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John D. Goddard, Henry F. Schaefer

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Author
Goddard, J.D.

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John D. Goddard and Henry F. Schaefer III

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The Photodissociation of Formaldehyde: Potential Energy Surface Features

John D. Goddard[*] and Henry F. Schaefer III

Department of Chemistry and Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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[*] National Research Council of Canada Postdoctoral Fellow.

Abstract

Features of the S_0 potential energy surface of formaldehyde relevant to its dissociation to molecular products, H_2 + CO, to radical formation, H + HCO, and to rearrangement to hydroxycarbene, HCOH, have been studied by means of *ab initio* calculations. A gradient procedure was used to locate and to characterize both equilibrium and transition state geometries. Basis sets of at least double zeta (DZ) quality were employed throughout and many calculations involved more flexible basis sets including polarization functions. Force constants, normal modes and vibrational frequencies were calculated at the SCF level for stationary points on the surface. Extensive configuration interaction (CI) calculations were also carried out.

For the molecular dissociation the energy barrier including the effects of polarization functions and electron correlation was 4.06 eV (93.6 kcal $mole^{-1}$, 32700 cm^{-1}). Correcting for changes in zero point vibrational energy gave an approximate activation energy of 3.76 eV (87 kcal $mole^{-1}$, 30300 cm^{-1}) with an estimated error of ± 0.2 eV (± 5 kcal $mole^{-1}$, ± 1700 cm^{-1}). The energy required for the rearrangement of formaldehyde to *trans*-hydroxycarbene was calculated to be 3.85 eV (89 kcal $mole^{-1}$, 31000 cm^{-1}) at the DZ + polarization + CI level with the inclusion of zero point corrections. The large imaginary frequencies associated with the reactive motion imply sharp and thin barriers through which tunneling is estimated to be of considerable importance. Based on the calculated features of the

Introduction

The photochemistry and photophysics of formaldehyde have attracted a great deal of attention in recent years. There are numerous reasons why a detailed understanding of the photochemistry of formaldehyde would be of very great value. As the smallest carbonyl containing molecule, it is not unreasonable to suspect that formaldehyde may serve as a prototype for the higher aldehydes and ketones. The spectroscopy of formaldehyde has been well studied[1], providing the prerequisite information for detailed tests of various theories[2] of radiative and nonradiative transitions in polyatomic molecules. Formaldehyde has practical use in laser isotope separation schemes for the enrichment of carbon, oxygen, and hydrogen isotopes.[3] Formaldehyde is an abundant and critically important interstellar species.[4] It also plays a very important role in the photochemistry of air pollution.[5] The mechanisms and quantum yields for formaldehyde photodissociation represent major uncertainties in the modelling of polluted atmospheres.[6] Clearly a careful theoretical examination of selected aspects of formaldehyde photochemistry would be of considerable importance to a number of areas of chemistry.

Experimental Background

Important processes following the production of the first excited singlet state of formaldehyde by absorption ($\pi^* \leftarrow n$, ${}^1A_2 \leftarrow {}^1A_1$) in the region 3530Å to 2300Å are:[7]

$$H_2CO\ (S_1,v') \rightarrow H_2 + CO \qquad \text{(I)}$$

$$\rightarrow H + HCO \qquad \text{(II)}$$

$$\rightarrow H_2CO(S_o,v'') + h\nu' \qquad \text{(III)}$$

The quantum yield for fluorescence (III) is usually negligible from a photochemical viewpoint[7] although D_2CO does fluoresce at energies near the S_1 origin in the zero pressure limit.[64] It is generally agreed[8] that the molecular process (I) predominates for energies near the S_1 origin at 3.495eV (80.6 kcal mole^{-1}, 28188 cm^{-1}) while the importance of the radical process (II) increases with increasing excitation energy. At 3130Å (3.96eV, 91.3 kcal mole^{-1}, 31900 cm^{-1}) Horowitz and Calvert[8] found that the sum of the quantum yields for processes I and II is approximately unity with the molecular quantum yield 0.32±0.03 and the radical quantum yield 0.68±0.03.

An overview of the experimental situation is given by Figure 1, adapted from Houston and Moore.[9] The overall dissociation of formaldehyde ($^1A_1$,S_0) to ground state molecular products, $H_2(^1\Sigma_g^+)$ and $CO(^1\Sigma^+)$ is nearly thermoneutral[10] and is symmetry allowed. S_0 formaldehyde also correlates by symmetry with the ground state radical products, $H(^2S_g)$ and $HCO(^2A')$, in a process which is overall endothermic by 3.79 eV (87.5 kcal mole^{-1}, 30600 cm^{-1}).[9] The lowest excited triplet state of formaldehyde ($^3A_2$, T_1, $^3(\pi^* \leftarrow n)$) with its origin at 3.124 eV (72.0 kcal mole^{-1}, 25194 cm^{-1})[11] also correlates by symmetry with radical products. The S_1 state ($^1A_2$, $^1(\pi^* \leftarrow n)$) of formaldehyde with origin at 3.495 eV (80.6 kcal mole^{-1} 28188 cm^{-1} correlates with ground state H plus a linear $^2\Pi$ excited state of HCO at ∿ 4.92 eV (113.5 kcal mole^{-1}, 39700 cm^{-1}).[11] Thus from symmetry considerations alone, it is most probable that the dissociation to ground state molecular products occurs on the S_0 surface, while the dissociation to ground state radicals could occur either on T_1 or on S_0.

In important experimental work, Houston and Moore[9] investigated the mechanism of the molecular photodissociation of formaldehyde by monitoring the appearance rate and vibrational distribution of the CO photochemical product. For pressures as low as 0.1 torr, the CO product appeared with a rate more than 100 times slower than the decay rate of the first excited singlet state of formaldehyde. This fact was interpreted as indicating the presence of a long-lived intermediate state between S_1 and molecular products. However, at low pressures (the collisionless regime[12]) there are no product studies and, indeed, it is possible that no H_2 + CO is produced in the absence of collisions.

Houston and Moore[9] examined various possibilities for the "intermediate state." An obvious candidate for the intermediate state is T_1. The mechanism would then be $S_1 \rightsquigarrow T_1 \rightsquigarrow S_0 \longrightarrow H_2 + CO$. Such an intermediate would explain the production of molecular products in the triplet benzene photosensitization of formaldehyde.[13] A nonradiative decay process such as $T_1 \rightsquigarrow S_0$ could then govern the lifetime. However, the triplet model lacks a direct collisionless mechanism for triplet production. Brand and Stevens[14] found $S_1 - T_1$ perturbations in the formaldehyde spectrum to be sparse, and the sharp lines due to those which do occur make it unlikely that the triplet vibronic level density at the S_1 origin is sufficiently high to allow T_1 to form a manifold for S_1 collision free decay.

Highly vibrationally excited S_o also presents itself as a natural intermediate. Yeung and Moore's calculated $S_1 \rightsquigarrow S_0$ internal conversion rates[2a] match the observed lifetimes of S_1 fairly well. However it must be postulated that these highly excited vibrational levels of S_o are so weakly coupled to the continuum that they exist for many microseconds before dissociation,[9] a hypothesis which is quite unlikely. It was also suggested that a geometry such as HCOH might play a role or that other processes, such as the formation of collision complexes, might be involved.[9]

Clark, Moore and Nogar[15a] have recently further investigated the radical dissociation of formaldehyde. At the S_1 origin for D_2CO, nonreactive quenching dominates and no photochemistry is observed. As the excitation energy increases, it appears that first molecular dissociation occurs and then at higher energy a threshold for the radical process is passed and a relatively constant proportion of radicals and molecules is produced with total quantum yield near unity. For H_2CO the results were similar but molecular dissociation began at the S_1 band origin with a quantum yield of 0.7.

Molecular dissociation and quenching competed between the S_1 origin and the threshold for radical production, with both processes apparently caused by collisions of ambient gas with an intermediate state formed by nonradiative decay of S_1. The branching between molecular dissociation and quenching was interpreted as involving an intermediate state which is near a dissociation threshold.

Clark, Moore, and Nogar[15a] found that dissociation to radicals, $H_2CO \rightarrow H + HCO$, exhibited an abrupt energy threshold between 3.686 and 3.773 eV (85 and 87 kcal mole^{-1}, 29728 and 30427 cm^{-1}), which is within experimental error of the best thermodynamic values of Benson, 3.768 ± 0.087 (86.9 ± 2, 30400 ± 700),[16a] and Warneck, 3.825 ± 0.069 eV (88.2 ± 1.6 kcal mole^{-1}, 30850 ± 550 cm^{-1}).[16b] More recent experimental work by Reilly, *et al.*[15b] has further confirmed the radical energy threshold to be 3.73 ± 0.04 eV (86 ± 1 kcal mole^{-1}, 30100 ± 350 cm^{-1}). Thus the photochemical dissociation occurred at or just below the thermochemical threshold. Therefore, there is no potential barrier along the radical dissociation pathway. The dissociation does not occur on the S_1 or T_1 surfaces which appear to have substantial barriers to radical dissocation.[17] In addition, the observed constancy of H-atom quantum yield for various rotational levels was interpreted by Tang, Fairchild, and Lee[18] as consistent with two competing photodissociation processes, the radical and the molecular, occurring from the S_0 manifold following the $S_1 \rightsquigarrow S_0$ internal conversion.

The constancy of the radical/molecule branching ratio above threshold observed by Clark, Moore and Nogar[15a] (where the H_2 + CO channel has ∿ 0.21 to 0.58 eV (∿ 4.9 to 13.4 kcal mole^{-1}, ∿ 1700 to 4700 cm^{-1}) and the H + HCO channel ∿ 0 to 0.37 eV (∿ 0 to 8.6 kcal mole^{-1}, ∿ 0 to 3000 cm^{-1}) excess energy implied that the dissociating species does not have a statistical distribution of internal energy (RRKM).[19] An explanation in terms of two competing channels for collision-induced dissociation of the intermediate state was not favored by these workers since a more gradual increase of radical yield above threshold would have been expected.

As will be discussed in the following section, theoretical work, particularly the study of Lucchese and Schaefer,[28] provided firm evidence that the lowest singlet state of hydroxycarbene, HCOH, lies only ∿ 52 kcal mole^{-1} above the ground state of formaldehyde. This theoretical prediction led E. K. C. Lee and co-workers to examine carefully possible experimental manifestations of the HCOH species. In a very recent paper, they have reported some evidence for the occurrence of hydroxycarbene in formaldehyde photolysis systems. Sodeau and Lee[20] postulated that glycoaldehyde ($CH_2(OH)CHO$), the primary product in the mercury arc lamp photolysis of formaldehyde in an Ar matrix, arose from the insertion of a singlet hydroxycarbene into the CH bond of a ground state formaldehyde molecule. They attributed an unusually large deuterium isotope effect which was observed to the intramolecular rearrangement, $CH_2O \rightarrow HCOH$. They further suggested that the long-lived precursor of $H_2 + CO$ in the gas phase photolysis might be <u>cis</u>-HCOH and that the photochemical isomerization involving hydrogen atom migration might be responsible for the radiationless decay of the $\tilde{A}\ {}^1A_2$ state of formaldehyde which shows a large deuterium isotope effect.[2e]

Theoretical Background

Early theoretical work on carbonyl photochemistry was limited to simple symmetry correlation arguments and attempted to identify and to qualitatively describe the nature of the photochemically active states.[21] More recently, *ab initio* SCF MO and CI calculations have appeared for both the radical[17,22,23] and molecular[24-26] dissociation of S_o, T_1 and S_1 formaldehyde. *Ab initio* SCF and CI calculations on hydroxycarbenes[27-30] have also been reported in the literature.

The most reliable previous work on the molecular dissociation of formaldehyde by Jaffe and Morokuma[26] involved *ab initio* MCSCF calculations with a split-valence (4-31G) basis set. Preliminary minimal basis set SCF calculations with CI on the S_o, S_1 and T_1 surfaces indicated that only a planar asymmetric pathway on S_o leads to molecular products with a barrier of less than 5eV (115 kcal mole^{-1}, 40300 cm^{-1}).[25] However, the barrier to molecular dissociation was found to be 4.85 eV (112 kcal mole^{-1}, 39100 cm^{-1}) at the minimal basis set + CI level, considerably in excess of the experimental threshold which was believed to be within ~0.05eV (~1 kcal mole^{-1}, a few 100 cm^{-1}) of the S_1 origin at

3.495eV (80.6 kcal $mole^{-1}$, 28188 cm^{-1}). In the 4-31G MCSCF calculations,[26] 18 configurations were included, having been selected to properly describe the H_2CO, H_2 + CO, and H + HCO limits. In addition, a 52 configuration CI consisting of all other valence shell double excitations was carried out at the equilibrium geometry for H_2CO and at the saddle point geometry. A C_s saddle point for the molecular dissociation pathway was located with a barrier height of 4.55eV (105 kcal $mole^{-1}$, 36700 cm^{-1}). At the MCSCF molecular transition state geometry, the 52 configuration CI gave 4.52eV (104.2 kcal $mole^{-1}$, 36500 cm^{-1}), and a polarized basis set MCSCF calculation (6-31G*) gave 5.22 eV (120 kcal $mole^{-1}$, 42100 cm^{-1}). The increase in the barrier with the addition of polarization functions was considered to be an artifact due to the lack of configuration and/or geometry optimization. Calculated force constants for H_2CO at the saddle point geometry were used as input to a normal mode analysis.[31] A good description of the molecular dissociation pathway involved motion of H_2 across the CO bond axis followed by the elongation of both CH bonds. The calculated zero-point vibrational energy of the five real vibrational modes for the transition state was 0.49eV (11.2 kcal mole^{-1}, 3900 cm^{-1}) as compared to the experimental value of 0.70eV (16.1 kcal mole^{-1}, 5600 cm^{-1})[11] for all six of the vibrational modes of H_2CO. A zero point energy correction thus lowers the barrier for $H_2CO \rightarrow H_2 + CO$ by ∿ 0.21 eV (∿ 4.9 kcal mole^{-1}, ∿ 1700 cm^{-1}) to 4.34 eV (100.1 kcal mole^{-1}, 35000 cm^{-1}).

The *ab initio* calculations on the radical dissociation of formaldehyde involved minimal Slater (Hayes and Morokuma)[17] or minimal Gaussian (STO-3G) (Grimbert and Salem)[23] basis set SCF plus CI. As the CH distance increased, the S_o surface monotonically increased in energy to form the ground state of H + HCO, with departure of the H atom in the HCO plane preferred.[17] The S_1 state monotonically increased to reach hydrogen atom plus the first excited (linear) state of the formyl radical.[17] The T_1 state reached a maximum (the saddle point or transition state), then decreased to ground state H + HCO. Hayes and Morokuma[17] calculated a barrier of 0.4 eV (9.2 kcal mole^{-1}, 3200 cm^{-1}) in T_1 above ground state HCO + H. As discussed previously, the presence of such a barrier was important in determining that formaldehyde probably dissociates to radical products on the

S_o surface. The barrier was attributed[17] to an avoided crossing of a π^* MO whose energy stayed relatively constant as the CH bond was stretched and a σ^* MO which drastically fell in energy.

Calculations on hydroxycarbene by Altmann et al.[27,29] have been reported which concentrated on formaldehyde as a model for the formation of oxacarbenes, as is observed experimentally in the photolysis of certain cyclic ketones. SCF calculations at the split-valence (4-31G) level[27] indicated that the easiest pathway for migration of H from C to O was in the plane of the molecule for S_o. At the 4-31G SCF level, s-trans hydroxycarbene (S_o) lay only ~2.2eV (~50 kcal mole^{-1}, ~17500 cm^{-1}) above formaldehyde (S_o), but the barrier for the rearrangement ($CH_2O \rightarrow HCOH$) was ~4.6eV (~105 kcal mole^{-1}, ~36700 cm^{-1}). Since this barrier was much greater than that for radical dissociation, it was argued that a dissociation-recombination mechanism would be preferred to a unimolecular rearrangement for the formation of hydroxycarbene from formaldehyde.

Much more extensive calculations involving polarized basis sets and treating electron correlation by large scale CI were carried out by Lucchese and Schaefer.[28] These calculations did not examine the S_o rearrangement barrier but did accurately locate the energy difference between formaldehyde (S_o) and s-trans hydroxycarbene (S_o). Using a double zeta plus polarization basis set plus extensive CI, the energy difference was 2.48eV (51.7 kcal mole^{-1}, 20000 cm^{-1}). Thus, S_o trans HCOH lay ∿ 1.26 eV (∿ 29 kcal mole^{-1}, ∿ 10100 cm^{-1}) below the experimental value for the S_1 origin in H_2CO.

Pople *et al.*[30] have located the transition state for the $CH_2O(S_o) \rightarrow$ s-*trans* HCOH (S_o) rearrangement using an SCF gradient method and a 6-31G* basis set. With the inclusion of polarization functions and of electron correlation effects by fourth order Møller-Plesset perturbation theory, the barrier height was found to be 4.06 eV (93.7 kcal mole^{-1}, 32800 cm^{-1}).

In this work, the transition state for the molecular dissociation of formaldehyde has been located at both the double zeta and double zeta plus polarization SCF levels by a gradient method. Extensive configuration interaction calculations allowed for the effects of electron correlation on the barrier height. Force constants have been calculated at the saddle point geometry and used in a normal mode analysis[38] to further characterize the transition state.

The radical dissociation of S_o formaldehyde has been examined by two configuration SCF (TCSCF) calculations with a double zeta basis set. The TCSCF calculations allow CH_2O to dissociate smoothly to ground state H + HCO. The TCSCF orbitals were further used in CI calculations based on two reference configurations designed to be of a quality comparable to calculations on the molecular pathway.

The transition state for the rearrangement of S_o formaldehyde to S_o s-*trans* hydroxycarbene was located at the double zeta basis set SCF level employing the gradient method. The effects of polarization functions and of configuration interaction on the rearrangement barrier have also been studied.

Theoretical Approach

The standard Huzinaga-Dunning[32] double zeta Cartesian Gaussian basis sets were employed in most calculations. A more flexible contraction of this basis set ((9s5p/4s)/[6s3p/3s])[32a] was also examined at the double zeta optimized geometries. Polarization was introduced by sets of standard p-type Cartesian Gaussian functions with exponent 0.8 centered on the hydrogens. In order to be able to analytically evaluate the gradients,[33] d functions on carbon and oxygen were simulated by linear combinations of standard p-type Gaussians with exponent 0.8 displaced slightly (± 0.1 Å) along the local Cartesian axes and fixed to be of opposite phase. At both the equilibrium and the distorted transition state geometries of formaldehyde, the simulated d polarization functions and ordinary d-type Cartesian Gaussians yielded the same total SCF energy to within 1×10^{-6} hartree. Limited optimization of the polarization function exponents was also studied. At a few points SCF calculations only were carried out using two sets of polarization functions on C, O, and H with exponents α_d(C and O) 1.2 and 0.4 and α_p(H) 1.0 and 0.33. To further assess any basis set limitations in the present work SCF calculations on critical points of the surface were also performed with a large (11s 7p 1d/6s 1p)/[7s 5p 1d/4s 1p] Gaussian basis set.[32c] The contraction was designed to allow maximum flexibility for the valence orbitals. The d function exponents were taken to be 0.8 for both C and O and a H p exponent of 1.0 was used.

SCF and gradient calculations were carried out using TEXAS,[33] an *ab initio* gradient (force) program which is a modified version of the MOLPRO system.[34] The energy gradients were evaluated analytically by the force method[35] and used in searching for the optimized geometries for formaldehyde, for the molecular transition state, and for the hydroxycarbene rearrangement saddle point. Starting from an initial guess at the transition state geometry, the gradient norm was minimized to accurately locate the saddle point geometry. At the final geometry, Cartesian forces of less than 1.0 millihartree/bohr were obtained. Second derivatives of the energy (force constants) in internal coordinates were calculated at the optimized geometries by numerical differencing of the analytically evaluated forces using central differences.[36] For the force constant calculations, the integral evaluation threshold was decreased as was the SCF convergence criterion in order to allow coordinate changes of ±0.001Å and ±0.5° in the numerical differencing. A check on numerical stability was made by examining the off-diagonal elements of the force constant matrix.[35b] Each coupling term was evaluated twice--once involving the force on the i-th coordinate evaluated at a displacement of the jth coordinate and once the force on the jth coordinate when the i-th coordinate was displaced. The agreement of the values to at least 2 parts in a thousand provided a check on numerical stability. The calculated transition state force constant matrix was diagonalize to check that there was one and only one negative eigenvalue for this geometry, as is required for a true saddle point.[37] A normal mode analysis was performed using a modified version of the NORCORD program[38] to further characterize both formaldehyde and the molecular transition state.

Near Hartree-Fock limit SCF geometries are generally quite reliable,[39] with bond lengths 0.01 to 0.02Å too short relative to experiment and bond angles accurate to a few degrees. Since the earlier 4-31G MCSCF calculations[26] showed that even at the saddle point for the molecular dissociation the Hartree-Fock configuration has a coefficient of greater than 0.97 in the MCSCF expansion, the DZ and DZ+POL SCF optimized geometries are expected to be reliable. The effects of electron correlation on the barrier height for the molecular dissociation were investigated by extensive configuration interaction calculations at the SCF optimized geometries. The direct CI method[40] was used as implemented[41] as part of the BERKELEY system[42] of minicomputer-based programs. The lowest two MO (the core) were frozen in all the CI calculations and the highest two virtual orbitals (the complements of the frozen core) deleted. With these minor restrictions, all singly and doubly excited Hartree-Fock interacting[43] configurations relative to the SCF configuration in C_{2v}: $(1a_1)^2$ $(2a_1)^2$ $(3a_1)^2$ $(4a_1)^2$ $(1b_1)^2$ $(5a_1)^2$ $(1b_2)^2$ $(2b_1)^2$ or in C_s: $(1a')^2$ $(2a')^2$ $(3a')^2$ $(4a')^2$ $(5a')^2$ $(6a')^2$ $(1a'')^2$ $(7a')^2$ were included. With the double zeta basis set 1137 $^1A_1$ configurations were involved for formaldehyde (C_{2v}) and 2121 $^1A'$ configurations for the molecular transition state (C_s). For the polarized basis set, 5025 $^1A_1$ (C_{2v}) or 10221 $^1A'$(C_s) configurations were employed.

Davidson's formula:[44] $(1 - C_o^2)\ \Delta E_{SD}$, where C_o is the coefficient of the Hartree-Fock configuration in the CI expansion and ΔE_{SD} the energy lowering due to singly and doubly excited configurations was applied to estimate the importance of higher (than double) excitations, specifically unliked clusters.

For the radical dissociation, TCSCF calculations[45] were employed since such a scheme has sufficient flexibility to give a proper description of the homolytic fission of the CH bond. The 7a' MO (in C_s symmetry) was represented by a Generalized Valence Bond (GVB) pair[46] to give what is essentially a TCSCF procedure involving configurations with $(7a')^2$ and $(8a')^2$ as the highest occupied molecular orbitals.

The GVB orbitals were used as the starting point for a CI calculation on the radial dissociation pathway using the BERKELEY general CI program[42] involving all singly and doubly excited Hartree-Fock interacting configurations with respect to the two reference configurations (C_s):

$$(1a')^2\ (2a')^2\ (3a')^2\ (4a')^2\ (5a')^2\ (6a')^2\ (1a'')^2\ (7a')^2$$

and

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (8a')^2$$

For the double zeta basis with the two core MO frozen and the two highest virtual orbitals deleted, 4055 $^1A'$ configurations (C_s symmetry) were included. An approximate unlinked cluster correction of the form $(1 - (C_1^2 + C_2^2))\Delta E_{SD}$ where C_1 and C_2 are the CI coefficients of the two reference configurations was also used.

The transition states for the rearrangement of CH_2O to HCOH were also located at the double zeta level by the force method. Analogous polarization basis set and direct CI calculations to those described above for the molecular transition state were carried out. In addition, larger direct CI calculations than previously reported[28] were carried out on s-*cis* and s-*trans* hydroxycarbene (S_0). The barriers to rotation and inversion from s-*cis* to s-*trans* hydroxycarbene were also calculated.

All calculations were performed on a Harris Slash 4 minicomputer.[47]

Results and Discussion

The Molecular Photodissociation of Formaldehyde

A. Structures and Energetics

The total energies of formaldehyde and of the transition state for the molecular dissociation at various levels of calculation are presented in Table 1. The geometries used were obtained at the DZ or DZ+POL SCF levels. The 4-31G MCSCF results of Jaffe and Morokuma[26] and the Garrison, Schaefer, and Lester[48] near Hartree-Fock limit energy of formaldehyde are included for comparison. The DZ+POL SCF energy of this work is 0.0204 hartree higher than the near Hartree-Fock limit value of formaldehyde.[48] Addition of a second set of d and p polarization functions to the DZ+POL basis resulted in an SCF energy of -113.9017 hartree for the DZ+POL optimized geometry which is within 0.0132 hartree of the near Hartree-Fock limit. The less contracted (9s 5p/4s) → [6s 3p/3s] basis set was used in calculations at the DZ ((9s 5p/4s) → [4s 2p/2s]) optimized geometries to examine the changes in the forces with increasing flexibility in the contracted basis. It has been suggested (e.g., reference 51) that a very flexible contraction scheme is of considerable importance in force calculations. The size of the forces on the DZ geometries with the [6s 3p/3s] basis allows an estimation of how different the [6s3p/3s] optimized geometry would be from the DZ one. The forces in the various internal coordinates increased from values of less than 1 x 10^{-3} hartree/bohr for the DZ SCF optimized geometries for formaldehyde and the molecular transition state to an average of 4 x 10^{-3} hartree/bohr for the [6s3p/3s] set. The force on the CO bond is the only one to increase dramatically and is of such a magnitude to suggest a shortening of this bond by ~ 0.01 Å in going from the DZ to the [6s3p/3s] basis sets. The energy barrier to the molecular dissociation decreased by only 0.02 eV (0.6 kcal $mole^{-1}$, 100 cm^{-1}) on going to the less contracted basis set. Since the increase in the forces was not excessively large and since the energy difference between formaldehyde and the molecular transition state was nearly constant, the DZ SCF optimized geometries were adopted as fairly representative of unpolarized basis set results.

The DZ SCF energy barrier for the molecular dissociation was calculated to be 4.93 eV (113.7 kcal $mole^{-1}$, 39700 cm^{-1}). The increased flexibility in the basis set given by polarization functions leads to a decrease in the barrier due to a relatively better description of the highly distorted molecular transition state structure. (see Figure 2). With the addition of polarization functions and the reoptimization of geometries the energy of formaldehyde decreases by 0.0638 hartree and that of the transition state by 0.0773 hartree. Thus, the DZ + POL SCF energy barrier is reduced to 4.56 eV (105.1 kcal mole^{-1}, 36800 cm^{-1}) which is, in fact, quite comparable to the 4-31G MCSCF result of 4.55 eV (104.9 kcal mole^{-1}, 36700 cm^{-1}).[26] The addition of a second set of polarization functions gave a further slight decrease in the barrier to a value of 4.49 eV (103.6 kcal mole^{-1}, 36200 cm^{-1}). The [7s 5p 1d/4s 1p] result for the DZ + POL optimized equilibrium geometry is -113.9134 and for the DZ + POL molecular transition -113.7464 yielding a value for the molecular dissociation barrier of 4.54 eV (104.8 kcal mole^{-1}, 36700 cm^{-1}). Extrapolating from these results along with accumulated experience it is probable that the Hartree-Fock limit barrier for the molecular dissociation is ∿4.4 eV (∿ 102 kcal mole^{-1}, ∿ 35500 cm^{-1}).

Effects of electron correlation on the barrier height were included by large scale CI calculations. The DZ + POL + CI energy of -114.1922 hartree for formaldehyde is probably the lowest total energy yet calculated for this molecule[52] and is 0.2977 hartree below the DZ + POL SCF energy of this work. More importantly, CI lowers the molecular dissociation energy barrier by 0.58 eV (13.4

kcal mole^{-1}, 4600 cm^{-1}) DZ basis set; or by 0.34 eV (7.8 kcal mole^{-1}, 2800 cm^{-1}) DZ + POL basis set. Clearly at the DZ level CI is not only introducing correlation but also compensating for basis set deficiencies, thus giving larger changes in comparison to the DZ + POL CI. The lowest barrier determined as the difference between two variationally calculated energies is 4.22 eV (97.3 kcal mole^{-1}, 34000 cm^{-1}) from the largest calculations. Since experience with CI calculations, particularly on transition states, is much more limited than with SCF work, it is more hazardous to estimate the limiting value for the barrier including correlation effects. Using Davidson's formula[44] to estimate the energy lowering due to unlinked clusters produces a further decrease in the barrier of 0.21 eV (4.8 kcal mole^{-1}, 1700 cm^{-1}) DZ + CI or 0.16 eV (3.7 kcal mole^{-1}, 1300 cm^{-1}) DZ + POL + CI. Recent work[53] has suggested that this correction formula, although possibly not of extremely high accuracy, does give the right trend and order of magnitude. In this light, it is certainly reasonable to adopt the position that the molecular dissociation barrier could be as low as 4.0 eV (92 kcal mole^{-1}, 32000 cm^{-1}).

In a more speculative vein, any calculated barrier will probably not be more than ~0.2 eV (~5 kcal $mole^{-1}$, ~1600 cm^{-1}) below this value.

The optimized geometries for formaldehyde and the molecular transition state at the DZ and DZ + POL SCF levels are given in Figure 2 along with the 4-31G MCSCF results[26] and the experimentally estimated r_e structure of formaldehyde.[49] Comparison of the theoretical and experimental geometries of formaldehyde allows an estimation of the experimental geometry of the molecular transition state for which, of course, only theoretical results are known. The SCF optimized geometries for formaldehyde are essentially identical with those recently reported by Bell.[52b] Slight differences in the DZ + POL SCF geometry are probably due to the choice of different p polarization function exponents on hydrogen. The DZ + POL SCF geometry gives CO and CH bond lengths slightly too short and an HCH angle very slightly too small relative to the experimental r_e structure.[49] The molecular dissociation transition states found in the DZ or DZ + POL SCF and force calculations are qualitatively quite similar to that found by Jaffe and Morokuma in their 4-31G MCSCF grid search.[25,26] The transition states are planar with one CH bond very much elongated and the other only slightly stretched relative to their values in formaldehyde. Interestingly, both hydrogens lie on the same side of the CO bond axis in the transition state. The distortion of the molecule from C_{2v} symmetry by the unequal stretching of the CH bonds allows the system to avoid what is an orbitally forbidden process in C_{2v} symmetry.[55] However, to attain the lower C_s symmetry in which the molecular dissociation is orbital symmetry allowed,a substantial price must be paid in terms of distortion energy, resulting in a high barrier.

For the DZ + POL SCF geometry, the HH distance in the transition state is very large compared with the experimental equilibrium bond length of the product H_2 ($r_e = 0.7416$ Å).[54] The DZ + POL CO distance is ~0.04 Å shorter than the calculated length in formaldehyde and at 1.151 Å lies somewhat closer to the experimental distance in the product carbon monoxide ($r_e = 1.1282$ Å) [54] as opposed to the reactant formaldehyde ($r_e = 1.203$ Å).[49] Comparing the DZ + POL SCF structure and the experimental r_e geometry of formaldehyde, it may be anticipated that the experimental r_e structure of the transition state would have CO and CH distances ~0.01 Å longer than and approximately the same angular variables as in the DZ + POL SCF calculated geometry.

B. Force Constants and Vibrational Frequencies

At the DZ SCF level, full sets of harmonic force constants were determined for the molecular transition state and, for comparative purposes, for formaldehyde. These force constants are reported in Tables 2 and 3. For formaldehyde, the calculated force field of Meyer and Pulay[51] and the experimentally determined general harmonic force field of Duncan and Mallinson[56] are also included. In the present work, the force constants have been calculated at the DZ SCF optimized geometry rather than at the experimental geometry as is frequently recommended.[35b,51,57] The procedure adopted here provides the most consistent comparison between formaldehyde and the transition state, where such a shift to an experimental geometry is impossible.

The formaldehyde force constants are given in symmetry coordinates to allow easier comparison with the earlier work. Considering the diagonal elements of the force constant matrix, the force constant corresponding to the CO stretch is ~12% larger than and the symmetric and asymmetric stretch constants ~16% smaller than the experimental values. However, it should be noted that diagonal stretching force constants are very sensitive to the choice of reference geometry.[35b] The symmetric bend and wag force constants give agreement with experiment, comparable to that of the previous calculation.[51] The diagonal out of plane deformation or wag force constants of planar molecules are commonly more seriously overestimated at the SCF level than are other force constants.[35b] The interaction force constants also show good agreement with experiment. In particular, F_{12} (CO/s.CH) is positive and large (0.76) for an interaction term and F_{23} (s.CH/s.bend) is small and negative. The calculated DZ SCF force constants are not of extremely high accuracy relative to experiment. However, with the possible exception of the imaginary frequency along the reaction coordinate for which anharmonicity may be of greater importance, there is no _a priori_ reason to assume that the force constants of the molecular transition state will not be of comparable accuracy to the formaldehyde ones. Thus, for purposes of calculating the change in zero point vibrational energies, the present force constants should be adequate.

At the molecular transition state, the force constant for the CO stretch in calculated to be 16.2 mdyn/Å at the DZ SCF level. On the basis of the result for the CO stretch in formaldehyde, this value is ~15% too large relative to experiment and thus the experimental CO stretching force constant at the transition state is probably ~14 mdyn/Å. Such a result may be compared with the experimental CO stretching constants (in mdyn/Å) in formaldehyde 12.9[56] formyl radical 14.2[58] and carbon monoxide 19.06.[54] As might be expected from a consideration of the optimized transition state geometry, the carbonyl group is most comparable to that in the formyl radical. The short CH bond at the saddle point has a normal stretching force constant of 4.86 mdyn/Å associated with it while the very long CH bond has a correspondingly small force constant. The large negative diagonal element for the one OCH bend is associated with motion along the reaction coordinate swinging the H_2 across the CO bond axis. In the coordinate system chosen in this work, a number of the interaction constants are quite large.

The calculated force constants were used to determine the normal modes and vibrational frequencies of formaldehyde and the molecular transition state. The results are shown in Figures 3 and 4. The experimental frequencies of formaldehyde are also included.[51] The DZ SCF formaldehyde vibrational modes which are principally stretches (the top three frequencies in Figure 3) are overestimated by 10-15% relative to experiment and a similar situation probably holds for the transition state. The modes in CH_2O which are principally in-plane bends (calculated to be 1435 and 1332 cm^{-1}) are in significantly better agreement with the experimental frequencies than are the stretches. It has been suggested that it may be possible to simply scale frequencies obtained from SCF calculations to agree with experiment. Clearly at the DZ basis set level of the force constant calculations in this work, the frequencies for modes dominated by stretching and bending would have to be treated differently. For simplicity, a scaling of -15% has been applied to all frequencies. This scaling chiefly corrects for the lack of CI and reduces the calculated stretching frequencies sufficiently to place them in good agreement (within 20 to 60 cm^{-1}) with experiment. The scaled values are given in parentheses in the figures. Such a scaling adversely affects the lower frequency modes which are chiefly bends and for these it may be more appropriate to consider the unscaled results when comparison to experiment is made. The calculated imaginary frequency of 2692i cm^{-1} for the molecular transition state suggests that the barrier is fairly thin and sharp as well as being quite high. Quantum mechanical tunneling of H_2 through such a barrier may be important to the molecular photodissociation process.

For formaldehyde, the zero point vibrational energy determined from the six calculated vibrational frequencies is 0.79 eV (18.3 kcal $mole^{-1}$, 6404 cm^{-1}) which may be compared with the experimental value of 0.70 eV (16.1 kcal $mole^{-1}$, 5631 cm^{-1}).[51] The calculated zero point vibrational energy of the five real vibrational modes of the transition state is 0.51 eV (11.7 kcal $mole^{-1}$, 4085 cm^{-1}). Thus a change in zero point energy of $\sim$ 0.3 eV (7 kcal $mole^{-1}$, 2400 cm^{-1}) lowers the calculated barrier from 4.06 eV (93.6 kcal $mole^{-1}$, 32700 cm^{-1}) to 3.76 eV (~87 kcal $mole^{-1}$, ~30300 cm^{-1}). A reduction of 4.9 kcal $mole^{-1}$ in the molecular dissociation barrier due to zero point corrections was calculated previously by Jaffe and Morokuma.[26]

The effect of CI on the geometries and force constants of formaldehyde and the molecular transition state was investigated by reoptimizing the CO bond length at the DZ + CI level and determining the CO stretching force constant by taking numerical second derivatives of the CI energies. As expected, the inclusion of electron correlation lengthens the bond distances and decreases the force constants relative to their SCF values. In formaldehyde, the CO bond length increases by 0.030 Å, from 1.217 to 1.247 Å, while the associated stretching force constant decreases by 2.8 mdyn/Å from 14.4 to 11.6 mdyn/Å with the inclusion of CI. The DZ CI results for formaldehyde are thus very similar to the Jaffe-Morokuma 4-31G MCSCF values[26] of R(CO) = 1.24 Å and F_{11}(CO) = 11.9 mdyn/Å. With CI, the CO distance in the molecular transition state changes by 0.035 Å from 1.170 to 1.205 Å and the force constant decreases by 2.7 mdyn/Å from 16.2 to 13.5 mdyn/Å. It is encouraging (in terms of the use of CI calculations at SCF optimized geometries to determine the dissociation barrier) that both the formaldehyde and the molecular transition state geometries undergo similar changes in bond lengths and force constants with the inclusion of electron correlation effects. The errors involved in using CI calculations at SCF geometries for formaldehyde and for the transition state may well approximately cancel.

The Radical Photodissociation of Formaldehyde

Calculations were carried out on $H_2CO(S_o)$ dissociating to H + HCO at the DZ basis set level to compare the energetic requirement with that for the molecular dissociation. The total energies for points along the assumed radical dissociation pathway are given in Table 4 and the potential curves illustrated by Figure 5. The single configuration restricted SCF results (OCSCF) are included merely to illustrate the well known inability of this method to give a reasonable description of dissociation to open shell species. At least a two configuration SCF (TCSCF) procedure is necessary to even qualitatively describe the radical dissociation. At the formaldehyde equilibrium geometry (R = 1), the TCSCF total energy is

0.0108 hartree below the OCSCF result. However, as R increases the second configuration in the TCSCF becomes increasingly important as evidenced by the larger energy lowerings relative to the OCSCF energy. By R = 5, the TCSCF curve levels off at the energy of $H(^2S) + HCO(^2A")$ while the OCSCF curve continues to rise.

The calculated TCSCF dissociation energy is 3.88 eV (89.5 kcal mole^{-1}, 31300 cm^{-1}) which may be contrasted with the previous minimal basis set + CI values for this quantity of 4.40 eV (101.5 kcal mole^{-1}, 35500 cm^{-1})[17] and ~4.63 eV (~107 kcal mole^{-1}, ~ 37000 cm^{-1}) (Figure 1 of reference 23). Subsequently, CI calculations were performed using all singly and doubly excited configurations with respect to the two reference configurations involved in the TCSCF calculation. Although the TCSCF + CI total energies decreased by nearly 0.2 hartree relative to the TCSCF results, the CI dissociation energy is calculated to be 3.82 eV (88.2 kcal mole^{-1}, 30,900 cm^{-1}) in excellent agreement with the TCSCF value of 3.88 eV (89.5 kcal mole^{-1}, 31,300 cm^{-1}). In this case, CI has merely shifted the potential curve down in total energy (see Figure 5) without much affecting the relative energies of formaldehyde and the radical products. Applying a quadruple excitation correction of the form $(1-(C_1^2 + C_2^2))\Delta E_{SD}$, where C_1 and C_2 are the CI coefficients of the two reference configurations in the DZ CI, leads to a barrier height of 3.79 eV (87.4 kcal $mole^{-1}$, 30600 cm^{-1}). The experimental values for the radical dissociation energy are 3.69 to 3.77 eV (85 to 87 kcal $mole^{-1}$, 29700 to 30400 cm^{-1})[15a] 3.77 ± 0.09 eV (86.9 ± 2 kcal $mole^{-1}$, 30400 ± 700 cm^{-1})[16a] and 3.825 ± 0.070 eV (88.2 ± 1.6 kcal $mole^{-1}$, 30850 ± 550 cm^{-1}).[16b]

The apparent agreement with experiment of the TCSCF and TCSCF + CI dissociation energies is remarkable. However, the experimental values implicitly include the zero point energy corrections between formaldehyde and the formyl radical. Using the experimentally observed vibrational frequencies, the zero point vibrational energy for $^{12}CH_2{}^{16}O$ is 0.70 (16.1 kcal $mole^{-1}$, 5631 cm^{-1})[51] and for $^{12}CH^{16}O$ 0.34 eV (7.8 kcal $mole^{-1}$, 2700 cm^{-1}). The change in zero point energy of $\sim$ 2900 cm^{-1} (0.36 eV, 8.3 kcal $mole^{-1}$) is, of course, chiefly associated with the loss of one CH stretch in the formyl radical relative to formaldehyde. Correcting the DZ-TCSCF or DZ-TCSCF CI radical dissociation barrier of 3.82 to 3.86 (88 to

89 kcal mole^{-1}, 30800 to 31100 cm^{-1}) by the zero point change gives a final barrier height of 3.47 to 3.51 eV (80 to 81 kcal mole^{-1}, 28000 to 28350 cm^{-1}). Including both the zero point vibrational energy correction and the quadruples correction for the DZ results, the calculations predict a barrier of 3.43 eV (79.1 kcal mole^{-1}, 27700 cm^{-1}).

Comparing the TCSCF and TCSCF + CI dissociation energies, it is apparent that correlation effects largely cancel between formaldehyde and hydrogen atom + formyl radical. The major change in theoretical procedure likely to affect the barrier height to radical dissociation would be the addition of polarization functions to the basis set. TCSCF calculations were carried out for formaldehyde at the DZ + POL SCF optimized geometry and for the separated radicals with R(CH) = 7 in units of the DZ + POL SCF optimized CH bond length. The total energies are formaldehyde -113.9058 and radicals -113.7644, and thus the calculated barrier is 3.85 eV (88.7 kcal mole^{-1}, 31000 cm^{-1}), which represents a slight increase relative to the DZ TCSCF value. The largest basis set TCSCF result ((11s 7p 1d/6s 1p)/[7s 5p 1d/4s 1p]) for the radical dissociation energy is 3.84 eV (88.5 kcal mole^{-1}, 30950 cm^{-1}). Applying the zero point energy correction to the DZ + POL barrier then gives 3.49 eV (80.4 kcal mole^{-1}, 28100 cm^{-1}) as the energy requirement for radical dissociation. A similar correction to the [7s 5p 1d/4s 1p] barrier yields an energy requirement of 3.48 eV (80.2 kcal mole^{-1}, 28050 cm^{-1}) for the radical reaction. The radical threshold is underestimated by ∿ 0.2 eV (5 kcal mole^{-1}, 1700 cm^{-1}) relative to the experimental value.

The Rearrangement of Formaldehyde to Hydroxycarbene

The total energies of formaldehyde, the rearrangement transition state and *trans*-hydroxycarbene at various levels of theory are presented in Table 5. Energy differences between the equilibrium structures CH_2O and *trans*-HCOH and the rearrangement transition state connecting them are given as are total energies of *cis*-hydroxycarbene and the height of the relaxed rotational barrier between *trans*- and *cis*-hydroxycarbene. All calculations were performed at fully optimized DZ SCF geometries. The most extensive previous CI calculations by Lucchese and Schaefer[28] gave energies of -114.1338 hartree for formaldehyde and -114.0154 hartree for *trans*-hydroxycarbene and thus an energy separation of 2.24 eV (51.7 kcal mole^{-1}, 18100 cm^{-1}). The largest CI calculations of the present work produced energies of -114.1922 hartree and -114.1084 hartree for CH_2O and trans-HCOH giving an energy difference of 2.28 eV (52.6 kcal $mole^{-1}$, 18400 cm^{-1}). Thus, it is confirmed that relative to the S_1 origin of formaldehyde (experimentally[9] at 3.495 eV (80.6 kcal $mole^{-1}$, 28188 cm^{-1})) hydroxycarbene is a low-lying isomer.

The trans conformer of hydroxycarbene lies slightly lower in energy than does the cis form at all levels of calculation in this work. Altmann, et al.[27] found the trans isomer 0.30 eV (6.9 kcal $mole^{-1}$, 2400 cm^{-1}) more stable than the cis with 4-31G SCF calculations while the most sophisticated calculation of Lucchese and Schaefer[28] places trans 5.8 kcal $mole^{-1}$ (0.25 eV, 2000 cm^{-1}) below cis. In the present work, the energy differences range from 7.7 kcal $mole^{-1}$ (0.33 eV, 2700 cm^{-1}) (DZ SCF) to 5.0 kcal $mole^{-1}$ (0.22 eV, 1700 cm^{-1}) (DZ + POL CI + QC) with trans the more stable. The addition of polarization functions to the basis set, configuration interaction, and the unlinked cluster correction all very slightly favor cis relative to trans thus somewhat reducing the energy separation from its DZ SCF value.

Optimized geometries at the DZ SCF level are shown in

Figure 6 for formaldehyde, the rearrangement transition state, trans- and cis-hydroxycarbene and the relaxed rotation transition state. In the isomeric hydroxycarbenes, the OH and CH bond distances are very similar and have values quite comparable to those calculated for H_2O or CH_2 (see references in [39]). The hydroxycarbene CO bond length of 1.337 Å is considerably shorter than a single CO bond distance such as the value of 1.437 Å (4-31G SCF) or 1.474 Å (experimental) in methanol.[39] Thus, it seems apparent that th CO bond in hydroxycarbene has some double bond character. The OCH bond angle of 103.8° in the trans form is quite comparable to that of the HCH angle of 102.4° in CH_2 ($^1A_1$).[39] The COH angle of 114.4° is larger than the HOH angle in water or the COH angle in methanol possibly to minimize unfavorable carbene lone pair--OH bond interactions. For the cis form the OCH and COH angles open up by 3.8° and 7.2° respectively and the CH and OH bonds lengthen slightly to relieve steric interactions between the hydrogens.

The geometry of the rotational transition state and the height of the barrier to rotation are consistent with the view that the CO bond in hydroxycarbene contains some double bond character. The relaxed rotation involves a transition state with a CO bond length of 1.376 Å at a conformation in which the CH and OH bonds are nearly orthogonal. The dihedral angle is 88.0° in a system where by convention the *cis* species is defined to have a dihedral angle of 0° and the *trans*, 180°. The lengthening of the CO bond by ∿ 0.04 Å relative to hydroxycarbene in the nearly orthogonal conformation is associated with the destruction of π bonding between C and O. At the DZ SCF level the calculated rotational barrier from *trans* to *cis* of 24.5 kcal mole^{-1} (1.06 eV, 8570 cm^{-1}) is in good agreement with the 4-31G SCF result of Altmann, *et al.*[27] The inclusion of electron correlation effects by CI raises the barrier by 2.9 to 3.0 kcal mole^{-1} (0.125 to 0.130 eV, 1010 to 1050 cm^{-1}) to ∿ 27.5 kcal mole^{-1} (∿ 1.19 eV, ∿ 9600 cm^{-1}). An SCF calculation including polarization functions gave a barrier of 27.7 kcal mole^{-1}. It is probable that the experimental rotational barrier would be quite large and ∿ 29 ± 3 kcal mole^{-1}. Although a detailed geometry optimization was not carried out, preliminary DZ SCF calculations on a structure with the HCO group linear (i.e., on a transition state for inversion at the carbene center) indicate that the energy required for inversion is substantially greater than that necessary for rotation.

The transition state for the rearrangement of formaldehyde to trans-hydroxycarbene was located by a gradient procedure at the DZ SCF level and is planar, in agreement with earlier grid search methods.[27] The transition state for the rearrangement more closely resembles trans-HCOH than CH_2O, particularly in the CO bond distance as might be anticipated on the basis of the Hammond postulate[59] for a reaction which is strongly endothermic if viewed in the sense $CH_2O \rightarrow HCOH$. The transition state geometry is quite similar to that found by Pople, et al.[30] at the 6-31G* SCF level of calculation.

Since the CH_2O to HCOH rearrangement represents a six dimensional optimization problem, any global view of the energy hypersurface has been lost and it is impossible to be absolutely certain that the transition state located is the only saddle point. However, it is probably the most important one in the sense of being the highest point on <u>the</u> minimum energy pathway from reactants to products.[61] The planar transition state described above is a true transition state[37] in the sense of the force constant matrix having one and only one negative eigenvalue, but this fact does not guarantee its uniqueness.

Searches for other possible transition states especially non-planar ones of lower symmetry than the planar (C_s) one found were undertaken from a number of different starting geometries. With other geometrical parameters close to the optimum values in the planar transition state the bridging H was moved out of the plane such that the dihedral angle (relative to a <u>cis</u> form) was 135°. The energy increased by only $\sim$ 1 kcal mole^{-1} but no transition state could be located in this region of space, as the forces on the internal coordinates were large and after ten SCF and gradient calculations it was clear that the system was returning to the previously located planar transition state geometry with a dihedral angle of 180°. Another series of calculations investigated the possibility of a concerted shift of the H_2 group across the CO axis and on to <u>cis</u>-hydroxy-carbene in a planar fashion. The energy was some 50 kcal mole^{-1}

(2 eV, 16000 cm^{-1}) higher than the rearrangement transition state previously located and there was no indication of the forces decreasing to zero as is required for a saddle point. Starting from geometrical variables similar to those for the planar transition state,but with the bridging H now in a plane at a dihedral angle of 90°, a further set of calculations was performed. The energy was ∿ 20 kcal $mole^{-1}$ (∿ 0.9 eV, ∿ 7000 cm^{-1}) higher than for the planar transition state and the force on the CO bond was always large in spite of any variations in the other geometrical parameters suggesting that the only transition state likely to be found in this region of the hypersurface is the simple rotational transition state with R(CO) = 1.376 Å already found and discussed above. All these calculations suggest(but, of course, do not prove) that there is no non-planar low energy transition state for the rearrangement of formaldehyde to hydroxycarbene with a geometry similar to the planar rearrangement transition state located.

The energy barrier for the rearrangement of formaldehyde to trans-hydroxycarbene via the planar transition state is 4.67 eV (107.7 kcal $mole^{-1}$, 37700 cm^{-1}) at the DZ SCF level. The addition of polarization functions reduces this barrier to 4.37 eV (100.7 kcal mole^{-1}, 35200 cm^{-1}) using the DZ SCF optimized geometries. The large basis set ([7s 5p 1d/4s 1p]) SCF result for the barrier at these geometries is 4.39 eV (101.2 kcal mole^{-1}, 35400 cm^{-1}). A Hartree Fock limit for this barrier of 4.53 eV (104.6 kcal mole^{-1}, 36500 cm^{-1}) has been suggested previously on the basis of 6-31G* calculations.[30] Single and double excitation CI using the DZ + POL basis further decreases this energy requirement by 0.39 eV (8.9 kcal mole^{-1}, 3100 cm^{-1}) to 3.98 eV (91.8 kcal mole^{-1}, 32100 cm^{-1}). This result may be compared with that of third order Møller-Plesset perturbation theory,[30] 4.18 eV (96.3 kcal mole^{-1}, 33800 cm^{-1}). With the inclusion of an approximate correction for unlinked cluster effects,[44] the barrier falls to 3.85 eV (88.8 kcal mole^{-1}, 31000 cm^{-1}). Fourth order singles, doubles, and quadruples Møller-Plesset perturbation theory[30] gave 4.06 eV (93.7 kcal mole^{-1}, 32800 cm^{-1}). Considering the reverse reaction, trans-hydroxycarbene to formaldehyde, the CI barrier with the polarized basis set is 1.70 eV (39.2 kcal mole^{-1}, 13700 cm^{-1}) which decreases to 1.56 eV (36.0 kcal mole^{-1}, 12600 cm^{-1}) with the use of the unlinked cluster correction.[44] This fairly large barrier does not support previous suggestions[28,60] that the singlet hydroxycarbene-formaldehyde rearrangement might possess a relatively small barrier by analogy with the singlet vinylidene-acetylene rearrangement for which the barrier is predicted[60] to be ∿ 0.37 eV (8.6 kcal $mole^{-1}$, 3000 cm^{-1}).

Harmonic force fields for both trans and cis hydroxycarbene were determined at the DZ SCF optimized geometries using forces obtained from DZ SCF calculations. The calculated force constants are presented in Table 6 and were used in the determination of the normal modes and vibrational frequencies illustrated in Figure 7. The same caution as advised earlier for the vibrational analysis of formaldehyde should also be taken with these results. The highest frequency mode is an OH stretch at 4075 (3646) cm^{-1} and 3965 (3370) cm^{-1} in trans and cis HCOH where the values in parentheses have been scaled down by 15%. The scaled values serve as the best prediction for the experimental frequency of the hydroxycarbene OH stretch. The two isomers have reasonably well separated frequencies and it should be possible to identify both of them experimentally by their infrared spectra if they can be matrix isolated. The predicted frequencies are also quite different from those of formaldehyde (recall Figure 3), the most likely precursor in hydroxycarbene synthesis.

DZ SCF force constants and vibrational frequencies were also determined for the rearrangement transition state and are presented in Table 7 and Figure 8. The strong coupling of the distance of the migrating hydrogen to carbon and the angle $O-C-H_{mig}$ is obvious. The large negative diagonal element for the $O-C-H_{mig}$ angle reflects the strong involvement of this coordinate in the rearrangement reaction path. The out of plane mode is of high frequency involving as it does both OH and CH stretching. The reaction coordinate has an associated vibrational frequency of 2705i cm^{-1} or 2299i cm^{-1} if scaled, which reflects a fairly thin barrier through which tunneling by H may be important in any experimental rearrangement.

These vibrational frequencies were used to calculate zero point vibrational energy corrections to the rearrangement barrier. For <u>trans</u>-HCOH the six calculated vibrational frequencies yield a zero point vibrational energy of 0.78 eV (17.9 kcal $mole^{-1}$, 6300 cm^{-1}). Recall that for CH_2O the calculated zero point energy was 0.79 eV (18.3 kcal mole^{-1}, 6400 cm^{-1}). The five real frequencies of the rearrangement transition state result in a zero point energy of 0.82 eV (18.8 kcal mole^{-1}, 6581 cm^{-1}). Thus zero point energy differences cause the best calculated CH_2O to HCOH rearrangement barrier of 88.8 kcal mole^{-1} (3.85 eV, 31100 cm^{-1}) to <u>increase</u> to 89.3 kcal mole^{-1} (3.87 eV, 31200 cm^{-1}). This slight increase in the rearrangement barrier due to changes in zero point energies may be contrasted with the <u>decrease</u> in the barriers observed for the molecular and radical dissociation processes when zero point energy corrections were considered. Both the molecular and the radical reactions possess very "loose" transition states and consequently less vibrational energy than the reactant formaldehyde. However, the rearrangement transition state is clearly a "tight" structure containing more vibrational energy thus giving a zero point correction in the opposite direction. Considering the reverse reaction, <u>trans</u>-HCOH to CH_2O, the best calculated barrier of 1.56 eV (36.0 kcal mole^{-1}, 12600 cm^{-1}) increases to 1.60 eV (36.8 kcal mole^{-1}, 12900 cm^{-1}) with consideration of zero point energy effects.

The best calculated barrier in this work for the rearrangement of formaldehyde to <u>trans</u>-hydroxycarbene of ∿ 3.86 eV (∿ 89 kcal mole^{-1}, ∿ 31100 cm^{-1}) is quite similar to the value of ∿ 3.77 eV (∿ 87 kcal mole^{-1}, ∿ 30400 cm^{-1}) predicted for the dissociation of formaldehyde to molecular products. A simple consideration of the transition states for these two processes (Figures 2 and 6) would suggest that both may be dynamically difficult in the sense of nuclear least motion. However, the molecular dissociation is readily observed experimentally and it would appear likely that the rearrangement to hydroxycarbene which energetically, and at least qualitatively dynamically, has similar requirements may also occur in formaldehyde photolysis systems.

The Mechanism of the Photodissociation of Formaldehyde

The present work provides what are the most accurate theoretical results yet determined for the transition state geometries and barrier heights of formaldehyde on its S_0 surface dissociating to give molecular or radical products or rearranging to hydroxycarbene. The most detailed picture of the mechanism of formaldehyde photolysis will only emerge when the results of this work as regards the potential energy surface are incorporated into detailed dynamics calculations. Some dynamics work[2d,62] on the dissociation of formaldehyde has begun to appear but it has been somewhat hampered by the previous lack of quantitatively reliable values for the barrier heights of the various processes.

In order to place the present calculated results in a better perspective relative to experiment, the S_0 to T_1 adiabatic excitation energy which is well known experimentally[11] to be 3.12 eV (72.0 kcal mole^{-1}, 25194 cm^{-1}) was calculated at the DZ + POL SCF + CI level of theory. The optimized T_1 geometry was taken from Bell.[52b] At the SCF level an S_0-T_1 excitation energy of 2.11 eV (48.6 kcal mole^{-1}, 17000 cm^{-1}) is predicted in the present work as compared to the near Hartree Fock limit value[48] of 2.18 eV (50.3 kcal mole^{-1}, 17600 cm^{-1}). A large scale CI using the T_1 SCF MO and including all Hartree-Fock interacting single and double excitations was performed. 12508 $^3A''$ configurations were explicitly included in this calculation which gives a T_1 state energy of -114.08485 hartree. Thus, the S_0-T_1 energy difference is 2.92 eV (67.4 kcal mole^{-1}, 23600 cm^{-1}) which may be compared, for example, with the Lucchese and Schaefer[28] result of 2.99 eV (68.9 kcal mole^{-1}, 24100 cm^{-1}) where important configurations were selected on the basis of perturbation theory. The inclusion of the approximate unlinked cluster correction[44] modifies the present result for the excitation energy to 3.01 eV (69.5 kcal mole^{-1}, 24300 cm^{-1}) to be compared with the experimental value of 3.12 eV (72.0 kcal mole^{-1}, 25194 cm^{-1}). Thus the best T_1 energy is $\sim$ 0.1 eV (2.5 kcal mole^{-1}, 900 cm^{-1}) too low. It is anticipated that for the S_1 energy (to which implicitly all experiment results are referenced) calculations of the quality of this work would give results in error by approximately the same amount and in the same direction as for T_1. Thus an S_0-S_1 adiabatic excitation energy of $\sim$ 3.38 eV ($\sim$ 78 kcal mole^{-1}, 27300 cm^{-1}) should result from theory as compared to the experimental value of 3.495 eV (80.6 kcal mole^{-1}, 28188 cm^{-1}).

The calculated barriers for the rearrangement and molecular dissociation involving as they do the energy differences between a stable equilibrium structure and a transition state may not be quite as accurately determined (i.e., within 0.1 eV (2.5 kcal mole^{-1}, 900 cm^{-1})) as the energy differences between two stable structures such as the S_0 and T_1 geometries. It is anticipated that the various barriers calculated in the present work may be reasonably assigned error estimates of $\sim \pm 0.2$ eV (± 5 kcal mole^{-1}, ± 1700 cm^{-1}). Collecting the most accurate theoretical results including zero point energy corrections from the previous sections, the molecular dissociation barrier is predicted to be 3.77 ± 0.22 eV (87 ± 5 kcal mole^{-1}, 30400 ± 1700 cm^{-1} and the hydroxycarbene rearrangement energy 3.86 ± 0.22 eV (89 ± 5 kcal mole^{-1}, 31100 ± 1700 cm^{-1}). The radical dissociation is of somewhat different character than either the molecular dissociation or the rearrangement in that the transition state is the infinitely separated radical fragments. Since it is usually the case that rearrangement barriers are slightly overestimated (e.g., [25, 26]) and that dissociation energies are underestimated in high level theoretical work, it is probable that the actual radical threshold should be slightly larger (by perhaps 3 to 5 kcal mole^{-1}) (0.13 to 0.22 eV, 1100 to 1700 cm^{-1}) and the molecular and rearrangement barriers smaller by a similar amount. It is clear that the energy requirements for the radical and molecular dissociation pathways are very similar,in agreement with experiment.[15a] It is also clear that the rearrangement to hydroxycarbene can not be definitely ruled out on energetic grounds and may play some role in formaldehyde photolysis.

The present results strongly suggest that there is a small 3-5 kcal mole^{-1} (0.13-0.22 eV, 1100-1700 cm^{-1}) barrier above the S_1 origin of formaldehyde to the three photochemical processes studies. Other work both experimental[9,15,63] and theoretical[2d,62] is divided on whether or not unimolecular photodissociation of formaldehyde should occur at the energy of the S_1 origin. The dissociation dynamics calculations of Elert, *et al.*[2d,62] could best rationalize the delayed appearance of CO product found by Houston and Moore[9] if there was a barrier (perhaps of 0.50 eV (11 kcal mole^{-1}, 4000 cm^{-1})) above the S_1 origin. Both H_2CO and D_2CO would then merely radiate at the S_1 origin and not undergo photochemistry. The time lag for CO appearance was then associated with collisional activation over the barrier. However, very recent experiments by Weisshaar, et al.[63] and by Luntz[64] have indicated that H_2CO decays nonradiatively in the zero pressure limit leaving open the question of zero pressure photochemistry by CH_2O at the energy of the S_1 origin. The results of the present work support the view that there is a small barrier above S_1 to molecular or radical dissociation or to isomerization to HCOH and thus that except for reaction due to tunneling, formaldehyde should not undergo truly unimolecular photodissociation at the S_1 origin.

The present calculations of vibrational frequencies clearly show that observed differences[15a] in reactivity of H_2CO and D_2CO may be understood in terms of normal isotope effects, i.e., differences in zero point energy and quantum mechanical tunneling effects. The vibrational analyses were repeated substituting D for H and the zero point energy corrections to the molecular dissociation and rearrangement barriers computed. For $CD_2O \rightarrow D_2 + CO$, the effective barrier height is 3.83 eV (88.4 kcal mole^{-1}, 30900 cm^{-1}) as compared to the value of 3.77 eV (87.0 kcal mole^{-1}, 30400 cm^{-1}) for CH_2O. Similarly, for CD_2O → trans-DCOD the corrected barrier is 3.98 eV (91.7 kcal mole^{-1}, 32100 cm^{-1}) while for CH_2O it is 3.87 eV (89.3 kcal mole^{-1}, 32100 cm^{-1}). Thus, the observed lower reactivity of CD_2O as compared to CH_2O for the molecular and radical dissociations[15a] is at least partially due simply to the lower zero point energies of the deuterated species.

As has been mentioned previously, the reaction coordinate frequencies of 2692i cm^{-1} (scaled: 2288i cm^{-1}) for the molecular dissociation and 2705i cm^{-1} (scaled: 2299i cm^{-1}) for the isomerization to hydroxycarbene are suggestive of relatively thin and sharp barriers through which quantum mechanical tunneling may be important. To provide an estimate of tunneling effects, the problem was treated in a very simple manner as a symmetric one dimensional Eckart barrier. The results suggested a significant role for tunneling.

In a very recent paper on tunneling corrections to the rate constant for unimolecular reactions within the standard transition state theory, Miller[65] has employed the calculated vibrational frequencies, energies and geometries of this work to show that tunneling effects are quite significant for rates of 10^9 sec^{-1} or slower in the collisionless photochemistry of formaldehyde. At energies near the S_1 origin at 80.6 kcal $mole^{-1}$ (3.495 eV, 28188 cm^{-1}) the rate of tunneling for $H_2CO \rightarrow H_2 + CO$ through a zero-point energy corrected barrier of height 87 kcal $mole^{-1}$ (3.77 eV, 30400 cm^{-1}) is large enough to explain the experimental observation of molecular products at the S_1 origin. *Trans*-HCOH also tunnels rapidly to CH_2O. At energies equal to the electronic excitation energy plus the relevant zero point energies Miller[65] finds that H_2CO dissociates to molecular products at a rate $\sim$ 41 times greater than D_2CO. The hydroxycarbene rearrangement reaction has a ratio k_{HCOH}/k_{DCOD} of $\sim$ 33 at these energies. Thus tunneling effects also serve to clearly differentiate between isotopically substituted formaldehydes.

Concluding Remarks

The present calculations provide decidedly more accurate values than previously available for energy barriers of critical importance to formaldehyde photochemistry. Significantly, the energy required for photochemical isomerization to hydroxycarbene is only slightly greater than that for the radical or molecular photodissociations. It is probable that some account of HCOH needs to be taken in formaldehyde photolysis.[66] Of equal significance, the calculations predict a small barrier above the S_1 band origin to any photochemical reaction by formaldehyde.

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Table 1 Total energies (in hartree) and energy differences (in eV, kcal mole^{-1}, and cm^{-1}) for formaldehyde and the molecular transition state at various levels of theory.

Level of Theory	Total Energy		ΔE		
	Formaldehyde	Molecular Transition State	eV	kcal mole^{-1}	cm^{-1}
DZ SCF	-113.8307	-113.6496	4.93	113.7	39700
$[6^s3^p/3^s]$SCF	-113.8391	-113.6588	4.91	113.1	39600
DZ + POL SCF	-113.8945	-113.7269	4.56	105.1	36800
DZ + DOUBLE POL SCF	-113.9017	-113.7366	4.49	103.6	36200
$(11^s7^p1^d/6^s1^p)/[7^s5^p1^d/4^s1^p)$	-113.9134	-113.7464	4.54	104.8	36700
Near Hartree-Fock Limit[a]	-113.9149	--	--	--	--
4.31G MCSCF[b]	-113.8029	-113.6356	4.55	104.9	36700
DZ + CI	-114.0353	-113.8756	4.35	100.3	35100
DZ + CI + QC[c]	-114.0519	-113.8997	4.14	95.5	33400
DZ + POL + CI	-114.1922	-114.0371	4.22	97.3	34000
DZ + POL + CI + QC[c]	-114.2185	-114.0693	4.06	93.6	32700

a. Reference [48] at the experimental geometry.
b. Reference [26].
c. Unlinked cluster quadruples correction. Reference [44].

Table 2 Calculated force constants[a] in symmetry coordinates[b] for formaldehyde at the DZ SCF optimized geometry.

Force Constant	Description	This Work DZ SCF at DZ optimized geometry	Previous Calculation [51] at experimental geometry	Exptl. [51,56]
F_{11}	CO	14.4	13.646	12.90±0.11
F_{12}	CO/s.CH	0.76	0.797	0.811±0.112
F_{13}	CO/s.bend	0.35	0.411	0.388±0.020
F_{22}	s.CH	4.2	4.885	4.999±0.034
F_{23}	s.CH/s.bend	-0.14	-0.131	-0.122±0.014
F_{33}	s.bend	0.63	0.634	0.572±0.003
F_{44}	as.CH	4.1	4.791	4.872±0.022
F_{45}	as.CH/rock	0.12	0.146	0.212±0.025
F_{55}	rock	0.91	0.907	0.838±0.003
F_{66}	wag	0.48	0.501	0.403±0.002

a. Units are mdyn $\mathring{A}^{-1}$ for stretching-stretching, mdyn $\mathring{A}/\mathrm{rad}^2$ for bend-bend and mdyn/rad for bending-stretching force constants.

b. Symmetry coordinates are defined by:

a_1: $S_1(\mathrm{CO}) = \Delta R$
$S_2(\mathrm{s.CH}) = 2^{-\frac{1}{2}}(\Delta r_1 + \Delta r_2)$
$S_3(\mathrm{s.bend}) = 6^{-\frac{1}{2}}(\Delta\beta_1 + \Delta\beta_2 - 2\Delta\alpha)$

b_1: $S_4(\mathrm{as.CH}) = 2^{-\frac{1}{2}}(\Delta r_1 - \Delta r_2)$
$S_5(\mathrm{rock}) = 2^{-\frac{1}{2}}(\Delta\beta_1 - \Delta\beta_2)$

b_2: $S_6(\mathrm{wag}) = \Delta\gamma$

where R is the CO bond lengths, r_1 and r_2 the two CH bond lengths, β_1 and β_2 the two HCO angles, α the HCH angle and γ the angle of O out of the HCH plane.

<u>Table 3</u> Calculated force constants[a] in internal coordinates[b] for the molecular transition state at the DZ SCF optimized geometry.

	$R(CO)$	$R(CH_1)$	$R(CH_2)$	$\sphericalangle(OCH_1)$	$\sphericalangle(OCH_2)$	Oo.o.p.(HCH)
$R(CO)$	16.2	1.19	0.01	0.87	-0.67	
$R(CH_1)$		0.70	-0.26	-0.81	0.83	
$R(CH_2)$			4.86	-1.13	2.00	
$\sphericalangle(OCH_1)$				0.60	1.10	
$\sphericalangle(OCH_2)$					-2.08	
Oo.o.p.(HCH)						0.33

a. Units are mdyn Å^{-1} for stretching-stretching, mdyn $\text{Å}/\text{rad}^2$ for bend-bend and mdyn/rad for bend-stretch force constants.

b. Internal coordinates are defined by:

$R(CO)$, $R(CH_1)$, $R(CH_2)$, $<OCH_1$, $<OCH_2$
and O out of the plane of HCH.

H_1 corresponds to the very long CH bond relative to formaldehyde and H_2 to the shorter bond. Recall Figure 2.

Table 4 One configuration SCF (OCSCF), two configuration SCF (TCSCF) and two configuration SCF plus configuration interaction (TCSCF + CI) calculations on the radical dissociation of formaldehyde.
Energies in hartree. R, the reaction coordinate, in units of the DZ SCF optimized CH bond length in formaldehyde which is 1.084 Å.

R	OCSCF	TCSCF	TCSCF + CI
1.0	-113.8307	-113.8415	-114.0376
1.5	-113.7496	-113.7852	-113.9807
2.0	-113.6586	-113.7277	-113.9264
3.0	-113.5479	-113.7005	-113.8990
5.0	--[a]	-113.6989	-113.8971
7.0	--[a]	-113.6989	-113.8971

[a] No satisfactory convergence was obtained for the OCSCF procedure. Approximate energies are R = 5.0, -113.48 hartree, and R = 7.0, -113.46 hartree.

Table 5. Total energies (in hartree) and energy differences (in eV, kcal mole^{-1} and cm^{-1}) for formaldehyde, the rearrangement[a] transition state, *trans*-hydroxycarbene, the rotational barrier[b] and *cis*-hydroxycarbene.

Level of Theory	Formaldehyde[c]	eV	ΔE kcal mole^{-1}	cm^{-1}	Rearrangement Transition State	eV	ΔE kcal mole^{-1}	cm^{-1}	*trans*-hydroxycarbene	eV	Rotational Barrier kcal mole^{-1}	cm^{-1}	*cis*-hydroxycarbene
DZSCF	-113.8307	4.67	107.7	37700	-113.6591	2.65	61.2	21400	-113.7566	1.06	24.5	8570	-113.7444
DZ+CI	-114.0353	4.34	100.0	35000	-113.8760	1.99	46.0	16100	-113.9493	1.19	27.4	9580	-133.9385
DZ+CI+QC[d]	-114.0519	4.23	97.5	34100	-113.8966	1.85	42.7	14900	-113.9647	1.19	27.5	9620	-113.9543
DZ+POL SCF	-113.8945	4.37	100.7	35200	-113.7340	2.24	51.8	18100	-113.8165	1.20	27.7	9690	-113.8072
DZ+POL CI	-114.1922	3.98	91.8	32100	-114.0459	1.70	39.2	13700	-114.1084	--	--	--	-114.1000
DZ+POL CI+QC[d]	-114.2185	3.85	88.8	31100	-114.0770	1.56	36.0	12600	-114.1344	--	--	--	-114.1265

a. Rearrangement from formaldehyde to *trans*-hydroxycarbene.

b. *Trans*- to *cis*-HCOH by relaxed rotation about the CO bond.

c. From Table 1.

d. Unlinked cluster quadruples correction. Reference [44].

Table 6. Calculated force constants[a] in internal coordinates[b] for trans- and cis-hydroxycarbene. DZ SCF results at DZ SCF optimized geometries.

trans-HCOH	R(CO)	R(CH)	R(OH)	∢ (OCH)	∢ (COH)	torsion
R(CO)	7.54	0.16	0.06	0.71	0.41	--
R(CH)		5.43	-0.06	0.13	0.02	--
R(OH)			9.25	0.09	0.13	--
∢ (OCH)				1.35	0.15	--
∢ (COH)					0.88	--
torsion	--	--	--	--	--	0.30

cis-HCOH	R(CO)	R(CH)	R(OH)	∢ (OCH)	∢ (COH)	torsion
R(CO)	7.43	0.20	0.09	0.62	0.36	--
R(CH)		4.91	0.05	0.15	-0.05	--
R(OH)			8.75	-0.14	0.09	--
∢ (OCH)				1.38	-0.02	--
∢ (COH)					0.84	
torsion	--	--	--	--	--	0.20

a. Units are mdyn Å^{-1} for stretching-stretching mdyn/rad for bending-stretching and mdyn Å/rad^2 for bend-bend interactions.

b. Internal coordinates defined by R(CO), R(CH), R(OH), ∢ (OCH) ∢ (COH) and torsion OH about the CO axis.

Table 7. Calculated force constants[a] in internal coordinates[b] for the rearrangement transition state. DZ SCF results at DZ SCF optimized geometries.

Rearrangement Transition State	R(CO)	$R(CH_1)$	$R(CH_2)$	∢ (OCH_1)	∢ (OCH_2)	o.o.p.
R(CO)	8.66	0.38	0.98	0.14	- 0.21	--
$R(CH_1)$		5.71	- 0.25	0.11	0.26	--
$R(CH_2)$			2.63	0.27	3.73	--
∢ (OCH_1)				1.05	- 0.75	--
∢ (OCH_2)					- 4.18	--
o.o.p.	--	--	--	--	--	0.20

a. Units are mdyn Å^{-1} for stretch-stretch, mydn/rad for bend-stretch and mydn $\text{Å}/\text{rad}^2$ for bend-bend.

b. Internal coordinates: R(CO), $R(CH_1)$, $R(CH_2)$ where H_2 is the bridging hydrogen, ∢ OCH_1, ∢ OCH_2 and H_2 out of the H_1CO plane.

Figure Captions

Figure 1. Experimental energy level diagram for formaldehyde. Adapted from Reference 9. Broken lines indicate symmetry correlations of the lowest states of CH_2O with radical and molecular products. The barrier heights are undetermined experimentally.

Figure 2. Optimized geometries of formaldehyde and of the molecular transition state at B. DZ and C. DZ + POL SCF levels of theory. A. 4-31G MCSCF results[26] and D. experimental r_e structure[49] of CH_2O for comparison. All structures are planar.

Figure 3. Calculated normal coordinates and their frequencies (in cm^{-1}) for formaldehyde. Experimental frequencies are underlined. Calculated frequencies decreased by 15% are given in parentheses.

Figure 4. Calculated normal coordinates and their frequencies (in cm^{-1}) for the molecular transition state. Calculated frequencies decreased by 15% are given in parentheses.

Figure 5. OCSCF, TCSCF and TCSCF+ CI DZ potential curves for the dissociation of H_2CO (S_0) to H + HCO. The geometrical parameters of the HCO fragment are frozen at the DZ SCF optimized values in formaldehyde (recall Figure 2). R is in units of the equilibrium CH bond length. Dissociation energy for TCSCF DZ + POL calculation at DZ + POL optimized geometries.

Figure 6. DZ optimized geometries for A. formaldehyde, B. the rearrangement transition state, C. s-trans and D. s-cis hydroxycarbene and E. the rotation barrier structure.

Figure 7. Calculated normal coordinates and their frequencies (in cm^{-1}) for a) trans- and b) cis-hydroxycarbene. Calculated frequencies decreased by 15% are given in parentheses.

Figure 8. Calculated normal coordinates and their frequencies (in cm^{-1}) for the transition state structure in the rearrangement of formaldehyde to trans-hydroxycarbene. Calculated frequencies decreased by 15% are given in parentheses.

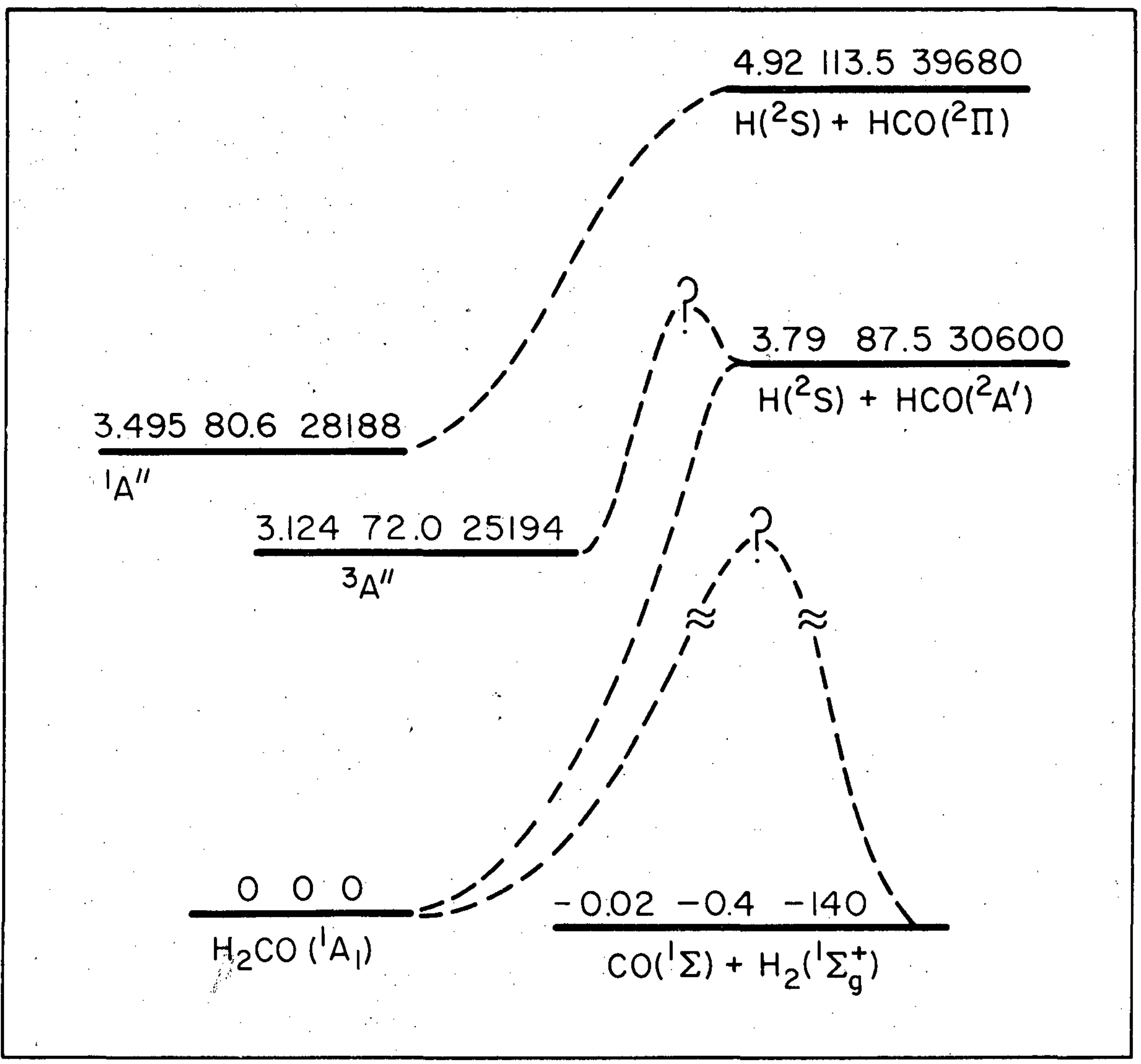

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Figure 1

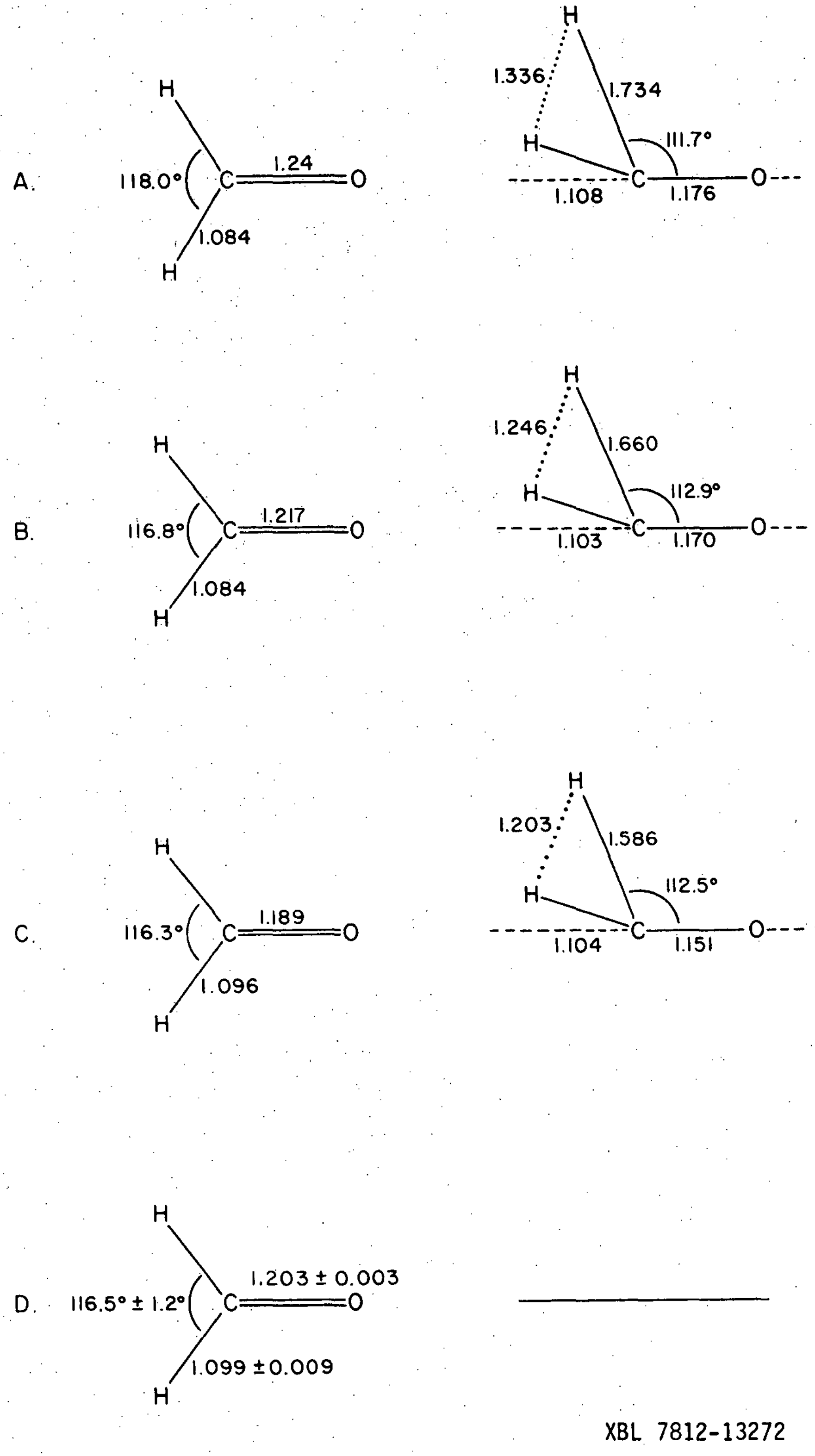
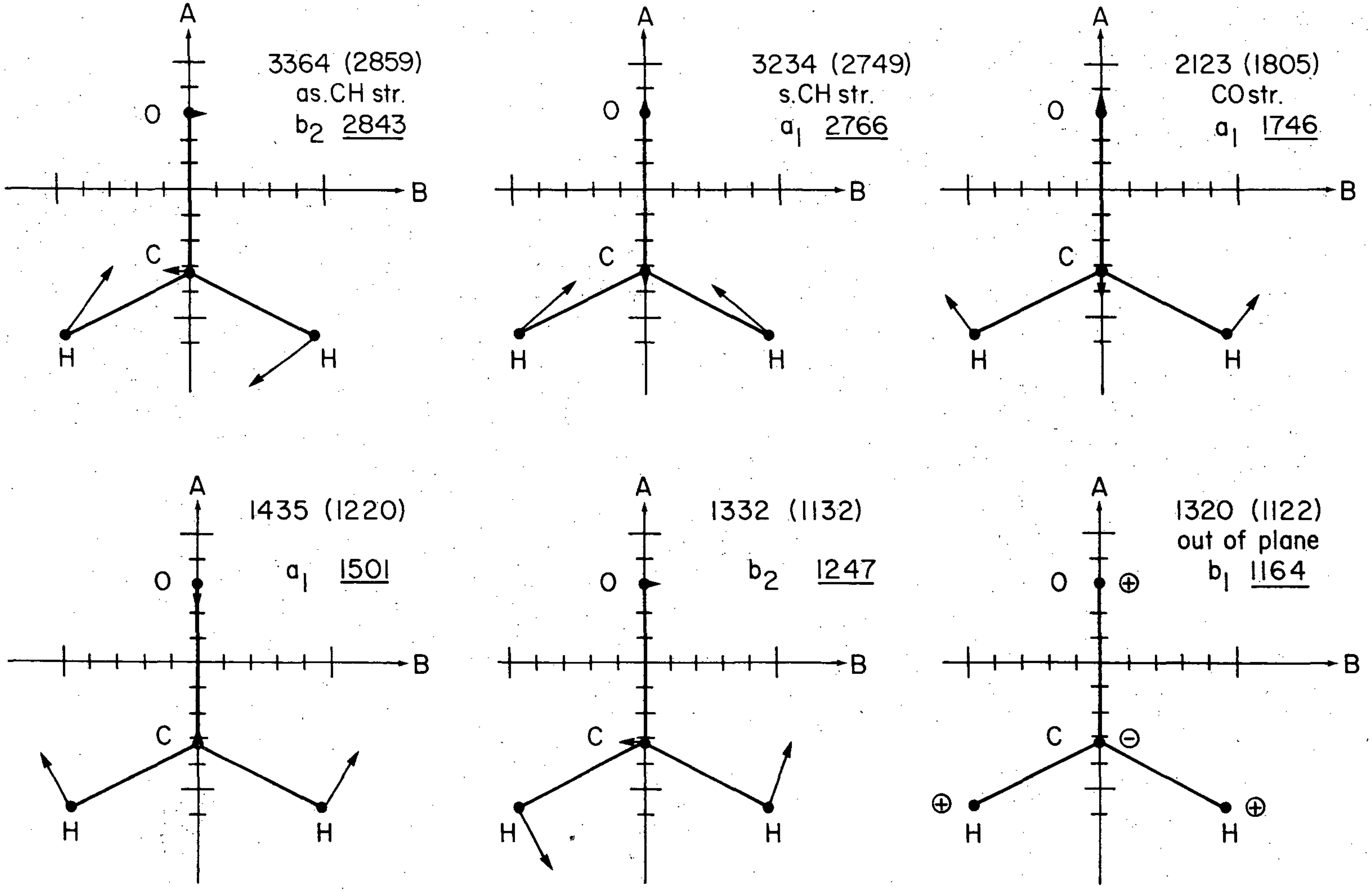
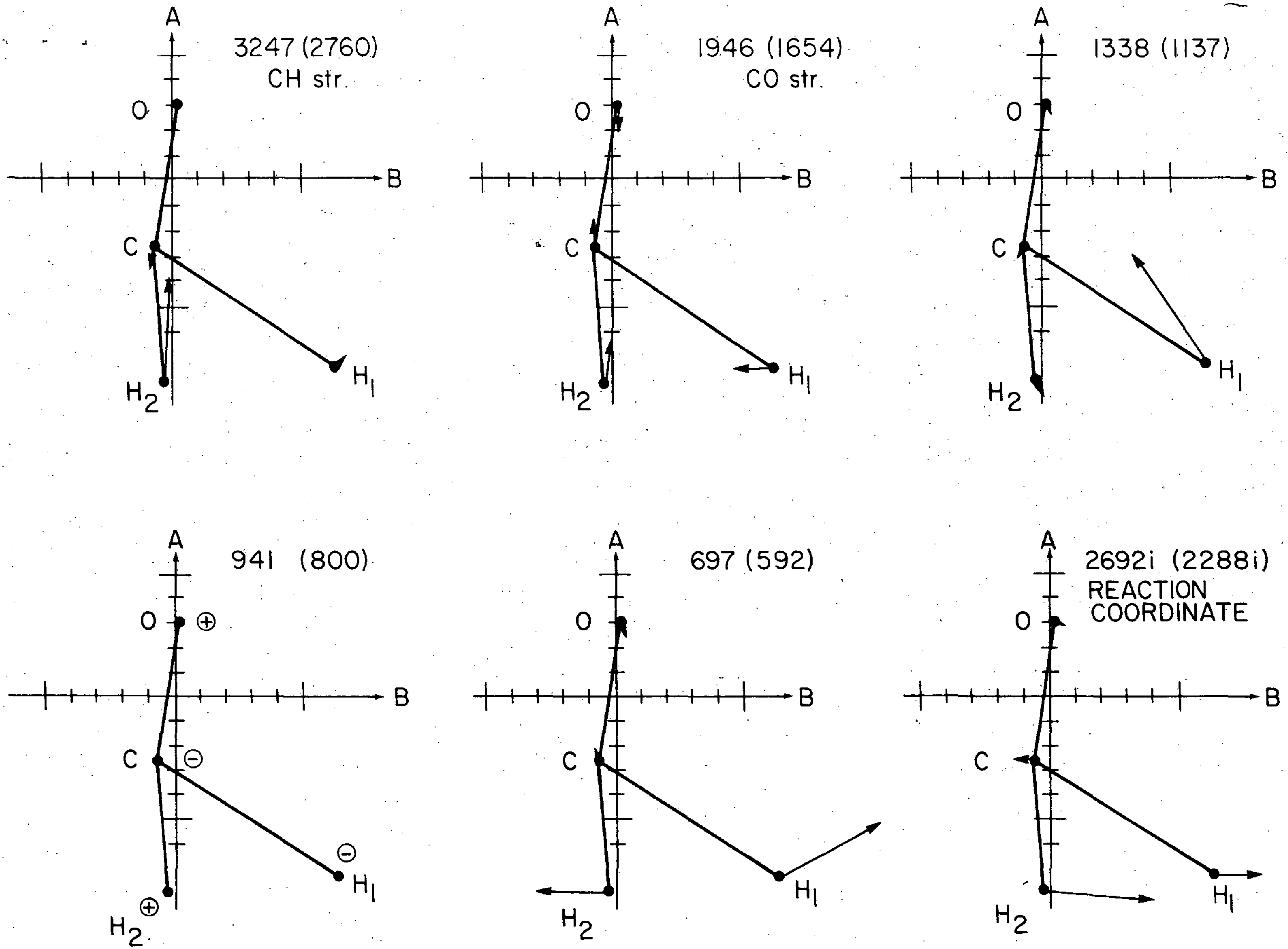

A.
H
118.0°
C
1.24
O
1.084
H
H
1.336
1.734
H
111.7°
1.108
C
1.176
O
B.
H
116.8°
C
1.217
O
1.084
H
H
1.246
1.660
H
112.9°
1.103
C
1.170
O
C.
H
116.3°
C
1.189
O
1.096
H
H
1.203
1.586
H
112.5°
1.104
C
1.151
O
D.
H
116.5° ± 1.2°
C
1.203 ± 0.003
O
1.099 ±0.009
H
XBL 7812-13272

Figure 2



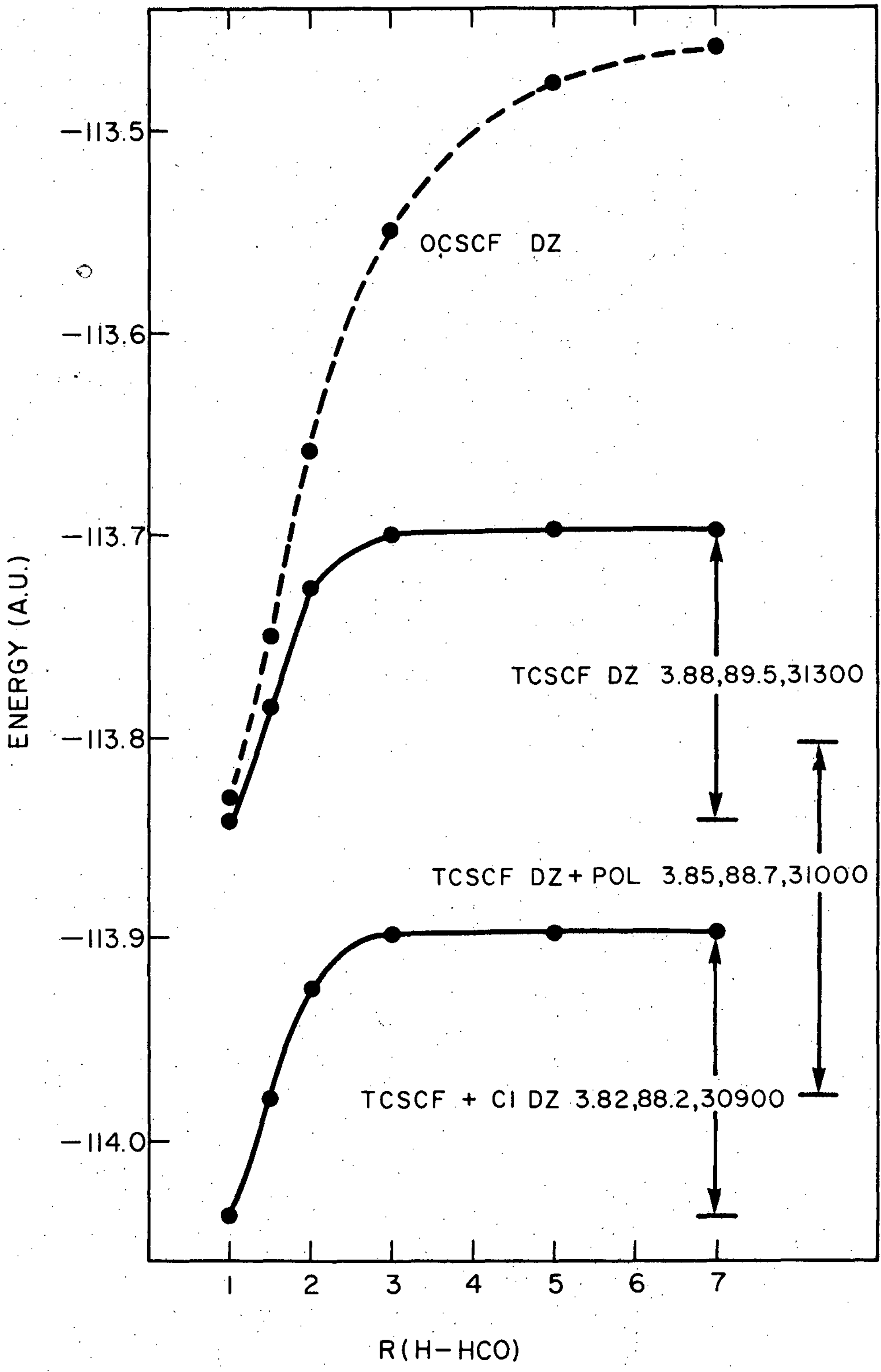
XBL 7812-13278

Figure 3



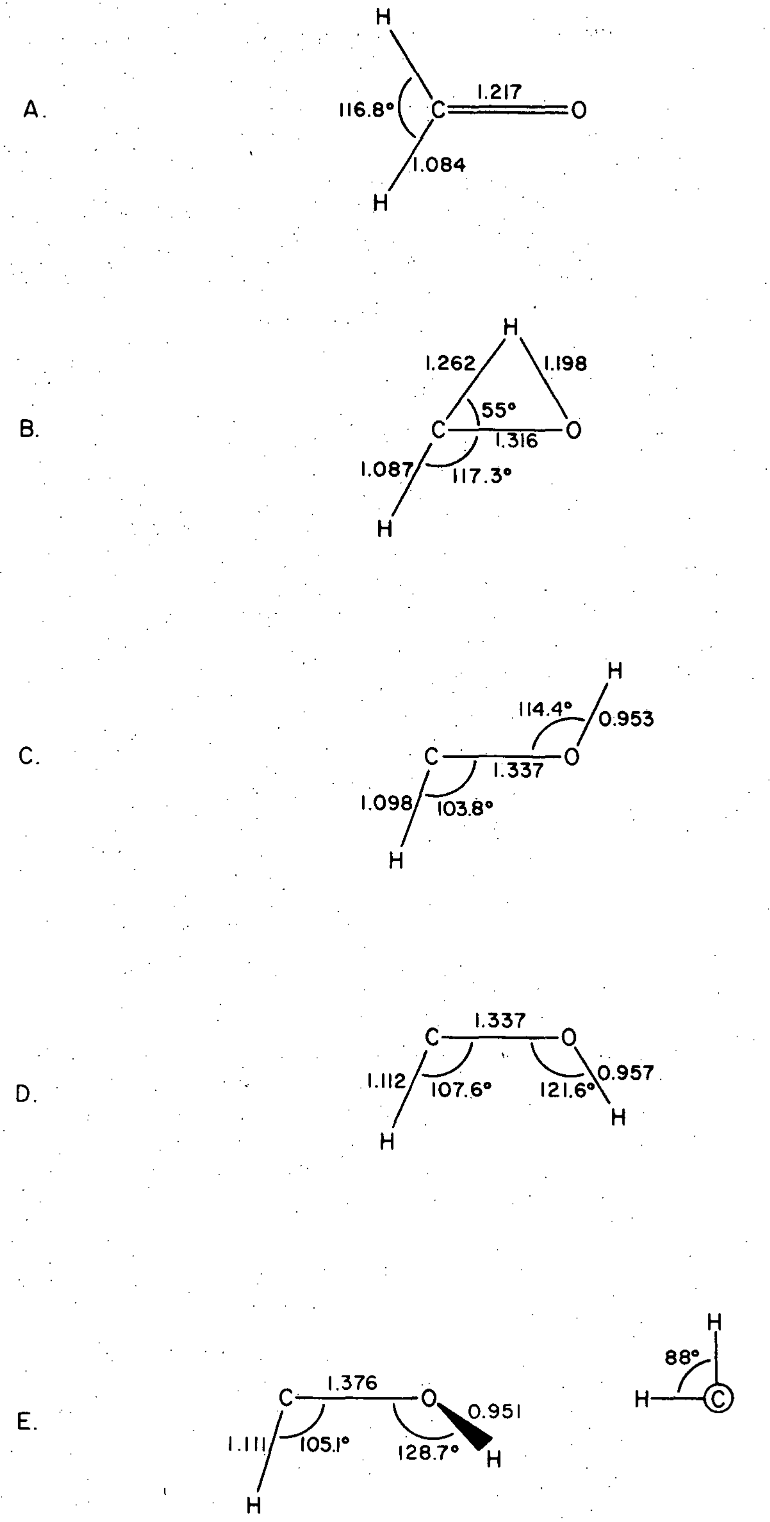
XBL 7812-13279

Figure 4



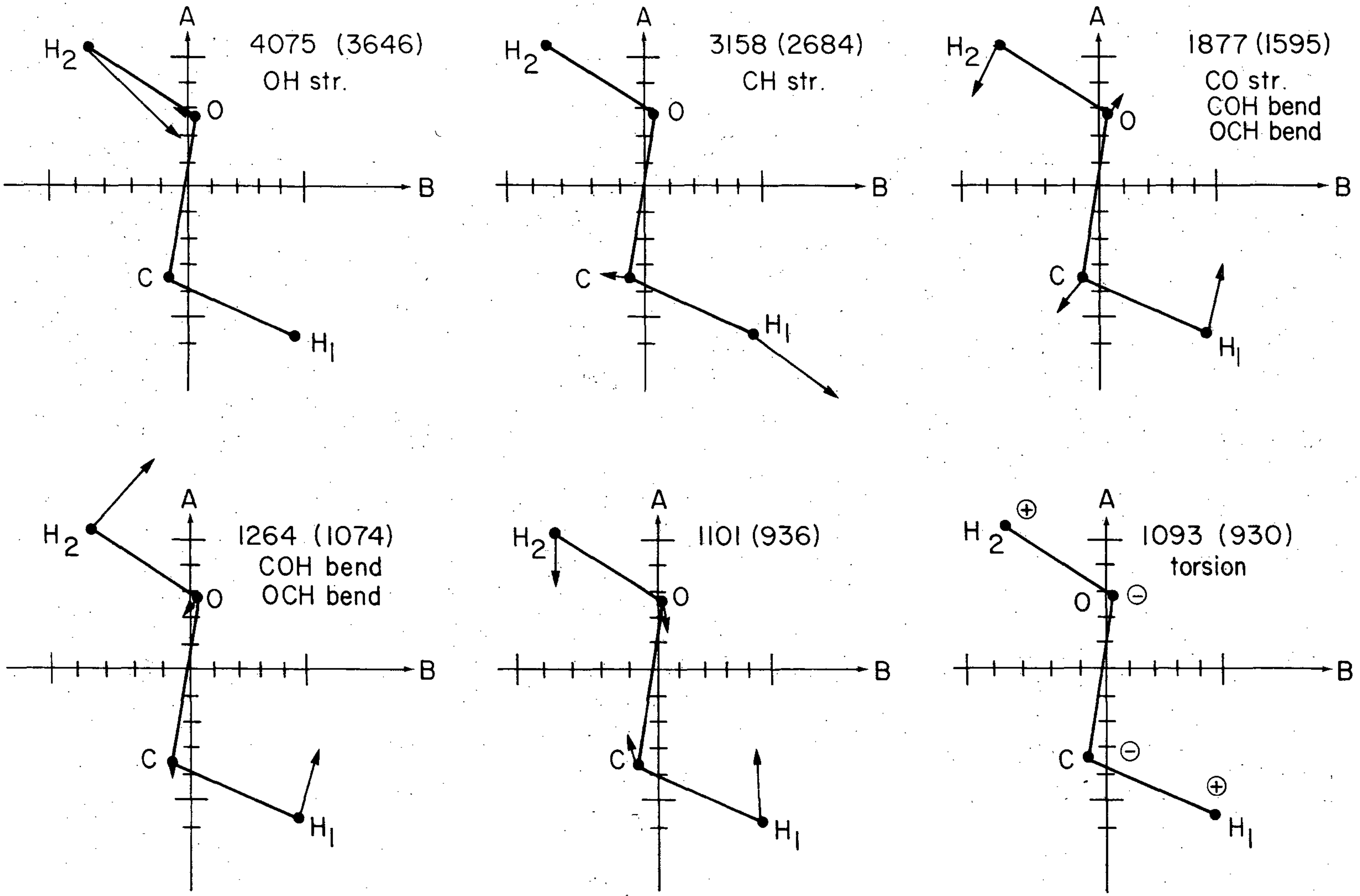
XBL 7812-13274

Figure 5



XBL 7812-13273

Figure 6



XBL 7812-13277

Figure 7a

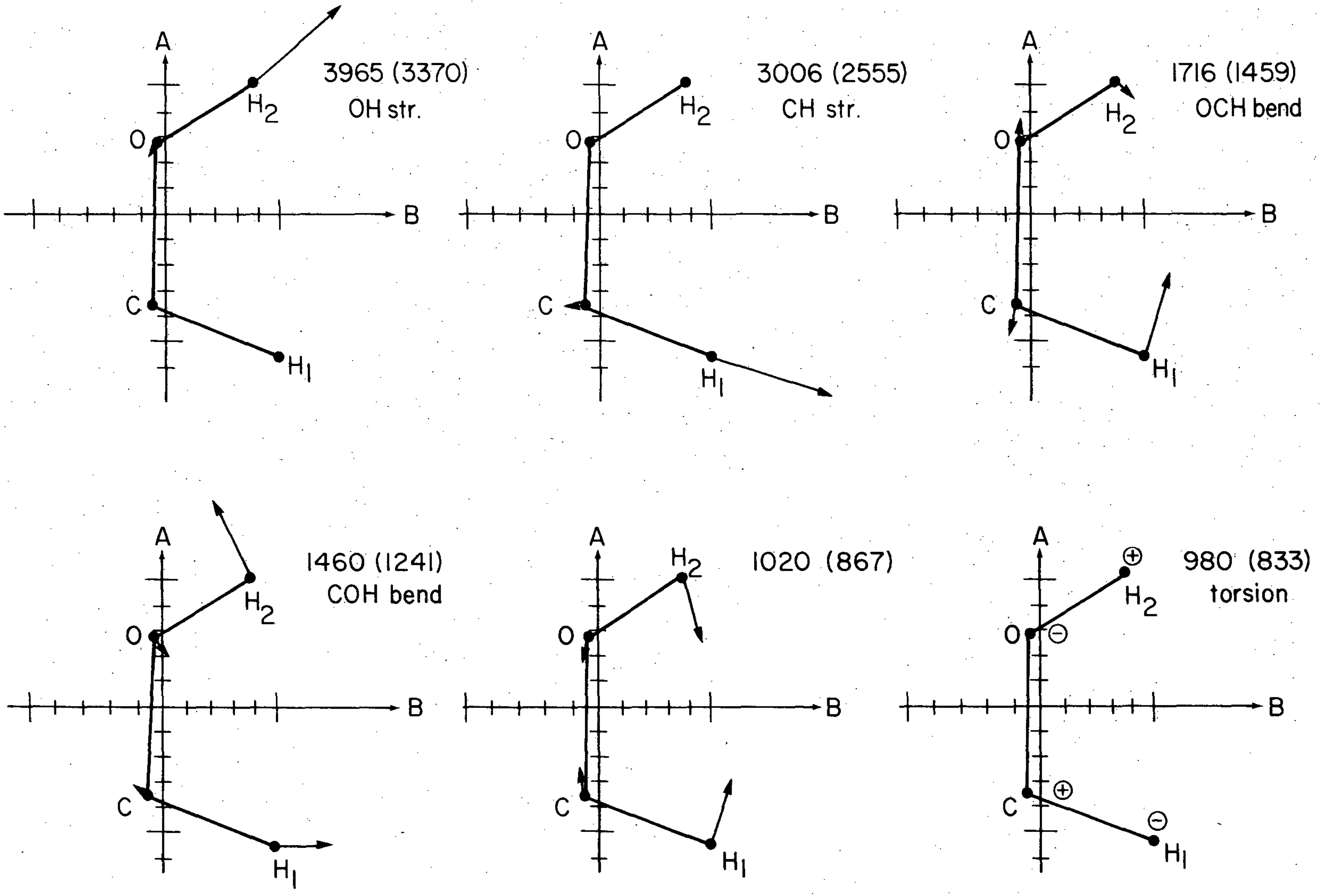


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Figure 7b

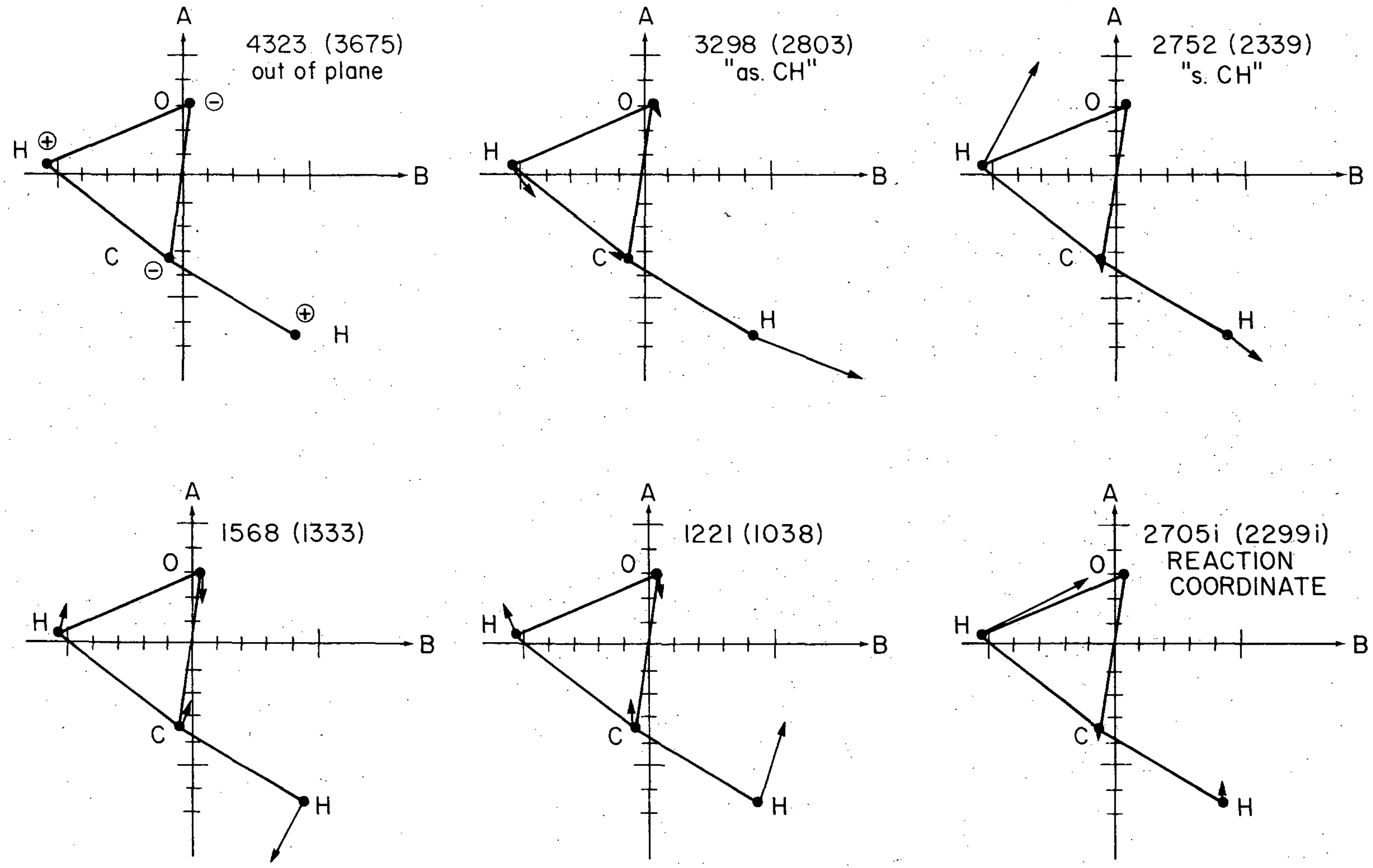

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Figure 8

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