## Excited Electronic States of Ketene

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Abstract: The geometries and excitation energies of the low-lying electronic states of $CH_2=C=O$ have been investigated using a priori theoretical methods. Three basis sets of contracted Gaussian functions were employed, double ζ (DZ), double ζ plus Rydberg (DZ + R), and double ζ plus polarization (DZ + P). Vertical transitions to 18 excited electronic states were considered, with DZ excitation energies ranging from 24 000 to 137 000 cm^{-1} and dipole moments from -4.1 to $+2.3$ D. The same states were studied with the DZ + P basis and very similar predictions made. The average differences in excitation energy and dipole moment were 2200 cm^{-1} and 0.33 D. For several states (including $^3B_1$ and $^1B_1$) excitation energies are lowered by as much as 30 000 cm^{-1} using the DZ + R basis. The predicted ground state dipole moment (1.81 D) is somewhat larger than the experimental value (1.41–1.44 D). The predicted ground state molecular structure compares quite favorably with experiment: $r(CO) = 1.168$ Å (1.161 ± 0.01), $r(CC) = 1.311$ (1.314 ± 0.01), $r(CH) = 1.070$ Å (1.079 ± 0.002), and $\alpha(HCH) = 120.1°$ (122.3 ± 0.2). For eight low-lying excited states, equilibrium geometries are predicted.

Ketene is a reactive gas phase species prepared by the decomposition of acetic acid or acetone. Perhaps typical of the conventional reactions of the ketene is that with water

$$H_2C=C=O + H_2O \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH$$
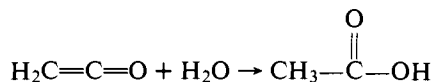
The subsequent reaction with acetic acid provides a useful commercial synthesis of acetic anhydride.[2a] In recent years, however, primary research interest has focused on the photochemistry of ketene. Specifically, ketenes $R_2C=C=O$ are a particularly convenient source[2b] of carbene radicals CR_2.

One of the most characteristic features of the photochemistry of ketene is a dependence on the wavelength of the absorbed radiation.[3] Both triplet and singlet methylene appear to be formed[4] at wavelengths less than 3700 Å, but the tripet fraction reported varies[5,6] from 26% at 2139 Å to 75% at 3660 Å. Since the first excited state (a $^3\Pi$) of the CO molecule is relatively high lying (48 000 cm^{-1}),[7] spin conservation requires that triplet and singlet methylene originate, respectively, with excited triplet and singlet states of ketene. Thus the nature and positions of the excited electronic states of ketene are expected to play a crucial role in any satisfactory understanding of the photodecomposition of ketene.

There have been a number of experimental studies of the electronic spectrum of ketene.[8-15] Perhaps the earliest interpretation of the ketene spectrum was that of Price, Teegan, and Walsh.[10] By analogy with ethylene, they assigned the six observed transitions between 54 680 and 75 180 cm^{-1} as the n = 3, 4, 5, 6, 7, and 8 members of a $\pi \rightarrow ns$ Rydberg series. The limit of the series (ionization potential) was placed at 9.60 ± 0.02 eV, a result recently confirmed by Baker and Turner.[16] In addition Price et al. suggested that (a) the 3200 Å (31 300

cm^{-1}) system of ketene probably arises from the excitation of a nonbonding electron on the oxygen atom, and (b) the band system around 2100 Å (47 600 cm^{-1}) may be interpreted as an excitation from the $C\equiv O$ bonding orbital to an antibonding upper orbital ($\pi + \pi \rightarrow \pi - \pi$).

Dixon and Kirby[12] carried out self-consistent-field (SCF) molecular orbital (MO) calculations in the Pariser–Parr–Pople approximation[17] in order to interpret their own ketene spectra as well as those of previous workers.[8-11] To discuss their conclusions we first note that the ground state orbital occupancy of ketene is (in our notation and ordering of orbitals)

$$1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 6a_1^2 7a_1^2 1b_2^2 1b_1^2 2b_2^2 2b_1^2 \quad (1)$$

Dixon and Kirby[12] predict the $^3A_2$ and $^1A_2$ states, corresponding to

$$\ldots 7a_1^2 1b_2^2 1b_1^2 2b_2^2 2b_1 3b_2 \quad (2)$$

to be the lowest excited states of ketene, lying at 22 400 and 25 700 cm^{-1}, respectively. They also predicted the existence of a low-lying (30 300 cm^{-1}) $^3A_1$ state arising from electron configuration

$$\ldots 7a_1^2 1b_2^2 1b_1^2 2b_2^2 2b_1 3b_1 \quad (3)$$

Although Dixon and Kirby's calculations were only carried out for the ground state equilibrium geometry, they concluded from the experimental progression that both the $^3A_2$ and $^1A_2$ states actually have in-plane bent CCO skeletons. Therefore the first two excited states of ketene are predicted to be $^3A''$ and $^1A''$ states, arising from

$$\ldots 7a'^2 8a'^2 1a''^2 9a'^2 2a'' 10a' \quad (4)$$

Finally, they concluded that two distinct electronic states were

responsible for the observed ketene spectrum, the $^3A_2$ ($^3A''$) with intensity maximum at 27 000 cm^{-1} and the $^1A_2$ ($^1A''$) being the stronger progression at 31 000 cm^{-1}.

Rabelais, McDonald, Scherr and McGlynn[13] have reported the spectrum of ketene between 3800 and 1940 Å, and interpreted it using a semiempirical Mulliken–Wolfsberg–Helmholtz approach.[18] Their analysis concurs with that of Dixon and Kirby concerning the role of the $^3A_2$ and $^1A_2$ states. Further, they suggest that the $^3A_1$ (in addition to the $^3A_2$) state is partially responsible for the absorption between 4635 Å (21 600 cm^{-1}) and 3700 Å (27 000 cm^{-1}). Finally, McGlynn and co-workers have identified another transition with allowed origin at 46 900 cm^{-1}, and suggested that it corresponds to the analogous $^1A_1$ state [arising from (3)] and has a geometry similar to that of the ground state. We note that Dixon and Kirby predicted this excited $^1A_1$ state to lie at 57 000 cm^{-1}.

The most recent experimental study of the electronic spectrum of CH_2CO is that of Laufer and Keller.[14] A primary conclusion is that the lowest singlet and triplet states of ketene lie no higher than 21 300 and 19 200 cm^{-1}. These excitation energies are significantly less than the previously accepted[12,19] values of 25 900 and 21 400 cm^{-1}. In even more striking contrast with earlier interpretations, Laufer and Keller conclude that the entire absorption spectrum in the 4700–2600-Å range is due to a single electronic transition, presumably $^1A_1 \rightarrow {}^1A_2$.

Before turning to additional theoretical work we note that the ground state vibrational frequencies and equilibrium geometry of ketene are reasonably established from microwave and infrared studies.[20-27] From the work of Cox, Thomas, and Sheridan[25] we take the bond distances

$$r(CO) = 1.161 \pm 0.01 \text{ Å}$$
$$r(CC) = 1.314 \pm 0.01 \text{ Å}$$

while the work of Moore and Pimentel[26] appears to provide the most reliable values for

$$r(CH) = 1.079 \pm 0.002 \text{ Å}$$
$$\alpha(HCH) = 122.3 \pm 0.2°$$

A final noteworthy semiempirical study is that of Yoshida and Kobayashi.[28] Using several parameterizations, including an INDO[29] scheme, they predicted the $^3A_2$, $^1A_2$, $^3A_1$, and second $^1A_1$ states to lie in the respective ranges 19 000–30 000, 22 000–31 000, 27 000–40 000, and 49 000–66 000 cm^{-1}. Their results are generally in agreement with those of Dixon and Kirby. In addition, Yoshida and Kobayashi assign the weak band observed by Knox, Norrish, and Porter[11] around 46 500 cm^{-1} to an n → σ* state, specifically the $^1B_1$ state, presumably that arising from the configuration

$$\ldots 7a_1{}^2 1b_2{}^2 1b_1{}^2 2b_2{}^2 2b_1 8a_1 \qquad (5)$$

There have been several ab initio studies of ketene reported in the literature.[30-37] Those of Del Bene[32] and Basch[36] are of most direct relevance to the present work. Del Bene used a minimum basis set to carry out SCF calculations for the ground state and single-excitation configuration interaction (CI) calculations for three excited states. The molecular geometries and relative energies of the ground $^1A_1$ state and the lowest $^3A''$ ($T_e = 19\,800$ cm^{-1}; vertical 29 900 cm^{-1}), $^1A''$ ($T_e = 26\,900$ cm^{-1}; vertical 34 700 cm^{-1}), and $^3A'$ ($T_e = 13\,800$ cm^{-1}, vertical 39 400 cm^{-1}) states were predicted. Consistent with the experimental analysis of Dixon and Kirby, Del Bene found the $^3A''$ and $^1A''$ states to be in-plane bent. Del Bene also concluded that her results supported Dixon and Kirby's assignment of the 4735–3700 Å band to the $^1A_1 \rightarrow {}^3A_2$ transition. This conclusion of course disagrees with Laufer and Keller's proposition that no singlet–triplet transitions have been observed in ketene. Del Bene also emphasized that the first singlet absorption ($^1A_1 \rightarrow {}^1A''$) in ketene is very different in

character from the lowest n → π* transition in formaldehyde.

Basch[36] was primarily concerned with the photodissociation of ketene to form methylene. He employed a double ζ basis set (twice as large as Del Bene's basis), augmented by a diffuse (Rydberg) 3s function on each carbon atom. Both SCF and small multiconfiguration (MC) SCF techniques were used. One of the most interesting results to come out of Basch's research is that the $^3B_1$ and $^1B_1$ states of ketene have significant Rydberg character. The calculated (vertical) $^1A_1 \rightarrow {}^1B_1$ excitation energy is 51 600 cm^{-1}, in reasonable agreement with the experimental $n = 3$ member (54 680 cm^{-1}) of the Price[10] Rydberg series.

The present research is best viewed as a continuation of previous efforts[12,13,28,32,36] to provide a theoretical understanding of the electronic spectrum of ketene. Although many questions remain, it seems quite likely that further theoretical progress during the next 5 years will bring about a detailed understanding of the spectrum of ketene, and the photodissociation which produces methylene.

Theoretical Approach

Three basis sets of contracted Gaussian functions were used in the present research. The first is the standard Huzinaga–Dunning double ζ (DZ) basis,[38,39] designated C(9s 5p/4s 2p), O(9s 5p/4s 2p), H(4s/2s). This basis set is essentially twice as large as that of Del Bene.[32] The total energy obtained at the predicted ground state equilibrium geometry is −151.6724 hartrees.

In the second basis set, Rydberg or diffuse functions are added to the DZ set. From the work of Basch,[36] these functions are required for a qualitative description of the $^3B_1$ and $^1B_1$ states. Using the even-tempered criterion of Raffenetti and Ruedenberg,[40] two additional primitive Gaussian functions of s and p type have been added to each C and O atom. For carbon the added s functions have exponents $\alpha = 0.0474$ and 0.0146, while the p functions have exponents $\alpha = 0.0365$ and 0.0117. For oxygen the analogous four exponents are $\alpha = 0.0862$, 0.0261, 0.0637, and 0.0190. For obvious reasons we refer to this basis set as double ζ plus Rydberg (DZ + R). The total energy obtained at the DZ predicted ground state equilibrium geometry is −151.6753 hartrees. For comparison, Basch reports a total energy of −151.6721 hartrees at the experimental geometry.

The final basis set was of the double ζ plus polarization (DZ + P) type. That is, a set of six d-like functions (d_{xx}, d_{yy}, d_{zz}, d_{xy}, d_{xz}, and d_{yz}) were added to the C and O atoms, while p_x, p_y, and p_z functions were added to each hydrogen. It is well known[41] that such polarization functions are often required for accurate predictions of molecular properties (e.g., dipole moments) and dissociation energies. The polarization exponents [α_d(C) = 0.75, α_d(O) = 0.80, α_p(H) = 1.00] were chosen on the basis of previous experience.[41] The total ground state energy obtained was −151.7555 hartrees, corresponding to a sizable absolute lowering of 0.0831 hartree (18 200 cm^{-1}) relative to the DZ result.

The general approach followed was to optimize geometries using only the DZ basis. That is, for the ground and lowest excited states the total energy was minimized with respect to chosen geometrical parameters. In addition, calculations were carried out on 18 excited states at the predicted ground state equilibrium geometry (vertical geometry) with all three basis sets. This makes possible a fairly detailed examination of the effects of Rydberg and polarization functions.

The three types of geometries studied most extensively are seen in Figure 1. First is the C_{2v} geometry characteristic of the ketene ground state. As determined experimentally,[22-26] there are four characteristic geometrical parameters. Of the two types of geometries belonging to point group C_s, the first ($C_s{}^1$) is that predicted by Del Bene[32] for the $^3A_1$ excited state, while

the second ($C_s{}^{II}$, for which the molecule is planar) corresponds to the structure suggested by Dixon and Kirby[12] and later by Del Bene[32] for the $^3A''$ ($^3A_2$) and $^1A''$ ($^1A_2$) excited states.

We have varied respectively six and five independent geometrical parameters for the $C_s{}^I$ and $C_s{}^{II}$ forms. The parameters were varied in the standard cyclic fashion. It was found that typically, the change in a given parameter in one pass through the cycle was around one-tenth of its change on the previous pass. The parameters were optimized until the expected improvement from an additional pass through the cycle was less than 0.002 Å for bond lengths and 0.05° for angles. As a check of this optimization procedure, the ground state parameters were passed through the optimization cycle one extra time. The average change in bond lengths was 0.0007 Å and the angle changed by less than 0.006°. The average energy lowering of the optimized excited states on the final pass was roughly 0.0003 hartree.

All of the ab initio results reported here were based on single configuration restricted Hartree–Fock wave functions.[42] The open-shell wave functions were obtained using the methods developed by Hunt, Hay, and Goddard,[43] as implemented in the Ohio State-Cal Tech-Berkeley version of POLYATOM.[44] Since the open-shell excited states are expected to have less correlation energy than the closed-shell ground state, several two-configuration SCF calculations were carried out for the ground state. These involved, in addition to configuration (1), the double excitations $7a_1{}^2 \rightarrow 3b_1{}^2$ ($E = -151.6739$), $7a_1{}^2 \rightarrow 3b_2{}^2$ ($E = -151.6753$), $2b_1{}^2 \rightarrow 3b_1{}^2$ ($E = -151.6955$), and $2b_1{}^2 \rightarrow 3b_2{}^2$ ($E = -151.6727$ hartrees). Of these it is seen that only the $2b_1{}^2 \rightarrow 3b_1{}^2$ configuration makes a large contribution (0.0242 hartree) to the correlation energy.

The computations were performed on the Harris Corporation Slash Four minicomputer. The shortest calculations were on the ground state using the DZ basis and required ~22 min (17 min for integrals; 5 min for 5 SCF iterations). The longest calculations involved excited states and the DZ + P basis, requiring 105 min for integrals and about 120 min for a average of 15 SCF iterations per state.

Ground State Properties

The DZ predicted ground state equilibrium geometry is compared with experiment in the abstract. For both the CO and CC distances the theoretical predictions are within experimental error. As Herzberg[15] points out, only the sum 2.475 Å is precisely determined from the spectra, and the predicted sum of 2.479 Å is only slightly greater. The CH distance differs by 0.009 ± 0.002 Å from experiment,[26] while the HCH bond angle is $2.2 \pm 0.2°$ smaller than the experimental value. On the whole, however, the agreement between the theoretical and experimental structures for ketene's ground state is very good. Del Bene[32] predicted only the CO and CC distances in her work, and found them to be respectively 0.019 Å longer and 0.014 Å shorter than the experimental values.

In Table I are given orbital energies at the DZ predicted equilibrium geometry. Both DZ and DZ + P results are displayed, along with Mulliken populations based on the DZ + P basis set. The orbital energies are quite similar for the two basis sets and may be compared with the experimental photoelectron spectrum via Koopmans theorem.[45] Baker and Turner[16] identify three adiabatic ionization potentials at 9.64, 14.62, and 16.08 eV and a fourth (for which the true adiabatic peak may be obscured by the second band) at 13.84 eV. The observed first ionization potential is clearly associated (in the molecular orbital picture) with the removal of an electron from the $2b_1$ orbital ($\epsilon = 0.3674$ hartree = 10.00 eV). However, the next three orbital energies [$\epsilon(2b_2) = 15.26$ eV, $\epsilon(1b_1) = 17.46$ eV, and $\epsilon(1b_2) = 17.89$ eV] are significantly higher than the observed adiabatic IP's. This is probably due to neglect of
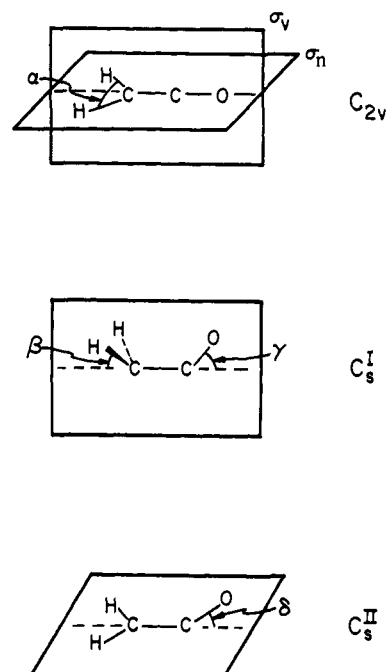

Figure 1. Ketene geometries. The ground state of ketene has C_{2v} symmetry. There are two distinct C_s symmetry types which are appropriate for low-lying excited states. In what is designated $C_s{}^1$, the reflection plane perpendicular to the molecular plane of the C_{2v} structure is preserved. The hydrogens can be positioned out of the original molecular plane at an angle β, and the oxygen at an angle γ. In $C_s{}^{II}$, the molecule is planar but the oxygen is bent away from the C–C axis at an angle, δ.

electronic reorganization in the positive ion states and their somewhat different geometries. It is also worth noting that correlation effects can alter the ordering of ionic states predicted on the basis of either Koopmans theorem or direct hole state calculations.[41]

The character of the individual orbitals may be seen from the Mulliken populations[46] in Table I. Since our qualitative conclusions concerning the valence orbitals are similar to previous ab initio studies,[30,32,33,36] the primary purpose of this data is as a reference set. Note that we concur with Del Bene's finding[32] that the greatest incremental (relative to isolated atoms) electron density resides around the methylene carbon atom (total atomic population 6.58). The O atom is somewhat less negatively "charged", while the central carbon population is only 5.52 "electrons".

Using the DZ, DZ + R, and DZ + P basis sets the ground state dipole moment is predicted to be 2.16, 2.22, and 1.81 D. The experimental dipole moments of CH_2CO (1.414 ± 0.01 D), $CHDCO$ (1.423 ± 0.014 D), and CD_2CO (1.442 ± 0.013) have been measured.[22] Since the heavier twice-deuterated species typically lies "lower" in the potential well, our value of μ at the predicted equilibrium should probably be closest to the experimental result for D_2CO. In any case, these results are consistent with the conventional wisdom[41] that the addition of polarization functions improves agreement with experiment. In addition, the magnitude of the remaining error, ~0.35 D, is about what is expected at the Hartree–Fock level of theory.[47]

Excited Electronic States

At the predicted equilibrium geometry, single configuration SCF calculations have been carried out for 18 excited electronic states. These results are summarized in Table II. Note that only for the lowest state of each space-spin symmetry (e.g., $^3A_2$) are the present results truly variational. However, it is hoped that the orbital structures of the other states will con-

Table I. Ground State Orbital Energies and Mulliken Populations for Ketene[a]

Orbital	ε (DZ)	ε (DZ + P)	Methylene carbon			Hydrogen		Carbon			Oxygen		
			s	p	d	s	p	s	p	d	s	p	d
1a₁	−20.6421	−20.6333	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	2.000	0.000	0.000
2a₁	−11.4165	−11.4035	0.000	0.000	0.000	0.000	0.000	2.000	0.000	0.000	0.000	0.000	0.000
3a₁	−11.2590	−11.2488	2.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4a₁	−1.5011	−1.4713	0.010	0.003	0.001	−0.001	−0.001	0.363	0.223	0.029	1.235	0.098	0.040
5a₁	−1.0708	−1.0582	0.953	0.082	0.017	0.088	0.004	0.327	0.346	0.014	0.042	0.033	0.002
6a₁	−0.7557	−0.7597	0.164	0.160	0.002	0.107	0.002	0.257	0.031	0.000	0.332	0.833	0.003
7a₁	−0.6855	−0.6830	0.073	0.650	0.018	0.186	0.003	0.032	0.374	0.001	0.102	0.376	−0.001
1b₂	−0.6687	−0.6573	0.000	0.670	0.000	0.228	0.004	0.000	0.401	0.000	0.000	0.457	0.007
1b₁	−0.6539	−0.6415	0.000	0.096	0.003	0.000	0.000	0.000	0.560	0.010	0.000	1.317	0.012
2b₂	−0.5610	−0.5609	0.000	0.434	0.007	0.179	0.002	0.000	0.172	0.033	0.000	0.985	0.008
2b₁	−0.3684	−0.3674	0.000	1.231	0.006	0.000	0.005	0.000	0.304	0.045	0.000	0.404	−0.001
	Function totals		3.199	3.326	0.054	0.787	0.019	2.979	2.412	0.133	3.711	4.503	0.070
	Atom totals			6.579			0.807		5.524			8.284	

[a] The calculation was carried out at the predicted ground state equilibrium geometry. Both double ζ (DZ) and double ζ plus polarization (DZ + P) basis sets were employed.

Table II. Vertical Excitation Energies for Ketene[a]

Electron configuration	State	Energy, cm⁻¹			Dipole moment, D		
		DZ	DZ + R	DZ + P	DZ	DZ + R	DZ + P
. . . 7a₁²1b₂²1b₁²2b₂²2b₁²	¹A₁	0	0	0	−2.16	−2.22	−1.81
. . . 7a₁²1b₂²1b₁²2b₂²2b₁ 3b₂	³A₂	24 120	23 670	25 570	−3.68	−3.72	−3.44
	¹A₂	25 700	25 270	27 520	−3.54	−3.58	−3.30
. . . 7a₁²1b₂²1b₁²2b₂²2b₁ 3b₁	³A₁	38 030	37 410	40 790	−3.25	−3.21	−3.04
	2 ¹A₁	39 700	39 180	42 920	−3.39	−3.39	−3.12
. . . 7a₁²1b₂²1b₁²2b₂2b₁²3b₂	2 ³A₁	47 030	46 490	49 440	0.07	0.04	0.56
	3 ¹A₁	48 440	47 890	51 470	0.07	0.03	0.55
. . . 7a₁²1b₂²1b₁²2b₂²2b₁ 8a₁	³B₁	69 810	44 330	69 820	−1.97	−0.85	−2.44
	¹B₁	76 500	45 930	75 670	−4.10	−0.90	−4.24
. . . 7a₁ 1b₂²1b₁²2b₂²2b₁²3b₂	³B₂	72 990	72 610	77 120	1.09	1.03	1.39
	¹B₂	80 970	80 500	84 680	0.66	0.61	1.12
. . . 7a₁²1b₂²1b₁²2b₂2b₁²3b₁	2 ³A₂	77 460	76 280	80 020	0.96	1.27	1.44
	2 ¹A₂	79 430	78 120	82 030	0.68	1.02	1.20
. . . 7a₁ 1b₂²1b₁²2b₂²2b₁²3b₁	2 ³B₁	98 930	98 020	103 110	2.29	2.58	2.55
	2 ¹B₁	103 510	102 450	108 110	1.61	2.03	1.95
. . . 7a₁²1b₂²1b₁²2b₂2b₁²8a₁	2 ³B₂	102 550	78 040	101 820	−2.19	−2.00	−1.94
	2 ¹B₂	108 880	79 070	108 060	−1.63	−1.13	−1.79
. . . 7a₁ 1b₂²1b₁²2b₂²2b₁²8a₁	3 ³A₁	132 370	111 390	132 100	−0.10	2.34	0.25
	4 ¹A₁	136 770	112 970	136 410	0.16	2.61	0.59

[a] All calculations were carried out at the predicted (DZ) ground state equilibrium geometry. A negative dipole moment implies polarity C⁺O⁻.

strain them in such a way as to provide physically reasonable results.[48]

Table II shows that the DZ and DZ + P predictions are quite comparable for all states considered. In general the excitation energies are slightly raised by the addition of polarization functions. The average difference between the two results is 2200 cm⁻¹. Similarly the DZ and DZ + P dipole moments are in rather close agreement, the average absolute value for the difference being 0.33 D.

The importance of Rydberg functions for the ³B₁ and ¹B₁ states is apparent from Basch's work.[36] Although the present DZ + P calculations place these states at 77 100 and 84 700 cm⁻¹ respectively, the DZ + R basis lowers these excitation energies to 44 300 and 45 900 cm⁻¹, respectively. The higher excitation energy (51 600 cm⁻¹) found by Basch[36] for the ³B₁ state is an indication of the effectiveness of the additional diffuse basis functions used in the present work. The Mulliken population analysis for the ³B₁ state shows the singly occupied 8a₁ orbital to be roughly speaking a linear combination of 3s functions on the methylene carbon (20%), central carbon (52%), and oxygen (15%) atoms. Note that the ³B₁ state is predicted to be the third lowest lying triplet state when Rydberg functions are included in the basis. We should observe however that both the ³B₁ and ¹B₁ states should have considerably less correlation energy than nearby (energetically) valence states (e.g., ³B₂ and ¹B₂). This is due to the fact that the 8a₁ orbital is spatially removed from the other orbitals and hence pair correlation energies[41] involving this orbital should

be small. Hence the true excitation energies of the ³B₁ and ¹B₁ states may be somewhat higher than the DZ + R values predicted in Table II.

Interestingly, the other states for which excitation energies are substantially reduced by the DZ + R basis also involve excitation of an electron to the 8a₁ orbital. Thus one can conclude that the Rydberg character of this orbital is relatively insensitive to the electronic state in which it appears. We must realistically point out that even using the DZ + R basis the 3 ³A₁ and 4 ¹A₁ states are too high lying (>110 000 cm⁻¹) to be taken as serious predictions. It is clear that correlation effects can be extremely large for states this high in energy. The reason for including these and several of the other entries in Table II is to illustrate that these electron configurations, although plausible, are in fact quite high lying.

The predicted dipole moments in Table II cover a rather broad range, from +2.55 D (2 ³B₁) to −4.24 D (¹B₁) with the DZ + P basis. It is of interest to attempt to correlate these predictions with the character of the different molecular orbitals. Note first that a negative dipole moment is taken here to imply polarity ⁺CO⁻. First consider the ³A₂ state with a dipole moment of the same polarity as the ground state but 1.63 D greater in magnitude. This electronic state is related to the ground state by the replacement of one of the 2b₁ spin orbitals by a 3b₂ spin orbital, or 2b₁ → 3b₂. Now inspection of the Mulliken populations (Table I) or a detailed orbital-by-orbital breakdown of the different contributions to the dipole moment shows that the 2b₁ orbital (predominantly methylene carbon

Table III. Results of Geometry Optimization of Ketene Electronic States[a]

| C_{2v} symmetry | | Final symmetry | | Structural parameters | | | | | | | |
State	Excitation	State	Excitation	R_{C-O}	R_{C-C}	R_{C-H}	α	β	γ	δ	Excitation energy, cm^{-1}
$^1A_1$	Ground state			1.171	1.311	1.070	120.1				0
$^3A_2$	$2b_1 \rightarrow 3b_2$	$C_s{}^{II}$ $^3A''$	$2a'' \rightarrow 10a'$	1.200	1.459	1.076	117.8			48.3	11 710
$^1A_2$		$C_s{}^{II}$ $^1A''$		1.201	1.455	1.076	118.3			49.1	13 940
$^3A_1$	$2b_1 \rightarrow 3b_1$	$C_s{}^I$ $^3A'$	$9a' \rightarrow 10a'$	1.190	1.519	1.069	124.1	23.9	53.3		15 220
2 $^1A_1$		$C_s{}^I$ $^1A'$		1.195	1.514	1.069	124.3	24.7	52.2		18 070
2 $^3A_1$	$2b_2 \rightarrow 3b_2$	$C_s{}^{II}$ $^3A'$	$2a'' \rightarrow 3a''$	1.422	1.315	1.077	116.6			51.7	23 020
3 $^1A_1$		$C_s{}^{II}$ $^1A'$		1.423	1.315	1.077	116.6			51.8	24 360

[a] Bond lengths are in angströms. Angles are in degrees and are defined in Figure 1.
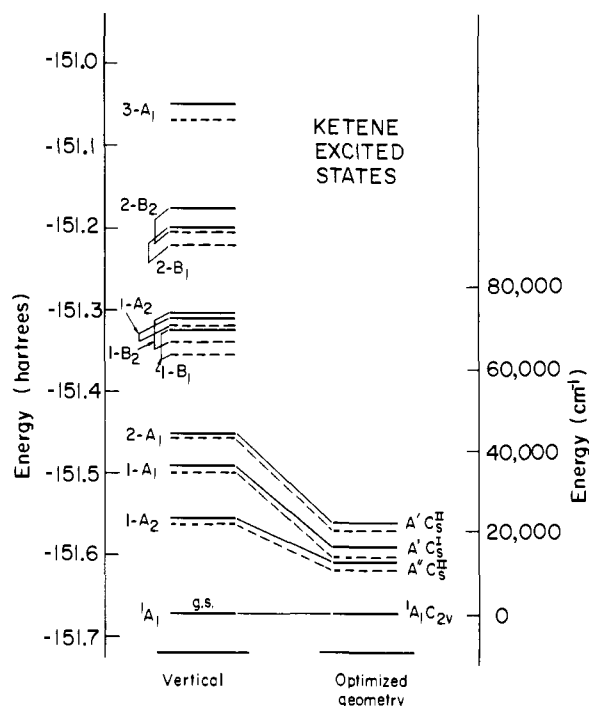

Figure 2. Ketene excited states. Symmetry designations correspond to Table I. Dotted lines represent triplet states and solid lines represent singlets. The vertical excitation energies are all for the same geometry, namely that of the $^1A_1$ ground state. The optimized results refer to geometries separately determined for each state, and the reduced symmetry and corresponding state designations are shown.
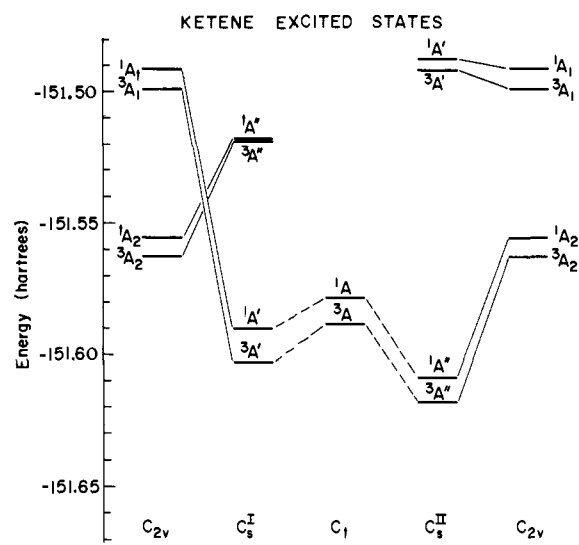

Figure 3. Correlation of lowest lying states. The C_{2v} vertical excitation energies of the lowest two singlets and triplets are connected by a solid line with their optimized energy level in $C_s{}^I$ or $C_s{}^{II}$ symmetry. Above the lowest states of each C_s symmetry are the energies of the other two states at the geometry of the lower singlet or triplet. Allowing the oxygen to internally rotate from $C_s{}^{II}$ to $C_s{}^I$ type structure reduces the molecular symmetry to C_1 or no symmetry. Thus, the lowest singlet and triplet must correlate, as shown by dotted lines. An intermediate geometry was chosen (see text) for the C_1 energy levels.

2p) makes a large positive contribution to the dipole moment. On the other hand, the $3b_2$ orbital makes a small but negative contribution. Thus the overall effect of the $2b_1 \rightarrow 3b_2$ excitation is to make the $^3A_2$ and $^1A_2$ dipole moments more negative than that of the $^1A_1$ ground state.

Next consider the $^3A_1$ and 2 $^1A_1$ states, which arise from excitation $2b_1 \rightarrow 3b_1$. The remarks of the previous paragraph again apply roughly to the $2b_1$ orbital, while the $3b_1$ orbital makes a small positive contribution to μ. Hence the $^3A_1$ dipole moment should be slightly *less* negative than that for $^3A_2$ but significantly more so than for the ground state. As seen in Table II the $^1A_1$, $^3A_2$, and $^3A_1$ dipole moments are -1.81, -3.44, and -3.04 D, in keeping with the simple model.

The 2 $^3A_1$ and 3 $^1A_1$ states, arising from the $2b_2 \rightarrow 3b_2$ excitation, have small positive dipole moments. This is due to the strong $^+CO^-$ character of the $2b_2$ orbital, which has its largest single contribution from the oxygen 2p orbitals. Similarly, the larger positive (1.44 and 1.20 D) dipole moments of the 2 $^3A_2$ and 2 $^1A_2$ states, arising from the $2b_2 \rightarrow 3b_1$ excitation, can be seen as a result of the earlier discussed difference between the $3b_2$ (slightly negative contribution to μ) and $3b_1$ (slightly positive) orbitals.

Finally, note that the $^3B_1$ and $^1B_1$ dipole moments change radically when diffuse functions are added to the basis.

To discuss the excitation energies for the different electronic states of ketene, it is helpful to first present the results of our geometry optimizations. These are seen in Table III and Figures 2 and 3. We now proceed to a discussion by electron configuration of these results.

The relative energies of both the $^3A_2$ and $^1A_2$ states are radically lowered by geometry optimization. In fact, comparison with experiment[12,14,19] shows unequivocally that these states lie significantly higher than the 11 700 cm^{-1} and 13 900 cm^{-1} predicted here. Note in Table II that polarization functions will raise these T_e results by 1000–2000 cm^{-1}. However, it appears clear that the effect of electron correlation will be to raise these excitation energies. This is as expected on intuitive grounds, and we hope to study these states in the near future using correlated wave functions. In the meantime, it appears that Hartree–Fock limit wave functions are not sufficiently reliable to discriminate between the 21 400 cm^{-1} experimental result of Dixon and Kirby[12] and the 19 200 cm^{-1} value of Laufer and Keller[14] for the excitation energy of the $^3A_2$ state.

A comparison with Del Bene's minimum basis set results for the lowest A_2 (A'') states is of interest. We find the DZ results

to yield much lower excitation energies. Also, she finds a separation of 7100 cm^{-1} between the $^3A''$ and $^1A''$ state, whereas a much smaller separation of 2200 cm^{-1} is predicted here. Thus it would appear that the minimum basis set yields energetic results quite different from those found near the Hartree-Fock limit, which is approached by our DZ + P results. However, these differences may at least in part be due to the fact that CI (including single excitations) effects were included in Del Bene's work. For the $^3A''$ state, we predict C–O and C–C bond distances of 1.200 and 1.459 Å, where Del Bene predicts 1.26 and 1.36 Å. Similarly, from the $^1A''$ states, the present predicted values are 1.201 and 1.455 Å, compared to Del Bene's 1.24 and 1.37 Å. The in-plane bond angle is predicted to be ~50° by both Del Bene and ourselves for both the $^3A''$ and $^1A''$ states.

The vertical and adiabatic excitation energies of the $^3A_1$ ($^3A'$) and $2\,^1A_1$ ($2\,^1A'$) states differ by 23 000 and 22 000 cm^{-1}, respectively. For the $^3A'$ state, this enormous relative energy lowering was predicted by Del Bene, whose calculations suggested that the T_e value for the $^3A'$ state is actually lower than those for the $^3A''$ and $^1A''$ states. Here, however, we find the $^3A'$ state to remain the third excited electronic state even after geometry optimization. In any case, the $^3A'$ and $^1A'$ states are quite low lying, and will have to be dealt with in any comprehensive discussion of ketene photodissociation. Since Del Bene did not allow for a nonzero value of the angle β (Figure 1) a detailed comparison of geometry predictions may not be meaningful. Our values of 23.9 and 24.7° for β certainly represent interesting predictions. One qualitative prediction of Del Bene's that we have confirmed is the very long (1.519 Å here, 1.54 in her work) CC bond distance for the $^3A'$ state. This C–C distance is nearly as long as the experimental value 1.536 Å found for the single bond of ethane.

The other two states in Table III for which geometry optimizations are reported are $^3A'$ and $^1A'$ states which arise from the excitation $2a'' \rightarrow 3a''$. We must be cautious about these predictions since the variational principle cannot be used to guarantee an upper bound to the energy. However one is hopeful[48] that the wave functions for these states will be very nearly orthogonal to the energetically lower wave functions of the same symmetry. Of course, if the same set of orbitals were used to describe all states, then for example the X $^1A'$, $2\,^1A'$, and $3\,^1A'$ states would be rigorously orthogonal. In any case, geometry optimization significantly lowers the energies of these states as well. Like the $^3A''$ and $^1A''$ states, these two states are of $C_s{}^{11}$ symmetry with angle δ about 50°. Although the C–C distance is comparable to the ground state, very long (1.42 Å) CO distances are found.

Finally it should be mentioned that for the lowest $^3B_2$ and $^1B_2$ states, geometry optimizations within the constraint of C_{2v} symmetry have been carried out. The primary difference with respect to the ground state structure is the lengthening of the CO bond from 1.17 to 1.38 Å. The excitation energies T_e for the $^3B_2$ and $^1B_2$ states are 63 400 and 70 800 cm^{-1}, notably lower than the vertical results 77 100 and 84 700 cm^{-1}. Finally, as pointed out by Basch and verified here using the DZ basis set, the $^3B_1$ and $^1B_1$ states dissociate directly to CH$_2$ + CO without a barrier.

Figure 3 gives a correlation diagram for the lowest electronic states of ketene. The particular point we wish to note here concerns the connection between the lowest $^3A'$ and $^3A''$ states. For geometries with no elements of symmetry, of course, these two states are of the same irreducible representation, namely ^3A. To study the changeover between the two states, a geometry roughly half-way between the two has been chosen: $R(\mathrm{CO}) = 1.20$ Å; $R(\mathrm{CC}) = 1.47$ Å; $R(\mathrm{CH}) = 1.07$ Å; $\alpha = 121°$; $\beta = 12°$; $\gamma = 27°$; $\delta = 24°$.

As seen in Figure 3, there appears to be a barrier between the $^3A'$ and $^3A''$ states. A reliable prediction of the nature and

position of this barrier would of course require examination of many other geometries. Also depicted in Figure 3 is the fact that when the $^3A''$ state (equilibrium geometry $C_s{}^{11}$) is studied with geometry appropriate to the $^3A'$ $C_s{}^1$ equilibrium, it becomes quite high in energy. An analogous result is found for the reverse situation and for the relevant singlet states.

Concluding Remarks

Several new directions for additional research are suggested by the present study. First it is clear that electron correlation has a large effect on the excitation energies of ketene. For the crucially important five lowest electronic states (X $^1A_1$, $^3A_2$, $^1A_2$, $^3A_1$, $2\,^1A_1$), the effects of both polarization and Rydberg basis functions appear small, and hence reliable configuration interaction (CI) studies could employ the manageable DZ basis set. To examine higher electronic states in a meaningful way, Rydberg functions must be added to the DZ basis. Given a reliable theoretical picture of the vertical and adiabatic excitation energies, electronic transition probabilities and Franck-Condon factors would greatly aid in the assignment of the experimental spectra. Following an unravelling of the ketene electronic spectra, the mechanism of photodissociation to CH$_2$ + CO may or may not be clear. In the latter case additional ab initio studies of possible pathways to dissociation could be extremely helpful.

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A Configuration Interaction Treatment of ¹E′ Trimethylenemethane

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Abstract: Configuration interaction is used to examine the wave function for the π electrons in ¹E′ trimethylenemethane from several different perspectives. It is shown that in the planar singlet, repulsion between the nonbonding electrons results in a modification of the MO's appropriate for ³A₂′ trimethylenemethane and that one component of the ¹E′ wave function consequently resembles closely that for an allyl radical plus an electron effectively localized in a p orbital. Some problems inherent in the SCF treatment of the ¹E′ state of D_{3h} trimethylenemethane are discussed.

Trimethylenemethane[1] has been of interest to theoreticians for more than a quarter of a century. A number of sophisticated theoretical treatments of triplet trimethylenemethane appeared before Dowd reported the synthesis and characterization of the molecule in this state.[2] Singlet trimethylenemethane, as the presumed intermediate in the rearrangements of methylenecyclopropanes, has an even longer experimental history than the triplet,[1] but only recently has the singlet been the subject of detailed theoretical study. In 1971 Dewar and Wasson[3] reported semiempirical MINDO/2 calculations which showed that, unlike the triplet which adopts a planar geometry, singlet trimethylenemethane prefers a conformation with one methylene group lying in a plane orthogonal to that containing the other two. This finding provided theoretical justification for previous proposals of this geometric preference for the singlet, which had been based on the experimentally observed preservation of optical activity in the rearrangement products of chiral methylenecyclopropanes,[4] the results of detailed stereochemical studies,[5] and the effect of substituents on migrating group selectivity and rate of rearrangement.[5a,6] Subsequent ab initio calculations[7,8] have also found the orthogonal geometry to be lower in energy than the planar one for the singlet, and an explanation of this phenomenon in terms of the effect of electron repulsion in this open-shell π system has been given.[9]

Although both of the ab initio calculations[7,8] agree with the MINDO/2 results in predicting that for the singlet, the orthogonal geometry is favored, the Yarkony and Schaefer[7] calculation found only a small (2.8 kcal/mol) energy difference between it and the planar one. In contrast, like MINDO/2,[3] the other ab initio calculation[8] predicted a substantially larger (>1 eV) energy difference between the two geometries. The Yarkony-Schaefer result is in much better accord with the experimental observation that racemization competes with rearrangement in chiral methylenecyclopropanes.[4,5a] That racemization is probably occurring via the planar singlet, rather than through the intermediacy of the triplet, is strongly indicated both by theoretical considerations and experimental data. If the triplet were

formed, it would not be expected to reclose to methylenecyclopropane,[10] and oxygen, an excellent scavenger of triplet trimethylenemethane,[11] has no effect on the distribution of products or the stereochemical characteristics of the rearrangement of optically active *trans*-2,3-dicyanomethylenecyclopropane.[12]

In a preliminary communication[13] it was argued that the Yarkony-Schaefer result[7] is correct and that, in order to avoid the high energy ionic terms, involving the nonbonding electrons, that appear in the familiar fully delocalized D_{3h} wave function for singlet trimethylenemethane, the optimum wave function for the planar singlet resembles closely that of an allyl radical plus an electron essentially localized in a p orbital. The overestimation of the energy preference for the orthogonal geometry by the other two calculations[3,8] on singlet trimethylenemethane was attributed to their failure to arrive at the correct wave function for the planar geometry. This failure was seen to result from the use in these calculations of approximate methods for dealing with open-shell systems, which led to the same set of MO's for singlet as for triplet trimethylenemethane.

In this paper configuration interaction is used to examine the wave function for the planar singlet from several different perspectives, in order to amplify and expand upon the points raised in the preliminary communication.[13]
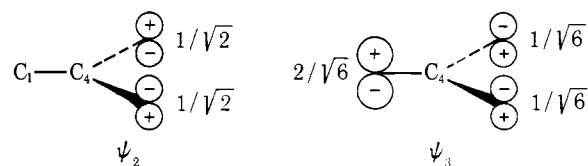
A Two-Electron Model

The familiar nonbonding MO's of planar (D_{3h}) trimethylenemethane are shown above. As has been pointed out previously,[9,13] unlike the case in [4n]annulenes,[14-16] these nonbonding MO's, or any linear combination of them, have amplitude on at least one common atom. Consequently, in the singlet state in which one electron is placed in each MO,