

WHAT CAN PHOTOCHEMISTS EXPECT FROM AB INITIO CALCULATIONS NOW AND IN THE NEAR FUTURE?

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Abstract - The state of the art of ab initio quantum-mechanical calculations for polyatomic molecules is reviewed, with particular reference to predictions of interest to photochemists. The major areas discussed are spectral predictions, substituent effects on energy gaps, and potential energy surfaces.

INTRODUCTION

My aim in this lecture is to provide experimental photochemists with some idea of the type of energetic information that they can expect from nonempirical or "ab initio" quantum-mechanical calculations on polyatomic species. To this end I shall use something of a "case study" approach, choosing examples from work which has been published recently or indeed which is still in progress.

One of the points I wish to emphasize is that all types of ab initio calculations are not of equal reliability. Ab initio computations come in a variety of different qualities and styles, with different degrees of sophistication appropriate to different occasions. The commonest type of such calculations is that which uses a so-called minimal set of atomic orbitals as a basis for expansion of molecular orbitals, and in which a single electron configuration is considered adequate to represent the electronic state of interest. As an example, the minimal basis set for the formaldehyde molecule would consist of a 1s atomic orbital, a 2s, and three 2p orbitals centered on each of carbon and oxygen, and a 1s orbital on each hydrogen; each MO would be expanded as a linear combination of these twelve atomic functions. If a so-called "double zeta" basis set were to be employed, there would be two 1s orbitals on each atom, and two 2s orbitals and six 2p orbitals on each heavy atom. The use of two functions, with different average radii, to represent each type of orbital adds flexibility in construction of the resultant MOs. Even greater flexibility can be imparted to the orbitals of the molecule by adding so-called "polarization functions" to the basis - these would correspond to 3d orbitals centered on carbon and oxygen in formaldehyde, and 2p orbitals on the hydrogens. (Orbitals with even higher angular momentum quantum numbers are employed in the most sophisticated calculations).

In most calculations, a single product wavefunction is employed to represent a low-lying state of the system. For example, the ground state of formaldehyde would be represented by the function

$$\psi_e = 1s_0^2 1s_C^2 2s_0^2 \sigma_{1,CH}^2 \sigma_{2,CH}^2 \sigma_{CO}^2 2p_0^2 \pi_{CO}^2$$

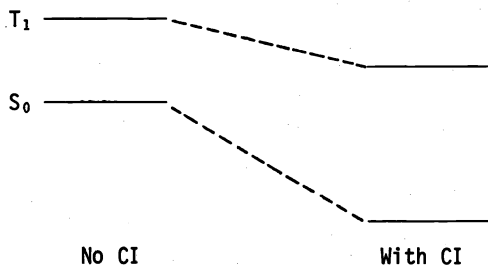
where $1s_0$ represents a molecular orbital which is predominantly $1s_0$ in character, etc. Such a single-determinant wavefunction is not a completely adequate representation of a multi-electron wavefunction, regardless of the quality of the basis set of orbitals used to construct each molecular orbital. This is so because such functions are incapable mathematically of incorporating the ability of electrons to instantaneously correlate their motion so as to avoid short interelectron distances. When comparing the relative energies of different closed shell molecules containing the same atoms and the same number of bonds, the errors in this correlation energy tend to be very similar and there is no particular need to evaluate explicitly the quantity. For example, Pople and coworkers (1) have reported relative energies for the ground states of C_4H_6 systems (Table 1).

TABLE 1. Relative energies of C₄H₆ isomers

Isomer	Relative Energy, in kcal mol ⁻¹		
	Calculated		Experimental
	No d on C	d orbitals on C	
1,3-Butadiene	0	0	0
2-Butyne	8.1	6.8	8.6
Cyclobutene	19.7	12.4	11.2
Methylenecyclopropane	25.1	20.2	21.7
Bicyclo[1.1.0]butane	46.6	30.4	25.6

(Note that d polarization functions on carbon are required to properly account for the strain in small rings).

Unfortunately the correlation energy error for a molecule tends to change drastically if the number of bonds and/or electron pairs is altered. For example, the correlation energy error associated with the relative motion of the two π electrons in the ground state of ethylene is rather substantial, whereas that for the same pair of electrons in the $\pi\pi^*$ triplet state is quite small. For this reason the S_0 - T_1 gap in ethylene would be underestimated using single-determinant wavefunctions for each state:



In general, accurate estimates of the energy difference between two excited states cannot be obtained unless one accounts for the change in correlation energy which occurs.

The most common technique of generating an electronic wavefunction which does properly correlate interelectronic motion is by expressing the electronic wavefunction as a linear combination of several different electron configurations. For example, to correlate the relative motion of the π electrons in the S_0 state of ethylene, the electronic wavefunction could be represented as an interaction between configurations in which the π bonding orbital π is doubly-occupied and π^* is empty, with those in which π is empty and π^* is doubly-occupied:

$$\Psi_e = x | \text{-----}(\pi)^2(\pi^*)^0 | + y | \text{-----}(\pi)^0(\pi^*)^2 |$$

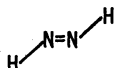
The weighing coefficients x and y determine the degree to which the two configurations interact, and they are evaluated by applying the variational principle. In the best ab initio calculations, thousands of different configurations are combined together to produce a very high quality wavefunction.

With this background in hand, I shall now discuss three current areas of application of ab initio calculations - namely the prediction of electronic spectra, the prediction of the effect of substituents and geometry upon the relative energies of states, and the calculation of potential surfaces for chemical reactions of excited states and of intermediates in photochemical reactions.

SPECTRAL PREDICTIONS

Near-quantitative predictions of vertical excitation energies to low-lying excited states are feasible now not only for diatomics but also for systems containing hydrogen atoms plus two first-row atoms. An interesting case in point is the N_2H_2 system. Very extensive calculations, which include a large amount of configuration interaction, were reported for

vertically-excited states of the most stable isomer, trans-diimide



by Vasudevan, Peyerimhoff, Buenker, Kammer, and Hsu (VPBKH) in 1975 (2). Almost all the low-lying states of this species involve excitation of an electron from the so-called n_+ molecular orbital, a species which is the result of symmetric combination of the in-plane lone pairs of the nitrogen atoms (see Fig. 1). On the basis of earlier calculations (3), the lowest-energy absorption band observed for trans-diimide and centered at about 3600Å had been assigned (4) as $^1(n_+ \pi^*)$. No other bands have been well-characterized experimentally. The vertical energy states predicted by VPBKH's calculations are illustrated in Fig. 2. Singlet states are shown by (thin) horizontal lines on the left, triplets on the right, and Rydberg states with near-degenerate singlets and triplets are positioned in the center. From previous experience with this type of calculation for formaldehyde, ethylene, O_2 and HNO it was expected that the lowest energy transitions should be accurate to two-tenths of an electron-volt (2). The discrepancy between the energy of 3.0 eV predicted for the transition to the $^1(n_+ \pi^*)$ state, and the experimental value of 3.5-3.6 eV obviously lies well outside this limit.

Vasudevan et al. feel sufficiently confident about their calculations that they attribute most of the 0.5 volt discrepancy to non-verticality in the transition. That explanation notwithstanding, calculations we have done recently (5) indicate that 0.1-0.2 eV of the discrepancy is due to the use of too small an HNN bond angle (110° as opposed to the experimental value of 106.8°) in the VPBKH calculations.

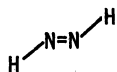
The second-lowest excited singlet predicted in the VPBKH calculations is a 6.1 eV transition and which involves principally an excitation from the n_+ orbital to a 3s orbital of the nitrogens. Although no such transition has yet been observed in the spectrum of trans-diimide, a 6.0 eV transition does occur in trans-azomethane, $CH_3-N=N-CH_3$ (2) (see dashed line in Fig. 2). Excitations in the trans-azomethane spectrum are also found at about 6.7 eV and which probably correspond to n_+ to 3p Rydberg transitions predicted between 6 and 7 eV (see Fig. 2).

The VPBKH calculations predict that the excitation of an electron from n_- , the out-of-phase combination of nitrogen lone pair orbitals (see Fig. 1), to the π^* MO should require 7.55 volts. This transition is seen in trans-azomethane at 7.8-8.0 eV, and may correspond to the absorption in diimide itself which has its 0-0 position at 7.2 eV (4). The $^1(\pi\pi^*)$ state is predicted to lie 11.7 eV above the ground state (i.e. at about 1060Å) by these calculations, in analogy with the results for formaldehyde in which the $\pi\pi^*$ singlet is very high in energy, the band at 1850Å being assigned as a transition to a Rydberg state rather than to $^1(\pi\pi^*)$. The inability of semiempirical MO methods to deal with Rydberg transitions becomes fatal in such cases!

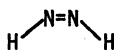
The valence-shell triplet states of trans-diimide are in rather different order than are the corresponding singlets (see right side of Fig. 2). The lowest triplet, predicted to lie only 2.1 eV above the ground state and seen in trans-azomethane (2) at about 2.7 eV, is $(n_+ \pi^*)$ as is S_1 , but the second triplet is predicted to be the $^3(\pi\pi^*)$ state at 5.3 eV. There is some evidence that T_2 in trans-azomethane lies a few tenths of a volt lower in energy than this (2). The $^3(n_- \pi^*)$ state lies higher than the $^3(\pi\pi^*)$, just above some Rydberg triplets, according to the VPBKH results.

There is every reason to expect ab initio calculations of this degree of sophistication for vertical excitation energies in other A_2H_2 systems in the near future. One can also look forward to the determination of the equilibrium geometries, and thus the prediction of 0-0 band energies, by ab initio calculations which include extensive configuration interaction and which employ large basis sets of orbitals.

In the recent past, such geometry searches in A_2H_2 systems have been done with small basis sets of orbitals and little or no CI. For example, in 1973 we reported calculated structures for the lowest two singlet and the lowest two triplet states of both cis and trans diimide (3), and for the S_0 and T_1 states of the isomer, 1,1-dihydrodiazine (7):



trans
diimide



cis
diimide



1,1-dihydrodiazine

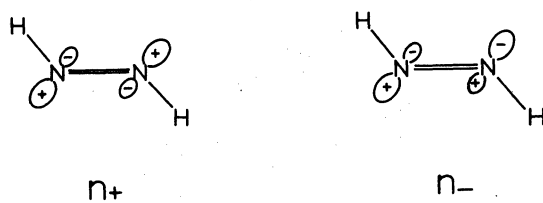
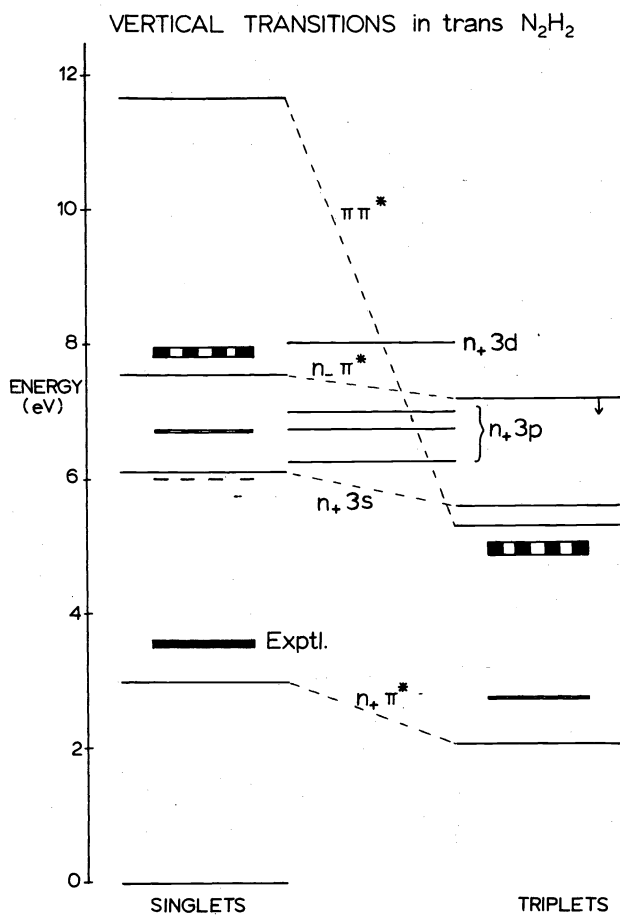


Fig. 1 Lone pair orbitals in diimide

Fig. 2 Vertical states in trans diimide

On the basis of these calculations, we were able to predict that the HNN angles in both the trans and cis forms increase substantially in the ($n\pi^*$) states compared to the ground state. The increase predicted for the trans singlet was 12° ; calculations by Vasudevan et al. (2) using a larger basis but including no CI give 14° . From the vibrational structure of the 3500A band of diimide, Back, Willis and Ramsay (4) estimate the increase to be $25 \pm 2^\circ$. While the ability of ab initio calculations to predict the occurrence of a large change in angle is useful, it would be comforting to know why the magnitude of the change differs by a factor of two from the experimental. Errors of this magnitude in predictions of bond angles for closed-shell ground states are not common, even when only a minimal basis set is employed. Perhaps the situation in the present case is complicated by the fact that twisting about the NN bond is predicted to occur with almost no energy of activation for the trans S_1 state, and that the bond angle in the twisted species should be larger still than in the planar form (3).

The expectation that a calculation which uses a minimal basis set of atomic orbitals and little or no CI can yield good geometric predictions for low-lying states is borne out by a wealth of calculations for closed-shell ground states by Pople and coworkers (8), and for the relatively smaller number of open-shell species for which comparisons can be made. As an example of both types, consider the predicted geometries shown in Fig. 3 for the S_0 states of trans-diimide and 1,1-dihydrodiazine and also for the low-lying triplet state of the latter. The agreement between the structures calculated at different levels of theory, and between these and the experimental results where available, is quite good. The 115° bond angle predicted around the amino nitrogen in the T_1 state of 1,1-dihydrodiazine is probably too high by 8° - 10° ; the 4-31G basis has chronic problems in dealing with the geometry about nitrogen and oxygen atoms which form only single bonds (8).

Although the predictions concerning the geometries of the nitrene are not much affected by use of a better basis set and inclusion of extensive configuration interaction, the relative energies of the singlet and triplet states are quite different at the two levels of calculation. When a minimal STO-3G basis (8) is used and the only CI applied is the important $(\pi)^2 \rightarrow (\pi^*)^2$ double excitation, the triplet is predicted to be the ground state since its energy is 26 kcal mol^{-1} superior to that of the closed-shell singlet (7). Upon use of the 4-31G basis (8) and the incorporation of CI (involving all but the lowest 4 MOs) the gap becomes only $1.6 \text{ kcal mol}^{-1}$ with the singlet predicted to be more stable than the triplet (9). However, even this calculation is not definitive, as no polarization functions are included in the basis set. Nevertheless it is likely that the S_0 and T_1 states of 1,1-dihydrodiazine lie rather close in energy.

In concluding this section, I should like to emphasize that ab initio calculations which employ large basis sets and extensive configuration interaction are capable of predicting energy transitions to within a few tenths of a volt. Less extensive, exploratory calculations must be regarded with caution as the differential error between the two states may be of the same order of magnitude as their energy gap.

EFFECT OF SUBSTITUENTS UPON RELATIVE ENERGIES OF STATES

In addition to semiquantitative predictions concerning the energies and geometries of low-lying states of small molecules and reactive intermediates, ab initio calculations are also useful in probing for substituent and geometric alterations which will alter the relative energy gaps between states in a desired manner. As an example in this area, consider the S_0 and T_1 states of carbenes :CRR'.

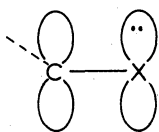
One of the great successes to date of ab initio calculations has been the consistent prediction, notwithstanding earlier experimental evidence to the contrary, that the T_1 state of CH_2 is strongly bent with an H-C-H angle of about 135° . These calculations also predict (correctly) that the triplet is the ground state of the system (10). The singlet-triplet splitting is overestimated in all but the most sophisticated calculations, chiefly for reasons associated with the lone pair of in-plane electrons in the S_0 state. The angular behavior of the lone pair orbital is described rather poorly unless d polarization functions are present in the basis set. Further, the correlation of motion between the two lone pair electrons is not accounted for adequately unless at least the electron configuration corresponding to a two-electron excitation from the lone-pair orbital to the (empty) p_π orbital is included as a component in the electronic wavefunction. (In contrast, the π extensive correlation in motion between the two unpaired electrons is included automatically and correctly in the triplet state wavefunction even without configuration interaction. Further, the poor description of the in-plane orbital involves only one electron for the triplet rather than two as in the singlet).

Thus the minimal STO-3G basis set calculation (using restricted MO methods for both open and closed shell species) with no CI places the S_0 state some 37 kcal mol^{-1} above the triplet (11). If the important $\sigma^2 \rightarrow \pi^2$ configuration interaction is included, this gap is lowered to 29 kcal mol^{-1} . The best theoretical calculation executed on CH_2 to date includes

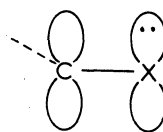
extensive polarization functions on the atoms and a large amount of CI, and predicts a gap of 9 kcal mol⁻¹, identical with the best 1975 experimental estimate (10). Unfortunately, the cost of repeating such calculations for many substituted carbenes would be prohibitive.

If we make the assumption that the "error" between the minimal basis set-limited CI calculation and the "full" calculation remains relatively constant (at the value of 20 kcal mol⁻¹ for CH₂), then the relatively inexpensive calculations by the simpler technique on substituted carbenes can prove quite useful. The molecular geometries predicted using such calculations are illustrated in Table 2 for several systems of interest; the corresponding energies are given in Table 3. (Note that Pople and coworkers have previously reported geometries for many of these species (12), although their method included no CI at all for the singlets and used unrestricted wavefunctions for the triplets.) The predicted bond angles about the divalent carbon in the acyclic systems are all within a few degrees of the 102° CH₂ value for the singlet state, and within a few degrees of 124° for the triplets (11). For this reason the character of the in-plane nonbonding orbital must be essentially identical in all acyclic systems, and thus lends support to our assumption that the "error" in the calculations should be very similar in such systems.

In the carbene calculations, we have been interested in finding substituents whose net effect would be to reverse the triplet-singlet ordering in CH₂ so as to make S₀ the ground state of the system. One way of effecting such a switch is to bond the divalent carbon to an atom X which has a lone pair of π electrons. The dative, two-electron π bond involving the lone pair on X with the empty p_π orbital on carbon could stabilize the singlet substantially.



2-electron π
bond in S₀



3-electron π
bond in T₁

The stabilization of the triplet by a three-electron π bond will be much less, and may even be destabilizing if the disparity in energy between the two p_π orbitals is large. The greatest π-bonding effects of X are found for X=N in H-C-NH₂. The predicted carbon-nitrogen bond length in the singlet is 1.35 Å, which is midway between the values predicted for C=N and C-N bonds by this method (12). In the best single-determinant representation of S₀, 0.30 electrons are transferred to the empty carbon p_π orbital from the nitrogen lone pair. Since two-electron excitation from the carbon in-plane lone pair to the carbon p_π orbital would create a destabilizing 4π electron, 2π orbital network, the contribution of the doubly-excited configuration to the ground-state wavefunction is only 1.8% for HCNH₂ compared to 5.8% for HCH. In contrast, the three-electron π bond in the T₁ state of HCNH₂ evidently is destabilizing, as the preferred geometry has the amino group flapped rather than planar, and the hydrogens twisted about the rather long CN bond. The singlet state is predicted to be more stable than the triplet by 28 kcal mol⁻¹ once the "correction" is applied (see Table 3).

Similar π-bonding effects occur, but to lesser extents, in HCOH and in HCF both of which should also possess singlet ground states. π bonding into the empty p_π orbital on carbon from two fluorines in FCF yields an S₀ state which should be 46 kcal mol⁻¹ more stable than T₁. Evidence from UV spectroscopy (13) supports the assignment of S₀ ground states for HCF and FCF; no direct experimental evidence seems to be available for the other systems.

Substitution of the hydrogens in CH₂ by neutral hydrocarbon groups is predicted to alter the S₀-T₁ gap by rather small amounts. Methyl groups lower the singlet relative to the triplet such that C(CH₃)₂ could well have both states populated thermally at normal temperatures. In contrast, conjugation of the carbene carbon with a vinyl group is predicted to yield a singlet state less stable (relative to the triplet) than that in CH₂.

It should be pointed out that in 1974 Staemmler (14) performed rather sophisticated *ab initio* calculations, which included polarization functions and a method of dealing with correlation energies, for four of the simpler systems listed in Table 3. The excellent agreement between his results (last column of Table 3) and our "corrected" values bolsters our confidence that the "correction" value of 20 kcal mol⁻¹ is valid for the acyclic systems we've considered.

The second technique known to stabilize the S₀ state of a carbene relative to the triplet is by reduction of the bond angle about the divalent carbon (15, 16). The variation in energy

		STO-3G Basis		4-31G Basis Extensive CI	Exptl.
		No CI	$\pi^2 \rightarrow (\pi^*)^2$ CI		
$\text{H}-\text{N}=\text{N}-\text{H}$ S_0	R_{NN}	1.21Å	1.25Å	1.29Å	1.252Å
	R_{NH}			1.02Å	1.028Å
	$\angle \text{HNN}$	109° (planar)		108.5°	106.8° (planar)
$\text{H} \diagdown \text{N}=\text{N}$ $\text{H} \diagup$ S_0	R_{NN}		1.276Å	1.260Å	--
	R_{NH}		1.041Å	1.02Å	--
	$\angle \text{HNN}$		124° (planar)	124°	--
$\text{H} \diagdown \text{N}=\text{N}$ $\text{H} \diagup$ T_1	R_{NN}	1.436Å		1.395Å	--
	R_{NH}	1.034Å		1.00Å	--
	$\angle \text{HNN}$	107.5° (flapped)		115° (flapped)	--

Fig. 3 Geometries of N_2H_2 isomers

ENERGY vs ANGLE IN CH_2

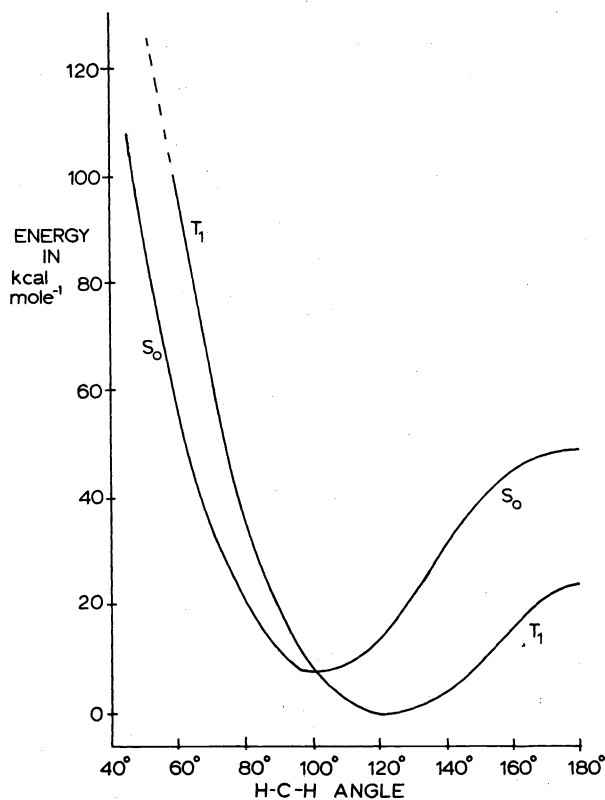


Fig. 4 Energies of S_0 and T_1 states of CH_2

TABLE 2. Geometries of carbenes





Carbene	Parameter	Singlet S_0	Triplet T_1
H-C-H	<HCH	102°[102.4°]	124°[136°]
H-C-NH ₂	NH ₂ conformation <HCN R_{CN}	Planar 104° 1.35A	Twisted, flapped (124°) 1.44A
H-C-OH	OH conformation <HCO R_{CO}	Planar 102° 1.34A	Twisted 123° 1.38A
H-C-F	<HCF R_{CF}	103°[101.6°] 1.32A[1.314Å]	121° 1.34A
F-C-F	<FCF R_{CF}	103°[104.9°] 1.32A[1.300A]	119° 1.34A
H-C-CH ₃	<HCC R_{CC}	104° 1.52A	124° 1.54A
H- \ddot{C} -CH=CH ₂	<H \ddot{C} C R_{CC} $R_{C=C}$	103° 1.51A 1.32A	124° 1.48A 1.32A
	<C \ddot{C} C R_{CC} R_{CC}	59° 1.53A 1.51A	56° 1.47A 1.56A
	<C \ddot{C} C R_{CC} $R_{C=C}$	55° 1.44A 1.32A	53° 1.47A 1.31A

TABLE 3. S_0 - T_1 splittings in carbenes

Carbene	Calculated Gap (kcal mol ⁻¹)		
	Ab Initio	"Corrected"	Staemmler
H-C-H	29	9	10
H-C-NH ₂	-8	-28	
H-C-OH	-4	-24	
H-C-F	6	-14	-11
F-C-F	-26	-46	-47
H-C-CH ₃	26	6	6
CH ₃ -C-CH ₃	24	4	
H-C-CH=CH ₂	32	12	
	5	-15(?)	
	-59	-79(?)	

of the T_1 and S_0 states of CH_2 with H-C-H bond angle is illustrated in Fig. 4. Since relative energies are of interest, the S_0 curve has been lowered by 20 kcal mol^{-1} , even though the "error" in the minimal basis set calculations may vary with angle.

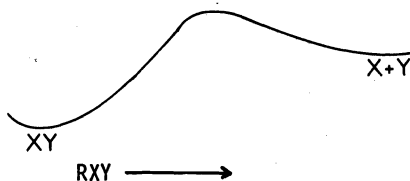
As previous workers have realized, carbenes which have singlet ground states by reason of small angle at C can be devised by incorporation of the carbene centre into a small ring. According to our calculations (11), the ground state of cyclopropylcarbene should be S_0 , with the triplet 15 kcal mol^{-1} above (assuming that the 20 kcal mol^{-1} correction is still valid at a 60° angle!). For cyclopropenylcarbene the singlet state is very much more stable than is the triplet according to our calculations (see Table 3). The large preferential increase in stability for S_0 in going from the saturated to the unsaturated 3-membered ring is due in part to the further decrease in the angle at C and in larger part to the existence of an aromatic 2π electron ring in the latter. According to our calculations, involvement in this aromatic ring network results in a single-determinant p_π orbital population of 0.36e, even greater than that for the $H\dot{C}NH_2$ singlet.

Dewar and coworkers (16) have previously reported semiempirical MINDO/2 calculations for both three-membered ring carbenes discussed above. They find a triplet ground state, with a T_1-S_0 split of $2.3 \text{ kcal mol}^{-1}$ for the cyclopropyl system, and a singlet ground state with a S_0-T_1 gap of $34.2 \text{ kcal mol}^{-1}$ for the cyclopropenyl. At present we are improving our computer programs so as to be able to include d orbitals on the carbon atoms in such systems, and we hope to provide a more realistic result as to the S_0-T_1 gaps in such compounds by using an improved basis set.

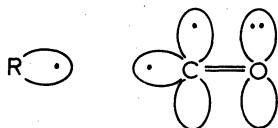
POTENTIAL ENERGY SURFACES

The calculation of potential energy surfaces for the reaction of ground-state molecules is a field still in its infancy; for this reason it is not surprising that rather few reaction surfaces for excited states of polyatomics have yet been generated. In contrast to ground state reactions for which the energy of the S_0 transition state is the only real quantity of interest, the location of real and avoided crossings of surfaces and the locations of "funnels" to the S_0 surface are often of as much interest as are barrier heights when dealing with photochemical processes. Since the reviews by Devaquet (17) and by Michl (18) at the last IUPAC Photochemistry Conference dealt with crossings in great detail, however, I shall not dwell upon the general aspects of this point.

Recently the mechanisms by which photochemical decompositions occur has been receiving some attention in terms of ab initio calculations. At first glance, one might think that computations which did not include extensive CI would be particularly unsuitable to follow decompositions, given the difficulties of molecular orbital theory in describing properly the homolytic dissociation of two-electron bonds in most closed-shell molecules. For example, the dissociation limit for H_2 corresponds to a mixture best described as 50% atomic hydrogen, 25% H^- and 25% H^+ if single-determinant (restricted) MO theory is employed (9). In contrast, restricted open-shell MO theory can describe correctly the dissociation of a three-electron $X\cdots Y$ bond into \dot{X} and \dot{Y} . The latter stages in the decomposition of certain free radicals and excited molecules correspond to the three-electron case. In many such systems, there exists an energy barrier, greater in magnitude than the reaction endothermicity, along the dissociation pathway:

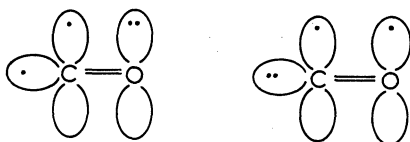


The origin of the barrier, and a good estimate of its magnitude, can be obtained from ab initio open-shell calculations which include some CI. As an example, consider first the decomposition to radical R and carbon monoxide of the free radicals RCO produced in various photochemical processes. At short RC distances and large RCO bond angles, the bonding in the ground states of such radicals is best described as consisting of a two-electron bond between the singly-occupied orbital of R and an sp-hybrid orbital on carbon:



The in-plane π linkage contains three-electrons and therefore is rather weak since there is little sharing between the "lone pair" on oxygen and the "singly-occupied" orbital on carbon.

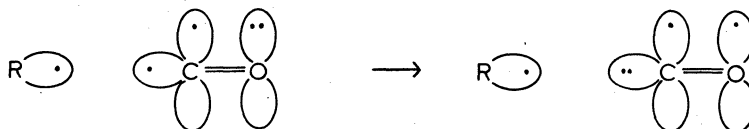
In the initial stages of the decomposition, the R-C distance is increased with a consequent reduction in the strength of that two-electron bond; very little reorganization of bonding occurs in the carbon-oxygen bonds. (For future reference it is pointed out here that single-determinant MO theory does not handle this stage of the dissociation very well, as the simple wavefunction contains ionic terms corresponding to $R^{\ominus} C^{\oplus} O$ and $R^{\oplus} C^{\ominus} O$ which are quite inappropriate at large R-C bond lengths.) Were the dissociation to continue in this manner, the resulting products would be ground state R^{\cdot} and electronically excited CO:



excited state

ground state

However, at some point in the carbon-carbon bond lengthening between 2\AA and 3\AA , the three-electron R-C bond structure becomes energetically superior to the two-electron, and the molecular orbitals of the nonlinear species switch over to adopt such an electronic environment:



Clearly the carbon-oxygen linkage corresponds to the triple bond of ground state CO, and in fact further lengthening of the R-C bond yields ground state carbon monoxide and ground state radical.

The potential energy profile for such processes (20) is sketched roughly in Fig. 5. The intended crossing between the curves is avoided (unless the molecule is linear in which case the curves correspond to states of different symmetry (19)) and ground state RCO dissociates into ground state CO (19). However, the substantial stretching of the R-C bond which has to occur before the switchover to the three-electron curve is feasible involves a substantial loss in bonding energy and gives rise to an activation energy barrier which is significantly larger than the reaction enthalpy. Experimental evidence from kinetic measurements (21) suggests that the total barrier height for CH_3CO decomposition is $17.2 \text{ kcal mol}^{-1}$, some 6 kcal mol^{-1} greater than the net loss in bonding energy. The *ab initio* calculations which has been reported for this process (22), and unpublished calculations from my own laboratory (20), both predict barriers approximately twice as high as the experimental value. We believe this error is due partially to the poor description of the two-electron C-C bond in the early stages of the reaction. Since no CI is included in these calculations, the energy increases too steeply as the C-C bond begins to stretch. Thus the calculated two-electron bond curve crosses the three-electron curve at too high an energy. The inclusion of CI to correlate the motion of the electron pair in the C-C bond will presumably yield a curve (dashed in Fig. 6) which intersects with the three-electron configuration at a longer C-C distance and will yield a more realistic barrier height. Calculations are presently underway at Western to test this hypothesis.

Preliminary calculations in our group indicate that the sensitized photochemical decomposition of ketene into methylene and CO is very similar to RCO $^{\cdot}$ dissociation in many respects (5). The analogy between the triplet and the radical processes becomes clear upon examination of the nature of the bonding in the S_0 and T_1 states of ketene. The ground state is best described as a hybrid of two structures, both of which contain four π electrons in the

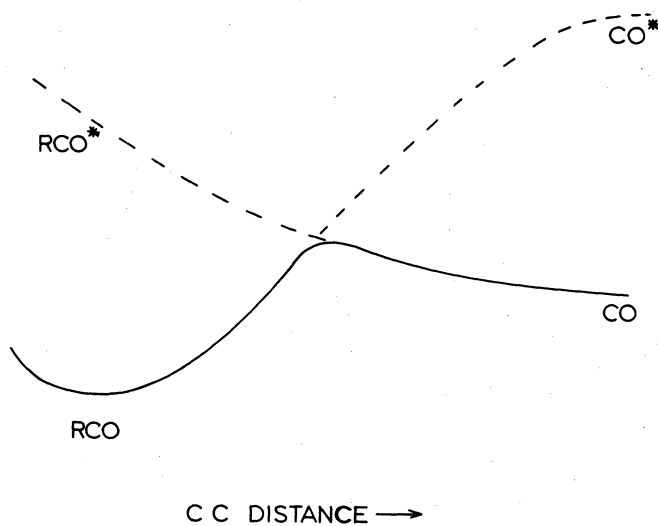


Fig. 5 Energy profile (schematic) for C-C bond dissociation in RCO systems

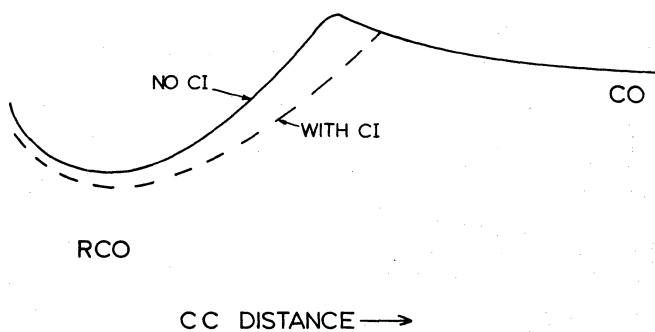
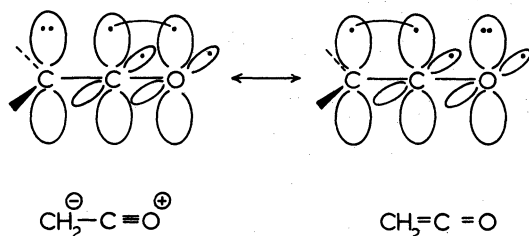
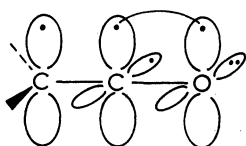


Fig. 6 Effect of CI on C-C dissociation in RCO

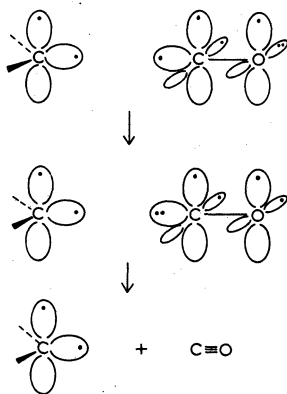
three p_{π} orbitals perpendicular to the molecular plane:



In the lowest triplet state, one of the four π electrons is excited into the antibonding MO formed by the quasi- π orbitals of carbon and oxygen (23). These in-plane MOs polarize such that the oxygen essentially carries a lone pair of electrons, and the carbon a single electron, as in RCO radicals. The three-electron π system perpendicular to the plane is best considered as a two-electron π bond between C and O, weakly conjugated to a singly-occupied p_{π} orbital on the methylene carbon:



Given the similarity in the carbonyl fragment of the electronic structure of the ketene triplet to that of RCO free radicals, it is not surprising that recent *ab initio* calculations of the geometry for the triplet (23) yield a CCO angle of 131.7° , very close indeed to the calculated value of 129° (20) for CH_3CO . The calculated carbon-carbon bond length of 1.459Å and the carbon-oxygen length of 1.200Å (23) correspond to essentially-single and essentially-double bonds, in agreement with the structure described above. Thus the triplet state decomposition of ketene can proceed through the same process of stretching the two-electron carbon-carbon σ bond followed by a switchover beyond 2Å to a three-electron C-C link and further dissociation to yield the triplet state of methylene and the ground state of carbon monoxide:



The similarity between the radical and triplet decomposition processes is illustrated vividly by the fact that their energy profiles are almost superimposable (Fig. 7). The transition states in both cases occur at 2.0Å; this is probably too early in the C-C bond stretching as these minimal basis set calculations include no CI. (Dykstra and Schaefer (24) plan to investigate the triplet decomposition using CI calculations, and no doubt their surface will be much more realistic than that given in Fig. 7.)

Even though the present calculations over-estimate the height of the barrier to ketene decomposition, the vertically-excited molecule is predicted to possess initially enough excess vibrational energy to dissociate (see dashed line near top left of Fig. 7). Much of this excess energy is contained in the C-C-O bending mode; the equilibrium CCO angle changes from 180° in the ground state to 131.7° in the triplet. If only excess vibrational energy in the carbon-carbon bond were to be available, the $17.6 \text{ kcal mol}^{-1}$ involved (dashed line near bottom left of Fig. 7) would be insufficient alone to allow the barrier to be mounted. It will be interesting to see how configuration interaction alters the heights of these

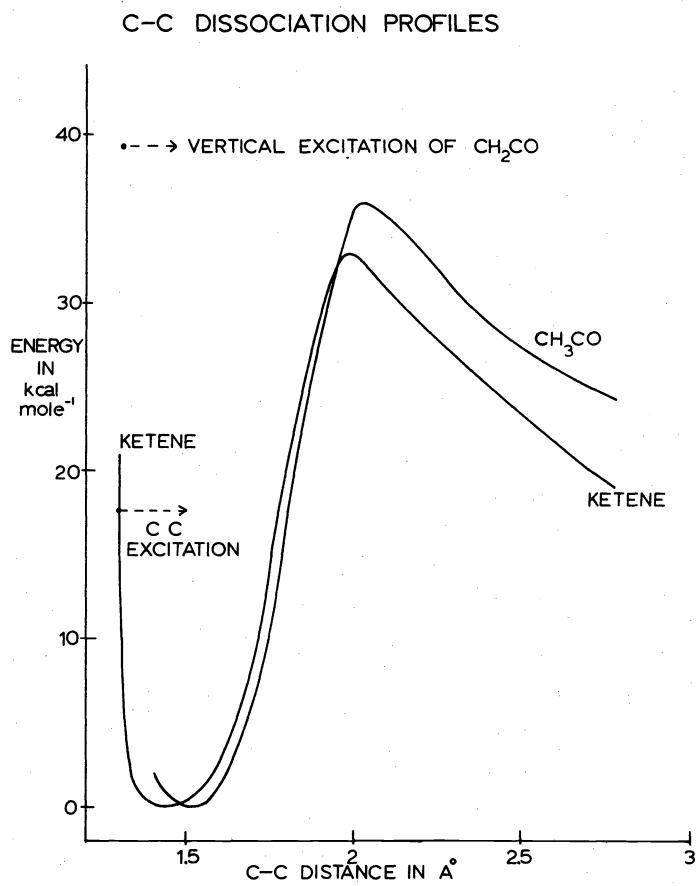


Fig. 7 C-C bond dissociation energy profiles (STO-3G) for CH₃CO and triplet ketene

two points on the surface. (Experimentally, the triplet state gas phase decomposition of ketene (25) involves an apparent activation energy of ~ 3.5 kcal mol⁻¹.) Quite obviously it is impossible to make meaningful predictions concerning the rate of decay predicted for the triplet with a probable uncertainty of a factor of 2 in the calculated barrier. *Ab initio* calculations of this sort can only yield a qualitative or, at best, a semiquantitative guide to barrier heights for chemical reactions, whether they be thermal or photochemical processes.

CONCLUSIONS

Near quantitative energetics for low-lying valence states of small polyatomic molecules can be obtained via *ab initio* calculations, provided that a large basis set (including polarization functions) and extensive configuration interaction are employed. In applications where a minimal basis set is used and little or no configuration interaction is employed, due caution must be exercised. Such calculations can be quite useful, however, in the prediction of trends within a closely-related series, in the preliminary investigation of a potential surface, and in attempts to understand the nature of the changes in electronic structure which occur as the result of a reaction or an electronic transition. A better appreciation on the part of the experimental photochemist of what can be realistically expected in terms of accuracy from a given type of *ab initio* calculation will improve the quality of dialogue between theoretician and experimentalist!

REFERENCES

1. J.S. Binkley, J.A. Pople, and W.J. Hehre, Chem. Phys. Letters **36**, 1-5 (1975).
2. K. Vasudevan, S.D. Peyerimhoff, R.J. Buenker, W.E. Kammer, and H. Hsu, Chem. Phys. **7**, 187-209 (1975).
3. N.C. Baird and J.R. Swenson, Can. J. Chem. **51**, 3097-3101 (1973).
4. R.A. Back, C. Willis, and D.A. Ramsay, Can. J. Chem. **52**, 1006-1012 (1974).
5. N.C. Baird, unpublished calculations.
6. A. Trombetti, Can. J. Phys. **46**, 1005-1011 (1968).
7. N.C. Baird and R.F. Barr, Can. J. Chem. **20**, 3303-3308 (1973).
8. See, for example, a) M.D. Newton, W.A. Lathan, W.J. Hehre, and J.A. Pople, J. Chem. Phys. **52**, 4064-4072 (1970), and b) W.A. Lathan, W.J. Hehre, L.A. Curtiss, and J.A. Pople, J. Amer. Chem. Soc. **93**, 6377-6387 (1971).
9. N.C. Baird and D.A. Wernette, unpublished calculations.
10. a) See V. Staemmler, Theoret. Chim. Acta (Berl.) **31**, 49-61 (1973) and references therein.
b) H.M. Frey and G.J. Kennedy, J. Chem. Soc. Chem. Comm., 233 (1975).
11. N.C. Baird and K.F. Taylor, unpublished calculations.
12. W.A. Lathan, L.A. Curtiss, W.J. Hehre, J.B. Lisle, and J.A. Pople, Prog. Phys. Org. Chem. **11**, 175-261 (1974).
13. See a) A.J. Merer and D.N. Travis, Can. J. Phys. **44**, 1541-1550 (1966);
b) C.W. Mathews, ibid. **45**, 2355-2374 (1967).
14. V. Staemmler, Theoret. Chim. Acta (Berl.) **35**, 309-327 (1974).
15. R. Hoffmann, G.D. Zeiss, and G.W. Van Dine, J. Amer. Chem. Soc. **90**, 1485-1499 (1968).
16. N. Bodor, M.J.S. Dewar, and J.S. Wasson, J. Amer. Chem. Soc. **94**, 9085-9102 (1972).
17. A. Devaquet, Pure Appl. Chem. **41**, 455-473 (1975).
18. J. Michl, Pure Appl. Chem. **41**, 507-534 (1975).
19. See a) N.C. Baird, J. Chem. Phys. **62**, 300-301 (1975), and b) G. Herzberg, Molecular Spectra and Molecular Structure, Vol. III, D. Van Nostrand, 1967, p. 468.
20. H.B. Kathpal and N.C. Baird, unpublished calculations.
21. K.W. Watkins and W.W. Word, Int. J. Chem. Kinetics **6**, 855-873 (1974).
22. P.J. Bruna, R.J. Buenker, and S.D. Peyerimhoff, J. Mol. Struct. **32**, 217-233 (1976).
23. C.E. Dykstra and H.F. Schaefer III, J. Amer. Chem. Soc. **98**, 2689-2695 (1976).
24. C.E. Dykstra, private communication to the author.
25. A.N. Strachan and D.E. Thornton, Can. J. Chem. **46**, 2353-2360 (1968).