal/mol, due to the neglect of the internal energy of the ketene precursor.[46]

according to the type of quantity being measured. Some try to determine the threshold energies for the formation of the singlet and the triplet from the same precursor,[36,39,41,45] or at least obtain the threshold for the singlet for comparison with heat of formation data for the triplet.[46–48] Others measure the equilibrium between the singlet and the triplet under conditions which promote rapid interconversion.[35,37,38,43,44] Several attempt to determine the excess energy of the photochemically produced singlet by RRKM analysis of the decomposition of its reaction products.[33,34,40]

Some of the representative experiments are discussed in more detail below, following a brief summary of the relevant properties of the two forms of methylene.

Reactions of methylene

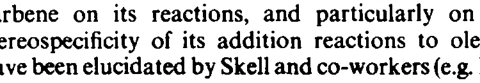
Singlet and triplet carbenes can be readily distinguished by their reaction products with other hydrocarbons.[1–5] The effects of the spin state of a carbene on its reactions, and particularly on the stereospecificity of its addition reactions to olefins, have been elucidated by Skell and co-workers (e.g. Refs 51–53). The singlet is very highly reactive, allowing its detection even in a large excess of the triplet species. The latter is singularly unreactive for a biradical,[54,55] except perhaps in some addition reactions with unsaturated hydrocarbons.[56] In reactions with saturated hydrocarbons, singlet methylene inserts,

$$^1CH_2 + RH \rightarrow RCH_3, \qquad (1)$$

while the triplet abstracts a H-atom,

$$^3CH_2 + RH \rightarrow CH_3^{\cdot} + R^{\cdot}. \qquad (2)$$

Perhaps the most interesting difference between the two species is their addition reaction to unsaturated hydrocarbons.[51–53] Both add across a double or triple bond, forming a cyclic product, but while the reaction of the singlet with olefins is stereospecific, that of the triplet is not. For example, the addition reaction of methylene with butene-2 results in dimethylcyclopropane (DMC),



$$CH_2 + CH_3CH{=}CHCH_3 \rightarrow CH_3\underset{\diagdown\,\diagup \atop CH_2}{CHCH}CH_3. \qquad (3)$$

In the case of the singlet, if *cis*-butene-2 is used, only the *cis* form of DMC is obtained[41,52] (together with the insertion products[44] 2-methylbutene-2 and pentene-2), while for the triplet both *cis* and *trans* DMC would be formed in equal amounts[41,52] (together with abstraction products[44]).

This difference in stereospecificity has been explained by Skell and co-workers[51–53] in terms of the spin coupling of the electrons involved in the reaction.[8] The antiparallel-spin lone-pair electrons of the singlet can recouple directly with the antiparallel-spin pair of electrons in the π-bond of the olefin, to form two new bonds in a concerted reaction without change in the steric structure. The two parallel-spin electrons of the triplet biradical, on the other hand, cannot recouple simultaneously with both antiparallel-spin π-bond electrons (since three of these four electrons would have their spins parallel). This results in a step-wise mechanism in which one bond is first formed between methylene and the olefin, producing a triplet intermediate, followed by a spin flip before the ring can close. In the interval between these steps there is essentially free rotation around the remaining σ bond of the olefin, resulting in complete scrambling of the steric structure. While this mechanism has not been entirely supported by theoretical studies,[57–60] it provides a simple explanation for the observed behavior.

Singlet and triplet methylene interconvert readily in the presence of a sufficient pressure of inert gases,[43,61,62] leading to an equilibrium mixture of the two forms, unless triplet scavengers, such as oxygen, are present.[43] In high enough concentration of transient species, the triplet can also disappear in the bimolecular reaction[43,61]

$$^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + H_2. \qquad (4)$$

Photochemical threshold experiments

As a representative experiment which determines the thresholds for the photochemical production of singlet and triplet methylene by analysis of their reaction products, we shall consider the work of Simons and Curry.[41] They photolyzed ketene by light from a high pressure xenon lamp passed through a monochromator. The threshold for the production of triplet methylene was determined by measuring the wavelength dependence of the quantum yield of CO produced in the decomposition of the ketene, while the singlet threshold was determined by reacting the methylene with an excess of *cis*-butene-2 and following the *cis*-DMC to *trans*-DMC ratio (measured by gas chromatography) as a function of wavelength. At wavelengths greater than about 340 nm that ratio was close to one, while at shorter wavelengths the ratio increased linearly with decreasing wavelength, due to the stereospecificity of the reaction of the singlet produced at the higher photon energies. The analysis of the data produced heats of formation $\Delta H^0_{f,298}$ of 99.0 $\pm$ 0.6 and 90.7 $\pm$ 1.0 kcal/mol for the singlet and triplet, respectively (ignoring the contribution of the internal energy of the ketene[46]), leading to an energy gap of 8.3 $\pm$ 1 kcal/mol.

Another threshold experiment by Kelley and Hase[39] was analyzed to yield an energy gap of 9 kcal/mol, but a later experiment by Hase and Kelley,[45] following the CH_2^- photoelectron spectroscopy work of Lineberger and co-workers,[42] was interpreted to yield a singlet–triplet gap of about 20 kcal/mol. As stated by the authors,[45] this interpretation (which involved ketene excimer formation to obtain two pathways for photolysis at 366 nm and to account for the nonlinearity of the Stern–Volmer CO plots) was strongly influenced by the "most credible" spectroscopic results of Lineberger and co-workers. This interpretation was challenged by Carr[63,64] (see also Lengel and Zare[46]).

Photochemical equilibrium experiments

As an example of the measurements of the equilibrium ratio of singlet and triplet concentrations, we shall consider the experiment of Lahmani.[43] She confirmed the reversibility of the interconversion by approaching the equilibrium from both directions. Direct photolysis of diazirine (cyclic CH_2N_2) at 315 nm produced singlet methylene, which was converted to an equilibrium mixture by collisions with up to 1000 Torr of SF_6. Triplet methylene was produced almost exclusively in photolysis experiments involving sensitization with triplet pyrazine or benzene. In either case, propane was included in the reaction mixture, and the relative concentrations of singlet and triplet methylene were determined by analyzing the resulting ratio of isobutane to n-butane. This ratio is 0.4 for the singlet, which reacts by insertion, and 4.0 for the triplet, which produces abstraction followed by radical recombination and disproportionation. Lahmani's result for the energy gap was 7.5 ± 0.7 kcal/mol.

Several equilibrium experiments were conducted by Frey and Kennedy,[37,38,44] yielding energy gaps between 8 and 9.1 kcal/mol. The latest of these[44] appeared after the publication of the CH_2^- photoelectron spectroscopy work,[42] but these authors maintained the validity of their own result, 8.7 ± 0.8 kcal/mol.

Photoelectron spectroscopy of CH_2^- *ions*

The question of the singlet–triplet energy gap in methylene was reopened in 1976 by the results of the laser photodetachment photoelectron spectroscopy of CH_2^- ions by Lineberger and co-workers.[42] Their experiment was ingenious in its directness, and its unexpected results stimulated a considerable amount of new work, both experimental and theoretical.

The experiment involved crossing a mass-selected CH_2^- ion beam with an argon ion laser (with a photon energy of 2.540 eV = 58.58 kcal/mol), and measuring the kinetic energy of the ejected electron. The process is

$$CH_2^- + h\nu \rightarrow CH_2 + e^- + \text{k.e.}, \qquad (5)$$

where k.e. represents the kinetic energy of the ejected electron. The internal energy difference between the negative ion and the neutral is then given by

$$E(CH_2) - E(CH_2^-) = h\nu - \text{k.e.} \qquad (6)$$

If all the CH_2^- ions are in the same internal energy level, each peak in the photoelectron spectrum would correspond to one of the internal energy levels of the CH_2 produced, thus allowing the direct determination of the energy differences between these levels. Ideally, there would be a single peak for each of the singlet and triplet electronic states, allowing unambiguous interpretation of the results. However, this picture is complicated by vibrational structure (rotational structure is not resolved in the PES), requiring identification of the vibrational levels, and particularly of the 0–0 transition.

The bond lengths in CH_2^- and in singlet and triplet CH_2 differ by no more than 0.05 Å (based on spectroscopic data[12,32] and theoretical calculations[65,66]), so stretching vibrations are not excited in the CH_2^- photodetachment. On the other hand, the bond angle of the triplet, 133.8°,[32] is quite different from that of the singlet, 102°,[12] and the ion, 103°,[65,66] which should produce a bending vibrational progression in the photoelectron spectrum for triplet formation, but only a single (0–0) peak for singlet. The actual spectrum[42] is reproduced in Fig. 1. The very strong central peak at an electron kinetic energy of 1.47 eV (peak G) has been identified as due to the singlet, while the partially resolved progression from about 2.32 eV to 1.61 eV (A–F) has been assigned to the triplet bending vibration.

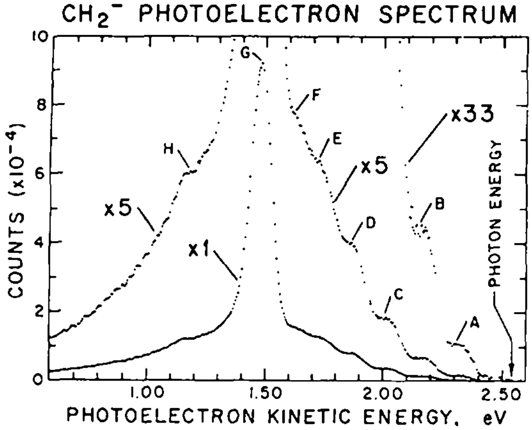


Fig. 1. The photoelectron spectrum of CH_2^-. Reprinted with permission from P. F. Zittel *et al.*, *J. Am. Chem. Soc.* **98**, 3731 (1976). Copyright (1976) American Chemical Society.

The principal problem in the interpretation of this spectrum is the identification of the 0–0 transition, connecting the zero-point vibrational levels of the CH_2^- ion and the triplet. If all the negative ions in the beam are in the ground vibrational level, then the lowest triplet energy obtained, corresponding to the highest electron kinetic energy (Eq. (6)), peak A, is likely to represent the 0–0 transition. This would yield a singlet–triplet energy gap T_0 (between the ground vibrational levels of the two species) of 0.845 eV (peak A minus peak G), or 19.5 kcal/mol. Two possibilities may modify this interpretation and shift the assigned position of the 0–0 transition in opposite directions. First, it is conceivable that the 0–0 transition peak should be to the right (higher kinetic energy side) of peak A, and is too weak to be observed. In that case the singlet–triplet gap would be even greater than 19.5 kcal/mol. Second, vibrationally excited CH_2^- ions may be present in the beam, and may produce "hot bands" on the high kinetic energy side of the spectrum, in which case the true 0–0 peak may be one of the peaks to the left of peak A, and the true singlet–triplet energy gap may be smaller.

Normally, hot bands can be identified by their sensitivity to source conditions, such as changes in the precursors or in the type of ion source or in the ion extraction voltage, which lead to changes in the internal energy distribution of the ions.[67] Also, examination of isotope shifts upon deuteration often helps in the vibrational assignment.[68] However, the CD_2^- photoelectron spectrum is rather poorly resolved[68] and the identification of its "peaks" (hardly discernible shoulders, in fact) with the corresponding peaks in the CH_2^- spectrum is far from unambiguous. Extensive variations in source conditions and precursors produced no significant changes in the PES spectrum,[42,68] leading Lineberger and co-workers to conclude that no hot bands were present.[42,68] This and a particular interpretation of the unresolved CD_2^- spectrum led them to assign peak A to the 0–0 transition and to conclude[42] that the singlet–triplet energy gap is 19.5 ± 0.7 kcal/mol.

In spite of the questions concerning the assignment of the 0–0 peak for triplet formation, the CH_2^- PES experiment was seen as the first *direct* determination of the singlet–triplet gap, and found to be very convincing by many researchers (e.g. Refs. 45, 69–73). The discrepancy between the result of 19.5 kcal/mol and the previously accepted value of 8–9 kcal/mol (Table 1) stimulated considerable discussion and much new work. At least two symposia (at the University of Colorado in Boulder in June 1978 and at the American

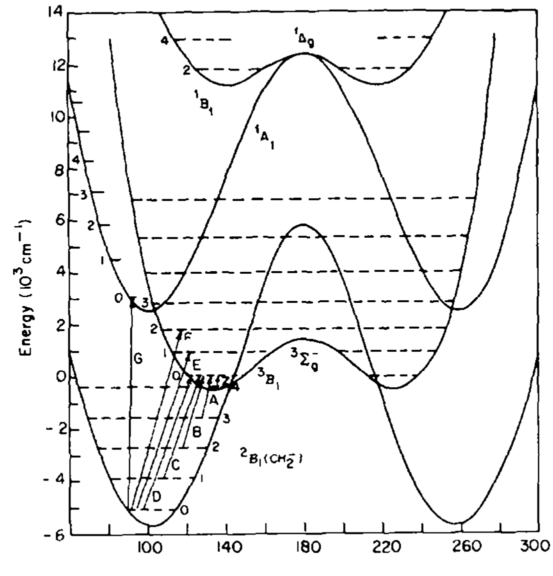


Fig. 2. Bending potential curves for CH_2 ($^3B_1$, $^1A_1$, $^1B_1$) and CH_2^- ($^2B_1$), based on data from Refs. 32, 50, 74, 75, 104, 105. The arrows show the proposed assignment of the transitions in the photoelectron spectrum of Fig. 1 (see Ref. 68 for transition Z). The vibrational numbering shown for $^1B_1$ is the linear molecule numbering used in Refs. 12, 104, 105. Bent molecule numbering is shown for all other states.

Chemical Society National Meeting in Miami Beach in September 1978) were devoted to a discussion of this question.

The latest spectroscopic data[50] unambiguously assigns the value of 9.05 ± 0.06 kcal/mol to the singlet–triplet gap. This would correspond to an assignment of peak D in the PES spectrum (at about 1.87 eV) as the 0–0 transition and implies that peaks A, B, and C are hot bands. There is no confirmed explanation for the insensitivity of these presumed hot bands to source conditions, though there is a theoretically based explanation[66] for the existence of exactly three hot bands in the spectrum. Theoretical calculations on the negative ion,[66] adjusted for the assumed errors in the calculated relative positions of the neutral and negative ion potential surfaces,[66,74] indicate that the fifth ($v = 4$) bending vibrational level of CH_2^- lies above the ground vibrational state of the triplet. This and higher vibrational levels of the ion would thus be unstable and would autodetach. Only three excited bending vibrational levels ($v = 1, 2, 3$) could thus be present in the CH_2^- beam, leading to three hot bands. More recent data[74,75] (Fig. 2) indicates that the $v = 4$ level of CH_2^- may actually lie just below the ground vibrational state of the triplet, producing a very weak fourth hot band (peak Z) seen in later PES studies.[68]

The original interpretation of the CH_2^- PES spectrum[42] requires an electron affinity value of 0.21 eV for triplet CH_2. Recent extensive *ab initio* calculations of the electron affinity by Davidson and co-workers[76] make it appear very unlikely that the electron affinity is as low as 0.21 eV, and indicate a value of 0.63 eV (after corrections based on similar electron affinity calculations on C and O atoms). This result is also in agreement with the assignment of peak D as the 0–0 transition. The assignment of the A, B, C peaks, with a spacing of about 0.15 eV (1200 cm^{-1}), to the bending progression of the triplet is also contradicted by the recent finding by Sears *et al.*[74,77] (using laser magnetic resonance spectroscopy) that the bending potential is rather anharmonic, with irregular level spacing and a fundamental bending frequency of only 963.1 cm^{-1}. A theoretical simulation of the CH_2^- photoelectron spectrum by Sears and Bunker,[75] based on spectroscopic data for the neutral and a theoretical potential surface for the ion,[66] succeeded in reproducing the observed spectrum when a singlet–triplet gap of 9.3 ± 0.6 kcal/mol and a negative ion beam temperature of 2500 K were assumed. They also discussed possible explanations for the insensitivity of the hot bands to source conditions. They suggested that the negative ions could be formed preferentially in an excited electronic state, possibly $^2A_1$, from which they decayed to a characteristic Franck–Condon vibrational population distribution of the ground state regardless of the original ion formation temperature. Alternatively, the negative ions could initially be formed with a high population of vibrationally excited levels, but the highly excited ions fragmented before reaching the photodetachment region (this is similar to the Harding and Goddard explanation,[66] except that those authors assumed autodetachment rather than fragmentation).

Singlet threshold by laser-induced fluorescence

Among the new studies stimulated by the questions raised by the CH_2^- PES results were the experiments of Lengel and Zare[46] and of Welge and co-workers,[47,48] designed to determine an upper limit on the heat of formation of singlet methylene with the help of laser-induced fluorescence. These experiments were fairly similar, and we shall discuss the Lengel and Zare study[46] here.

Ketene vapor in a fast flow system was photolyzed by light from a nitrogen laser (337.1 nm, equivalent to 84.82 kcal/mol), and the singlet methylene produced was monitored by laser-induced fluorescence using a tunable dye laser to excite specific lines of the $^1B_1 \leftarrow {}^1A_1$ "red bands" transition which had been analysed by Herzberg and Johns.[12] This method of detection allowed the identification of the vibration–rotation states of the singlet methylene being produced, and thus made it possible to account for the internal energy of the methylene. A fluorescence threshold was found for the $J = 4$ rotational state of the (0, 0, 0) ground vibrational state of $CH_2(^1A_1)$. The threshold for the formation of singlet methylene in the (0, 0, 0) state was also confirmed by using a tunable, frequency doubled dye pump laser instead of the nitrogen laser. The contribution of ketene internal energy to the dissociation process was also determined (this was overlooked in the first of the papers by Welge and co-workers[47]), by following the fluorescence intensity as a function of ketene temperature. The energy difference between the ground vibration–rotation states of ketene and the photolysis products ($CH_2 + CO$) was then determined on the assumption that there was no CO internal energy or product recoil energy at threshold. To the extent that this last assumption may not have been entirely valid, the value obtained for the singlet heat of formation (using known heat of formation data for ketene and CO), and thus for the singlet–triplet gap, must be considered an upper bound. However, it is unlikely that this overestimation would be significant.[46]

The heat of formation deduced by Lengel and Zare was[46]

$$\Delta H^0_{f,0}(CH_2, {}^1A_1) = 101.7 \pm 0.5 \text{ kcal/mol.} \quad (7)$$

This compares with 101.9 ± 0.5 deduced by Welge and co-workers,[48] and 101.1 ± 1.0 obtained from the threshold photochemical experiment of Simons and Curry[41] after correction for the internal energy of the ketene.[46]

The heat of formation of triplet methylene has been determined[78–80] by measuring the appearance potential of CH_2^+ ions from various precursors and comparing with the known $^3CH_2$ ionization energy[13] and the precursor heat of formation. A value of 92.8 ± 1.0 kcal/mol can also be deduced from the Simons and Curry[41] threshold data after correction for ketene internal energy.[46] Based on the various sources, Lengel and Zare adopted the value

$$\Delta H^0_{f,0}(CH_2, {}^3B_1) = 93.6 \pm 0.6 \text{ kcal/mol,} \quad (8)$$

compared to 92.1 ± 1.0 used by Welge and co-workers.[48] Comparing Eqs (7) and (8), we find a singlet–triplet gap (or an upper bound for it) of 8.1 ± 0.8 kcal/mol, compared to 9.8 ± 1.5 deduced by Welge.[48]

Recoil kinetic energy of photolysis fragments

Another interesting experiment stimulated by the methylene uncertainty was that of Lee and co-workers,[49] who measured fragment recoil velocities from ketene photodissociation in a molecular beam. Unfortunately, it was not possible to obtain sufficient concentrations of both singlet and triplet methylene at a single photolysis wavelength, so two separate experiments had to be carried out, at two different wavelengths, to determine the fragment velocities for singlet and triplet dissociation. Otherwise the two experiments were identical, eliminating various factors which could introduce uncertainties into the interpretation.

The ketene in the molecular beam (which is cooled in the expansion, so that no significant internal energy contributions remain) is crossed with either an XeF (351 nm) or XeCl (308 nm) excimer laser. The dissociation product velocities at various laboratory angles are determined by time of flight to a detector, passing through an ionizer and a quadrupole mass selector. The maximum product velocities observed are assumed to correspond to the production of ground vibration–rotation states of CH_2 and CO.

The analysis of the results produced heats of formation $\Delta H^0_{f,0}$ of 102.6 and 94.1 kcal/mol for singlet and triplet methylene, respectively, and a singlet–triplet gap of 8.5 ± 0.8 kcal/mol.

Direct spectroscopic determination of the singlet–triplet gap

Finally, we shall consider the direct spectroscopic determination of the singlet–triplet energy gap by McKellar *et al.*[50] This employed laser magnetic resonance spectroscopy, in which Zeeman modulation of far-IR laser spectra is used to observe perturbations and even direct transitions between the singlet and triplet manifolds. The spin-orbit coupling interaction responsible for the perturbations was studied with the help of extensive *ab initio* calculations, and the identification of the perturbing levels was facilitated by the use of the nonrigid bender Hamiltonian analysis of the triplet potential surface.[81]

The value obtained[50] for the singlet–triplet energy gap was

$$T_0 = 3165 \pm 20 \text{ cm}^{-1} = 9.05 \pm 0.06 \text{ kcal/mol.} \quad (9)$$

The quoted uncertainty represents an estimate of the possible errors in extrapolating the triplet rotation–bending levels from the perturbing levels (involving mostly $v_2 = 3$) down to the ground level. This result must be considered the most reliable and most accurate value at present for the singlet–triplet energy gap in methylene.

McKellar *et al.*[50] also estimated the zero-point vibrational contributions to the singlet–triplet gap, in order to determine T_e, the energy difference between the equilibrium geometries (potential energy surface minima) of the singlet and triplet. This quantity is the one most directly comparable with results of theoretical calculations of the energy difference. The determination of T_e is complicated by the absence of sufficient experimental data on the stretching vibrations. McKellar *et al.* used their data for the bending vibrations, which give zero-point energies of 670 and 499 cm^{-1} for the singlet and triplet, respectively, and assumed that the stretching contributions are very similar in both states and thus do not contribute to the difference. This resulted in[50] $T_e = 8.56 \pm 0.09$ kcal/mol. Actually, *ab initio* calculations[82,83] and new experimental data[84] indicate that the zero-point energy difference for the stretching vibrations is at least as large as, and opposite in sign to, the bending difference. Based on the gradient configuration interaction calculations of Osamura *et al.*,[83] the stretching zero-point energy difference (ignoring anharmonicity effects) is 293 cm^{-1} (triplet greater than singlet), giving a total zero-point contribution of 122 cm^{-1}, or 0.35 kcal/mol. Moore and co-workers[84] have recently determined the fundamental stretching frequencies of the singlet as $\nu_1 = 2805.9$ cm^{-1} and $\nu_3 = 2864.5$ cm^{-1}. The corresponding values for the triplet have been estimated by Bunker and Jensen[32] as 2950 ± 40 and 3080 ± 40 cm^{-1}, respectively. In the absence of sufficient data for anharmonicity corrections, using just half the difference in $\nu_1 + \nu_3$ for the two species, we obtain a stretching contribution to the zero-point energy difference of 180 ± 60 cm^{-1}, and a total zero-point difference of 10 ± 60 cm^{-1}, or 0.03 ± 0.17 kcal/mol. This leads to

$$T_e = 9.08 \pm 0.18 \text{ kcal/mol} \quad (10)$$

as the best current estimate of the equilibrium geometry singlet–triplet energy difference in methylene.

IV. THEORETICAL DETERMINATION OF THE SINGLET–TRIPLET ENERGY GAP

When faced with a discrepancy of 10 kcal/mol between experimental determinations of an energy difference in a molecule as small as methylene, it would seem natural to turn to theoretical calculations for a resolution. Unfortunately, the range of reported results for the singlet–triplet gap from quantum mechanical calculations of various types is substantially greater than the range of experimentally derived values, extending from near zero[14,19] to more than 50 kcal/mol.[85] It should not be surprising, then, that computational quantum chemistry has faced a credibility problem. However, the problem is at least partially due to a lack of discrimination between different levels and types of theoretical treatments.

Quantum mechanical calculations of molecular properties are carried out at many levels and for a variety of reasons. Many are designed to test variations in methodology, rather than to obtain useful information about specific molecules (why else would there be so many calculations on a few well-known small molecules?). Many others are qualitative in nature and intended primarily for interpretive rather than predictive purposes. But also, because of the great difficulty of high-quality quantum calculations even for small molecules, many are carried out at a level which is quite inadequate for the questions they are intended to answer. It will be shown here that if the various calculations are properly classified according to the adequacy of their treatment, a very definite theoretical conclusion emerges, favoring a value of about 10 kcal/mol for the singlet–triplet gap, and definitely ruling out a value around 20 kcal/mol.

Among the various reviews of previous theoretical work on methylene,[6–9] the detailed review of Gaspar and Hammond[8] covers practically all papers on the subject published until the end of 1972 (and two more for 1973–1974). The reviews by Borden and Davidson[9] update the record of *ab initio* calculations to about 1981. Here we shall not review all the earlier papers individually again, but focus on classes of calculations and on selected and recent papers. This will be preceded by a brief discussion of the electronic structure of the molecule.

The electronic structure of methylene

Excellent discussions of the electronic structure of the methylene molecule have been given by Harrison[6] and by Gaspar and Hammond.[8] Only the principal features needed for the subsequent discussion of the calculations will be described here.

For an understanding of the electronic structure of both singlet and triplet methylene, it is useful to compare the linear and bent forms of the molecule. The carbon atomic orbitals contributing to each of the molecular orbitals in the two forms are shown in Table 2. Also indicated are the hybridizations appropriate for the valence bond descriptions of the linear and 120° bent forms. The hydrogen atomic orbitals contribute to the bonding MOs, which are $2\sigma_g$ and $1\sigma_u$ in the linear case and the corresponding $2a_1$ and $1b_2$ in the bent case. The two π orbitals of the linear molecule and $1b_1$ in the bent case are nonbonding. The $3a_1$ MO of the bent molecule, which has minor contributions form the hydrogen AOs, is primarily nonbonding. Diagrammatic representations of the MOs can be found in Refs 6 and 8.

Table 2. Contributions of carbon atomic orbitals to the methylene molecular orbitals for linear and bent configurations[a]

Linear			Bent		
MO	AO	hyb.	MO	AO	hyb.
$1\sigma_g$	1s		$1a_1$	1s	
$2\sigma_g$	2s	sp	$2a_1$	$2s+2p_z$	sp^2
$1\sigma_u$	$2p_y$		$1b_2$	$2p_y$	
$1\pi_u$	$2p_z$		$3a_1$	$2s-2p_z$	
	$2p_x$		$1b_1$	$2p_x$	

[a] An unconventional choice of axes for the linear configuration is made in order to facilitate comparison with the bent case. The hybridizations appropriate for valence bond structures in the linear and 120° bond angle forms are indicated in the columns marked "hyb."

Table 3. Correlation diagram for the electronic states of methylene[a]

Linear		Bent	
State	Configuration	State	Configuration
$^3\Sigma_g^-$	$^3(\pi_y\pi_z)$	$^3B_1$	$^3(3a_1 1b_1)$
$^1\Delta_g$	$\pi_y^2-\pi_z^2$	$^1A_1$	$3a_1^2-\lambda 1b_1^2$
	$^1(\pi_y\pi_z)$	$^1B_1$	$^1(3a_1 1b_1)$
$^1\Sigma_g^+$	$\pi_y^2+\pi_z^2$	$^1A_1^*$	$1b_1^2+\lambda 3a_1^2$

[a] See Harrison.[7] The axes for the orbitals are those of Table 2. Only the uppermost two (nonbonding) orbitals are shown. The coefficient λ is small. The states are arranged in order of increasing energy, with the ground state at the top.

In all the low-lying electronic states of the molecule, six of the eight electrons fill the inner-shell and two bonding orbitals, leaving two electrons to divide between the remaining nonbonding orbitals. The different electron configurations that can be obtained for these two electrons in the linear and bent geometries, and the resulting electronic states, are shown in Table 3. The two nonbonding (π) MOs are degenerate in the linear case, leading to the triplet-coupled $\pi_y\pi_z$ configuration and a $^3\Sigma_g^-$ state as the ground state in this case. As the molecule is bent, the π_z orbital becomes $3a_1$, acquires some 2s character, and is stabilized. This favors the $3a_1^2$ configuration, and results in a reduction in energy for the $^1A_1$ state (and increase for the excited $^1A_1^*$), reaching a minimum for a bond angle of 102.4°.[12] The structure of the bent singlet is then similar to that of the water molecule, except that there is only one (σ) lone pair instead of two (σ and π). The B_1 states, both singlet and triplet, also decrease in energy upon bending, but to a much lesser extent, reaching a minimum at 133.8° for the triplet,[32] and a shallower minimum[66,86,87] at about 140° for the singlet.[12,65,66,70,88] A plot of the bending potential curves of these states (and of the ground $^2B_1$ state of CH_2^-) is shown in Fig. 2.

As shown in Table 3, the $^3B_1$ ground state is characterized principally by a single-term wave function (single determinant) at all bending angles. A single-configuration SCF wave function should therefore provide a reasonable zero-order description of this state, and a single-reference configuration interaction calculation which includes all single and double excitations (SD–CI) relative to the SCF configuration can be expected to be reasonably reliable. The $^1A_1$ state, on the other hand, requires a two-term zero-order description at 180°, and while the contribution of the $1b_1^2$ term decreases from 50% at 180° to as little as 2% at 100°,[89] it still is important enough at the equilibrium angle to have a very significant effect on the computed singlet–triplet energy gap. Similarly, for CI calculations to provide a balanced treatment for $^3B_1$ and $^1A_1$, a two-reference treatment (2R–CI), in which all single and double excitations relative to *two* configurations are included for the singlet (but not for the triplet) is required. This particular characteristic of the singlet state was recognized in the relatively early work of Harrison and Allen,[25] and was taken into account in the calculations of O'Neil *et al.*[90] and in most subsequent treatments. The neglect of this requirement is likely to affect the results of perturbation theory (Møller–Plesset)[69] and certain types of semiempirical calculations, as well as SD–CI.

Before proceeding to a survey of the computational results, it is important to note again that the most direct results of the theoretical calculations give T_e, the energy difference between the potential surface minima of the singlet and triplet states, rather than T_0 (the energy difference between the ground vibrational states). As noted previously, the contribution of zero-point vibrational energy is estimated at

$$T_e - T_0 = 0.03 \pm 0.17 \text{ kcal/mol.} \qquad (11)$$

There has also been some discussion of the possible role of relativistic corrections,[91] but recent calculations[92,93] indicate that their contribution to the singlet–triplet gap is only 0.04 kcal/mol, increasing the estimated difference between the computed non-relativistic value T_e^{nr} and the measured T_0 to about 0.07 kcal/mol, so that we estimate

$$T_e^{nr} = 9.12 \pm 0.20 \text{ kcal/mol.} \qquad (12)$$

Semiempirical results

A list of the most important semiempirical calculations of the singlet–triplet gap (not including qualitative speculations and rough estimates) is given in Table 4. It is seen that two of these treatments, the semiempirical valence bond/atoms-in-molecules approach of Jordan and Longuet-Higgins[16] and the MINDO/3 calculations of Dewar *et al.*,[94] obtained very good results, within about 1 kcal/mol of the estimated T_e^{nr} value of Eq. (12) (but the VB/AIM treatment predicted the triplet to be linear). However, the problem with all of these approaches is that without independent information on the correct value, there is no reliable way to choose between the various results.

Unlike *ab initio* treatments, there is no systematic sequence of improvements available here to establish trends and assess convergence, and thus no guidance for selection of the most reliable prediction. While trends in the errors of semiempirical calculations on sequences of related or similar molecules can be helpful in estimating errors in cases for which independent data are not available, this approach is less useful when dealing with unusual cases, such as radicals, transition states, or nonclassical structures.

Dewar[71] has determined the mean errors for calculations of heats of atomization of 209 compounds by the MINDO/3 and MNDO methods at 15.7 and 7.5 kcal/mol, respectively. Normally one would expect much of the error in heats of atomization to cancel when taking the difference between two states of the same molecule, but of course the individual errors in particular cases may be significantly greater than the mean and can vary erratically. Dewar[71] has answered a symposium discussion question about his results for the singlet–triplet gap in methylene by saying: "By MINDO/3 we find 9 kcal/mol and the MNDO/2 [*sic*] value is about 30 kcal/mol—both are about 10 kcal/mol out from the experimental value." Of course we now know that the correct experimental value is about 10, not 20, so that most of the NDO results, with the notable (and probably accidental) exception of MINDO/3 and INDO/GVB, are off by 5–20 kcal/mol.

Among the other semiempirical methods, extended Hückel theory cannot discriminate between different spin multiplicities of an electronic configuration without *ad hoc* corrections[98] (prior to correction for electron repulsion effects, it predicts the $3a_1^2$ configuration to lie 13 kcal/mol below the $3a_1 1b_1$ configuration[98]). In the CNDO[23] and INDO[24] treatments of Pople *et al.*, no value was reported for the singlet–triplet gap.

All this is not meant to detract from the great usefulness of semiempirical methods for interpretive and, in many cases, predictive and even quantitative value. It does mean, though, that such methods cannot be called upon to resolve a question involving a 10 kcal/mol discrepancy, at least for an unusual species like methylene.

Table 4. Some semiempirical determinations of the singlet–triplet gap

Year	Authors	Ref.	Method[a]	T_e^{nr} (kcal/mol)
1952	Niira and Oohata	22	VB	44
1962	Jordan and Longuet-Higgins	16	VB/AIM	10.4
	Pedley	17	VB	14
	Ellison	18	VB	14.3
1964	Dixon	19	AIM	0–14
1972	Bodor, Dewar and Wasson	58	MINDO/2	28.3
1974	Dewar, Haddon and Weiner	94	MINDO/3	8.7
	Wadt and Goddard	86	INDO/GVB	7.4[b]
1976	Takabe, Takahashi and Fukutome	95	MINDO/2' (UHF)	17
1977	Lee and Li	96	INDO	15.1
1978	Dewar and Rzepa	97	MNDO	25.3

[a] Key for methods:
VB = semiempirical valence bond;
AIM = atoms-in-molecules;
INDO = intermediate neglect of differential overlap;
MINDO = modified INDO;
MNDO = modified neglect of diatomic overlap;
GVB = generalized valence bond.

[b] This is a computed T_0 value.

Ab initio *Calculations*

Representative examples of *ab initio* results for the singlet–triplet gap in methylene, organized according to the types of basis sets and wave functions employed, are collected in Table 5. In this table, the basis sets improve from left to right, and the type of wave function generally improves from top to bottom. Clearly, the energy gap generally diminishes as the calculation is improved in either dimension.

Considering the basis set variation first, it is obvious that no reliable prediction can be obtained from a basis set which does not include polarization functions. The errors for these "unpolarized" basis sets, compared to the corresponding "very large" basis results, range from 7 to 22 kcal/mol. The smallest basis for which useful estimates can be obtained is DZP, with errors of up to 2.4 kcal/mol. The EBP results agree with the VL values to within 0.1–0.8 kcal/mol, and thus can usually be expected to provide "chemical accuracy" (~1 kcal/mol) with the right type of wave function.

The first row of Table 5 gives the SCF results for the gap, and it is seen that these converge to a "Hartree–Fock limit" (infinite basis) value [70,89] near 25 kcal/mol. Again, it is clear that no useful prediction for the singlet–triplet gap can be expected from any single-configuration SCF calculation. (Using "unrestricted" SCF, or UHF, for the open-shell triplet can only increase the computed SCF gap.[69]) The reason for the sizable failure of SCF theory in this case is obvious from the earlier discussion of the electronic structure of methylene, where it was seen that two configurations are needed for a reasonable zero-order description of the $^1A_1$ state, but only one is needed for $^3B_1$. Using a two-configuration MCSCF wave function for the singlet and ordinary SCF for the triplet (denoted 2C–SCF in the table) results in convergence to a large-basis limit of [76,100] 10.7 kcal/mol, which corresponds to an error of only 1.6 kcal/mol relative to the best experimental estimate, Eq. (12).

Table 5. Some *ab initio* results for the singlet–triplet gap (T_e^{nr}, kcal/mol), according to basis set and type of wave function

Type of wave function[a]	Basis set[b]					
	MBS	DZ	EB	DZP	EBP	VL
SCF	40.1[c]	32.4[d,e]	31.5[f]	26.2[e]	25.0[e]	24.8[f]
2C–SCF	32[g]	22.8[d,e]	22.0[f]	12.8[e]	11.1[e]	10.7[h,i]
SD–CI		23.7[e]		14.6[e]	13.2[e]	13.1[j]
SD(Q)–CI		22.0[e]		12.4[e]	10.9[e]	10.8[j]
2R–CI		22.2[e]		12.2[e]	10.6[e]	9.8[h]
MR–CI						10.5[j]

[a] Key for wave functions:
SCF = self-consistent field;
2C–SCF = two-configuration SCF for singlet (one for triplet);
SD–CI = single and double excitations CI, single reference;
SD(Q)–CI = SD–CI plus quadruples correction, single reference;
2R–CI = two-reference SD–CI for singlet (one for triplet);
MR–CI = multireference CI.

[b] Key for basis sets:
MBS = minimal basis set, (2s1p) for carbon, (1s) for hydrogen;
DZ = double zeta, (4s2p; 2s);
EB = extended basis, without polarization functions, (9s6p; 4s);
DZP = double zeta with polarization functions, (4s2p1d; 2s1p);
EBP = extended basis with polarization functions (6s4p2d; 3s2p);
VL = very large bases, from (8s5p3d; 4s1p) to (9s7p2d1f; 5s2p).

[c] Lathan *et al.*, Ref. 99.

[d] O'Neil *et al.*, Ref. 90.

[e] Bauschlicher and Shavitt, Ref. 89.

[f] Meadows and Schaefer, Ref. 70.

[g] Harrison and Allen, Ref. 25.

[h] Werner and Reinsch, Ref. 100 (see also Ref. 110 for a more recent result of 9.4 kcal/mol).

[i] Feller *et al.*, Ref. 76.

[j] Saxe *et al.*, Ref. 101.

After Meadows and Schaefer[70] obtained an energy gap of 10.9 kcal/mol by the 2C–SCF method in 1975, they learned of the CH_2^- photoelectron spectrum results[42] and concluded that the 2C–SCF approach grossly overcorrects for the difference in character between the singlet and the triplet. In a late addition to their paper[70] they employed an indirect approach to the determination of the $^1A_1$–$^3B_1$ gap. This approach, which has been discussed in detail by Harrison,[7] is based on the assumption that it should be easier to compute the $^1B_1$–$^3B_1$ energy difference by *ab initio* methods, since these two states share the same electron configuration and differ only in multiplicity. The $^1A_1$–$^3B_1$ gap can then be obtained by subtracting the presumably known $^1B_1$–$^1A_1$ energy difference (which gives rise to the "red bands" of the singlet, studied by Herzberg and Johns[12]). Meadows and Schaefer obtained an energy difference of 40.0 kcal/mol for $^1B_1$–$^3B_1$ in large-basis SCF calculations on both states.[70] Subtracting what they presumed to be the 0–0 $^1B_1$–$^1A_1$ excitation energy of 20.3 kcal/mol (obtained by substituting $v = l = 0$ in Eq. (6) of Herzberg and Johns[12]), they obtained a $^1A_1$–$^3B_1$ gap of 19.7 kcal/mol, in remarkable agreement with the experimental value[42] of Lineberger and co-workers! This agreement is destroyed, though, in improved configuration interaction calculations, which can account for the difference in the electron correlation energy between the singlet and triplet states of the same configuration. Of several computations[86–88,102,103] of the $^1B_1$–$^3B_1$ energy difference, the best appear to be those of Bauschlicher[88] and of Römelt *et al.*,[102] obtaining 35.6 and 37.4 kcal/mol, respectively. Bauschlicher[88] extrapolates his results (on the basis of comparisons with corresponding results for CH) to a corrected value of 33.4 kcal/mol. Furthermore, as noted by Duxbury[104] and by Ashfold *et al.*,[105] the Herzberg and Johns[12] analysis of the vibronic levels of the $^1B_1$–$^1A_1$ transition has been misinterpreted by several quantum chemists,[66,88,103,106] including Meadows and Schaefer.[70] The $^1A_1$ and $^1B_1$ states can be considered as the two Renner–Teller components of the linear $^1\Delta_g$ state (Fig. 2). Herzberg and Johns used the linear-molecule vibrational numbering appropriate for the vibronic treatment of $^1\Delta_g$, in which the lowest vibrational level which can be associated with the quasilinear upper state has $v_2 = 2$ (see, e.g. Jungen and Merer;[107] a detailed analysis of the Renner–Teller effect in the $^1\Delta_g$ state of CH_2 has been given by Duxbury, Ashfold *et al.*,[104,105] and a recent *ab initio* treatment has been presented by Perić *et al.*[108]). Thus the extrapolated lowest vibronic transition energy in the $^1B_1$–$^1A_1$

system is obtained[12,104] as 23.6 kcal/mol, which, coupled with the estimated[88] 33.4 kcal/mol $^1B_1$–$^3B_1$ difference, is compatible with a $^1A_1$–$^3B_1$ energy gap of about 9 kcal/mol.

Returning now to an examination of the results in Table 5, we note that the SD–CI treatments (CI with all single and double excitations relative to a single configuration for each state) converge to a value of[101] 13.1 kcal/mol, reflecting a residual lack of balance between the two states in this approach. While the configuration interaction calculations succeeded in reducing the SCF energy gap from about 25 to 13 kcal/mol, they could not entirely overcome the deficiency of a single-configuration zero-order description of the singlet.

This deficiency can be remedied in at least two ways. The first, denoted SD(Q)–CI in the table, involves the use of a "cluster correction", such as the Davidson correction,[109] to account for the principal effects of quadruple excitations in a CI expansion. After the double excitations, these quadruple excitation terms are usually the most important higher-order contributions to the wave function, and while the Davidson correction (which is essentially a type of rescaling of the double excitation contribution in SD–CI) is only approximate, it has been very successful in many applications in reducing bias and extending the usefulness of SD–CI calculations. The correction is very sensitive to the magnitude of the coefficient of the SCF configuration in the SD–CI expansion, and produces a bigger shift in the energy of the singlet state, in which that coefficient is smaller. It thus accounts for the greater importance of some of the quadruple excitations (those which are double excitations relative to the secondary $1b_1^2$ configuration) in the $^1A_1$ wave function. We see from Table 5 that the SD(Q)–CI approach can produce a satisfactory 10.8 kcal/mol result[101] for the singlet–triplet gap.

More satisfactory is the 2R–CI approach, in which all single and double excitations relative to both the $3a_1^2$ and $1b_1^2$ configurations are included in the $^1A_1$ CI calculation. With the very large (9s7p2d1f; 5s2p) basis set used by Werner and Reinsch,[100] this produced the very good result of 9.8 kcal/mol for T_e^{nr}, an error of only about 0.7 kcal/mol relative to Eq. (12) (an even better result, $T_e^{nr} = 9.4$ kcal/mol, was obtained in unpublished calculations by Werner,[110] using a (9s6p3d2f; 5s2p) basis).

Also included in Table 5 is a multireference CI result by Saxe *et al.*,[101] in which all single and double excitations relative to a full-valence CI (with the $1a_1$ orbital doubly occupied and the three lowest-occupancy natural orbitals deleted) were included. The result of 10.5 kcal/mol probably reflects the somewhat smaller basis set (8s5p3d; 4s1p), without f functions, compared to most of the other entries in the VL column.

Other results comparable to those listed in Table 5 have also been published. Among the additional recent treatments are some which have been mentioned in connection with the $^1B_1$ state,[87,88,102] as well as that of Davidson *et al.*[111] All well-designed calculations produced T_e^{nr} values of about 11 kcal/mol or smaller. A few nonvariational treatments should also be mentioned. Among these are the IEPA (independent electron pair approximation) calculations of Staemmler,[112,113] which produced a singlet–triplet gap of 9.2–10 kcal/mol, and the D-MBPT (many-body perturbation theory limited to double-excitation diagrams) treatment of Kenney *et al.*,[114] which extrapolates to a linearizeal coupled cluster result of 12.4 kcal/mol. Nichols and Yeager[115] carried out multiconfiguration SCF (MCSCF) and multiconfigurational random phase approximation (MC-RPA, based on MC-time-dependent Hartree–Fock) calculations, with results of 8.1 and 14.5 kcal/mol, respectively. Jensen *et al.*[116] used RPA propagator calculations based on an AGP (antisymmetrized geminal power) reference state and obtained 11.1 kcal/mol. Pople *et al.*[69,117] used the UMP (unrestricted Møller–Plesset) approach, which is an MBPT treatment based on an unrestricted SCF reference state, and obtained 15.3 kcal/mol at the third-order level (UMP3)[69] and 14.3 in fourth order (UMP4).[117] Both these results appear to reflect the single-reference nature of the theory. Extrapolation of the UMP4 result for basis set limitations and higher-order terms produced an improved estimate of 11.4 kcal/mol.[117] An alternative derivation of the singlet–triplet gap was also presented,[117] based on the "isogyric" reaction (in which the number of unpaired electron spins is conserved),

$$CH_2(^1A_1) + 2H \rightarrow CH_2(^3B_1) + H_2. \qquad (13)$$

This approach, which produced a singlet–triplet gap estimate of 7.7 kcal/mol, has the disadvantage of introducing the errors of bond dissociation calculations into the determination of the energy difference between the two states of CH_2.

Finally, we consider the question of error estimates and empirical corrections of *ab initio* results. In many cases, such estimates and corrections can be obtained by carrying out analogous calculations on related systems for which reliable data are available. A crude estimate of this type, based on calculations on the C atom and on CH, was given in the early work on CH_2 by Foster and Boys,[15] but did not employ the appropriate states of C and CH in the analysis of the singlet–triplet gap. As discussed by Bauschlicher and Shavitt,[89] the splittings in these systems analogous to the methylene $^1A_1$–$^3B_1$ gap are the $^2\Pi$–$^4\Sigma^-$ gap in CH and the ^3P–^5S splitting in C (in corresponding order). Furthermore, before error corrections based on such an analysis become quantitatively useful, the errors should be small to start with, so that the estimated corrections cannot themselves be subject to significant errors. Using this approach, Bauschlicher and Shavitt extrapolated their best computed values for T_e^{nr}, 10.9 and 10.6 kcal/mol for SD(Q)–CI and 2R–CI, respectively, to an estimated value of 9 kcal/mol, in excellent agreement with the best experimental estimate, Eq. (12). A similar approach was used by Bauschlicher[88] in the determination of the $^1B_1$–$^3B_1$ gap (using the $^2\Sigma^-$ state of CH as analogous to $^1B_1$ in CH_2) and by Feller *et al.*[76] in the calculation of the electron affinity of CH_2 (they used analogies with the C and O atoms).

V. CONCLUSIONS

In both experimental and theoretical work, the principal uncertainty is often not in the raw data collected, but in their interpretation. Experimental measurements are frequently interpreted and adjusted on the basis of simplified theoretical models. In interpreting theoretical results, account should be taken of systematic errors (based on comparisons with related systems for which other data are available), as well as possible nonsystematic inaccuracies. When trying to resolve a discrepancy between theoretical and experimental results, both should be examined carefully and critically, with particular attention to all aspects of interpretation. This has been put cogently by Gaspar and Hammond, who said:[8] "Even more insidious has been the willingness of the theoretician to accept as true the pronouncements of the experimentalist, and *vice versa*."

As amply documented in the Gaspar and Hammond review,[8] the early attempts to understand the methylene molecule were beset with misidentified and misinterpreted data, with inappropriate analytical techniques, with unfounded speculations, and with erroneous estimates. The early theoretical treatments were mostly of little, if any, validity. Even authors of more advanced calculations, both semiempirical and *ab initio*, tended to overestimate the reliability of their results. From the theoretical point of view, it is seen that for problems such as the singlet–triplet gap in methylene there is no alternative to sophisticated and laborious calculations. Even if simple models sometimes produce correct answers, there is no independent way, in general, to recognize when this has happened.

As far as the methylene discrepancies are concerned, these have now been essentially resolved. The only remaining significant open question involves the uncharacteristic behavior of the hot bands in the CH_2^- photoelectron spectrum. While tentative explanations for this behavior have been proposed,[66,75] no experimental confirmation of the mechanism responsible for the hot band intensities has been obtained.

Postscript—With this review all but complete, the author has just learned of the results of a new CH_2^- photoelectron spectroscopy experiment which has been carried out by Lineberger and co-workers,[118] using a flowing afterglow technique. In this method all the CH_2^- ions are expected to relax to their ground vibrational level before undergoing photodetachment. As expected, the peaks labeled A, B, C in Fig. 1 have disappeared in this experiment, confirming the identity of peak D as the 0–0 transition and giving a singlet–triplet gap of 9 kcal/mol. The presence of vibrationally excited CH_2^- has also been demonstrated recently by Lee and co-workers,[119] who have determined the radiative decay rates of the vibrationally excited states. Their results are consistent with a $^{3}CH_2$ electron affinity of 0.65 eV.[75]

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