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Publication Date

1975-08-01

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Submitted to Journal of the American
Chemical Society

LBL-4092
Preprint c. |

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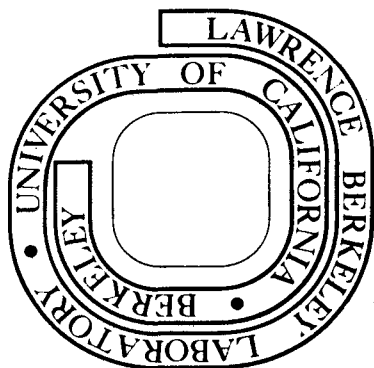
Clifford E. Dykstra and Henry F. Schaefer III

August 1975

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

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LBL-4092

Excited Electronic States of Ketene

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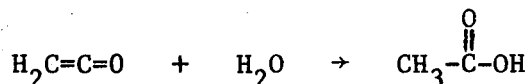
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Abstract

The geometries and excitation energies of the low-lying electronic states of $\text{CH}_2=\text{C}=\text{O}$ have been investigated using a priori theoretical methods. Three basis sets of contracted gaussian functions were employed, double zeta (DZ), double zeta plus Rydberg (DZ + R), and double zeta plus polarization (DZ + P). Vertical transitions to eighteen 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 debye. 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 debye. For several states (including $^3\text{B}_1$ and $^1\text{B}_1$) 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 debye) is somewhat larger than the experimental value (1.41-1.44 debye). The predicted ground state molecular structure compares quite favorably with experiment: $r(\text{CO}) = 1.168 \text{ \AA}$ (1.161 ± 0.01), $r(\text{CC}) = 1.311$ (1.314 ± 0.01), $r(\text{CH}) = 1.070 \text{ \AA}$ (1.079 ± 0.002), and $\alpha(\text{HCH}) = 120.1^\circ$ (122.3 ± 0.2). For eight low-lying excited states, equilibrium geometries were predicted.

Introduction

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



The subsequent reaction with acetic acid provides a useful commercial synthesis of acetic anhydride.¹ In recent years, however, primary research interest has focused on the photochemistry of ketene. Specifically ketenes $\text{R}_2\text{C}=\text{C}=\text{O}$ are a particularly convenient source² 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 formed⁴ at wavelengths less than 3700 \AA , but the triplet fraction reported varies from 26% at 2139 \AA ⁵ to 75% at 3660 \AA .⁶ Since the first excited state (a $^3\Pi$) of the CO molecule is relatively high-lying ($48,000 \text{ cm}^{-1}$),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 photo-decomposition 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 \AA ($31,300 \text{ cm}^{-1}$) system of ketene probably arises from the excitation of a nonbonding electron on the oxygen atom, and b) the band system around 2100 \AA ($47,600 \text{ cm}^{-1}$) may be interpreted as an excitation from the $\text{C}\equiv\text{O}$ bonding orbital to an antibonding upper orbital ($\pi + \pi \rightarrow \pi - \pi$).

Dixon and Kirby¹² carried out self-consistent-field (SCF) molecular orbital (MO) calculations in the Pariser-Parr-Pople approximation¹⁷ 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)

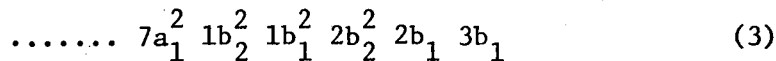
$$1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 6a_1^2 7a_1^2 1b_2^2 1b_1^2 2b_2^2 2b_1^2 \quad (1)$$

Dixon and Kirby¹² predict the 3A_2 and 1A_2 states, corresponding to

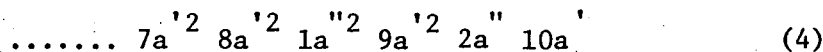
$$\dots\dots\dots 7a_1^2 1b_2^2 1b_1^2 2b_2^2 2b_1^2 3b_2 \quad (2)$$

to be the lowest excited states of ketene, lying at $22,400 \text{ cm}^{-1}$ and $25,700 \text{ cm}^{-1}$

respectively. They also predicted the existence of a low-lying ($30,300 \text{ cm}^{-1}$) 3A_1 state arising from electron configuration



Although Dixon and Kirby's calculations were only carried out for the ground state equilibrium geometry, they concluded from the experimental progressions 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



Finally, they concluded that two distinct electronic states were responsible for the observed ketene spectrum, the 3A_2 (${}^3A''$) with intensity maximum at $27,000 \text{ cm}^{-1}$ and the 1A_2 (${}^1A''$) being the stronger progression at $31,000 \text{ cm}^{-1}$.

Rabelais, McDonald, Scherr and McGlynn¹³ have reported the spectrum of ketene between 3800 and 1940 \AA , and interpreted it using a semi-empirical 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 \AA ($21,600 \text{ cm}^{-1}$) and 3700 \AA ($27,000 \text{ cm}^{-1}$). Finally, McGlynn and co-workers have identified another transition with allowed origin at $46,900 \text{ cm}^{-1}$, 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 $57,000 \text{ cm}^{-1}$.

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 $21,300 \text{ cm}^{-1}$ and $19,200 \text{ cm}^{-1}$. These excitation energies are significantly less than the previously accepted^{12,19} values $25,900 \text{ cm}^{-1}$ and $21,400 \text{ cm}^{-1}$. In even more striking contrast with earlier interpretations, Laufer and Keller conclude that the entire absorption spectrum in the $4700\text{-}2600 \text{ \AA}$ 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 Sheridan²⁵ we take the bond distances

$$r(\text{CO}) = 1.161 \pm 0.01 \text{ \AA}$$

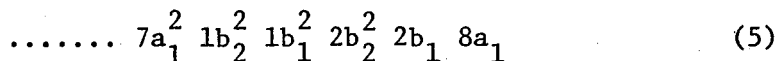
$$r(\text{CC}) = 1.314 \pm 0.01 \text{ \AA}$$

while the work of Moore and Pimentel²⁶ appears to provide the most reliable values for

$$r(\text{CH}) = 1.079 \pm 0.002 \text{ \AA}$$

$$\alpha(\text{HCH}) = 122.3 \pm 0.2^\circ$$

A final noteworthy semiempirical study is that of Yoshida and Kobayashi.²⁸ Using several parameterizations, including an INDO²⁹ 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 cm^{-1} , 22,000-31,000 cm^{-1} , 27,000-40,000 cm^{-1} , 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 Porter¹¹ around 46,500 cm^{-1} to an $n \rightarrow \sigma^*$ state, specifically the 1B_1 state, presumably that arising from the configuration



There have been several ab initio studies of ketene reported in the literature.³⁰⁻³⁷ Those of Del Bene³² and Basch³⁶ 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 $^3A''$ ($T_e = 19,800 \text{ cm}^{-1}$; vertical 29,900 cm^{-1}), $^1A''$ ($T_e = 26,900 \text{ cm}^{-1}$; vertical 34,700 cm^{-1}) and $^3A'$ ($T_e = 13,800 \text{ cm}^{-1}$, 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 Å - 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 $n \rightarrow \pi^*$ transition in formaldehyde.

Basch³⁶ was primarily concerned with the photodissociation of ketene to form methylene. He employed a double zeta basis set (twice as large as Del Bene's basis), augmented by a diffuse (Ryberg) 3s function on each carbon atom. Both SCF and small multi-configuration (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 $51,600 \text{ cm}^{-1}$, in reasonable agreement with the experimental $n = 3$ member ($54,680 \text{ cm}^{-1}$) of the Price⁹ 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 five 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 zeta (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 Raffinetti 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 $\alpha = 0.0474, 0.0146$, while the p functions have exponents $\alpha = 0.0365, 0.0117$. For oxygen the analogous four exponents are $\alpha = 0.0862, 0.0261, 0.0637, \text{ and } 0.0190$. For obvious reasons we refer to this basis set as double zeta 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 zeta plus polarization (DZ + P) type. That is, a set of six d-like functions ($d_{xx}, d_{yy}, d_{zz}, d_{xy}, d_{xz}, \text{ and } d_{yz}$) were added to the C and O atoms, while $p_x, p_y, \text{ and } p_z$ functions were added to each hydrogen. It is well known⁴¹ that such polarization functions are often required for accurate predictions of molecular

properties (e.g. dipole moments) and dissociation energies. The polarization exponents [$\alpha_d(c) = 0.75$, $\alpha_d(0) = 0.80$, $\alpha_p(H) = 1.00$] were chosen on the basis of previous experience.⁴¹ The total ground state energy obtained was -151.7555 hartrees, corresponding to a sizeable absolute lowering 0.0831 hartrees ($18,200 \text{ cm}^{-1}$) 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^I) is that predicted by Del Bene³² 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 Kirby¹² and later by Del Bene³² for the ${}^3A''$ (3A_2) and ${}^1A''$ (1A_2) excited states.

We have varied respectively 6 and 5 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 \AA 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 \AA 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 hartrees.

All of the ab initio results reported here were based on single configuration restricted Hartree-Fock wavefunctions.⁴² The open-shell wavefunctions 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 hartrees) 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 minutes (17 minutes for integrals; 5 minutes for 5 SCF iterations). The longest calculations involved excited states and the DZ + P basis, requiring 105 minutes for integrals and about 120 minutes for an 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 Herzberg¹⁵ points out, only the sum 2.475 \AA is precisely determined from the spectra, and the predicted sum of 2.479 \AA is only slightly greater. The CH distance differs by $0.009 \pm 0.002 \text{ \AA}$ from experiment,²⁶ while the HCH bond angle is $2.2 \pm 0.2^\circ$ 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 Bene³² predicted only the CO and CC distances in her work, and found them to be 0.014 and 0.019 \AA longer 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 Turner¹⁶ 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 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 populations⁴⁶ 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 finding³² 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 debye. The experimental dipole moments of CH₂CO (1.414 ± 0.01 debye), CHDCO (1.423 ± 0.014 debye), and CD₂CO (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 D₂CO. In any case, these results are consistent with the conventional wisdom⁴¹ that the addition of polarization functions improves agreement with experiment. In addition, the magnitude of the remaining error, ~ 0.35 debye, 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 constrain 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 debye.

The importance of Rydberg functions for the 3B_1 and 1B_1 states is apparent from Basch's work.³⁶ Although the present DZ + P calculations place these states at $77,100$ and $84,700 \text{ cm}^{-1}$ respectively, the DZ + R basis lowers these excitation energies to $44,300$ and $45,900 \text{ cm}^{-1}$, respectively. The higher excitation energy ($51,600 \text{ cm}^{-1}$) found by Basch³⁶ for the 3B_1 state is an indication of the effectiveness of the additional diffuse basis functions used in the present work. The Mulliken population analysis for the 3B_1 state shows the singly-occupied $8a_1$ 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 3B_1 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 3B_1 and 1B_1 states should have considerably less

correlation energy than nearby (energetically) valence states (e.g. 3B_2 and 1B_2). This is due to the fact that the $8a_1$ orbital is spatially removed from the other orbitals and hence pair correlation energies⁴¹ involving this orbital should be small. Hence the true excitation energies of the 3B_1 and 1B_1 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 $8a_1$ 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 3A_1 and $^4^1A_1$ states are too high lying ($> 110,000 \text{ cm}^{-1}$) 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 debye (2^3B_1) to -4.24 debye (1B_1) 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 3A_2 state with a dipole moment of the same polarity as the ground state but 1.63 debye greater in magnitude.

This electronic state is related to the ground state by the replacement of one of the $2b_1$ spin orbitals by a $3b_2$ spin orbital, or $2b_1 \rightarrow 3b_2$. Now inspection of the Mulliken populations (Table I) or a detailed orbital-by-orbital breakdown of the different contributions to the dipole moment show that the $2b_1$ orbital (predominantly methylene carbon 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 the 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 debyes, 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 debye) 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 Tables 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 $11,700 \text{ cm}^{-1}$ and $13,900 \text{ cm}^{-1}$ predicted here. Note in Table II that polarization functions will raise these T_e results by $1000 - 2000 \text{ cm}^{-1}$. 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 $21,400 \text{ cm}^{-1}$ experimental result of Dixon and Kirby¹² and $19,200 \text{ cm}^{-1}$ value of Laufer and Keller¹⁴ 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 $7,100 \text{ cm}^{-1}$ between the $^3\text{A}''$ and $^1\text{A}''$ state, whereas a much smaller separation of $2,200 \text{ cm}^{-1}$ 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. For the $^3\text{A}''$ 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, for the $^1\text{A}''$ 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 $\sim 50^\circ$ by both Del Bene and ourselves for both the $^3\text{A}''$ and $^1\text{A}''$ states.

The vertical and adiabatic excitation energies of the $^3\text{A}_1$ ($^3\text{A}'$) and 2^1A_1 ($2^1\text{A}'$) states differ by 23,000 and 22,000 cm^{-1} respectively. For the $^3\text{A}'$ state, this enormous relative energy lowering was predicted by Del Bene, whose calculations suggested that the T_e value for the $^3\text{A}'$ state is actually lower than those for the $^3\text{A}''$ and $^1\text{A}''$ states. Here, however, we find the $^3\text{A}'$ state to remain the third excited electronic state even after geometry optimization. In any case, the $^3\text{A}'$ and $^1\text{A}'$ 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 non-zero 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 $^3\text{A}'$ 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 hopeful⁴⁸ 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^{II} symmetry with angle δ about 50°. Although the C-C distance is comparable to the ground state, very long (1.42 Å) C-O 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 $\text{CH}_2 + \text{CO}$ 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 change-over between the two states, a geometry roughly half-way between the two has been chosen:

$$R(CO) = 1.20 \overset{\circ}{\text{A}}$$

$$R(CC) = 1.47 \overset{\circ}{\text{A}}$$

$$R(CH) = 1.07 \overset{\circ}{\text{A}}$$

$$\alpha = 121^\circ$$

$$\beta = 27^\circ$$

$$\gamma = 12^\circ$$

$$\delta = 24^\circ$$

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^{II}) is studied with geometry appropriate to the ${}^3A'$ C_s^I 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.

Acknowledgments

We thank Professors John Simons and C. Bradley Moore for helpful discussions. The Berkeley Theoretical Chemistry mini-computer is supported by the National Science Foundation, Grants GP-39317 and GP-41509X.

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TABLE I. Ground state orbital energies and Mulliken populations for ketene. The calculation was carried out at the predicted ground state equilibrium geometry. Both double zeta (DZ) and double zeta plus polarization (DZ + P) basis sets were employed.

Orbital	$\epsilon(\text{DZ})$	$\epsilon(\text{DZ+P})$	Methylene Carbon			Hydrogen		Carbon			Oxygen		
			s	p	d	s	p	s	p	d	s	p	d
1a ₁	-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
2a ₁	-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
3a ₁	-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
4a ₁	- 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
5a ₁	- 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
6a ₁	- 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
7a ₁	- 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
1b ₂	- 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
1b ₁	- 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
2b ₂	- 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
2b ₁	- 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			

00004307897

TABLE II. Vertical Excitation Energies for Ketene.^a

Electron Configuration	State	Energy (in cm ⁻¹)			Dipole Moment (in Debyes)		
		DZ	DZ + R	DZ + P	DZ	DZ + R	DZ + P
... 7a ₁ ² 1b ₂ ² 1b ₁ ² 2b ₂ ² 2b ₁ ²	¹ A ₁	0	0	0	-2.16	-2.22	-1.81
... 7a ₁ ² 1b ₂ ² 1b ₁ ² 2b ₂ ² 2b ₁ ² 3b ₂	³ A ₂	24,120	23,670	25,570	-3.68	-3.72	-3.44
	¹ A ₂	25,700	25,270	27,520	-3.54	-3.58	-3.30
... 7a ₁ ² 1b ₂ ² 1b ₁ ² 2b ₂ ² 2b ₁ ² 3b ₁	³ A ₁	38,030	37,410	40,790	-3.25	-3.21	-3.04
	² ¹ A ₁	39,700	39,180	42,920	-3.39	-3.39	-3.12
... 7a ₁ ² 1b ₂ ² 1b ₁ ² 2b ₂ ² 2b ₁ ² 3b ₂	² ³ A ₁	47,030	46,490	49,440	0.07	0.04	0.56
	³ ¹ A ₁	48,440	47,890	51,470	0.07	0.03	0.55
... 7a ₁ ² 1b ₂ ² 1b ₁ ² 2b ₂ ² 2b ₁ ² 8a ₁	³ B ₁	69,810	44,330	69,820	-1.97	-0.85	-2.44
	¹ B ₁	76,500	45,930	75,670	-4.10	-0.90	-4.24
... 7a ₁ 1b ₂ ² 1b ₁ ² 2b ₂ ² 2b ₁ ² 3b ₂	³ B ₂	72,990	72,610	77,120	1.09	1.03	1.39
	¹ B ₂	80,970	80,500	84,680	0.66	0.61	1.12
... 7a ₁ ² 1b ₂ ² 1b ₁ ² 2b ₂ ² 2b ₁ ² 3b ₁	² ³ A ₂	77,460	76,280	80,020	0.96	1.27	1.44
	² ¹ A ₂	79,430	78,120	82,030	0.68	1.02	1.20
... 7a ₁ 1b ₂ ² 1b ₁ ² 2b ₂ ² 2b ₁ ² 3b ₁	² ³ B ₁	98,930	98,020	103,110	2.29	2.58	2.55
	² ¹ B ₁	103,510	102,450	108,110	1.61	2.03	1.95

Table II. Continued.

...	$7a_1^2$	$1b_2^2$	$1b_1^2$	$2b_2^2$	$2b_1^2$	$8a_1$	2	3B_2	102,550	78,040	101,820	-2.19	-2.00	-1.94
							2	1B_2	108,880	79,070	108,060	-1.63	-1.13	-1.79
...	$7a_1$	$1b_2^2$	$1b_1^2$	$2b_2^2$	$2b_1^2$	$8a_1$	3	3A_1	132,370	111,390	132,100	-0.10	2.34	0.25
							4	1A_1	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^- .

TABLE III. Results of Geometry Optimization of Ketene Electronic States.^a

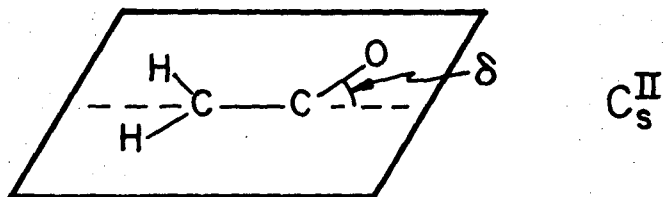
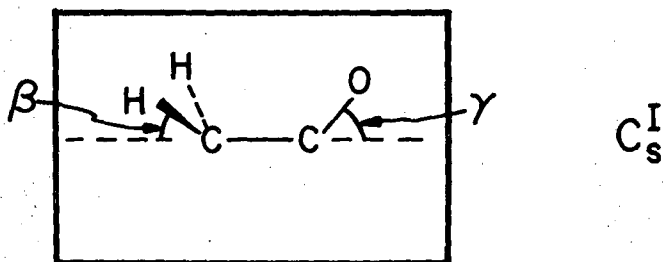
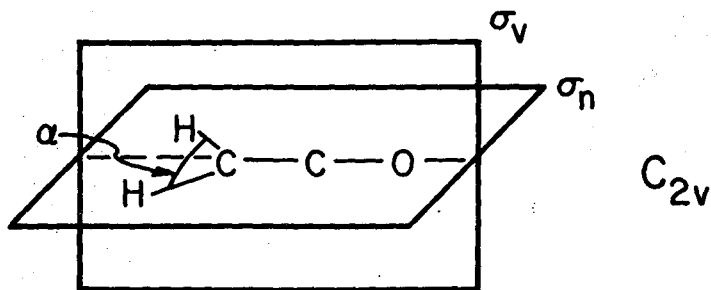
<u>C_{2v} Symmetry</u>		<u>Final Symmetry</u>		<u>Structural Parameters</u>						<u>Excitation Energy</u>		
<u>State</u>	<u>Excitation</u>	<u>State</u>	<u>Excitation</u>	<u>R_{C-O}</u>	<u>R_{C-C}</u>	<u>R_{C-H}</u>	<u>α</u>	<u>β</u>	<u>γ</u>	<u>δ</u>	<u>(in cm⁻¹)</u>	
¹ A ₁	ground state			1.171	1.311	1.070	120.1				0	
³ A ₂	2b ₁ → 3b ₂	C _s ^{II}	³ A''	2a'' → 10a'	1.200	1.459	1.076	117.8	-	-	48.3	11,710
¹ A ₂		C _s ^{II}	¹ A''		1.201	1.455	1.076	118.3	-	-	49.1	13,940
³ A ₁	2b ₁ → 3b ₁	C _s ^I	³ A'	9a' → 10a'	1.190	1.519	1.069	124.1	23.9	53.3	-	15,220
2 ¹ A ₁		C _s ^I	¹ A'		1.195	1.514	1.069	124.3	24.7	52.2	-	18,070
2 ³ A ₁	2b ₂ → 3b ₂	C _s ^{II}	³ A'	2a'' → 3a''	1.422	1.315	1.077	116.6	-	-	51.7	23,020
3 ¹ A ₁		C _s ^{II}	¹ A'		1.423	1.315	1.077	116.6	-	-	51.8	24,360

^a Bond lengths are in Angstroms. Angles are in degrees and are defined in Figure 1.

FIGURE CAPTIONS

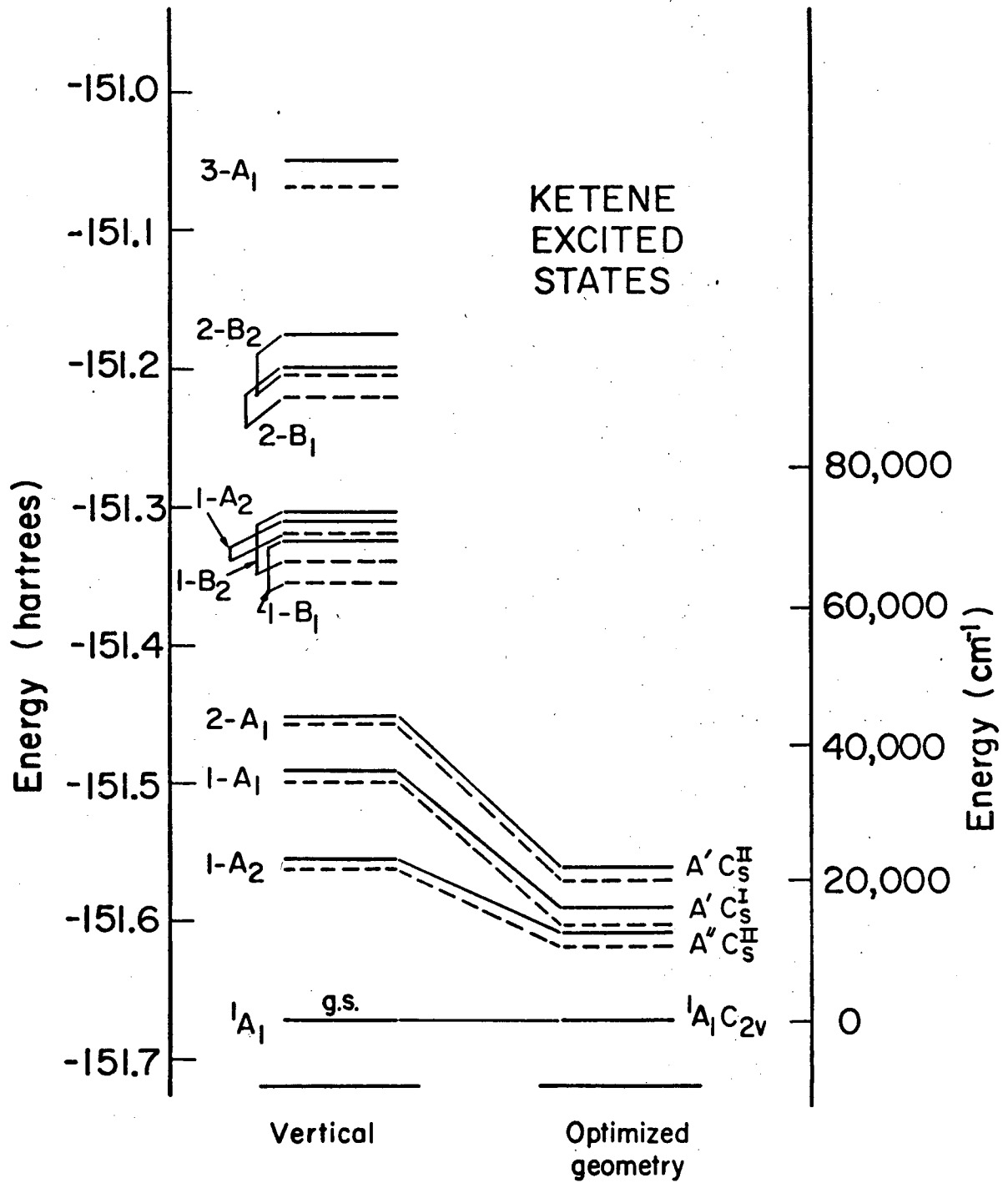
- Figure 1.** Ketene Geometries. The ground state of ketene has C_{2v} symmetry. There are two distinct C_s symmetry types which are appropriate for low-lying excited states. In what is designated C_s^I , the reflection plane perpendicular to the molecular plane of the C_{2v} structure is preserved. 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 .
- 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.



XBL757-4443

Fig. 1



XBL757-4445

Fig. 2

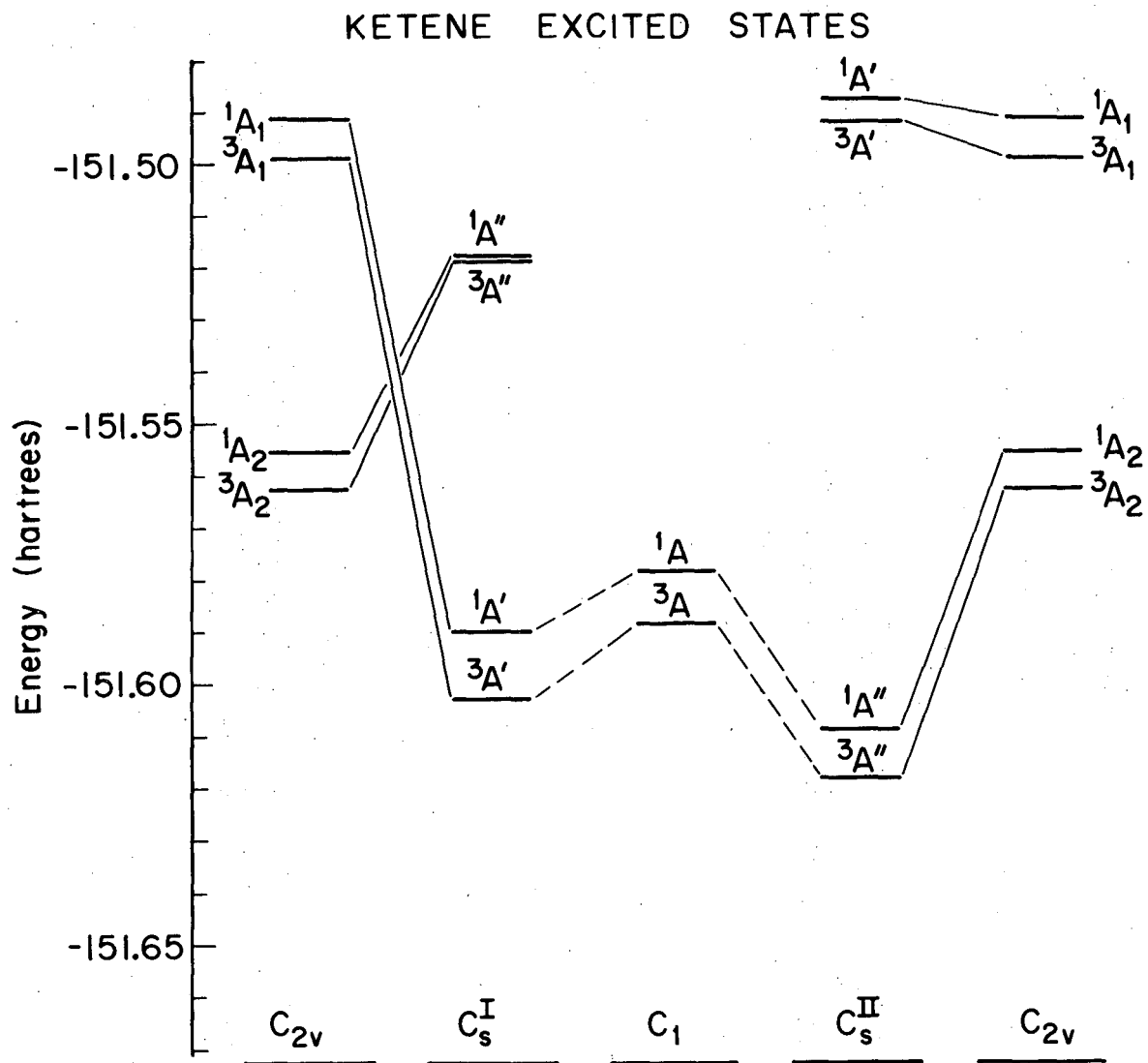


Fig. 3

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