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TECHNICAL REPORT ARBRL-TR-02240

AB INITIO PREDICTION OF THERMOCHEMICAL
PARAMETERS FOR FLAME SPECIES

George F. Adams
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May 1980



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
BALLISTIC RESEARCH LABORATORY
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I. INTRODUCTION

Formaldehyde is a ubiquitous flame zone species. Reactions between formaldehyde and various oxidizers provide a major portion of the heat released in the primary flame zone of nitrate esters and nitramines.¹ Any model or description of propellant combustion must account for the oxidation of formaldehyde. A precise model requires detailed modeling of the flame chemistry, and thus rate coefficients for chemical reactions. Since experiment cannot measure rate coefficients for all the elementary flame reactions, it is important to develop and test methods for estimating those rate coefficients.

Thermochemical kinetics, described and justified in Benson's monograph, provides one approach to estimate rate coefficients for several classes of chemical reactions.² These methods require thermochemical parameters, such as heat-of-formation, entropy and heat capacity, for each chemical species involved in the chemical reaction. For many compounds, these data can be found in the various compendia of thermochemical data; but for other species, accurate thermochemical data are not available. Furthermore, to estimate rate coefficients for unimolecular reactions of radical species requires thermochemical data for evanescent transition-state species; data not susceptible to direct measurement. This report describes the application of many-body perturbation theory to predict thermochemical parameters for some flame zone reactions that involve formaldehyde, and for several other species that are important in models that include formaldehyde.

The chemical reactions to be examined are:



¹R. A. Fifer, "High Temperature Pyrolysis of Methyl and Ethyl Nitrate", *Seventeenth Combustion Institute Symposium, University of Leeds, England, 1978*.

²S. W. Benson, *Thermochemical Kinetics*, John Wiley, New York, 1976.

This selection implies neither that all of these reactions are important flame-zone reactions nor that other reactions are unimportant. The selected reactions represent only a fraction of the many flame-zone reactions that involve formaldehyde.

Reactions (I) and (II) both include the methoxy radical, CH_3O . Accurate predictions of the heat-of-reaction for each of these processes should provide enough information to determine the heat-of-formation for this radical. Several unimolecular reactions that remove formaldehyde from a flame are given by equations (III), (V) and (VI), while reaction (IV) competes with the bimolecular reaction between the formyl radical and formaldehyde. For each of the listed reactions, theoretical predictions of the heat-of-reaction are obtained. Activation energy barriers are estimated for reactions (IV), (V) and (VI).

The theoretical methods employed in this study are described in the next section and in several appendices. Succeeding sections describe details of the electronic structure calculations and results of the thermochemical estimates for each reaction; the final section discusses the implications for chemical models of the flame zone.

II. DISCUSSION OF THEORETICAL METHODS

For many years electronic structure theorists have attempted to derive simple schemes for predicting or calculating thermochemical parameters for chemical species. The best known of the models, MINDO, developed by Dewar and co-workers, predicts thermochemical data with fair accuracy for hydrocarbons.³ However, the performance of the method diminishes for non-hydrocarbon organic species because there are insufficient empirical data to develop fitting parameters. In practice, this means that the method fares poorly when used to study oxygen containing compounds.

When Snyder and Basch used *ab initio* molecular orbital methods to study the heats-of-reaction of closed-shell molecules,⁴ they obtained fair agreement between theory and experiment. Although improved agreement might result from an increase in the size of the atomic basis sets used in the calculations, recent research suggests that more fundamental problems must be addressed. In particular, the accurate prediction of relative energies requires accounting for the correlation between

³M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Organic Chemistry", Plenum Press, New York, 1975.

⁴L. C. Snyder and H. Basch, "Heats of Reaction from Self-Consistent Field Energies of Closed-Shell Molecules", *J. Am. Chem. Soc.* 91, 2189 (1969).

electron motions, an effect that is not treated in self-consistent field calculations.^{5,6,7}

Historically, estimates of molecular correlation energy were obtained by using the method of configuration interaction (CI)* to improve the wavefunction obtained from a molecular orbital (MO) SCF calculation. In the past several years, theoretical techniques based upon the linked-diagram theorem have been extended to molecular applications, and several comparisons of the various theoretical approaches to the correlation problem have been published.^{5,8} In recent works, Pople suggests a set of desiderata for computational techniques:

(a) The method should be size-consistent. An energy calculated for an assembly of isolated molecules should equal the sum of the energies calculated for individual molecules.

(b) The method should be invariant under transformations within a set of degenerate MO's.

(c) The method should be variational. The energy should be an upper-bound to the energy obtained by an exact solution to the electronic Schrodinger equation.

Few theoretical methods satisfy all three criteria simultaneously. Spin-unrestricted Hartree-Fock theory (UHF) often satisfies all three criteria, but the method takes no account of correlation effects between electrons of different spins. A complete solution of the configuration interaction problem for a given basis set satisfies all three criteria, but such calculations are practical only for small molecular systems. As pointed out by Pople, there is a need for theories at an intermediate level that account for electron correlation.⁵

⁵J. A. Pople, R. Krishnan, H. B. Schlegel and J. S. Binkley, "Electron Correlation Theories and Their Application to the Study of Simple Reaction Potential Surfaces", *Int. J. Quantum Chem.* 14, 545 (1978).

⁶R. J. Bartlett, I. Shavitt and G. D. Purvis, "The Quadratic Force Field of H₂O Determined by Many-Body Methods that Include Quadruple Excitation Effects", submitted to *J. Chem. Phys.*

⁷J. D. Goddard and H. F. Schaefer, III, "The Photodissociation of Formaldehyde: Potential Energy Surface Features", *J. Chem. Phys.* 70, 5117 (1979).

⁸R. J. Bartlett and G. D. Purvis, "Many-Body Perturbation Theory, Coupled-Pair Many-Electron Theory, and the Importance of Quadruple Excitations for the Correlation Problem", *Int. J. of Quantum Chem.* 14, 561 (1978).

* A description of the method of configuration interaction is given in Appendix A.

The technique most often used to estimate correlation energy is a truncated CI calculation. Generally, the many electron wave function consists of the Hartree-Fock configuration, Φ_0 , plus all configurations obtained by double-excitations of electrons from one-electron functions occupied in Φ_0 to the virtual orbitals of Φ_0 .* A configuration interaction calculation that uses such a many-electron wave function is called configuration-interaction with double-excitations (CID). CID calculations satisfy criteria (2) and (3), but do not satisfy the size-consistency requirements, since the wave-function cannot account for simultaneous double-excitations in different molecules.

Among alternatives to conventional CI are theoretical techniques based on the linked-diagram theorem.^{9,10} One of these techniques is the couple-cluster approach (CCA).^{11,12} When the cluster analysis is limited to a consideration of only two-body terms, which include both the double-excitations included in CID and the simultaneous double-excitation omitted by the CID, the method is called coupled cluster with double substitutions (CCD),⁵ or coupled-pair many-electron theory (CPMET).¹³ Relative to a Hartree-Fock reference function, this theory satisfies criteria (1) and (2), but does not satisfy the variational requirement.**

Another linked-diagram related approach is many-body perturbation theory (MBPT).⁸ This technique uses the Moller-Plesset partitioning of

⁹K. A. Brueckner, "Two-Body Forces and Nuclear Saturation. III. Details of the Structure of the Nucleus", *Phys. Rev.* 97, 1353 (1955).

¹⁰K. A. Brueckner, "Many-Body Problem for Strongly Interacting Particles. II. Linked Cluster Expansion", *Phys. Rev.* 100, 36 (1955).

¹¹J. Cizek, "On the Correlation Problem in Atomic and Molecular Systems. Calculation of Wavefunction Components and Ursell-Type Expansion Using Quantum Field-Theoretical Methods", *J. Chem. Phys.* 45, 4256 (1966).

¹²J. Paldus, J. Cizek and I. Shavitt, "Correlation Problems in Atomic and Molecular Systems. IV. Extended Coupled Pair Many-Electron Theory and its Application to the BH₃ Molecule", *Phys. Rev.* A5, 50 (1972).

¹³J. Cizek, "On the Use of the Cluster Expansion and the Technique of Diagrams in Calculations of Correlation Effects in Atoms and Molecules", *Adv. Chem. Phys.* 14, 35 (1969).

* Virtual orbitals are those one-electron functions that are not occupied in the reference function Φ_0 .

** A description of coupled-pair many-electron theory is given in Appendix B.

the molecular Hamiltonian,¹⁴ such that the Hartree-Fock solution is taken to be the unperturbed Hamiltonian, H_0 , and the residual part of the molecular Hamiltonian is treated as the perturbation, V . Bartlett and co-workers have pioneered molecular applications of many-body perturbation theory,^{8,15} a technique that satisfies desiderata (1) and (2), but like CCD, does not satisfy a variational principle.*

Reliable predictions of potential energy hypersurfaces and thermochemical parameters require that computational methods exceed the Hartree-Fock self-consistent-field level of accuracy and, thus, must include correlation. The choice of method used to estimate the correlation energy in such studies depends upon the importance of size-consistency effects and the related size-extensivity criterion.** Whenever these effects are important, truncated CI methods, such as CID, do not give accurate representations of potential energy hypersurfaces. Size-extensive methods, such as CCD and MBPT, provide more uniform representations of potential energy hypersurfaces than does a truncated CI calculation. Bartlett, et al., concluded that the effect of size-consistency on electronic structure calculations was important, even for calculating the potential energy near the equilibrium structure for a molecule as small as water.⁶ Since size-consistency and size-extensivity depend upon the number of electrons, theoretical methods that satisfy these criteria should predict more accurate values for thermochemical parameters than a method such as CID. Consequently, this study, in the main, uses fourth-order MBPT to estimate relative energies. The MBPT calculations are supplemented by CCD calculations for some crucial molecular configurations. The latter calculations serve to check the convergence of the MBPT calculations.⁸

Several appendices discuss, in more formal terms, the theoretical methods mentioned above, and provide a discussion of some aspects of size-consistency and size-extensivity in molecular calculations. Most of the information presented in the appendices can be found in various papers by Bartlett, et al.^{6,8,15}

III. DETAILS OF THE CALCULATIONS

The electronic states of the molecules discussed in this report are represented at the Hartree-Fock level by unrestricted Hartree-Fock (UHF)

¹⁴C. Moller and M. S. Plesset, "Note on an Approximation Treatment for Many-Electron Systems", *Phys. Rev.* 46, 618 (1934).

¹⁵R. J. Bartlett and D. M. Silver, "Some Aspects of Diagrammatic Perturbation Theory", *Int. J. of Quantum Chem.* 9S, 183 (1975).

* A description of many-body perturbation theory is given in Appendix C.

** Size-consistency and size-extensivity are discussed in Appendix D.

wavefunctions. For closed shell molecules, such as formaldehyde and carbon monoxide, these wavefunctions are just those that would be obtained with a restricted Hartree-Fock (RHF) calculation. As noted in Section II, a UHF calculation usually satisfies all of Pople's desiderata.

The computations reported here refer to a double-zeta plus polarization atomic basis set consisting of contracted Gaussian-type functions.* Dunning's 4s3p¹⁶ contraction of Huzinaga's 9s5p primitive set¹⁷ was used for the first-row atoms. The carbon and oxygen basis sets were each augmented by a single set of d-orbital polarization functions with exponents 0.75 and 0.85, respectively. The hydrogen basis set included the 3s contraction of Huzinaga's 4s primitive set, with scaled exponents ($\delta = 1.2$), augmented by a p-type polarization function with orbital exponent 1.0. All integrals over atomic basis functions were calculated with the MOLECULE integral program.¹⁸

The SCF, MBPT and CCD calculations were performed using the program PRPGTR.¹⁸ The different calculations include SCF; fourth-order MBPT including all double-excitation diagrams that contribute, D-MBPT(4); fourth-order MBPT including all single- and double-excitation diagrams, SD-MBPT(4); fourth-order MBPT including all single-, double-, and quadruple-excitation diagrams that contribute, SDQ-MBPT(4); and coupled-pair many-electron theory, CCD. Although relative energies reported represent energy differences between calculations using the full MO-basis, molecular structure parameters were optimized at SD-MBPT(4) level with the restriction that the core-orbitals were not correlated with the remainder of the MO-basis. Molecular structure optimization was performed for all molecular configurations reported, except the transition states of formaldehyde reactions leading to (a) molecular products, and (b) hydroxycarbene. In these two cases, we use transition state geometries predicted by Goddard and Schaeffer.⁷

¹⁶T. H. Dunning, Jr., "Gaussian Basis Sets for Use in Molecular Calculations. I. Contraction of (9s, 5p) Atomic Basis Sets for First-Row Atoms", *J. Chem. Phys.* 53, 2823 (1970).

¹⁷S. Huzinaga, "Gaussian-Type Functions for Polyatomic Systems. I.", *J. Chem. Phys.* 42, 1293 (1965).

¹⁸MOLECULE was written by J. Almlof. The program is described in "Proceedings of the Second Seminar on Computational Problems in Quantum Chemistry", Strasbourg, France, 1972 (1973). PRPGTR includes program GRNFNC, written by G. D. Purvis and program UMBPT, written by R. J. Bartlett and G. D. Purvis.

*This is the smallest basis set that can provide predictions of chemical accuracy.

IV. DISSOCIATION OF METHANOL: $\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}$

The dissociation of methanol, CH_3OH , to radical products methoxy, CH_3O , and hydrogen, H , is not generally important in flame zone chemistry schemes except for the pyrolysis of methanol. This reaction offers a mechanism to estimate the heat-of-formation of the methoxy radical, hence the inclusion in this study. Previous research by Redmon, et al.,¹⁹ and Adams, et al.,²⁰ demonstrated that MBPT predicts heats-of-reaction and dissociation energies that agree well with available experimental values. Since heat-of-formation data exist for methanol and hydrogen, the heat-of-formation of methoxy can be calculated if the theory predicts an accurate value for the dissociation energy of methanol.*

To predict the heat-of-reaction for the dissociation of methanol,** electronic energies must be calculated for methanol, methoxy radical and the hydrogen atom. Since linked-diagram related methods, such as MBPT and CCD, are size-consistent, the electronic energies of the products are additive, so that separate calculations are performed for each of the products. This feature offers two benefits in the calculations for methanol. First, two separate calculation save computer time and reduce required computer resources when compared to the supermolecule calculation. Second, separation of the product channel to two calculations permits a thorough analysis of the Jahn-Teller energy lowering for the methoxy radical.

A theoretical study of methoxy by Yarkony, et al., showed that the ground electronic state for the molecule in a configuration with C_{3v} symmetry belonged to the two-dimensional (E) irreducible representation of the point group.²¹ The Jahn-Teller theorem states that a molecule cannot

¹⁹L. T. Redman, G. D. Purvis and R. J. Bartlett, "The Unimolecular Isomerization of Methyl Isocyanide to Methyl Cyanide", *J. Chem. Phys.* **69**, 5386 (1978).

²⁰G. F. Adams, G. D. Bent, G. D. Purvis and R. J. Bartlett, "The Electronic Structure of the Formyl Radical, HCO ", to be published, *J. Chem. Phys.*, 1979.

²¹D. R. Yarkony, H. F. Schaefer III. and S. Rothenberg, "Geometries of the Methoxy Radical (X^2E and A^2A_1 States) and the Methoxide Ion", *J. Am. Chem. Soc.* **96**, 656 (1974).

*It's clear that $\Delta H_f^0(\text{CH}_3\text{O})$ can also be estimated by predicting the dissociation energy of the radical to form formaldehyde and hydrogen and combining this result with known heats-of-formation of the products. This calculation will be described in the next section.

**The heat-of-reaction for a dissociation reaction is often called the dissociation energy. Both expressions will occur in this report.

exist in a degenerate electronic state, requiring, therefore, a distortion of the molecular configuration to destroy the spatial symmetry of the state.²² Yarkony, et al., considered a single vibrational mode that destroyed the C_3 symmetry axis, and predicted a Jahn-Teller energy lowering of 0.2 kcal mole⁻¹.²¹ A more recent calculation, including correlation effects and considering the coupling of all three e-type vibrational modes for methoxy, predicts different effects:²³

- (a) Mode-coupling increases the magnitude of the Jahn-Teller energy reduction.
- (b) The ground-state electronic energy of the distorted molecule is 0.75 kcal mole⁻¹ less than the minimum energy for the C_{3v} molecule.

In addition to optimizing the energy relative to the structural parameters for methoxy, the structural parameters for methanol were also determined. The calculations to optimize energy with respect to structure were performed using the fourth-order MBPT with all double-excitations, but the core orbitals were not permitted to correlate with the valence electrons. A variety of experimentally determined structural parameters²⁴⁻²⁸ and the parameters predicted by these calculations appear in Table 1. The agreement between the predicted parameters and the recent empirically-derived parameters of Gerry, et al.,²⁸ is excellent. Predicted structural parameters for the methoxy radical are presented in

²²H. A. Jahn and E. Teller, *Proc. Roy. Soc., Ser. A*, 161, 220 (1937).

²³G. D. Bent, G. F. Adams, G. D. Purvis and R. J. Bartlett, "The Electronic Structure of Methoxy Radical. Jahn-Teller and Spin-Orbit Energy Lowering", manuscript in preparation.

²⁴K. Kimuro and M. Kubo, "Structure of Dimethyl Ether and Methyl Alcohol", *J. Chem. Phys.* 30, (1959).

²⁵T. Nishikawa, no title available, *J. Phys. Soc. Japan* 11, 781 (1956).

²⁶P. Venkateswarlu and W. Gordy, "Methyl Alcohol. I. Microwave Structure", *J. Chem. Phys.* 23, 1195 (1955).

²⁷R. M. Lees and J. G. Baker, "Torsion-Vibration-Rotation Interactions in Methanol. I.", *J. Chem. Phys.* 48 5299 (1968).

²⁸M. L. C. Gerry, R. M. Lees and G. Winnewisser, "The Torsion-Rotation Microwave Spectrum of ¹²CH₃¹⁸OH and the Structure of Methanol", *J. Mol. Spec.* 61, 231 (1967).

TABLE 1. STRUCTURAL PARAMETERS FOR METHANOL, CH₃OH^a

	<u>Ref. 24</u>	<u>Ref. 25</u>	<u>Ref. 26</u>	<u>Ref. 27</u>	<u>Ref. 28</u>	<u>This Work</u>
R _{CH}	1.095	1.096	1.096	1.0936	1.0937	1.093
R _{OH}	0.96	0.953	0.956	0.9451	0.963	0.963
R _{CO}	1.428	1.427	1.427	1.4246	1.4214	1.432
HCH	109° 28'	109° 4'	109° 2'	108° 38'	108° 32'	107° 9'
COH	109°	108° 24'	108° 52'	108° 32'	108° 2'	107° 2'
Methyl Tilt	...	3° 18'	3° 20'	3° 16'	3° 12'	2° 12'

^aBond length units, Å.

Table 2. After determining the optimal structures for methanol and methoxy, MBPT calculations including the correlation of the core orbital electrons were done.

The results of the electronic structure calculations for methanol and the methoxy radical provide part of the information needed to estimate the dissociation energy of methanol. In addition to the electronic part of this heat-of-reaction, there are contributions from the vibrational, rotational and translational degrees of freedom. Thus,

$$\Delta H_R = \Delta H_R^{el} + \Delta H_R^{vib} + \Delta H_R^{rot} + \Delta H_R^{tr} .$$

At 0 K, rotational and translational degrees of freedom do not contribute to ΔH_R , and ΔH_R^{vib} equals the difference between the zero-point energies of the reactant and the products. Since the hydrogen atom has no vibrational degrees of freedom, only methanol and methoxy contribute to ΔH_R^{vib} . Tables 3 and 4 contain summaries of the molecular information, including electronic energy predictions and vibrational frequencies, for methanol and methoxy, respectively. All the vibrational frequencies for methanol are known from experimental data, but only three methoxy frequencies have been observed.²⁹ Thus, six frequencies for methoxy must be estimated. Estimation of the heat-of-reaction for reaction (1),



is outlined in Table 5.

A fourth-order MBPT calculation, that includes all single-, double-, and quadruple-excitation diagrams that contribute at fourth-order, predicts a value for the electronic part of the heat-of-reaction. This calculation predicts that the dissociation is endothermic, requiring an energy of 107.3 kcal mole⁻¹ to break the oxygen-hydrogen bond. To compare this number with experiment, however, the correction for the change in zero-point vibrational energy that occurs during the dissociation must be included. This correction reduces the energy required for dissociation at 0 K to 98.3 kcal mole⁻¹. This number corresponds to $\Delta H_{R,0}^0$. Since most experimentally tabulated values for the heat-of-reaction are given for T = 300 k, the effects of translational and rotational degrees of freedom on the dissociation energy must be included. As the details

²⁹P. C. Engelking, G. B. Ellison and W. C. Lineberger, "Laser photodetachment spectrometry of methoxide, deuteromethoxide and thiomethoxide. Electron affinities and vibrational structure of CH₃O, CD₃O and CH₃S", *J. Chem. Phys.* 69, 1826 (1978).

TABLE 2. STRUCTURAL PARAMETERS FOR THE METHOXY
RADICAL, CH₃O^a

r _{CO}	1.405
r _{CH'}	1.081
r _{CH''}	1.085
H'CH''	108° 36'
H''CH''	112° 6'
H'CO	111° 30'
H''CO	103° 54'

^aBond length units, Å.

TABLE 3. ELECTRONIC ENERGY PREDICTIONS AND
VIBRATIONAL FREQUENCIES FOR METHANOL, CH₃OH

<u>Electronic</u>		<u>Energy (h)</u>
	SCF	-115.07437
	D-MBPT(4)	-115.49415
	SD-MBPT(4)	-115.49713
	SDQ-MBPT(4)	-115.49199
<u>Vibration</u>	<u>Mode</u>	<u>Frequency (cm⁻¹)</u>
	OH stretch	3681
	CH ₃ stretch	3005
	CH ₃ stretch	2965
	CH ₃ stretch	2844
	Methyl bend	1477
	Methyl bend	1477
	Methyl bend	1455
	COH	1345
	CO stretch	1073
	Methyl rock	1165
	Methyl rock	1060
	torsion	270

TABLE 4. ELECTRONIC ENERGY PREDICTIONS AND
VIBRATIONAL FREQUENCIES FOR METHOXY RADICAL, CH₃O

<u>Electronic</u>		<u>Energy (h)</u>
	UHF	-114.45319
	D-MBPT(4)	-114.82484
	SD-MBPT(4)	-114.82802
	SDQ-MBPT(4)	-114.82321
<u>Vibration</u>	<u>Mode</u>	<u>Frequency (cm⁻¹)</u>
	ν_1 , C-H stretch (a_1)	2980
	ν_2 , H umbrella (a_1)	1325
	ν_3 , C-O stretch (a_1)	1020
	ν_4 , C-H stretch (e)	3010
	ν_5 , H bend (e)	1380
	ν_6 , rock (e)	680

TABLE 5. DETAILS OF THE ESTIMATION OF THE DISSOCIATION ENERGY FOR METHANOL

	CH ₃ OH	→	CH ₃ O	+	H
Electronic Energy (hartree)	-115.49199		-114.82321		-.49778
ΔE^{el}			.17099h = 107.3 kcal mole ⁻¹		
Zero-point vibrational energy (kcal mole ⁻¹)	31.1		22.1		0.
ΔE^{vib}			-9.0 kcal mole ⁻¹		
$\Delta E_R(0\text{ K})$			98.3 kcal mole ⁻¹		
Translational Energy (300 K) (kcal mole ⁻¹)	0.9		0.9		0.9
ΔE^{tr}			+0.9 kcal mole ⁻¹		
Rotational Energy (300 K) (kcal mole ⁻¹)	0.9		0.9		0.
ΔE^{rot}			0.		
$\Delta E_R(300\text{ K})$			99.2 kcal mole ⁻¹		
$\Delta H_R^\circ(300\text{ K}) = \Delta E_R^\circ(300\text{ K}) + RT = 99.8\text{ kcal mole}^{-1}$					

Experimental values:

100.9 kcal mole⁻¹ (Reference 29)

104.0 kcal mole⁻¹ (Reference 30)

in Table 5 show, the translational energy increases during the course of the reaction, while the rotational energy does not change. Summing the various energy contributions, the theoretical analysis predicts that the energy of reaction is 99.2 kcal mole⁻¹. Comparison with observed enthalpies requires addition of a term $\Delta(pV)$ to the energy. This term is evaluated by using the expression, $\Delta(pV) = \Delta n(RT)$. For $T = 300$ K, the $\Delta(pV)$ term contributes 0.6 kcal mole⁻¹, giving an estimated dissociation energy, $\Delta H_{R,300}^0 = 99.8$ kcal mole⁻¹.

Two experimental values for the dissociation energy of methanol have been reported recently. Batt and McCulloch derived $\Delta H_{R,300}^0$ for methanol using thermochemical parameters derived from chemical kinetic data.³⁰ They derived a value of 3.9 kcal mole⁻¹ for the heat-of-formation of the methoxy radical, leading to a predicted methanol dissociation energy of 104.0 kcal mole⁻¹. Engelking, et al., measured the electron affinity of the methoxy radical, and estimated that the heat-of-formation for CH₃O was 0.7 kcal mole⁻¹.²⁹ This heat-of-formation required that the methanol dissociation energy equal 100.9 kcal mole⁻¹. The results of the MBPT calculations support the experimental value reported by Engelking, et al.

If the heats-of-formation for methanol and hydrogen are assumed to be -48.0 kcal mole⁻¹ and 52.1 kcal mole⁻¹, respectively, the theoretical calculations predict that the heat-of-formation of the methoxy radical is 0.3 kcal mole⁻¹. A summary of the calculation to estimate this quantity appears in Table 6. This estimate agrees well with the experimental value of Engelking, et al.²⁹ This prediction can be checked, however, by calculating the dissociation energy for the methoxy radical and combining that result with the known heats-of-formation of formaldehyde and hydrogen. This calculation is presented in the next section.

In general, good quality, correlated, ab initio calculations tend to underestimate heats-of-reaction. Even the excellent calculations of Goddard and Schaefer underestimated the formaldehyde dissociation energy by about 7 kcal mole⁻¹.⁷ This characteristic is due, in part, to the finite basis sets employed in molecular calculations, since such a basis always describes the products better than it describes the reactant. Such a condition guarantees that the electronic energy of the products is relatively lower than that of the reactant. Reliable estimates of the magnitude of the error introduced are not available, but the fact that theoretical techniques underestimate dissociation energies is general and must be emphasized.

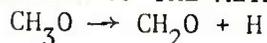
³⁰L. Batt and R. D. McCulloch, "Pyrolysis of Dimethyl Peroxide", *Int. J. Chemical Kinetics* 8, 491 (1976).

³¹G. F. Adams, "A Priori Estimation of Rate Constants for Unimolecular Decomposition Reactions", ARBRL-TR-02143 (1979). (AD#A069132)

TABLE 6. ESTIMATE OF METHOXY RADICAL HEAT-OF-FORMATION

CH_3OH	\rightarrow	CH_3O	$+$	H
$\Delta H_{\text{R},300}^{\circ}$				$99.8 \text{ kcal mole}^{-1}$
$\Delta H_{\text{f},300}^{\circ} (\text{CH}_3\text{O})$	$=$	$\Delta H_{\text{R},300}^{\circ} - \Delta H_{\text{f},300}^{\circ} (\text{H}) + \Delta H_{\text{f},300}^{\circ} (\text{CH}_3\text{OH})$		
$\Delta H_{\text{f},300}^{\circ} (\text{H})$		$52.1 \text{ kcal mole}^{-1}$		
$\Delta H_{\text{f},300}^{\circ} (\text{CH}_3\text{OH})$		$-48.0 \text{ kcal mole}^{-1}$		
$\Delta H_{\text{f},300}^{\circ, \text{th}} (\text{CH}_3\text{O})$		$-0.3 \text{ kcal mole}^{-1}$		

V. DISSOCIATION OF THE METHOXY RADICAL:



The dissociation of the methoxy radical to form formaldehyde, CH_2O , and hydrogen is a reaction that appears in almost all chemical models that describe the oxidation of formaldehyde, or that contain significant contributions by formaldehyde chemistry. Experimental studies of the dissociation reaction are hampered by the lack of molecular information. A theoretical study of the radical offers opportunities to estimate the dissociation energy and heat-of-formation of the radical, and to predict a value of the critical energy that is required for dissociation.

Molecular information characterizing the methoxy radical was discussed in the previous section, and the data are summarized in Table 4. To predict the dissociation energy for the methoxy radical requires electronic energy and vibrational frequency values for formaldehyde. Formaldehyde, CH_2O , is a closed-shell molecule with spatial symmetry corresponding to the point group, C_{2v} . Many publications describe prior theoretical studies of the formaldehyde molecule, with the most important of these summarized in the recent paper by Goddard and Schaefer.⁷

Equilibrium molecular structure parameters for formaldehyde, summarized in Table 7, were predicted by optimizing the energy as a function of three parameters; the CH bond distance, the CO bond distance and the HCH bond angle, using frozen-core D-MBPT(4) calculations. Excellent agreement obtains between the predicted and the experimental values for the structural parameters.³² Electronic energy predictions and vibrational frequencies³² for formaldehyde appear in Table 8. The electronic energy predicted by the fourth-order MBPT calculation that includes all single-, double- and quadruple-excitation diagrams that contribute at that order is lower than that predicted by any of the previous theoretical studies of formaldehyde. However, because of the non-variational property of the linked-diagram related calculation, this energy cannot be identified as an upper bound to the true energy.

Details for the dissociation energy calculation are presented in Table 9. Theory predicts a significantly less endoergic dissociation energy for the methoxy radical than for formaldehyde. On the other hand, the predicted dissociation energy, $22.2 \text{ kcal mole}^{-1}$, is likely less than the critical energy for dissociation, since it is expected that the dissociation of methoxy will have an energy barrier to overcome. In this way the reaction resembles the dissociation reaction of the formyl radical.²⁰

Having predicted a value for the heat-of-reaction, an estimate of the heat-of-formation for the methoxy radical can be obtained. The arithmetic of this estimate appear in Table 10. With the heat-of-formation

³²K. Yamada, T. Nagakura, K. Kuchistu and Y. Morino, "Band Contour Analysis of the ν_1 and ν_2 Fundamentals of Formaldehyde", *J. Mol. Spectroscop.* 38, 70 (1971).

TABLE 7. STRUCTURAL PARAMETERS FOR FORMALDEHYDE^a

	<u>Reference 32</u>	<u>This Work</u>
R _{CH}	1.099	1.102
R _{CO}	1.203	1.211
HCH	116°30'	116°11'

^aBond length units, Å.

TABLE 8. ELECTRONIC ENERGY PREDICTIONS AND VIBRATIONAL FREQUENCIES FOR FORMALDEHYDE, CH₂O

Electronic		Energy (h)
	SCF	-113.8974
	D-MBPT(4)	-114.28321
	SD-MBPT(4)	-114.28868
	SDQ-MBPT(4)	-114.28296
Vibration	Mode	Frequency (cm ⁻¹)
	CH stretch (b ₂)	2843
	CH stretch (a ₁)	2766
	CO stretch (a ₁)	1746
	CH ₂ bend (a ₁)	1501
	CH ₂ bend (b ₂)	1251
	CH ₂ rock (b ₁)	1167

TABLE 9. DETAILS OF THE ESTIMATION OF THE DISSOCIATION ENERGY FOR METHOXY RADICAL

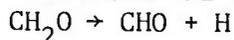
	CH ₃ O	→	CH ₂ O	+	H
Electronic Energy (hartree)	-114.82321		-114.28296		-.49778
ΔE^{el}			.04238h = 26.5 kcal mole ⁻¹		
Zero-point vibrational energy (kcal mole ⁻¹)	22.1		16.2		0.
ΔE^{vib}			-5.9 kcal mole ⁻¹		
$\Delta E_R(0\text{ K})$			20.7 kcal mole ⁻¹		
Translational Energy (300 K) (kcal mole ⁻¹)	0.9		0.9		0.9
ΔE^{tr}			0.9 kcal mole ⁻¹		
Rotational Energy (300 K)	0.9		0.9		
ΔE^{rot}			0.0		
$\Delta E_R^\circ(300\text{ K})$			21.6 kcal mole ⁻¹		
$\Delta H_{R,300}^\circ = E_R^\circ(300\text{ k}) + RT = 22.2\text{ kcal mole}^{-1}$					

TABLE 10. ESTIMATE OF THE METHOXY RADICAL HEAT-OF-FORMATION

CH_3O	\rightarrow	$\text{CH}_2\text{O} + \text{H}$
$\Delta H_{\text{R},300}^{\circ}$		22.2 kcal mole ⁻¹
$\Delta H_{\text{f},300}^{\circ}(\text{CH}_3\text{O}) = \Delta H_{\text{f},300}^{\circ}(\text{CH}_2\text{O}) + \Delta H_{\text{f},300}^{\circ}(\text{H}) - \Delta H_{\text{R},300}^{\circ}$		
$\Delta H_{\text{f},300}^{\circ}(\text{CH}_2\text{O})$		-26.0 kcal mole ⁻¹
$\Delta H_{\text{f},300}^{\circ}(\text{H})$		52.1 kcal mole ⁻¹
$\Delta H_{\text{f},300}^{\circ,\text{th}}(\text{CH}_3\text{O})$		3.9 kcal mole ⁻¹

of formaldehyde assumed to be $-26.0 \text{ kcal mole}^{-1}$,^{2,33} the heat-of-formation result is $3.9 \text{ kcal mole}^{-1}$, a value that differs by about 4 kcal mole^{-1} from the value obtained using the methanol dissociation energy. A major part of the difference between the two estimates results from the systematic underestimation of dissociation energies by theoretical methods. Note that the error decreases the heat-of-formation estimate obtained from the methoxy radical dissociation energy. More accurate predictions of ΔH_f^0 require an estimate of the magnitude of the error in predicted dissociation energies.

VI. DISSOCIATION OF FORMALDEHYDE TO RADICAL PRODUCTS:



Thermal dissociation of formaldehyde produces radical products hydrogen atom (^2S) and formyl radical, HCO ($X^2\text{A}'$). Interestingly, the dissociation to molecular products H_2 ($^1\Sigma^+$) and CO ($^1\Sigma^+$) is almost thermo-neutral, while the observed dissociation energy for formaldehyde is approximately $88 \text{ kcal mole}^{-1}$.³³ Both sets of products correlate by symmetry with the ground electronic state of formaldehyde, $\text{S}_0(X^1\text{A}_1)$. Electronic excitation of formaldehyde to the first singlet excited state, $\text{S}_1(\text{A}^1\text{A}')$, requires less energy than the threshold energy for dissociation. Photochemical experiments indicate that excitation of formaldehyde to the S_1 state leads to three major processes,³⁴



Experimentalists generally agree that process (I), production of molecular products, dominates for energies near the S_1 origin (3.495 eV , $80.6 \text{ kcal mole}^{-1}$). The importance of the radical process increases with increasing excitation energy. For an excitation energy of $91.3 \text{ kcal mole}^{-1}$ the sum of quantum yields for processes (I) and (II) is almost one with molecular quantum yield 0.32 ± 0.03 and the radical quantum yield

³³P. Warneck, "Photoionization von Methanol und Formaldehyd", *Z. Naturforsch A26*, 2047 (1971).

³⁴R. D. McQuigg and J. G. Calvert, "The Photodecomposition of CH_2O , CD_2O , CHDO and $\text{CH}_2\text{O}-\text{CD}_2\text{O}$ Mixtures at Xenon Flash Lamp", *J. Am. Chem. Soc.* **91**, 1590 (1969).

0.68 ± 0.03 .³⁵ Although many experimental studies of the photodissociation of formaldehyde have been reported, there is little agreement as to the detailed mechanism that would explain the observed chemistry.

Goddard and Schaefer reviewed the various mechanistic possibilities in their report on extensive configuration interaction (CI) studies of the features of the potential energy surfaces relevant to the photodissociation of formaldehyde.⁷ These include the dissociation to radical products by breaking a CH bond, the dissociation to molecular products via an intermediate on the S_0 surface, and the rearrangement of formaldehyde to hydroxycarbene, HCOH, on the S_0 surface. The CI study provided improved values for energy barriers for dynamical processes in formaldehyde photochemistry, including the prediction that the energy required for photochemical isomerization to hydroxycarbene is only slightly greater than the energy needed for dissociation to either radical or molecular products. Mechanistic studies of formaldehyde photodissociation should, therefore, consider the presence of the hydroxycarbene molecule. The CI calculations also predict small barriers above the S_1 band origin to any photochemical reaction of formaldehyde.

The CI calculation for the dissociation to radical products predicts the heat-of-reaction to be about 79 kcal mole⁻¹, a value below the experimental threshold of about 86 kcal mole⁻¹.³⁶ CI calculations, in general, underestimate dissociation energies and overestimate barriers to reaction, in part due to variations in the MO basis as the molecular structure is changed. Many-body perturbation theory uses the same diagrams at every point on the potential energy surface, a fact that may reduce the inherent error in a theoretical study. The dissociation of formaldehyde to radical products provides an excellent example to test this contention.

The results of MBPT calculations for the ground electronic state of formaldehyde were presented in Table 8. Electronic structure calculations for the formyl radical include a thorough study of structures surrounding the equilibrium conformation, as well as a number of structures in the hypersurface associated with dissociation to hydrogen and carbon monoxide. The predicted structural parameters for the equilibrium conformation are given in Table 11, along with parameters deduced from a number of

³⁵A. Horowitz and J. G. Calvert, "The Quantum Efficiency of the Primary Processes in Formaldehyde Photolysis at 3130Å and 25½°C", *Int. J. Chem. Kinet.* 10, 713 (1978).

³⁶J. H. Clark, C. B. Moore and N. S. Nogar, "The Photochemistry of Formaldehyde. Absolute Quantum Yields, Radical Reaction and NO Reactions", *J. Chem. Phys.* 68, 1264 (1978).

TABLE 11. STRUCTURAL PARAMETERS FOR THE FORMYL RADICAL, HCO^a

	<u>Ref. 37</u>	<u>Ref. 38</u>	<u>Ref. 40</u>	<u>Ref. 41</u>	<u>Ref. 42</u>	<u>This work</u>
R _{CH}	1.08	1.145	1.1102	1.1465	1.125	1.111
R _{CO}	1.198	1.176	1.1715	1.1783	1.175	1.188
HCO	119.5	123.3	127.426	122.7	124.95	124

^aBond lengths units, A.

experimental studies.³⁷⁻⁴² Because of the more precise data obtained by Brown and Ramsey,⁴² the structure predicted in that publication should be more accurate than the other empirical structures. The theoretical bond lengths and angle predictions agree well with the Brown and Ramsey parameters.

A summary of the electronic structure calculations for the predicted equilibrium conformation of the radical appears in Table 12. The wave function, not a pure spin state, has a multiplicity equal to 2.01, indicating that the zero-order wave function contains only small contamination from excited states. The vibrational frequencies listed in Table 12, taken from the data of Brown and Ramsey, correspond to a vibrational zero-point energy of 7.8 kcal mole⁻¹ for the radical.

The heat-of-reaction estimate for the dissociation of formaldehyde to radical products, outlined in Table 13, parallels the previous dissociation energy calculations. An electronic energy barrier of 93.4 kcal mole⁻¹, predicted by the MBPT calculations, is significantly higher than the CI barrier, 88.5 kcal mole⁻¹.⁷ Since the zero-point energy differences are virtually identical, the predicted dissociation energy for the threshold reaction, 85 kcal mole⁻¹, is larger than the value predicted by the CI calculations, 80.2 kcal mole⁻¹.⁷ As noted by Goddard and Schaefer, the CI calculations underestimate the threshold by about 5 kcal mole⁻¹.

³⁷G. Herzberg and D. Ramsey, "The 7500 to 4500 Å Absorption System of the Free HCO Radical", *Proc. Roy. Soc. (London)* A233, 34 (1955).

³⁸J. E. Ogilvie, "The Vibrational Fundamentals and Structure of Triatomic Radicals formed by Photolytic Hydrogen-Atom Reactions", *Spectrochim. Acta* A23, 737 (1969).

³⁹S. Saito, "Laboratory Observations of the $101 \leftarrow 0_{00}$ Transitions for the HCO and DCO Free Radicals by Microwave Spectroscopy", *Astrophys. J.* 178, L95 (1972).

⁴⁰J. A. Austin, D. A. Levy, C. A. Gottlieb and H. E. Radford, "Microwave Spectrum of the HCO Radical", *J. Chem. Phys.* 60, 207 (1974).

⁴¹J. Ogilvie, "Structures of Triatomic Radicals HCO, HNO, and HOO", *J. Mol. Struct.* 31, 407 (1976).

⁴²J. M. Brown and D. A. Ramsey, "Axis Switching in the $\tilde{A}^2A' - \tilde{X}^2A'$ Transitions of HCO: Determination of Molecular Geometry", *Can. J. Phys.* 53, 2232 (1975).

TABLE 12. ELECTRONIC ENERGY PREDICTIONS AND VIBRATIONAL FREQUENCIES
FOR FORMYL RADICAL, HCO

Electronic		Energy (h)
	UHF	-113.2769
	D-MBPT(4)	-113.6343
	SD-MBPT(4)	-113.64155
	SDQ-MBPT(4)	-113.63634
Vibration	Mode	Frequency(cm^{-1})
	CH Stretch	2488
	CO Stretch	1861
	HCO Bend	1080

TABLE 13. DETAILS OF THE ESTIMATION OF THE DISSOCIATION ENERGY FOR FORMALDEHYDE

	CH ₂ O	→	CHO	+	H
Electronic Energy (hartree)	-114.28296		-113.63634		-.49778
	ΔE^{el}		.14884h = 93.4 kcal mole ⁻¹		
Zero-point Vibrational Energy (kcal mole ⁻¹)	16.2		7.8		0.
	ΔE^{vib}		-8.4 kcal mole ⁻¹		
	$\Delta E_R(0\text{ K})$		85.0 kcal mole ⁻¹		
Translational Energy (kcal mole ⁻¹)	0.9		0.9		0.9
	ΔE^{tr}		0.9 kcal mole ⁻¹		
Rotational Energy (kcal mole ⁻¹)	0.9		0.9		0.
	ΔE^{rot}		0.		
	$\Delta E_R + pV = 86.5\text{ kcal mole}^{-1}$				
Experimental Values, $\Delta H_{R,300}^\circ$:	85	- 87	kcal mole ⁻¹ (36)		
	86.9 ± 2	kcal mole ⁻¹ (43)			
	88.2 ± 1.6	kcal mole ⁻¹ (33)			

The MBPT calculations predict a dissociation energy slightly below the experimental values of Walsh and Benson⁴³ and Warneck.³³

The predicted dissociation energy leads to an estimate of the heat-of-formation of the formyl radical by a calculation outlined in Table 14. The predicted value, $\Delta H_{f,300}^{\circ}(\text{HCO}) = 8.4 \text{ kcal mole}^{-1}$, is slightly less than the value inferred from Warneck's recent study, $9.9 \text{ kcal mole}^{-1}$.³³ As noted previously, underestimation of the heat-of-reaction leads to underestimation of the heat-of-formation of a product species, so this result does not surprise.

Before discussing alternate dissociation mechanisms for formaldehyde, the dissociation of formyl radical will be investigated, in order to obtain another estimate of $\Delta H_{f,300}^{\circ}$ for the radical.

VII. DISSOCIATION OF THE FORMYL RADICAL: $\text{CHO} \rightarrow \text{CO} + \text{H}$

A recent paper by Adams, et al., describes a complete theoretical study of the formyl radical using linked-diagram related methods.²⁰ This section reviews the results of that publication.

Formyl radical, HCO, dissociates into ground state hydrogen and carbon monoxide along a single potential energy surface. This surface is expected to have a substantial energy barrier ($> 5 \text{ kcal mole}^{-1}$) above the dissociation energy of the radical. The major objectives of the theoretical study of the formyl radical potential energy hypersurface were to predict the height of this energy barrier and to specify the structure of the activated complex at the barrier. Table 15 lists the predicted structural parameters for the transition state. The barrier height, (the difference in electronic energy between the equilibrium configuration and the saddle point) corresponds to a critical energy of $18.5 \text{ kcal mole}^{-1}$. The predicted transition state properties were used in an a priori statistical analysis of the dissociation kinetics for the radical.⁴⁴

To estimate the dissociation energy of the formyl radical, the electronic energy of carbon monoxide is required. Table 16 lists the results of the MBPT calculations as well as the value assigned to the CO stretching frequency. Optimization of the CO bond length resulted in exact agreement between the experimental and theoretical values, $2.1276b$.

⁴³R. Walsh and S. W. Benson, "Kinetics and Mechanisms of Gas-Phase Reactions between Iodine and Formaldehyde and the Carbon-Hydrogen Bond Strength in Formaldehyde", *J. Am. Chem. Soc.* 88, 4570 (1966).

⁴⁴G. F. Adams, "Estimation of a Rate Coefficient for the Decomposition of the Formyl Radical", manuscript to be submitted.

TABLE 14. ESTIMATE OF THE FORMYL RADICAL HEAT-OF-FORMATION

CH_2O	\rightarrow	$\text{CHO} + \text{H}$
$\Delta H_{\text{R},300}^{\circ}$		86.5 kcal mole ⁻¹
$\Delta H_{\text{f},300}^{\circ} (\text{HCO}) = \Delta H_{\text{R},300}^{\circ} - \Delta H_{\text{f},300}^{\circ} (\text{H}) + \Delta H_{\text{f},300}^{\circ} (\text{CH}_2\text{O})$		
$\Delta H_{\text{f},300}^{\circ} (\text{H})$		52.1 kcal mole ⁻¹
$\Delta H_{\text{f},300}^{\circ} (\text{CH}_2\text{O})$		-26.0 kcal mole ⁻¹
$\Delta H_{\text{f},300}^{\circ} (\text{HCO})$		8.4 kcal mole ⁻¹

TABLE 15. MOLECULAR PARAMETERS OF THE FORMYL RADICAL AT THE SADDLEPOINT

<u>Electronic Energy</u>		<u>(²A')</u>
(Hartrees)		
UHF		-113.2488
SD-MBPT(4)		-113.6048
Barrier Height		23.1 kcal mole ⁻¹
<u>Structural Parameters</u>		
R_{CH}	3.35 b	
R_{CO}	2.15 b	
HCO	115°	

TABLE 16. ELECTRONIC ENERGY PREDICTIONS AND VIBRATIONAL FREQUENCY FOR CARBON MONOXIDE, CO

Electronic		Energy (Hartree)
	SCF	-112.76646
	D-MBPT(4)	-113.11047
	SD-MBPT(4)	-113.11732
	SDQ-MBPT(4)	-113.11235
Vibrational		Frequency (cm ⁻¹)
	CO Stretch	2170.

The calculation to predict the formyl radical dissociation energy is summarized in Table 17. This example differs from the previous estimates of dissociation energy, since the change in rotational energy for the reaction differs from zero. The predicted heat-of-reaction is lower than the suggested experimental values.^{33,45}

The predicted heat-of-formation of the formyl radical, detailed in Table 18, exceeds the value obtained in the calculation based upon the dissociation energy of formaldehyde. As was the case with estimates of ΔH_F^O for methoxy, the systematic underestimation of dissociation energies leads to predicted values of ΔH_F^O that differ significantly for the radical as product or reactant. To estimate heats-of-formation more accurately requires data about the magnitude of the error in the predicted heat-of-reaction. One approach, used initially by Bauschlicher and Shavitt,⁴⁶ systematically improves the basis set until the quantity calculated does not vary with the basis set change. Although this technique may work for a particular problem, employing such an approach for all theoretical studies requires computer resources not currently available.

An alternative, pragmatic approach is to use the verified differences between experimental and theoretical values of dissociation energies to estimate the degree to which theory underestimates the physical quantity. For the reactions discussed in this report, Warneck's experimental dissociation energy for formaldehyde is least subject to revision. The theoretical prediction underestimates Warneck's measurements by 1.7 kcal mole⁻¹. This example, combined with the results published by Redmon, et al.,¹⁹ suggests that theory underestimates dissociation energies by approximately 1.5 kcal mole⁻¹, and that addition of this quantity to the original theoretical estimates corrects the dissociation energy in a reasonable way. The original and modified theoretical estimates are compared with experimental dissociation energies in Table 19. This modification improves the agreement between theory and experiment, a not unexpected result of this choice of correction factor. Modified heat-of-formation estimates for methoxy and formyl are outlined in Tables 20 and 21, respectively. Use of the "correction" factor reduces the difference between the two ΔH_F^O values for methoxy to 1.2 kcal mole⁻¹ (2.1 kcal mole⁻¹ and 3.3 kcal mole⁻¹), and reduces the difference between the formyl radical estimates to 1.4 kcal mole⁻¹ (9.9 kcal mole⁻¹ and 11.3 kcal mole⁻¹). These heat-of-formation estimates fall within the error limits of the experimental values, and thus it seems justified to claim that this method predicts accurate values for dissociation energies and heats-of-formation.

A comment about the intrinsic accuracy of dissociation energy data clarifies the significance of the theoretical results. Most published dissociation energies have error limits of several kilocalories per mole.

⁴⁵M. A. Haney and J. C. Franklin, "Excess Energies in Mass Spectra of Some Oxygen Containing Compounds", *Trans. Far. Soc.* 65, 1794 (1969).

⁴⁶C. Bauschlicher and I. Shavitt, "Accurate *ab initio* calculations on Singlet-Triplet Separation in Methylene", *J. A. Chem. Soc.* 100, 739 (1978).

TABLE 17. DETAILS OF THE ESTIMATION OF THE DISSOCIATION ENERGY FOR FORMYL RADICAL

	CHO	→	CO	+	H
Electronic Energy (hartree)	-113.63634		-113.11235		-.49778
ΔE^{el}			.02621h = 16.4 kcal mole ⁻¹		
Zero-point Vibrational Energy (kcal mole ⁻¹)	7.8		3.1		0.
ΔE^{vib}			-4.7 kcal mole ⁻¹		
$\Delta E_R(0\text{ K})$			11.7 kcal mole ⁻¹		
Translational Energy (300 K) (kcal mole ⁻¹)	0.9		0.9		0.9
ΔE^{tr}			0.9 kcal mole ⁻¹		
Rotational Energy (300 K) (kcal mole ⁻¹)	0.9		0.6		0.
ΔE^{rot}			-0.3 kcal mole ⁻¹		
$\Delta E_R^\circ(300\text{ K})$			12.3 kcal mole ⁻¹		
$\Delta H_{R,300}^\circ = \Delta E_R^\circ(300\text{ K}) + pV = 12.9\text{ kcal mole}^{-1}$					
Experimental Values: 15.5 ± 1.5 Reference 33					
17 ± 2. Reference 45					

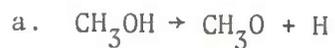
TABLE 18. ESTIMATE OF THE FORMYL RADICAL HEAT-OF-FORMATION

CHO	→	CO + H
$\Delta H_{R,300}^{\circ}$		12.9 kcal mole ⁻¹
$\Delta H_{f,300}^{\circ} (\text{CHO}) = \Delta H_{R,300}^{\circ} - \Delta H_{f,300}^{\circ} (\text{CO}) - \Delta H_{f,300}^{\circ} (\text{H})$		
$\Delta H_{f,300}^{\circ} (\text{H})$		52.1 kcal mole ⁻¹
$\Delta H_{f,300}^{\circ} (\text{CO})$		-26.4 kcal mole ⁻¹
$\Delta H_{f,300}^{\circ} (\text{HCO})$		12.8 kcal mole ⁻¹

TABLE 19. MODIFIED HEAT-OF-REACTION PREDICTIONS (kcal mole⁻¹)

<u>Reaction</u>	<u>$\Delta H_{R,300}^{\circ,th}$</u>	<u>$\Delta H_{R,300}^{\circ,th} + 1.5$</u>	<u>Experiment</u>
$\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}$	99.6	101.3	100.9 (29) 104.0 (30)
$\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} + \text{H}$	22.2	23.7	...
$\text{CH}_2\text{O} \rightarrow \text{CHO} + \text{H}$	86.5	88.0	88.2 (33)
$\text{CHO} \rightarrow \text{CO} + \text{H}$	12.9	14.4	15.4 (33) 17.0 (45)

TABLE 20. MODIFIED HEAT-OF-FORMATION ESTIMATES, METHOXY (kcal mole⁻¹)



$$\Delta H_{\text{R},300}^{\circ} \quad 101.3$$

$$\Delta H_{\text{f},300}^{\circ} (\text{CH}_3\text{OH}) \quad -48.0$$

$$\Delta H_{\text{f},300}^{\circ} (\text{H}) \quad 52.1$$

$$\Delta H_{\text{f},300}^{\circ, \text{th}} (\text{CH}_3\text{O}) \quad 1.2$$

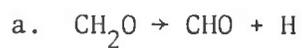


$$\Delta H_{\text{R},300}^{\circ} \quad 23.7$$

$$\Delta H_{\text{f},300}^{\circ} (\text{CH}_2\text{O}) \quad -26.0$$

$$\Delta H_{\text{f},300}^{\circ, \text{th}} (\text{CH}_3\text{O}) \quad 2.4$$

TABLE 21. MODIFIED HEAT-OF-FORMATION ESTIMATES, FORMYL (kcal mole⁻¹)

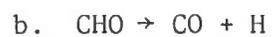


$$\Delta H_{\text{R},300}^{\circ} \quad 88.0$$

$$\Delta H_{\text{f},300}^{\circ} (\text{CH}_2\text{O}) \quad -26.0$$

$$\Delta H_{\text{f},300}^{\circ} (\text{H}) \quad 52.1$$

$$\Delta H_{\text{f},300}^{\circ, \text{th}} (\text{CHO}) \quad 9.9$$



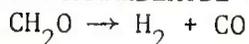
$$\Delta H_{\text{R},300}^{\circ} \quad 14.4$$

$$\Delta H_{\text{f},300}^{\circ} (\text{CO}) \quad -26.4$$

$$\Delta H_{\text{f},300}^{\circ, \text{th}} \quad 11.3$$

For molecules such as formaldehyde which permit sophisticated experimental studies, thermochemical data are accurate and precise. But for species such as the formyl radical, often the suggested empirical values lie outside the respective suggested error limits. The error limits suggested by Warneck³³ for the dissociation energy of formyl barely contain the dissociation energy reported by Haney and Franklin.⁴⁵ The MBPT calculations predict that both values are too high, and that this dissociation energy is less than 15 kcal mole⁻¹. Since both theory and experiment have minimum error limits of ± 3 kcal mole⁻¹, the difference between our theoretical estimates and available experimental data is inconsequential.

VIII. DISSOCIATION OF FORMALDEHYDE TO MOLECULAR PRODUCTS:



The formation of molecular products in the dissociation of formaldehyde occurs via one of several competitive mechanisms. Two possible reaction channels were studied by Goddard and Schaefer, leading to identification of two reaction intermediates.⁷ One intermediate occurs on the S_0 potential energy curve that leads to direct formation of the molecular products, $\text{H}_2 + \text{CO}$. The other intermediate occurs on the S_0 surface between ground state formaldehyde and the metastable species, hydroxycarbene. In addition to determining the structure of each intermediate, Goddard and Schaefer predicted the vibrational frequencies for the two evanescent species, thus facilitating the task of estimating zero-point energy differences. The rearrangement to hydroxycarbene provides an example of the importance of the 1,2-hydrogen shift in chemistry.

The configuration interaction calculations used by Goddard and Schaeffer underestimate the dissociation energy of formaldehyde (to form radical products) by about 5 kcal mole⁻¹, an error considerably larger than that attained by the MBPT calculation reported in section VI. It is important to investigate the predictions of MBPT for the transition state geometries to determine whether the two theoretical approaches again obtain different results.

The approach to these MBPT calculations differs from that reported in the previous sections. Rather than determining the optimal structural parameters for the transition states, this study uses the structures reported by Goddard and Schaefer. The results of the MBPT calculations for the molecular products and rearrangement transition states, as well as the Goddard-Schaefer predictions for the real vibrational eigenvalues, are presented in Tables 22 and 23, respectively. In addition, Table 24 contains the results of a "supermolecule" calculation for the molecular products, H_2 and CO . Tables 22, 23 and 24 contain all the molecular data needed to estimate thermochemical parameters relevant to the dissociation of formaldehyde to molecular products.

TABLE 22. ELECTRONIC ENERGY PREDICTIONS AND VIBRATIONAL FREQUENCIES FOR THE MOLECULAR PRODUCTS TRANSITION STATE

Electronic		Energy (hartree)
	SCF	-113.73169
	D-MBPT(4)	-114.13206
	SD-MBPT(4)	-114.13991
	SDQ-MBPT(4)	-114.13256
Vibrational	Mode	Frequency (cm ⁻¹)
	CH Stretch	2760
	CO Stretch	1654
	HCO	1137
	HCO	800
	HCH	592

TABLE 23. ELECTRONIC ENERGY PREDICTIONS AND VIBRATIONAL FREQUENCIES FOR THE HYDROXYCARBENE TRANSITION STATE

Electronic		Energy (hartree)
	SCF	-113.73666
	D-MBPT(4)	-114.13652
	SD-MBPT(4)	-114.14547
	SDQ-MBPT(4)	-114.13911
Vibrational	Mode	Frequency (cm ⁻¹)
	"out-of-plane"	3675
	CH	2803
	CH	2339
	HCH	1333
	HCH	1038

TABLE 24. ELECTRONIC ENERGY PREDICTIONS AND VIBRATIONAL FREQUENCIES
FOR MOLECULAR PRODUCTS, H₂ + CO

Electronic		Energy (hartree)
	SCF	-113.89766
	D-MBPT(4)	-114.27622
	SD-MBPT(4)	-114.28317
	SDQ-MBPT(4)	-114.27797
Vibrational	Mode	Frequency (cm ⁻¹)
	H ₂ Stretch	4150
	CO Stretch	2150

Isomerization of formaldehyde to form hydroxycarbene exemplifies a 1,2-hydrogen shift. This class of chemical reactions plays an important role in many organic reaction mechanisms. A recent review by Schaefer elucidates the main features of the 1,2-hydrogen shift, while providing a survey of the experimental literature.⁴⁷ Goddard and Schaefer located the transition state for the isomerization using a gradient-SCF technique.⁷ This calculation also provided estimates of the vibrational force constants, from which the vibrational frequencies for the transition state can be derived. Interestingly, the zero-point energy of the transition state exceeds that of the equilibrium molecule by 0.5 kcal mole⁻¹. The estimate of the barrier height, outlined in Table 25, reflects the increase of the critical energy relative to the electronic energy barrier. The SDQ-MBPT(4) results predict an electronic energy barrier equal to 90.3 kcal mole⁻¹, corresponding to a critical energy equal to 90.8 kcal mole⁻¹. This number exceeds the Goddard-Schaefer prediction for the barrier, 89.3 kcal mole⁻¹, and the predicted heat-of-reaction to radical products, 85 kcal mole⁻¹. However, the difference between the two linked-diagram method calculations, 5.8 kcal mole⁻¹, is much less than the difference between the two CI predictions, 9.3 kcal mole⁻¹.

The final formaldehyde dissociation calculation, outlined in Table 26, corresponds to the direct formation of molecular products. An electronic energy barrier, 94.4 kcal mole⁻¹, is reduced by the zero-point energy change, -6.6 kcal mole⁻¹, to yield a predicted critical energy for this dissociation pathway of 87.8 kcal mole⁻¹, and, like the barrier to rearrangement, exceeds the energy required to dissociate to radical products.

The calculation of the heat-of-reaction for the dissociation of formaldehyde to molecular products is outlined in Table 27. The electronic energy difference, 3.13 kcal mole⁻¹, leads to a predicted heat-of-reaction, -2.1 kcal mole⁻¹, that underestimates the suggested empirical value by 1.8 kcal mole⁻¹.

The results reported here agree with the Goddard-Schaefer electronic structure calculations and support their proposed mechanisms for the photochemical dissociation of formaldehyde to form molecular products. In fact, the MBPT results predict that the energy requirements for the production of molecular products via either of the proposed mechanisms approach the energy requirements for thermal dissociation to radical products. To determine whether these results are an artifact of the MBPT method, double-excitation coupled-cluster calculations paralleling the many-body calculations were performed. Table 28 contains the result

⁴⁷H. F. Schaefer, III, "The 1,2-Hydrogen Shift: A Common Vehicle for the disappearance of Evanescent Molecular Species", *Accts. Chem. Research*, in press.

TABLE 25. BARRIER HEIGHT FOR FORMALDEHYDE TO HYDROCARBENE ISOMERIZATION

	H ₂ CO	→	(HCOH) [‡]
Electronic Energy (hartree)	-114.28296		-114.13911
	ΔE^{el}		.14385h = 90.3 kcal mole ⁻¹
Zero-point Vibrational Energy* (kcal mole ⁻¹)			
	ΔE_{zp}		0.5 kcal mole ⁻¹
	ΔE_o^{\ddagger}		90.8 kcal mole ⁻¹

* Zero-point vibrational energies calculated by Goddard and Schaefer(7). Although their predicted zero-point energy for formaldehyde is greater than the experimental value, the change in zero-point energy between species seems to be insensitive to this error.

TABLE 26. BARRIER HEIGHT FOR DISSOCIATION OF FORMALDEHYDE TO MOLECULAR PRODUCTS

	CH ₂ O	→	(CH ₂ O) [‡]
Electronic Energy (hartree)	-114.28296		-114.13256
	ΔE^{el}		.1504h = 94.4 kcal mole ⁻¹
Zero-point Vibrational Energy* (kcal mole ⁻¹)	18.3		11.7
	ΔE_{zp}		-6.6 kcal mole ⁻¹
	ΔE_o^{\ddagger}		87.8 kcal mole ⁻¹

* Zero-point energies predicted by Goddard and Schaefer (7).

TABLE 27. HEAT-OF-REACTION FOR THE DISSOCIATION
OF FORMALDEHYDE TO MOLECULAR PRODUCTS

	CH ₂ O	→	H ₂	+	CO
Electronic Energy (hartree)	-114.28296				-114.27797
ΔE^{el}			.00499h = 3.13 kcal mole ⁻¹		
Zero-point Vibrational Energy (kcal mole ⁻¹)	16.2				9.1
ΔE_{Zp}			-7.1 kcal mole ⁻¹		
ΔE_R°			-3.9 kcal mole ⁻¹		
Translational Energy (kcal mole ⁻¹)	0.9		0.9		0.9
ΔE^{tr}			0.9 kcal mole ⁻¹		
Rotational Energy (kcal mole ⁻¹)	0.9		0.6		0.6
ΔE^{rot}			0.3 kcal mole ⁻¹		
ΔE_R° (300 K)			-2.7 kcal mole ⁻¹		
$\Delta H_{R,300}^\circ = E_R^\circ$ (300 K) + pV			= -2.1 kcal mole ⁻¹		

TABLE 28. RESULTS OF CCD CALCULATIONS FOR
FORMALDEHYDE CHEMISTRY

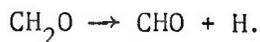
<u>Molecule</u>	<u>CCD Energy (hartree)</u>
CH ₂ O, equilibrium	-114.27718
Transition state, rearrangement	-114.12930
Transition state, molecular products	-114.12407
CHO, equilibrium	-113.6288

of the CCD calculations of the electronic energy for several of the molecular and intermediate structures relevant to formaldehyde dissociation, while Table 29 contains a comparison of the CI, MBPT and CCD predictions of thermochemical quantities. The CCD calculations predict the highest values for the thermochemical quantities, with a notably large barrier predicted for the rearrangement reaction. In sum, the calculations suggest that the rearrangement barrier exceeds the barrier for dissociation to molecular products.

In their discussion of the CI results, Goddard and Schaefer comment that configuration interaction calculations generally underestimate heats-of-reaction and overestimate barrier heights. The expected error in the dissociation energy calculations equals about 5 kcal mole⁻¹, while the expected error in the barrier height calculation is approximately 2 kcal mole⁻¹. Linked-diagram calculations have, to date, underestimated dissociation energies by 1 to 2 kcal mole⁻¹, and overestimated rearrangement barriers by similar amounts.¹⁹ Assuming these error estimates, the relative energy differences indicated in Table 29 reduce to almost zero. Therefore, using energy as the criterion for reaction, all three of the proposed reaction channels should be considered when seeking a mechanism to describe the photo dissociation of formaldehyde. The inferences with respect to the thermal dissociation of formaldehyde are considered in the next section.

IX. THE UNIMOLECULAR THERMAL DISSOCIATION OF FORMALDEHYDE

Combustion chemistry models customarily assume that the thermal dissociation of formaldehyde produces radical products,



Experimental studies by Clark, Moore and Nogar demonstrated that the dissociation to radical products exhibits an abrupt energy threshold between 85 and 87 kcal mole⁻¹.³⁶ Such a value falls within the error bars of the thermodynamic estimates of Walsh and Benson, 86.9 ± 2 kcal mole⁻¹, and Warneck, 88.2 ± 1.6 kcal mole⁻¹.³³ Recent work by Reilly, Clark, Moore and Pimentel confirms the radical threshold at 86 ± 1 kcal mole⁻¹.⁴⁸ The MBPT and CCD calculations, corrected for T = 300 K, predict the radical threshold at 86.6 and 87.8 kcal mole⁻¹, respectively. As noted in the previous section, the relative energy calculations suggest that the dissociation to molecular products should compete with the radical product channel.

⁴⁸J. P. Reilly, J. H. Clark, C. B. Moore and G. C. Pimentel, to be published. Results quoted by Goddard and Schaefer.⁷

TABLE 29. COMPARISON OF CI, MBPT(4) AND CCD CALCULATIONS
 (UNITS: kcal mole⁻¹)

<u>Reaction</u>	<u>CI</u>	<u>SDQ-MBPT(4)</u>	<u>CCD</u>
CH ₂ O → CHO + H	~80.	85.0	86.2
CH ₂ O → (HCOH) [‡]	88.8	90.8	93.3
CH ₂ O → (CH ₂ O) [‡]	87.	87.8	89.5

Several other results of the photochemical experiments relate to this discussion. These experiments involve excitation into the first excited singlet state, S_1 , and subsequent dissociation to either radical or molecular products. For energies below the radical threshold, formaldehyde (S_1) dissociates to molecular products with quantum yield 0.9. For energies equal to and greater than the radical threshold, the total quantum yield is near 1.0, with radicals accounting for about forty per cent of the dissociation. The abrupt threshold for radical products demonstrates that no barrier occurs in this reaction channel, and this implies that the dissociation does not occur on the S_1 hypersurface.

No mechanism to explain the photodissociation of formaldehyde has yet received the acceptance of the chemical community. Goddard and Schaefer's theoretical study suggests that formaldehyde (S_1) undergoes internal conversion to formaldehyde (S_0), followed by dissociation that is enhanced by quantum mechanical tunneling to molecular products. These proposed reactions occur on the S_0 hypersurface, so there is no priori reason why molecular products may not occur during thermal dissociation, since the transition state for this channel is energetically competitive with the dissociation to radical products. However, dynamical considerations strongly favor the formation of radical products. The "loose" transition state representative of that dissociation reaction guarantees that the entropy of activation for this channel will exceed that characteristic of a "tight" transition state. The two transition states found by Goddard and Schaefer are "tight" transition states. Consequently, the dissociation to radical products should occur more rapidly, in a chemical kinetics sense, than the dissociation to molecular products, provided that the non-fixed internal energy distribution is statistical. In photodissociation, the constancy of the molecular/radical branching ratio above the radical threshold implies that the reacting species does not have a statistical distribution of non-fixed internal energy.

The connection between the confusion associated with the mechanism of photodissociation of formaldehyde and the simplistic thermal dissociation mechanism defies easy definition. That some anomaly in thermal dissociation may occur under extreme conditions of temperature and pressure seems likely, but it may be that under extreme conditions the dissociation reaction is ignorable relative to competing bimolecular reactions.

X. SUMMARY

The calculations described in this report have important implications for research in flame zone chemistry. For the first time an a priori model predicts heats-of-reaction as accurately as the best experiments. In addition, heats-of-formation can be estimated with moderate accuracy. This accuracy is improved if a pragmatic correction to the heat-of-reaction estimate is used.

The results of calculations of dissociation energies and barrier heights for a series of formaldehyde reactions support the photodissociation mechanism proposed by Goddard and Schaefer.⁷

The linked-diagram based calculations described in this report appear to predict thermochemical quantities more accurately than do truncated configuration interaction calculations.

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Finally, we acknowledge the contributions of Drs. Rodney Bartlett and George D. Purvis of Battelle Columbus Laboratories. Their pioneering work in the development and efficient programming of the MBPT method and their unstinting assistance of our research has made this research possible.

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APPENDIX A. THE CORRELATION PROBLEM AND THE METHOD
OF CONFIGURATION INTERACTION

The standard approach to electronic structure theory for many researchers is the Hartree-Fock self-consistent field method, a technique based upon a variational principal. For a normalized approximate wave-function ψ , the expectation value of the electronic Hamiltonian operator, corresponding to the electronic energy, has the form,

$$E = \langle \psi | H | \psi \rangle \tag{A-1}$$

The variational principle guarantees that this expectation value, E , exceeds the true value of the electronic energy; that is, the expectation value is an upper bound.

The Hartree-Fock wave-function may be written as an antisymmetrized product

$$\Psi_{\text{HF}} = A(m) \phi_1(1)\phi_2(2)\dots\phi_m(m), \tag{A-2}$$

where A is the antisymmetrizer for m -electrons and the ϕ_i 's are one-electron spin orbitals, products of a spatial orbital χ and a one-electron spin function. This function has a convenient expression as a Slater-determinant

$$\Psi_{\text{HF}} = \frac{1}{\sqrt{m!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \dots & \phi_m(1) \\ \vdots & \vdots & & \vdots \\ \vdots & \vdots & & \vdots \\ \phi_1(m) & \phi_2(m) & \dots & \phi_m(m) \end{vmatrix} \tag{A3}$$

The Hartree-Fock wave-function corresponds to the determinant for which the orbitals in equation (2) have been varied to give the lowest possible electronic energy.

Minimizing the energy resulting from a single-determinant wave-function leads to a complicated set of integro-differential equations, the Hartree-Fock equations. The conceptual importance of the Hartree-Fock approach is that the HF wave function is the best wave function that can be constructed by assigning each electron to a separate orbital or function that depends only upon the coordinates of that electron.

In practice, the one electron functions, ϕ_i , are expanded in terms of a finite set of analytical basis functions,

$$\phi_i = \sum_j C_{ij} \chi_j. \quad (\text{A-4})$$

Because of the finite basis, only approximate solutions of the HF equations occur. The lowest-energy single-determinant wave function available in the finite basis, the so-called self-consistent field (SCF) wave-function, represents the level of theoretical sophistication most commonly encountered in the chemical literature. SCF wave-functions suffice to describe the structure and properties of molecules near equilibrium in the ground electronic state. This level of calculation does not suffice to describe potential energy curves and surfaces, transition states, or excited electronic states. The difference between the best Hartree-Fock approximation of the electronic energy and the exact energy calculated using the non-relativistic Schrodinger equation is the correlation energy. The name reflects the physical concept that the Hartree-Fock potential contains the average, rather than the instantaneous, inter-electron potential, and thus neglects the correlation between the motions of electrons.*

To circumvent the error introduced by the HF approximation, excited electronic configurations were added to the Hartree-Fock wave function, leading to the method of configuration interaction (CI). A CI wave function can be represented as a sum of Slater determinants, and the energy is determined by variation of the expansion coefficients until a minimum energy is obtained. Were the basis set of one electron functions (MO's) complete, the result of a complete CI calculation would approach the exact numerical solution of the N-particle Schrodinger equation.

The CI wave function, with ϕ_0 the HF solution, has the form,

$$\psi = \phi_0 + \sum_{i,a} C_i^a \phi_i^a + \sum_{i>j} C_{ij}^{ab} \phi_{ij}^{ab} + \dots, \quad (\text{A-5})$$

where, for instance, ϕ_i^a represents the configuration obtained by exciting an electron from orbital i of ϕ_0 to an orbital a in the virtual orbital space. Equation (A-5) has the more compact form,

* As pointed out by Shavitt (1), this definition of correlation energy neglects non-dynamical effects caused by near degeneracies and rearrangements of electrons within partially filled shells. This leads, in the case of potential energy curves that are always poorly described by RHF wave functions, to the counterintuitive idea that the correlation energy increases as the electrons move apart with the separating atoms.

^{A1} I. Shavitt, "The Method of Configuration Interaction", in Modern Theoretical Chemistry, Vol. III. Methods of Electronic Structure Theory, edited by H. F. Schaefer, III, Plenum, New York, 1977.

$$\Psi = \sum_{s=1}^m C_s \phi_s \quad (\text{A-6})$$

where the ϕ_s represent pre-determined expansion functions and the coefficients C_s represent the variational parameters used to minimize $E[\Psi]$. This form of the wave-function leads to the generalized matrix eigenvalue equation,

$$\underline{\underline{H}} \underline{\underline{c}} = E \underline{\underline{S}} \underline{\underline{c}}, \quad (\text{A-7})$$

with the matrix elements, H_{st} and S_{st} , defined by

$$H_{st} \equiv \langle \phi_s | H | \phi_t \rangle \quad (\text{A-8})$$

$$S_{st} \equiv \langle \phi_s | \phi_t \rangle, \quad (\text{A-9})$$

and the column vector $\underline{\underline{c}}$ has the coefficients c_s as components.

The principal computational step of a CI calculation is the evaluation of the matrix elements, H_{st} . Choosing the molecular orbital basis set to be orthonormal facilitates this evaluation, for then the matrix elements equations have the form

$$H_{st} = \langle \phi_s | H | \phi_t \rangle = \sum_{i,j} a_{ij}^{st} h_{ij} + \sum_{ijkl} b_{ijkl}^{st} g_{ijkl}, \quad (\text{A-10})$$

with the orbital integrals defined by

$$h_{ij} \equiv \langle \phi_i(\vec{r}_1) | h_1 | \phi_j(\vec{r}_1) \rangle \quad (\text{A-11})$$

$$g_{ijkl} \equiv \langle \phi_i(\vec{r}_1) \phi_k(\vec{r}_2) | g_{12} | \phi_j(\vec{r}_1) \phi_l(\vec{r}_2) \rangle, \quad (\text{A-12})$$

where $g_{12} = r_{12}^{-1}$.

The orbital integrals are obtained from analogous basis-set integrals

$$\bar{h}_{pq} = \langle \chi_p(\vec{r}_1) | h_1 | \chi_q(\vec{r}_1) \rangle, \quad (\text{A-13})$$

$$\bar{g}_{pqrs} = \langle \chi_p(\vec{r}_1) \chi_r(\vec{r}_2) | g_{12} | \chi_q(\vec{r}_1) \chi_s(\vec{r}_2) \rangle; \quad (\text{A-14})$$

by means of the transformation

$$h_{ij} = \sum_{p,q} U_{pi}^* \bar{h}_{pq} U_{qj} \quad (\text{A-15})$$

$$g_{ijkl} = \sum_{p,q,r,s} U_{pi}^* U_{qj} U_{rk}^* U_{sl} \bar{g}_{pqrs}, \quad (\text{A-16})$$

where

$$\phi_i = \sum_{p=1}^m \chi_p U_{pi} \quad (\text{A-17})$$

The transformation of the two-electron integrals, equation (A-16), requires extensive computational resources, thus, demanding efficient implementation of this step.

The computational steps required for a CI calculation can be outlined as follows:

1. Choose an analytical basis set (χ_p) and compute the basis set integrals, equations (A-13) and (A-14).
2. Choose the orbitals (ϕ_i), by an SCF or similar calculation, and transform the basis-set integrals to molecular orbital integrals.
3. Choose and construct a set of symmetry adapted configuration functions, Φ , appropriate to the state under consideration, and compute the Hamiltonian matrix, \underline{H} , in terms of these CF's.
4. Compute the several lowest eigenvalues of the matrix \underline{H} .

A full CI calculation, including all possible N-tuple excitations for the N-electron problem, provides the exact solution to the problem. Full CI calculations satisfy all of Pople's desiderata.² Unfortunately, full CI calculations for even relatively small molecules require impractical amounts of computer time and hardware resources. On the other hand, a truncated CI expansion suffers from three interrelated problems:

^{A2}J. A. Pople, R. Krishnan, H. B. Schlegel and J. S. Binkley, "Electron Correlation Theories and Their Application to the Study of Simple Potential Surfaces", *Int. J. Quantum Chem.*, 14, 545 (1978).

1. The convergence of the method for a given level of excitation is slow.
2. The number of configurations increases nonlinearly with the level of excitation included.
3. Truncated CI calculations are not size-consistent.

In most applications of CI, only double-excitations relative to a single determinant are included in the wave-function expansion. The magnitude of the size-consistency error for such a wave-function may be reduced by including quadruple excitations in the wave-function, or by replacing the single determinant by a multi-determinantal reference function, thereby including the most significant quadruple excitation contributions.³

For many problems, the method of configuration interactions remains the most reliable and best understood theoretical technique available for the study of molecular electronic structure. However, the difficulty and expense of constructing and diagonalizing the Hamiltonian matrix have encouraged alternative methods to estimate the correlation effect. Each of the following appendices outlines a successful alternative to CI, while future reports will describe the development of a powerful new theoretical method, the graphical unitary group approach.^{4,5,6}

^{A3}R. J. Buencker and S. D. Peyerimhoff, "Energy Extrapolations in CI Calculations", *Theor. Chim. Acta* 39, 217 (1975).

^{A4}I. Shavitt, "Graph Theoretical Concepts for the Unitary Group Approach to the Many-Electron Correlation Problem", *Int. Journ. Quantum Chem.* 11, 131 (1977).

^{A5}B. R. Brooks and H. F. Schaefer, III, "The Graphical Unitary Group Approach to the Electron Correlation Problem. Methods and Preliminary Application, Including the Vertical Electronic Spectrum of Ketene", *J. Chem. Phys.* 70, 5092 (1979).

^{A6}P. E. M. Siegbahn, "Generalizations of the Direct CI Method. I. Single Replacements from a Complete CI Root Function of any Spin, First Order Wave functions", *J. Chem. Phys.* 70, 5391 (1979).

APPENDIX B. THE COUPLED CLUSTER APPROACH

The coupled cluster approach develops an alternative to the CI method by considering the origin of particular levels of excitation in CI.^{1,2} The basic element in CCA is a cluster expansion where one-body, two-body, ..., n-body clusters are the fundamental entities. A coupled cluster wave-function is represented by,

$$\psi_{cc} = e^T \phi_0 \quad (B-1)$$

where T is separated into the various cluster terms,

$$T = T_1 + T_2 + T_3 + \dots \quad (B-2)$$

In the occupation number representation,

$$T_1 = \sum_{i,a} t_{i,a}^a A_a^+ A_i \quad (B-3)$$

$$T_2 = \sum_{\substack{i>j \\ a>b}} t_{ij}^{ab} A_a^+ A_i A_b^+ A_j \quad (B-4)$$

⋮

where the t's are antisymmetrized components to be determined. Expanding the exponential operator gives a new expression for the coupled cluster wavefunction,

^{B1}J. Cizek, "On the Correlation Problem in Atomic and Molecular Systems. Calculation of Wave Functions", *J. Chem. Phys* 45, 4256 (1966).

^{B2}J. Paldus and J. Cizek, "Relation of Coupled Pair Theory, CI, and Some Other Many-Body Approaches", *Energy, Structure and Reactivity*, Smith and McCrae, Eds. (Wiley, New York, 1973).

$$\Psi_{CC} = (1 + T_1 + T_2 + \dots + 1/2 T_1^2 + 1/2 T_2^2 + \dots + T_1 T_2 + \dots) |\Phi_0\rangle \quad (B-5)$$

Similarly, a CI wavefunction has the form,

$$\Psi_{CI} = (1 + C_1 + C_2 + \dots) |\Phi_0\rangle, \quad (B-6)$$

where the C_i 's refer to excitation-levels relative to Φ_0 . By relating terms in equations (B-5) and (B-6), it follows that

$$\begin{aligned} C_1 &= T_1 \\ C_2 &= T_2 + 1/2 T_1^2 \\ C_3 &= T_3 + T_1 T_2 + (1/3!) T_1^3 \\ C_4 &= T_4 + 1/2 T_2^2 + T_1 T_3 + (1/4!) T_1^4 + (1/2!) T_1^2 T_2. \end{aligned} \quad (B-7)$$

The quadruple-excitation term in CI consists of several different parts: a four-body term, a product of two-body terms which is said to be "disconnected", and additional disconnected products that involve T_1 . For Φ_0 represented by SCF-orbitals, Brillouin's theorem justifies ignoring all terms that include T_1 up to fourth-order. Furthermore, for closed-shell problems, the most important contributors to the correlation energy are the two-body cluster terms, T_2 . This leads to the basic premise of coupled-pair theory, that T_2 approximates T .² In particular, coupled-pair many-electron theory (CPMET), developed by Cizek, uses the wave-function,

$$\Psi_{CPMET} = e^{T_2} |\Phi_0\rangle = (1 + T_2 + 1/2 T_2^2 + \dots) |\Phi_0\rangle \quad (B-8)$$

Pople³ calls this approximation coupled-cluster double-excitation, or CCD. The CCD (CPMET) wavefunction has the explicit form,

^{B3}J. A. Pople, R. Krishnan, H. B. Schlegel and J. S. Binkley, "Electron Correlation Theories and Their Application to the Study of Simple Reaction Potential Surfaces", *Int. J. Quantum Chem.* 14, 545 (1978).

$$\Psi_{\text{CCD}} = \phi_0 + 1/4 \sum_{ijab} A_{ij}^{ab} t_{ij}^{ab} \phi_0 + 1/32 \sum_{ijab} \sum_{klcd} A_{ij}^{ab} A_{kl}^{cd} t_{ij}^{ab} t_{kl}^{cd} \phi_0 + \dots \quad (\text{B-9})$$

The operator product $t_{ij}^{ab} t_{kl}^{cd}$ is zero if any coincidences occur among the eight indices, and represents a quadruple excitation otherwise. In the latter case, Ψ_{CCD} becomes,

$$\Psi_{\text{CCD}} = \phi_0 + 1/4 \sum_{ijab} A_{ij}^{ab} \psi_{ij}^{ab} + 1/32 \sum_{ijab} \sum_{klcd} A_{ij}^{ab} A_{kl}^{cd} \psi_{ijkl}^{abcd} + \dots \quad (\text{B-10})$$

Explicit equations for the coefficients, A, are obtained by requiring that the projection of the function

$$\langle (H - E) | \Psi_{\text{CCD}} \rangle \quad (\text{B-11})$$

on ϕ_0 and ψ_{ij}^{ab} equals zero. Thus

$$\langle \phi_0 | (H - E) | \Psi_{\text{CCD}} \rangle = 0 \quad (\text{B-12})$$

$$\langle \psi_{ij}^{ab} | (H - E) | \Psi_{\text{CCD}} \rangle = 0. \quad (\text{B-13})$$

These equations suffice to determine the coefficients, A, and the energy, E. Details of the reduction of these formal equations to expressions including integrals involving one- or two-electrons are given by Pople, et al,³ and Bartlett and Purvis.⁴ Substitution of Ψ_{CCD} (B-10), in equation (B-12) yields an expression for the energy in terms of two-electron integrals and the coefficients, A. Substitution of the energy expression in (B-13) permits elimination of energy as a variable, and leaves an equation relating the coefficients, A, with the one- and two-electron molecular integrals. That equation, however, requires an iterative solution.

^{B4}R. J. Bartlett and G. D. Purvis, "Many-Body Perturbation Theory, Coupled-Pair Many-Electron Theory, and the Importance of Quadruple Excitations for the Correlation Problem", *Int. J. Quantum Chem.* 14, 561 (1978).

As implemented by Pople, et al,³ and Bartlett and Purvis,⁴ the CCD method includes excitations relative to a single-determinant expression for Φ_0 . The technique satisfies the size-consistency and invariance desiderata,³ but does not satisfy a variational principle. Furthermore, CCD calculations require more computer time than comparable calculations done using many-body perturbation theory. However, CCD is more reliable than MBPT when more than a single reference function is important in the calculation of the electronic energy. This point has been demonstrated for the case of the $1\Sigma_g^+$ potential curve of Be_2 .⁴

APPENDIX C. MANY-BODY PERTURBATION THEORY

The development of molecular many-body perturbation theory (MBPT) followed the introduction of the occupation number representation ("second quantization"), from which the diagrammatic description of ordinary time-independent perturbation theory follows.¹ Chapters five through eight in Raimes' book outline the important elements of the theory and describe the important linked-diagram theorem: only linked diagrams contribute to the energy of the ground state.² Since the literature of many-body perturbation theory is extensive, only an overview is given here.³

Prerequisite to developing MBPT is the partitioning of the mathematical space in which the molecular problem is defined. The mathematical space for the N-electron problem is partitioned into the zero-order reference function, D_0 , and the remaining configurations, $|\underline{h}\rangle$, chosen to be orthogonal to D_0 , so that

$$P = |\underline{h}\rangle\langle\underline{h}|\underline{h}\rangle^{-1}\langle\underline{h}|. \quad (C-1)$$

Assuming the Moller-Plesset separation of the molecular Hamiltonian⁴ the defining equations of perturbation theory become,

$$H = H_0 + v, \quad (C-2)$$

$$V = \sum_{\sigma < \beta} r_{\sigma\beta}^{-1} - \sum_{\sigma} v^{\text{eff}}(\sigma), \quad (C-3)$$

$$[h(1) + v^{\text{eff}}(1)]_p(1) = \epsilon_p \chi_p(1), \quad (C-4)$$

$$H_0 = \sum_i [h(i) + v^{\text{eff}}(i)], \quad (C-5)$$

^{C1}S. Raimes, *Many-Electron Theory*, North-Holland, New York (1972).

^{C2}J. Goldstone, *Proc. Roy. Soc. (London)*, A239, 267 (1957).

^{C3}R. J. Bartlett and G. D. Purvis, "Many-Body Perturbation Theory, Coupled-Pair Many-Electron Theory, and the Importance of Quadruple Excitations for the Correlation Problem", *Int. J. Quantum Chem.* 14, 561 (1978).

^{C4}C. Moller and M. S. Plesset, "Note on an Approximation Treatment for Many-Electron Systems", *Phys. Rev.* 46, 618 (1934).

$$H_0 \phi_0 = E_0 \phi_0, \quad (C-6)$$

$$E_1 = \langle \phi_0 | V | \phi_0 \rangle, \quad (C-7)$$

$$E_0 = \sum_i \epsilon_i, \quad (C-8)$$

$$E_{\text{SCF}} = E_0 + E_1. \quad (C-9)$$

All excited electronic configurations, represented by (\underline{h}) , are eigenfunctions of H_0 because they are composed of SCF orbitals determined by equation (C-4). The total energy, E , is given by

$$E = E_0 + E_1 + E_{\text{CORR}}, \quad (C-10)$$

where E_{CORR} is the correlation energy. In Rayleigh-Schrodinger perturbation theory (RSPT), the energy expression has the form,

$$\Delta E = E - E_0 = E_1 + E_{\text{CORR}} = \sum_{m=2}^{\infty} \langle \phi_0 | V [(E_0 - H_0)^{-1} P(V - \Delta E)]^m | \phi_0 \rangle. \quad (C-11)$$

Another expression for the energy derives from the linked-diagram expansion,

$$\Delta E = \sum_{m=2}^{\infty} \langle \phi_0 | V [(E_0 - H_0)^{-1} V]^m | \phi_0 \rangle_L, \quad (C-12)$$

where the subscript "L" denotes the limitation to linked diagrams. As an instructive example, consider the second-order term; E_2 ,

$$E_2 = \langle \phi_0 | V | \underline{h} \rangle \langle \underline{h} | (E_0 - H_0)^{-1} | \underline{h} \rangle \langle \underline{h} | V | \phi_0 \rangle^*. \quad (C-13)$$

Since only double-excitations can mix across the Hamiltonian with a Hartree-Fock reference function, the second-order energy expression reduces to

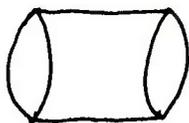
*The restriction to linked-graphs removes the ϕ_0 component from $V|\phi_0\rangle$ at second-order, so that only excited configurations can mix with that product. Consequently the use of $|\underline{h}\rangle\langle\underline{h}|$ as the projection operator is justified.

$$E_2 = \sum_K \langle \Phi_0 | v | h_K \rangle \langle h_K | v | \Phi_0 \rangle / (E_0 - E_K^0). \quad (C-14)$$

Since $\sum_K h_K = 1/4 \sum_{ij} \sum_{ab} D_{ij}^{ab}$, representing the double-excitations from the reference function, the second-order energy can be written in terms of two-electron integrals as,

$$E_2 = 1/4 \sum_{ij} \sum_{ab} |\langle ij || ab \rangle|^2 / (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b), \quad (C-15)$$

where the double bar indicates an antisymmetrized integral. This integral is represented by the graph



At second-order, the use of graphical representations adorns with elegance an otherwise straightforward problem. At higher-orders, however, the derivation of the energy expression using the operator equation becomes tedious, so the rules for directly drawing the linked-diagrams simplify the analysis. Bartlett and Silver have published a useful discourse on rules for constructing the linked-diagrams.⁵

Formally, the linked-diagram expansion excludes unlinked-diagrams and this guarantees size-extensivity, order-by-order. However, theoretical methods based upon the linked-diagram theorem do not satisfy a variational principal. As implemented by Bartlett and Purvis, MBPT provides a powerful tool to estimate correlation energy at a relatively low cost. The method is limited to problems for which Φ_0 is well-approximated by a single-determinant reference function. Extension of the technique to permit the zeroth-order function to be a multi-reference function have been derived, however, so this shortcoming in the theory should soon be removed.⁶

^{C5}R. J. Bartlett and D. M. Silver, "Some Aspects of Diagrammatic Perturbation Theory", *Int. J. Quantum Chem.* 95, 183 (1975).

^{C6}G. D. Purvis and R. J. Bartlett, private communication.

APPENDIX D. UNIFORM APPROXIMATION CRITERIA

Reliable predictions of potential energy hypersurfaces require computational accuracy that exceeds the Hartree-Fock SCF level. While doubts remain about the extent and types of electron correlation effects that must be included to obtain accurate results, theoretical methods that meet certain criteria may provide more uniform approximations for energy calculations over the entire potential hypersurface.

Two important uniform approximation criteria are "size-extensivity" referring to the proper dependence of energy and related properties on the size of the system*,¹ and "size-consistency" and separability.^{2,3,4} Size extensivity is a characteristic of models based upon the linked-diagram theorem. While size consistency and separability are often equivalent to size extensivity, size consistency may impose additional requirements in some cases.

A method is considered size consistent if the energy of a system made up of two subsystems, A and B, infinitely far apart is equal to the sum of the energies of A and B computed separately by the same method. For closed-shell systems dissociating to closed-shell fragments, an RHF (restricted Hartree-Fock) reference function satisfies the size-consistency criteria, and size extensivity (or the absence of unlinked diagrams) guarantees size-consistency for a correlated model based upon that reference function. On the other hand, to satisfy size consistency when considering separation to open-shell fragments requires a UHF (unrestricted Hartree-Fock) reference function. Since either an RHF or a UHF reference function can be used to generate a linked-diagram, size-extensive expansion, the condition of size consistency applied to a correlated calculation based on a single determinant reference function imposes the requirement of a UHF-type reference function in addition to the use of a linked-diagram expansion.

^{D1}R. J. Bartlett and G. D. Purvis, "Many-Body Perturbation Theory, Coupled-Pair Many Electron Theory, and the Importance of Quadruple Excitations for the Correlation Problem", *Int. J. Quantum Chem.*, 14, 561 (1978).

^{D2}J. A. Pople, J. S. Binkley, and R. Seeger, "Electron Correlation Theories and Their Application to the Study of Simple Reaction Potential Surfaces", *Int. J. Quantum Chem.*, 14, 545 (1978).

^{D3}H. Primas, in Modern Quantum Chemistry, edited by O. Sinanoglu, Academic Press, NY, 1965.

^{D4}W. Kutzelnigg, in Methods of Electronic Structures Theory, edited by H. F. Schaefer, III, Plenum, New York, 1947.

*The term "size-extensivity" occurs in thermodynamics. An extensive property is proportional to the size of a homogeneous system. For a homogeneous system of N units, energy predicted by a size-extensive method equals N times the energy predicted for a single unit.

A significant consequence of size extensivity occurs when studying chemical reactions, such as



The heats-of-formation, ΔH_f , computed separately by a size extensive method, combine to equal the heat-of-reaction, ΔH_R ,

$$\Delta H_R = \Delta H_f(C) + \Delta H_f(D) - \Delta H_f(A) - \Delta H_f(B).$$

Were the heats-of-formation for each species obtained by a truncated CI calculation, this simple addition does not equal the heat-of-reaction. Instead, to obtain a proper ΔH_R requires supermolecule calculations of A-B and C-D at large internuclear separation.

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