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Methylene: A Paradigm for Computational Quantum Chemistry

HENRY F. SCHAEFER III

The year 1970 has been suggested as a starting date for the "third age of quantum chemistry," in which theory takes on not only qualitative but also quantitative value. In fact, each of the years 1960, 1970, 1972, and 1977 is of historical value in the unraveling of the structure and energetics of the CH₂ molecule, methylene. What took place for methylene, namely the establishment of credibility for theory, has subsequently taken place for many other molecules. Three important roles for quantitative theory are outlined: (i) theory precedes experiment; (ii) theory overturns experiment, as resolved by later experiments; and (iii) theory and experiment work together to gain insight that is afforded independently to neither. Several examples from each of the three classes are given.

THE EXCELLENT RECENT REVIEW BY GODDARD (1) OF theoretical research at California Institute of Technology points to the year 1970 as the origin of "the coming of age of quantitative quantum chemistry." That year provided a sufficiently definitive theoretical prediction (2) of the bent structure of methylene to challenge directly the linear experimental structure of Herzberg (3). In their 1975 review, Gaspar and Hammond also hinted at the uniqueness of that prediction (4): "In 1970 Bender and Schaefer reported by far the most elaborate calculation carried out to date on methylene, or indeed almost any molecule."

Certainly one may point to earlier possible dates (5) for the birth of quantitative predictions in molecular electronic structure theory. Perhaps the most obvious is 1933, with the famous theoretical treatment of the hydrogen molecule by James and Coolidge (6) appearing in the first volume of the *Journal of Chemical Physics*. James and Coolidge were successful in proving for the first time that Schrödinger's equation was quantitatively trustworthy for molecules as well as atoms. Another choice would be the year 1968, with the appearance of Kolos and Wolniewicz's landmark paper (7) on the dissociation energy of H₂. Kolos and Wolniewicz challenged the experimental error ($\pm 0.3 \text{ cm}^{-1}$) for D_e(H-H), and their results were subsequently confirmed by new spectroscopic measurements (8). However, both James and Coolidge and Kolos and Wolniewicz used wave functions explicitly incorporating interelectronic coordinates. Since these methods have never been effectively extended to molecular systems of more than two electrons, they are in this sense unconnected to the many successes of quantum chemistry during the past 15 years.

It will be contended here that methylene is a paradigm for

quantitative theoretical chemistry. That is, theory may now claim some of the prerogatives typically reserved in chemistry for experiment. Specifically, when state-of-the-art theoretical methods are intelligently applied to many problems involving molecules as large as naphthalene, the results may be treated in the same way that one treats reliable experiments. I will first provide an account of four phases of the methylene problem and then turn to some more general conclusions.

The Structure and Energetics of CH₂: Four Critical Years

We take the four years 1960, 1970, 1972, and 1977 to be of special value in the unraveling of the structure and energetics of the CH₂ molecule.

1960. No discussion of the theoretical contributions to the methylene problem is complete without reference to the pioneering work of Foster and Boys (9). Although, for reasons that will become apparent, Foster and Boys' work did not contribute to the paradigm in view here, it is a monument to the efforts of early workers in the field of ab initio molecular quantum mechanics. In fact, their study of CH₂ was one of the earliest ab initio investigations (10) of any nonlinear polyatomic molecule.

The study of Foster and Boys was purely predictive in nature, since there were no published spectroscopic data for CH₂ when their paper was submitted in 1959. A basis set of eight Slater functions was used: 1s, 1s', 2s, 2p_x, 2p_y, 2p_z on carbon and a single 1s function on each hydrogen atom. Although a self-consistent field (SCF) calculation was not carried out, orbitals approaching SCF quality were obtained by decreasing the importance of single excitations (to less than 10 percent) in the configuration interaction (CI). Large CI (for 1960) was carried out, including 128 determinantal expansion functions for the ³B₁ state. Thirteen different geometries were investigated, resulting in a ³B₁ equilibrium geometry of 129°. The ¹A₁ state was predicted to have a bond angle of 90° and to lie 24.5 kcal per mole higher in energy than the ³B₁ state.

Foster and Boys did not challenge experiment for the simple reason that there were no experiments to challenge. Understandably, at this early stage in the development of ab initio theory, the authors made no particular claims concerning the quantitative reliability of their predictions.

The appearance of Herzberg's 1961 Bakerian Lecture (3) boded ill for the theoretical efforts of Foster and Boys. On the basis of his analysis of the electronic spectrum of CH₂, Herzberg concluded that the molecule in its triplet ground state is linear. Herzberg noted the work of Foster and Boys (9), stating "Our experimental values are distinctly different from these predictions but not excessively so, when the approximate nature of the calculations is considered" (3).

The completion of the discrediting of Foster and Boys' 1960

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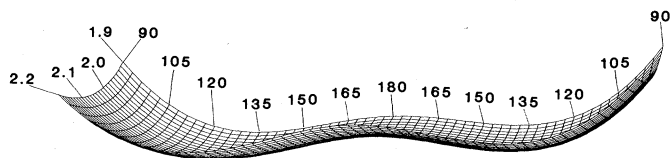


Fig. 1. Perspective plot for the potential energy surface of the lowest triplet state of methylene (36).

paper was carried out by Jordan and Longuet-Higgins (11) in 1962. At the time Longuet-Higgins was professor and head of theoretical chemistry at Cambridge, while Boys occupied a lesser post in the same department. Furthermore, Longuet-Higgins was widely known (12) for his negative attitude toward theorists such as Boys who made serious use of computers. Jordan and Longuet-Higgins prefaced their 1962 paper with the words "It may be that future theoretical progress will require elaborate variational calculations such as those of Foster and Boys on CH_2 , but until the results of such machine experiments can be interpreted physically, there would seem to be a place for more empirical theories such as that which we now describe." Jordan and Longuet-Higgins then proceeded to show from their empirical theory that the triplet ground state of CH_2 is linear. Their result not only questioned Foster and Boys' 1960 paper on CH_2 , but along with Herzberg's remarks quoted above it also cast grave doubt on the overall trustworthiness of any *ab initio* procedure. Certainly if such methods were unable to predict the structure of a molecule as simple as CH_2 , they would appear to be of little value.

1970. Before proceeding to the specific CH_2 events of 1970, two important theoretical papers appearing in the 1960's should be noted. The first (13) of these, by Pople and Segal, appeared in 1966. They utilized the CNDO (complete neglect of differential overlap) method, which they had introduced (14) in the previous year. It is fair to say that the CNDO method has been, overall, the most important semiempirical method introduced to quantum chemistry. Pople's systematic studies of the structures and energetics of simple molecules allowed users of the CNDO method to appreciate both its strengths and its weaknesses. In recent years, Pople has committed himself entirely to *ab initio* theory and has pressed the same systematization to the highest levels of theory (15).

Pople and Segal (13) used the CNDO/2 method to predict that the bond angle of triplet methylene is 141.4° , in qualitative agreement with the prediction of Foster and Boys (9). However, in the aftermath of Herzberg's and Longuet-Higgins' repudiation of Boys' prediction, Pople and Segal chose not to challenge the experimental linear structure. Rather, they noted (13) "this is a situation where the CNDO approximation is least satisfactory," adding that CNDO "neglects the one-center exchange integral." They concluded "this triplet stabilization is probably a maximum in the linear form and its inclusion would very likely modify the calculated bond angle."

Second, note must be made of the 1969 *ab initio* valence bond study of Harrison and Allen (16). Their work was especially significant from a theoretical perspective, representing one of the earliest rigorous quantum mechanical treatments of any polyatomic molecule within the valence bond framework. Using a minimum basis set of atomic SCF orbitals, Harrison and Allen reported theoretical studies of the lowest 3B_1 , 1A_1 , and 1B_1 states of CH_2 .

Harrison and Allen predicted CH_2 to be bent, with bond angle 138° . But they also hesitated to challenge Herzberg's experimental linear structure (16): "We certainly wish the present results to be regarded with conservatism and there is certainly room for a greatly improved theoretical treatment." More specifically referring to their bond angle predictions, Harrison and Allen stated "Because of the

very flat potential curves of the 3B_1 , and 1B_1 states, the predicted equilibrium angles of 138° and 148° , respectively, could be changed significantly with minor changes in the atomic bases."

The 1970 theoretical treatment by Bender and Schaefer (2) brought to bear on the methylene problem theoretical methods that had previously been applied only to atoms and diatomic molecules (17). The contracted Gaussian double-zeta basis set developed by Dunning (18) was used in conjunction with SCF and CI methods. The CI treatment included the SCF wave function

$$1a_1^2 2a_1^2 1b_2^2 3a_1 1b_1 \quad ^3B_1 \quad (1)$$

plus all configurations of 3B_1 symmetry arising from orbital occupancies differing by one or two orbitals from the SCF function, with the restriction that the $1a_1$ orbital be always doubly occupied. This yielded a total of 408 3B_1 configurations, a rather large variational treatment for the year 1970. An iterative natural orbital procedure (19) was then used in several subsequent CI calculations to obtain the most rapidly convergent expansion of the above type.

The CI potential energy surface for triplet methylene is displayed in Fig. 1 and clearly shows that the molecule is bent. The precise bond angle predicted by Bender and Schaefer was 135.1° . This bent structure was found to lie 7 kcal per mole below the optimized linear geometry, and it was concluded that no higher level of theory could remove such a barrier. Thus methylene became the first polyatomic molecule for which it could be claimed that theory was more reliable than the conclusions of a distinguished experimentalist. And thus began methylene's role as a paradigm for quantitative quantum chemistry. An interesting aside is that Herzberg's original analysis (3) allowed for the possibility that CH_2 was bent, but he eventually chose the linear structure because it seemed more reasonable.

Essentially concurrently with Bender and Schaefer's paper (2) appeared the experimental electron spin resonance (ESR) study of Bernheim and colleagues (20). They state "Our measurements, which were made on CH_2 trapped in xenon at 4.2 K, verify that the ground state is indeed triplet and show that triplet CH_2 is slightly bent under these conditions." These investigators did not speculate on whether the observed slight bending was due to the xenon matrix as opposed to the gas-phase conditions of Herzberg's experiments. However, there was no indication of a perceived serious disagreement with Herzberg, nor was a specific value of the CH_2 bond angle put forth.

Three months later (15 November 1970), Wasserman, Yager, and Kuck (21) reported a second ESR study of triplet methylene. These investigators approached the structural dilemma more aggressively, concluding that the CH_2 triplet bond angle lies between 128° and 143° . Their most probable value was 136° , in remarkably close agreement with Bender and Schaefer's prediction of 135.1° .

The work of Wasserman (21) was followed by a second paper (22) from Bernheim's group, who determined that the bond angle is 137.7° from additional observations on CD_2 . At this point, the laboratory findings of the two ESR groups led Herzberg (23) to reexamine his deductions from electronic spectroscopy. He graciously concluded "The considerations given here point strongly toward the bent structure of the triplet ground state (3B_1) of CH_2 , as first suggested by the electron-spin resonance work and the *ab initio* calculations."

The experimental papers by Bernheim and Skell, by Wasserman, and by Herzberg forced many to reconsider the role of *ab initio* theory in chemistry. Instead of having been an early failure, the work of Foster and Boys (9) was now shown to be qualitatively correct. Equally important, state-of-the-art theory (2) had challenged the most distinguished spectroscopic group in the world and been vindicated. A new role for theory, "full partner with experiment" [to use the title of Goddard's recent paper (1)], had been charted.

I conclude this section by quoting Goddard's brief summary of the triplet CH₂ structural problem (1):

Everyone believed the molecule to be linear until the increasingly accurate theoretical studies in the late 1960's finally led Bender and Schaefer to insist in 1970 that CH₂ is bent by 135°. Indirect experimental evidence for such highly bent CH₂ came quickly, followed by a reinterpretation of the spectroscopic studies to confirm the bent geometry predicted by theory.

1972. Despite having established beyond doubt the nonlinearity of methylene, experiment was unable to agree upon a precise value for the bond angle of triplet methylene (21–24). Bernheim's group favored 138°, Wasserman's group 130°, and Herzberg allowed the range 128° to 148°. Therefore, McLaughlin, Bender, and Schaefer set out to attempt to place error bars on the theoretical prediction of the bond angle of triplet CH₂.

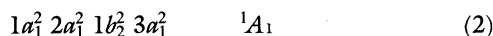
This second theoretical study (25) of the geometry of triplet methylene was carried out with the use of a still larger basis set. Specifically, polarization functions were included, a set of 3*d* functions on carbon and a set of 2*p* functions on hydrogen. The basis set, technically designated C(5*s*3*p*1*d*), H(3*s*1*p*), could be described as triple-zeta plus polarization. Although it is now fairly routine to predict the structures of small polyatomic molecules with such basis sets at the CI level of theory, it was without precedent in 1972. The particular configuration interaction method used, involving "first-order" wave functions (26), was designed to treat only the structure-sensitive part of the correlation energy. In this way a basis set nearly twice as large as that used in 1970 could be utilized, while the total number of ³B₁ configurations increased only from 408 to 617.

In this manner the bond angle of triplet methylene was predicted (25) to be 134.0°. It was further stated "We estimate that our theoretical bond angle of 134° is reliable to within 2°. Thus we feel that the present calculations provide the most reliable value to date, theoretical or experimental, for the bond angle of the ³B₁ ground state of methylene."

Such a statement of preference for theory over experiment was not expected to be warmly received all around. A response from "experiment" was given by Ramsay (27) 1 year later, when he stated "theoretical chemistry has now reached the happy level of acceptance" of making predictions "not entirely inaccurately." With respect to the prediction of 134° ± 2° for the CH₂ bond angle, Ramsay stated "he could choose a bond angle of 150° almost as easily as one of 135°." It is apparent that the reliability of ab initio theory was still a topic of some controversy.

Fortunately, the equilibrium bond angle of triplet methylene is no longer a matter of debate. A definitive experiment, involving laser magnetic resonance, was reported in 1983 by Bunker and Jensen (28). They concluded that the equilibrium bond angle is 133.8° ± 0.1°. It is seen that, despite the skepticism of Ramsay and others, the 1972 ab initio prediction of 134° ± 2° was eventually confirmed.

The year 1972 also marked the appearance of two significant theoretical predictions (29, 30) of the energy difference between the lowest singlet and triplet electronic states of CH₂. The singlet state arises in simple molecular orbital theory from the electron configuration



These two states had been known for some time to lie in close proximity energetically. In 1972 there were two competing experimental values for the singlet-triplet energy separation (ΔE_{ST}), with two groups (31, 32) of experimentalists giving values near 2 kcal per mole and three others (33–35) giving values in the range of 6 to 10 kcal per mole.

The first theoretical paper, that of Hay, Hunt, and Goddard (29),

is also of historical significance as one of the first applications of an important new theoretical method, the generalized valence bond (GVB) method. These investigators used a double-zeta basis set augmented by a set of *d* functions on the carbon atom. Using the GVB molecular orbitals in connection with a CI procedure, they predicted that singlet CH₂ lies 11.5 kcal per mole above the triplet ground state.

The second theoretical paper, by Bender and colleagues (30), used the full triple-zeta plus polarization basis set described earlier (25). With this large basis set, they first reported a single-configuration (Eq. 1) SCF treatment of triplet methylene and a two-configuration SCF treatment of singlet methylene (30):

$$\psi = C_1 1a_1^2 2a_1^2 1b_2^2 3a_1^2 + C_2 1a_1^2 2a_1^2 1b_2^2 1b_1^2 \quad (3)$$

This approach had previously been used by Bender and colleagues with a smaller basis set (36) and recognizes the fact that the SCF treatment of triplet methylene (1) utilizes both the 3*a*₁ and 1*b*₁ molecular orbitals, while the single-configuration SCF treatment of the singlet state (2) completely ignores the 1*b*₁ orbital. This triplet SCF/singlet two-configuration SCF procedure allows the singlet state to partake of the 1*b*₁ orbital and provides a much more nearly equivalent theoretical treatment of the two states. Subsequent theoretical examinations (37, 38) have provided general validation of this approach. The singlet-triplet separation predicted in this way by Bender and colleagues was 11.7 kcal per mole.

Bender and colleagues (30) also reported a more complete variational treatment of electron correlation in the CH₂ molecule (419 configurations for singlet CH₂; 617 configurations for the triplet state) using first-order wave functions (26). This approach led to a singlet-triplet separation of 14.0 kcal. However, such an approach does not begin with the two-configuration SCF description (3) of the singlet state, so that further correction was required to allow a definitive prediction. After considering several possible sources of error, Bender's group concluded in the abstract of their paper (30) "Results from these wave functions plus additional small corrections lead to a prediction of 11.0 ± 2 kcal per mole of the singlet-triplet energy difference." This was perhaps the first ab initio-based energetic prediction with error bars for any polyatomic molecule. Furthermore, the authors concluded that the experimental values (31, 32) for ΔE_{ST} of approximately 2 kcal must be incorrect.

1977. It should now be apparent that the events of 1970 and 1972 provided something of a heady experience for workers in the young field of computational quantum chemistry. In the latter year the theoretical group at California Institute of Technology headed by Goddard (29) and at the University of California at Berkeley headed by myself (25, 30) had teamed together [each paper (29, 30) refers to the other as being in press] to adjudicate an important dispute among experimentalists concerning the value of the CH₂ singlet-triplet energy difference. The lower values (~2 kcal per mole) (31, 32) were clearly wrong, while the values (33–35) near 8 kcal per mole were in acceptably close agreement with theory (11 ± 2 kcal per mole).

This state of self-satisfaction was rudely terminated in 1976 with the appearance of the first direct experimental measurement of ΔE_{ST} (CH₂). Since Goddard and Shavitt have covered this territory well in their excellent reviews (1, 39), I note only that Zittel and colleagues (40) found a value for ΔE_{ST} of 19.5 ± 0.7 kcal per mole via laser photodetachment of the CH₂⁻ anion.

For many experimentalists, this development reinforced the old prejudices (3, 12) associated with the original theoretical predictions of Foster and Boys (9). For example, a conference (41) was convened by J. A. Berson and W. C. Lineberger in June 1978 at the University of Colorado to inquire into the apparent inconsistency between theory and experiment with respect to the CH₂ singlet-

triplet energy gap. In the context of another dispute (involving myself) between theory and experiment (later resolved in favor of theory), Platz and Berson (42) stated "These discrepancies are reminiscent of and perhaps related to the still unexplained disagreement among the values for the S-T gap in CH₂."

Moreover, the reverberations of Zittel's experiment (40) were by no means restricted to the North American continent. The flavor of the atmosphere is perhaps best reflected in an exchange (43) that took place in London on 17 February 1977 between R. B. Woodward, the greatest organic chemist of his time, and M. J. S. Dewar:

WOODWARD: What do you find for the triplet-singlet splitting in methylene?

DEWAR: By MNDO/3 we find 9 kcal/mole and the MNDO/2 value is about 30 kcal/mole—both are about 10 kcal/mole out from the experimental value. We are less embarrassed than Schaefer is!

This is hardly the sort of exclamatory sentence in which a scientist desires to see his or her name mentioned.

After an inevitable period of self-doubt and introspection, the theoretical groups at Cal Tech and Berkeley took it upon themselves to determine, at the very least, why theory had failed for $\Delta E_{ST}(\text{CH}_2)$. Much higher levels of theory were applied to the problem, with the perplexing result (44, 45) that the very same qualitative result for ΔE , 10 to 11 kcal, was obtained. Moreover, that same qualitative conclusion was reached independently by three distinguished theoretical chemistry groups in Sweden (46), Columbus, Ohio (38), and West Germany (47). At this point it became clear that the laser photodetachment experiment was in conflict not just with two theoretical groups from California, but with the entire field of computational quantum chemistry.

Between 1972 and 1980 a number of experimental studies (48–55) provided indirect measurements of $\Delta E_{ST}(\text{CH}_2)$ in the range of 6 to 8 kcal per mole. However, the fact that only Zittel's experiment (40) was a direct measurement severely hindered acceptance of these experiments. This remained the case despite the fact that Harding and Goddard (45, 56) proposed a simple explanation of the laser photodetachment experiment, namely that the three observed bands were hot bands, arising from vibrationally excited CH₂⁻ molecules.

In 1982 a major breakthrough (57) on the methylene problem occurred in Lee's laboratory at Berkeley. In the second direct experimental measurement of the singlet-triplet gap, Lee and his co-workers used the molecular beam photodissociation of ketene to determine a value for ΔE_{ST} of 8.5 ± 0.8 kcal per mole. They concluded (57) that their result was "in reasonable agreement with recent ab initio quantum mechanical calculations."

The following year, McKellar and colleagues (58) observed and identified spectroscopic transitions between the \tilde{X}^3B_1 and \tilde{a}^3A_1 states of CH₂ using far-infrared laser magnetic resonance. These experiments yielded the precise splitting value for $\Delta E_{ST}(\text{CH}_2)$ of 9.05 ± 0.06 kcal per mole. The final chapter of the story was written 1 year later when Leopold, Murray, and Lineberger (59) constructed a new laser photodetachment apparatus and found ΔE_{ST} to be approximately 9 kcal per mole. Perhaps most encouraging of all from the theoretical perspective was the fact that the seemingly brash 1972 prediction for the value of $\Delta E_{ST}(\text{CH}_2)$ of 11 ± 2 kcal per mole by Bender and colleagues (30) had stood the test of 13 years of excruciatingly careful experimental investigation.

The identification in this section of methylene as a paradigm for quantitative quantum chemistry requires that CH₂ be prime exemplar of a subsequent pattern of findings. This has in fact turned out to be the case, with theory being confirmed by experiment in many situations. Here I cite several examples from theoretical research at Berkeley over the past 15 years. In every case cited, experiment has ultimately confirmed the specific predictions of theory. The interac-

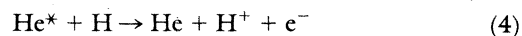
tions between theory and experiment are readily cast into three distinct categories.

Theory Precedes Experiment

The category is most typical of the different positive relations between theory and experiment. And one must be selective here in claiming credit for theory. It is obvious that one can easily make many reliable but uninteresting predictions from theory—such predictions could be readily confirmed by equally uninteresting experiments. Thus I restrict this category to predictions that are either contrary to intuition or of substantive importance to the body of chemical knowledge.

The existence of low-lying quartet states of the CN radical. The Wigner-Witmer symmetry rules may be used to predict the existence of several low-lying quartet states of the CN radical, one of the most exhaustively spectroscopically characterized species (60) of all diatomic molecules. This qualitative suggestion was made by Heil and myself and was backed up with ab initio predictions in 1971 (61). Twelve years later the theoretical prediction for the ⁴Π state of CN was confirmed by Kuchitsu's group (62, 63) at the University of Tokyo. Other predictions by Heil (61) concerning the doublet states of CN have been confirmed (64) in Herzberg's laboratory in Ottawa.

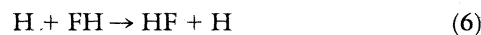
Penning ionization of H by He (1s2s³S, ¹S).* Perhaps the simplest Penning and associative ionization processes are those involving metastable helium namely



The theoretical understanding of this process involves not just the determination of diatomic potential energy curves, but also the much more challenging evaluation of the ionization width Γ (or lifetime $\hbar\Gamma$) as a function of internuclear distance. The first such ab initio study was reported by the Berkeley theory group (65) in 1972. Two years later Magnuson and Neynaber (66) studied the same system experimentally with merging beams techniques, concluding that the relative cross sections " Q_R are in excellent agreement with theoretical predictions by Miller, Slocomb, and Schaefer."

The existence of a novel class of molecular complexes including Li-H₂O. A theoretical study (67) appearing in 1977 predicted surprisingly large binding energies for the complexes Li-NH₃ (15 kcal), Li-H₂O (13 kcal), Li-HF (4 kcal), Na-NH₃ (6 kcal), and Na-H₂O (5 kcal). These results almost immediately stimulated Margrave's group at Rice University to carry out ESR and infrared spectroscopic studies (68) of lithium and sodium codeposited with H₂O or NH₃ in argon matrices. The theoretical prediction of strong binding between alkali atoms and polar molecules was quickly confirmed and has served to instigate much additional research, both theoretical and experimental (69).

The high activation energy for D + HF exchange. As a test of the validity of different semiempirical potential energy surfaces (such as bond energy–bond order, London-Eyring-Polanyi-Sato, and diatomics in molecules), an ab initio CI study of the simple exchange reaction

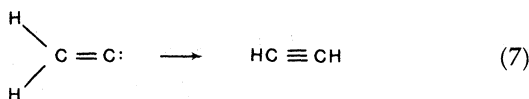


was undertaken (70) in 1975. The surprising result was a very large theoretical barrier height (ab initio, 49 kcal; estimated, ≥ 40 kcal), in serious disagreement with all 13 available semiempirical predictions. Moreover, such a high barrier was inferred by not a few scientists (71) to be inconsistent with the low experimental barrier (72) for

the analogous chlorine reaction. However, 3 years later Polanyi's group was able to confirm the prediction from Berkeley by means of chemiluminescence depletion with mass spectrometry (73). They concluded "It is correspondingly encouraging that the ab initio calculations yielded this result well in advance of experimental observation." Subsequently the activation energy for the chlorine reaction was reexamined experimentally and found to be higher than previously imagined (74).

The heat of formation of hydroxycarbene. In 1977 the unknown molecule hydroxycarbene, HCOH, was predicted (75) to lie 51.7 kcal above H₂CO, and a higher level of theory revised this prediction slightly to 52.6 kcal 2 years later. By 1981 the energetics, structure, and infrared and electronic spectra had all been predicted via state-of-the-art theory (75). The first experimental evidence for the existence of HCOH as a fleeting intermediate was presented in 1978 by Sodeau and Lee (76). However, the critical experiment was that of Pau and Hehre (77) in 1982, who used ion-cyclotron double-resonance spectroscopy. They determined that HCOH lies 54.2 kcal above formaldehyde, in close agreement with the theoretical predictions (75).

The existence of vinylidene as a very shallow minimum on the C₂H₂ potential energy hypersurface. Vinylidene, H₂C=C:, is the prototype unsaturated carbene and there has been much discussion as to whether it has any stability with respect to the isomerization to acetylene.



The two most complete ab initio studies of the problem predicted activation energies of 1.8 kcal (78) and 0.9 kcal (79), respectively, with some concern that the barrier might disappear entirely (79). However, recent photoelectron spectra (80) of the vinylidene anion show vibrational structure in the ground-state neutral molecule up to 12 kcal per mole. Although this excitation energy cannot be directly taken as an activation energy for rearrangement, it does appear to imply the existence of some barrier. In this sense Lineberger's experiment confirms theory's 1978 prediction (81) of vinylidene as a real molecular species.

Theory Overtakes Experiment, as Resolved by Subsequent Experiments

The methylene examples discussed above fall into this category of interaction between theory and experiment, but there have been many other examples since 1970.

The activation energy for D₂ + H₂ four-center exchange. This was a bone of contention between theory and experiment 3 years before Bender and I became involved in 1972. Shock-tube experiments by Bauer and Ossa (82) and by Burcat and Lifshitz (83) placed the activation energy for



at approximately 40 kcal per mole. This result was sharply contested by the theoretical groups of Goddard (84), Shavitt (85), and Karplus (86), who all favored bimolecular barriers in the vicinity of 100 kcal per mole. The purpose of our contribution (87) was to assess explicitly the importance of triple and quadruple excitations to the barrier height. However, these higher order correlation effects were found not to affect the earlier theoretical predictions. Much rancor ensued over the H₄ dilemma, ending only in 1983, when Lifshitz showed (88) that hydrogen atoms had been present in the

shock-tube experiments. Burcat and Lifshitz' paper (83) was entitled "The reaction H₂ + D₂ ⇌ 2HD. A long history of erroneous interpretation of shock tube results."

The unexpected inner crossing of the B³Σ_u⁻ and ³Π_u electronic states of O₂ and its relation to predissociation in the Schumann-Runge bands. Nearly 50 years ago Flory (who was later to receive the Nobel Prize for polymer chemistry), in explaining the important Schumann-Runge bands of the O₂ molecule, proposed a predissociation mechanism (89) based on the repulsive ³Π_u potential curve crossing the bound B³Σ_u⁻ state on the latter's outer limb. Twenty years later (1957) Wilkinson and Mulliken (90) proposed an opposite and rather surprising mechanism for the observed predissociation: namely, that the crossing occurs on the inner limb of the B state. Ab initio studies by Harris and Schaefer (91) in 1968 confirmed this proposal. However in 1969 Murrell and Taylor (92) analyzed the spectra again and took sharp exception to this view. Further spectroscopic observations (93) appeared to support Murrell and Taylor in this view, instigating a new ab initio study (94) at Berkeley in 1971 that served to confirm the 1968 predictions. This problem was eventually resolved in favor of Wilkinson and Mulliken and Schaefer and Harris (90, 91) by Julienne and Krauss (95), whose elegant and careful analysis emphasized the importance of spin-orbit coupling.

The molecular quadrupole moment of ozone. As part of his series of pioneering studies of the molecular Zeeman effect, Flygare in 1969 reported experimental quadrupole moments for the ozone molecule (96). Two years later, theoretical studies with Rothenberg (97) predicted quadrupole moments nearly an order of magnitude smaller. This was surprising since a prior comparison between theory (98) and experiment (96) for the valence-isoelectronic SO₂ molecule gave excellent agreement. The discrepancy was resolved 6 years later by Mack and Muenter (99), who used molecular-beam electronic resonance spectroscopy. They conclude their paper "the theoretical θ values for ozone are now in better agreement with experiment than for SO₂, as would be expected. Considering the great difficulty of many types of experimental measurements, this agreement is heartening."

The singlet-triplet separation for trimethylenemethane. In a 1974 paper primarily concerned with the triplet ground state of trimethylenemethane (TMM), or C(CH₂)₃, Yarkony predicted that the lowest singlet state lies 18.4 kcal per mole higher (100). Although Yarkony's description of singlet TMM was well received theoretically (101), it was sharply challenged experimentally by Dowd and Chow (102) and Platz and Berson (103). The former (102) concluded that ΔE_{ST}(TMM) must be less than 7.3 kcal, and the latter (103) found a value less than 3.5 kcal for a closely related compound. Hood, Pitzer, and Schaefer (104) carefully reexamined the problem theoretically, with complete geometry optimization for the singlet state. The final ab initio prediction was 14.1 kcal, still far from the two experimental values for ΔE_{ST}(TMM). Four years later the discrepancy was resolved in the form of five consecutive papers in the *Journal of the American Chemical Society* on TMM by Berson and co-workers. In the second of these, Mazur and Berson (105) state "The energy separation between the singlet and triplet biradicals, ≳13.3 kcal/mole, is in poor agreement with our previously reported value."

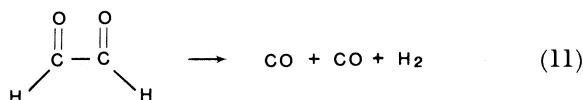
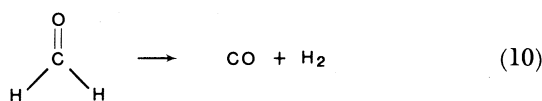
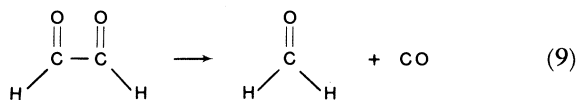
The prediction that the "aromatic" carbene cycloheptatrienyliene is in fact cyclohepta-1,2,4,6-tetraene. The C₇H₆ isomer cycloheptatrienyliene (1) is a simple 6π-electron "aromatic" carbene, and its



1

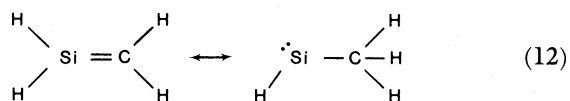
synthesis in the late 1960's by Jones at the University of Florida was a major achievement (106). In light of the long-standing interest in such species, a complete structural optimization was carried out in collaboration with the Australian quantum chemists Radom and Vincent (107). However, the surprising result was that the planar aromatic carbene structure (1) was predicted to lie 15.8 kcal above a less symmetric structure, in which the supposedly carbene carbon atom is in fact allene-like. This prediction was confirmed the following year by Chapman and co-workers at UCLA (108). They observed the infrared and ultraviolet spectra in an argon matrix at 10 K and properly named the compound cyclohepta-1,2,4,6-tetraene.

The triple dissociation of glyoxal in the absence of collisions. It has been known for 20 years that one of the products of glyoxal photodissociation is molecular hydrogen, with a two-step mechanism of the type represented by Eqs. 9 and 10 assumed (109). In 1981 Osamura and



myself (110) pointed out that the established activation energy for Eq. 10 is too high for this mechanism to be operative for glyoxal. We also showed that the one-step triple dissociation mechanism given by Eq. 11 is allowed by considerations of orbital symmetry (110). Later in the same year a detailed ab initio treatment (111) supported the hypothesized low barrier for the unconventional triple dissociation. Shortly thereafter, molecular-beam experiments by Lee and co-workers (112) confirmed the so-called "triple whammy" mechanism.

The structure and energy surface for rearrangement of silaethylene. Between 1978 and 1982, the Berkeley group made clear predictions concerning the geometrical structure of silaethylene, its energy with respect to methylsilylene, and the barrier height for interconversion (Eq. 12). These three predictions were vigorously protested by at



least four different experimental groups, as described in a separate account (113). Since the publication of that account (113), new experiments (114–117) have vindicated all three predictions.

Nonexistence of the experimentally assigned \tilde{B}^1A'' state of HCN. One of the dozen most important papers in the history of molecular spectroscopy is Herzberg and Innes's 1957 work (118) showing that, unlike the linear ground state, several of the excited states of HCN are distinctly bent. They concluded that the second excited singlet state of HCN, the \tilde{B}^1A'' state, has a bond angle of 114.5°. However, theoretical studies (119) in 1974 predicted a bond angle of 164° for the \tilde{B}^1A'' state. In the following year the problem was reconsidered (120) at a higher level of theory, but with no change in the final results. Finally, in late 1984 the conflict was resolved by the new spectroscopic studies of Bickel and Innes (121), who concluded that the observed $\tilde{B}^1A'' \rightarrow \tilde{X}^1\Sigma^+$ transitions were in fact part of the $\tilde{A}^1A'' \rightarrow \tilde{X}^1\Sigma^+$ system.

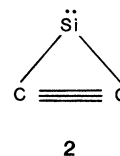
Theory and Experiment: Symbiosis

In April 1979, a news report in *Nature* heralded the arrival of the "third age of quantum chemistry" (122). After describing a particular example (described in the second paragraph below), the author concludes (122) "This work represents a near perfect instance of theory being in harmony with experiment, each aspect vital to the other and the combination much more than the sum of the separated parts." This is an exciting way for a theorist to contribute to science and is much less traumatic than the examples described above.

The identification of the interstellar molecules HNC and HCO⁺. In 1973 there were two well-known interstellar microwave lines that had never been observed in the laboratory. The simple triatomic molecules HNC and HCO⁺ were suggested as the carriers of these lines, but they proved difficult to observe terrestrially. Therefore we undertook to predict the positions of these lines theoretically. The theoretical frequencies fit those observed in interstellar space to 1 part in 500, and it was concluded that the molecules had been properly identified (123, 124). Five years later laboratory microwave measurements became possible (125, 126), and the theoretical structures for HNC and HCO⁺ proved to have been very accurate— to within 0.003 Å in all four bond distances.

The identification of the triplet-triplet electronic spectrum of acetylene. This is the case that provided the substance for the 1979 news article heralding the third age of quantum chemistry (122). The earliest experimental study of triplet acetylene to provide any structural inferences was that of Burton and Hunziker (127) in 1972. From the mercury-photosensitized reactions of acetylene, they tentatively postulated that the lowest triplet state has a *trans*-bent or linear structure. This suggestion was refuted in 1978 by detailed ab initio studies by Wetmore and myself (128) on the structures of the four lowest *cis* and *trans* triplet states of C₂H₂. However, in the course of visually examining the theoretical structures for the two lowest *cis* triplet states determined at Berkeley, Hunziker suspected that he had obtained some years earlier a (previously unidentified) spectrum corresponding to the $\tilde{a}^3B_2 \rightarrow \tilde{b}^3A_2$ transition. Subsequent experiments (129) confirmed Hunziker's keen intuition and led to the correctly analyzed spectrum of triplet C₂H₂.

The unusual cycloalkyne structure of the SiC₂ molecule. In 1983, during attempts to analyze their visible spectrum of jet-cooled SiC₂, Smalley and his colleagues hit a severe stumbling block. The assumption (130) (in analogy with the valence-isoelectronic C₃ molecule) of a linear structure led to bond distances several tenths of an angstrom shorter than would appear reasonable. They requested that the Berkeley group make a reliable theoretical prediction of the structure of SiC₂. This suggestion was pursued, only to give the result of a rather conventional linear structure. However, after the theory was pressed to the state of the art, the strongly bent structure (2) fell energetically below the linear geometry (131). With this

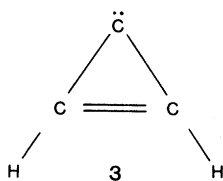


information in hand Smalley and co-workers (132) were immediately able to analyze the spectrum and to find close agreement with the theoretical equilibrium geometry.

Precise predictions of the infrared spectra of H₃O⁺, NH₄⁺, and H₂CN⁺. Beginning in 1979, I was instructed by R. J. Saykally to make reliable predictions of the infrared spectra of several simple polyatomic ions. The idea was that Saykally would then look for these species in his new laboratory at Berkeley. Yamaguchi and I

promptly delivered predictions (133) for NH_4^+ but, with no experimental results forthcoming, proceeded at a more leisurely pace to work on HO_2^+ . About the time the HO_2^+ theoretical work was finishing up, Saykally completed the development of an important new experimental technique, velocity-modulation infrared laser spectroscopy (134). Observing many transitions in the vicinity of 3500 cm^{-1} , Saykally's first thought was that he had found HO_2^+ . However, we assured him that the O–H stretching frequency in HO_2^+ occurs some 300 cm^{-1} lower (135). Thereafter, Saykally put us on a furious (2 weeks elapsed time) search for the infrared spectrum of H_3O^+ . The predicted frequencies of H_3O^+ were consistent (within a few inverse centimeters) with his observations, and the theoretical infrared intensities clinched the assignment (136, 137). Subsequently the Berkeley group's ab initio predictions (133, 138) for NH_4^+ and H_2CN^+ have assisted Saykally (139) and Oka (140, 141) in the observation of these elementary molecular ions.

The identification of the infrared spectrum of the elusive cyclopropenyli-dene molecule. Before 1984, an elusive C_3H_2 isomer, cyclopropenyli-dene (3), had been unsuccessfully pursued by experimentalists for



more than two decades (142). Therefore when Reinhart Hoffmann, a sabbatical visitor to Berkeley, told me in 1981 of his plans to synthesize cyclopropenyli-dene, I was skeptical. However, Hoffmann insisted that his goal was reachable, told me something of the history of this hypothetical aromatic 2π -electron species, and eventually enlisted my group's theoretical support. In June 1983, Lee and Bunge (143) delivered a theoretical structure and vibrational frequencies for this isomer (3). The match with the matrix-isolated infrared spectrum was good but not compelling, so the experimentalists sent us back for the infrared intensities. These were delivered in early 1984, and the perfect fit provided conclusive evidence that the molecule prepared in the laboratory was indeed cyclopropenyli-dene (144). In early 1985, the same molecule was observed by microwave spectroscopy in both the laboratory and interstellar space (145). The experimental structure agrees well with that predicted from theory.

Concluding Remarks

The 1970 controversy concerning the structure of methylene provided the first example, based on general theoretical methods, of ab initio theory squarely and successfully challenging an important conclusion from experimental chemistry. The CH_2 predictions from 1972 were likewise eventually resolved in favor of theory. Thus the methylene molecule played a singular role in the development of quantitative quantum chemistry.

However, the methylene examples are by no means isolated incidents. In the second half of this account, thumbnail sketches have been presented of 20 additional cases illustrative of the predictive powers of computational quantum chemistry. In every case important theoretical predictions (some highly controversial) were eventually confirmed by laboratory experiments. Since all of the examples given involved a single theoretical research group, it goes without saying that many other examples could readily be brought forward. It is clear that theoretical chemistry has entered a new stage, the third age of quantum chemistry, with the goal of being no less than "full partner with experiment."

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