

Electronic States of Organic Molecules. 3. Photoelectron Spectra of Cycloalkenes and Methylenecycloalkanes¹

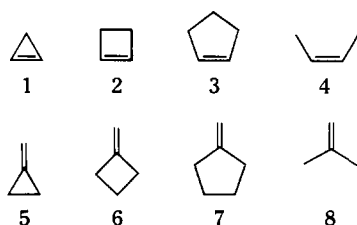
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Abstract: The photoelectron spectra (He(I) and He(II)) of a series of cycloalkenes (C₃-C₅) and methylenecycloalkenes (C₃-C₅) are presented along with those of related open chain compounds. The calculated MO energies using a 4-31G basis set are also given. A good correlation between ionization potentials and MO energies was found, but the correlation did not have a zero intercept. The correlation was useful in assigning the bands in the photoelectron spectra of the larger molecules for which overlapping bands could not experimentally be resolved and suggests a relationship between the neutral molecule MO energy and the sum of the correlation and reorganization energies on going to the ion.

One of the most important of the techniques which give information concerning ground state molecular orbital energy levels is photoelectron spectroscopy.³ To the extent that Koopmans' theorem⁴ is applicable, the Hartree-Fock orbital energies are obtained directly. It seems likely that it will be possible in the near future to calculate the error associated with relating ionization potentials to MO energy levels.⁵ The photoelectron spectra are also an important tool in achieving an understanding of the optical spectra.

We present the photoelectron spectra for a series of cycloalkenes (1-3) and of methylenecycloalkanes (5-7),⁶ as well as for the related *cis*-2-butene (4) and isobutene (8). These



series were chosen because trends in the ionization potentials with structure could be useful in assigning the IP's and because the molecules were small enough so that the restricted Hartree-Fock wave functions could readily be calculated. The spectra were obtained using both He(I) and He(II) excitation, since it appeared possible that the difference in relative cross section might be useful in assigning the IP's. The observed values are given in Tables I and II and the spectra are reproduced in Figures 1 and 2. Since most of the bands have no vibrational structure, it was not generally possible to obtain adiabatic ionization potentials. The values given in the tables are the vertical ionization potentials.

The first ionization potential for each compound certainly corresponds to ionization from the π MO.³ As is generally observed, the band has vibrational structure. For most of the molecules, the frequency is on the order of 1300-1500 cm⁻¹ and can only be attributed to the C=C stretching mode.

The remaining ionization potentials are generally assigned by assuming a one-to-one correspondence between the experimental values and the complements of the MO energies.⁷ It is important to see how the flexibility of the basis set affects the energy levels. Ethylene is a useful example and the results are indicated in Figure 3.^{8,9} The IP's in ethylene are sufficiently widely spaced so that it is unlikely that a direct correlation between observed and calculated values will be incorrect. The 2G and 3G calculations are minimal basis sets (1s, 2s, 2p_x, 2p_y,

2p_z per carbon), in which each atomic orbital is represented by two or three Gaussian functions, respectively. The DZ (double ζ) calculation doubles the size of the basis set by replacing each of the above with two atomic orbitals having different exponents. The 6-31* basis set adds d functions at carbon.

A particularly interesting observation is that the double ζ MO energies may be rather well reproduced if one uses a 3G basis set for the σ bonds and a double ζ basis set for the π bond. This is not unreasonable. There is considerable flexibility in the construction of the σ MO's, since each may involve a number of basis functions. However, a minimal basis (3G) only has two basis functions with which to construct two π MO's. The inclusion of another π -type basis function at each carbon increases the flexibility of that basis set, so that it is more comparable to that used for the σ MO's.

Whereas there is a large change in calculated MO energy levels on going from a 3G to a DZ basis set, the use of a more flexible 6-31G* basis set⁹ did not lead to a further large change in energies. This suggests that the DZ set may be adequate for all hydrocarbons. It may also be noted that there is a fairly good linear relationship between the 3G and DZ MO energies.

The general energy level distribution in the calculated MO's and the observed spectra are quite similar and suggests that a direct correlation may be adequate for those molecules for which the bands in the photoelectron spectrum are sufficiently well resolved. Beside ethylene, cyclopropene, cyclobutene, and methylenecyclopropane appear to meet this criterion. With cyclopropene, seven valence state bands are predicted and seven are found. Similarly, with cyclobutene, ten bands are predicted and ten are found. In the case of methylenecyclopropane, ten bands are predicted, but only nine are found. A comparison of the spacings in the energy levels in the photoelectron spectrum and in the results of the calculation makes it clear that the 1b₁ MO corresponds to the missing band as the spectrum. It may have too low an intensity to be observed or it may be part of the band at 15.75 eV which is quite broad.

Using these molecules, the observed and calculated energies were compared.¹⁰ The fit was reasonable with the STO-3G energies, the correlation line being given by

$$-IP = 0.770E_{MO} - 3.17$$

with a root mean square error of 0.26 eV. The energies also were calculated using a 4-31G basis set (essentially equivalent to DZ) and a better fit was found (Figure 4). Here, the correlation was given by

Table I. Photoelectron Spectra and MO Energy Levels^a of Cycloalkenes

| Compd | Symmetry | 4-31G, eV | | Vertical IP, eV |
|----------------------|------------------|-----------|--------|-----------------|
| | | Calcd | Scaled | |
| Ethylene | 1b _{3u} | 10.25 | 10.13 | 10.51 |
| | 1b _{3g} | 13.73 | 12.82 | 12.70 |
| | 3a _g | 15.91 | 14.50 | 14.70 |
| | 1b _{2u} | 17.56 | 15.77 | 15.78 |
| Cyclopropene | 2b _{1u} | 21.47 | 18.79 | 18.87 |
| | 2b ₁ | 9.57 | 9.60 | 9.82 |
| | 3b ₂ | 11.38 | 11.00 | 10.95 |
| | 6a ₁ | 13.30 | 12.48 | 12.59 |
| | 1b ₁ | 16.27 | 14.78 | 14.95 |
| Cyclobutene | 5a ₁ | 18.50 | 16.50 | 16.68 |
| | 2b ₂ | 20.72 | 18.21 | 18.28 |
| | 4a ₁ | 22.42 | 19.52 | 19.51 |
| | 2b ₁ | 9.37 | 9.45 | 9.59 |
| | 5b ₂ | 12.31 | 11.72 | 11.04 |
| | 7a ₁ | 12.56 | 11.91 | 11.80 |
| | 1a ₂ | 13.70 | 12.79 | 12.84 |
| | 6a ₁ | 14.39 | 13.33 | 13.40 |
| | 1b ₁ | 17.01 | 15.35 | 15.54 |
| | 5a ₁ | 18.32 | 16.36 | 16.44 |
| Cyclopentene | 4b ₂ | 19.08 | 16.95 | 17.19 |
| | 3b ₂ | 23.84 | 20.62 | 20.72 |
| | 12a' | 9.01 | 9.17 | 9.20 |
| | 7a'' | 12.78 | 12.08 | ~11.6 |
| | 11a' | 12.88 | 12.17 | ~12.0 |
| | 6a'' | 13.12 | 12.34 | ~12.2 |
| | 10a' | 13.23 | 12.43 | ~12.6 |
| | 9a' | 14.17 | 13.15 | 13.08 |
| | 5a'' | 15.05 | 13.83 | ~14. |
| | 8a' | 17.49 | 15.72 | ~15.8 |
| | 7a' | 18.13 | 16.21 | ~16.1 |
| | 4a'' | 19.52 | 17.28 | 17.3 |
| | 6a' | 21.19 | 18.57 | 19.0 |
| | 3a'' | 25.59 | 22.25 | 22.0 |
| <i>cis</i> -2-Butene | 5a' | 26.17 | 22.42 | |
| | 2b ₁ | 9.06 | 9.21 | 9.20 |
| | 6b ₂ | 12.57 | 11.92 | 11.57 |
| | 7a ₁ | 13.81 | 12.88 | 12.63 |
| | 5b ₂ | 14.45 | 13.37 | 13.71 |
| | 6a ₁ | 15.11 | 13.88 | |
| | 1a ₂ | 15.30 | 14.03 | 14.06 |
| | 1b ₁ | 15.66 | 14.31 | ~14.5 |
| | 5a ₁ | 17.78 | 15.94 | 16.02 |
| | 4b ₂ | 19.39 | 17.18 | 17.31 |
| | 4a ₁ | 24.21 | 20.91 | 20.38 |
| | 3b ₂ | 26.62 | 22.77 | 22.03 |

^a The data for ethylene, cyclopropene, and cyclobutene were included in the calculation of the correlation line and intercept. The scaled values for the other compounds are values predicted using the correlation.

$$-\text{IP} = 0.772E_{\text{MO}} - 2.22$$

with a root mean square error of 0.22 eV. Since the range of ionization potentials is 14 eV, the error is quite small. The scaled values of the MO energies are given in Tables I and II.

The use of a scaling factor has been suggested previously,¹¹ but the generality of the nonzero intercept does not appear to have been recognized.¹² It cannot be an artifact resulting from the basis set which was used, since the vertical ionization potentials for ethylene are correlated with the near Hartree-Fock limit 6-31G* energies⁹ by

$$-\text{IP} = 0.768E_{\text{MO}} - 2.47$$

with a root mean square error of 0.06 eV. The error is not much larger than the uncertainty in the experimental values.

Table II. Photoelectron Spectra and MO Energy Levels^a for Methylenecycloalkanes

| Compd | Symmetry | 4-31G, eV | | Vertical IP, eV |
|-----------------------|------------------|-----------|---------------------|-----------------|
| | | Calcd | Scaled | |
| Methylenecyclopropane | 2b ₁ | 9.62 | 9.64 | 9.57 |
| | 4b ₂ | 11.43 | 11.04 | 10.47 |
| | 8a ₁ | 11.84 | 11.36 | 11.35 |
| | 1a ₂ | 14.05 | 13.06 | 13.08 |
| | 3b ₂ | 15.96 | 14.54 | 14.52 |
| | 7a ₁ | 17.38 | 15.63 | 15.75 |
| | 1b ₁ | 17.56 | 15.76 | |
| | 6a ₁ | 19.75 | 17.46 | 17.45 |
| | 2b ₂ | 22.66 | 19.71 | 19.72 |
| | 5a ₁ | 26.35 | 22.56 | 22.20 |
| Methylenecyclobutane | 3b ₁ | 9.24 | 9.35 | 9.35 |
| | 5b ₂ | 11.79 | 11.32 | 10.93 |
| | 10a ₁ | 12.31 | 11.72 | 11.68 |
| | 4b ₂ | 12.81 | 12.11 | ~12.2 |
| | 2b ₁ | 13.56 | 12.68 | 12.72 |
| | 1a ₂ | 14.98 | 13.78 | 13.53 |
| | 3b ₂ | 16.14 | 14.68 | 14.53 |
| | 9a ₁ | 17.10 | 15.42 | |
| | 1b ₁ | 17.69 | 15.87 | 15.72 |
| | 8a ₁ | 18.94 | 16.84 | 17.05 |
| Methylenecyclopentane | 7a ₁ | 22.34 | 19.46 | 19.54 |
| | 2b ₂ | 24.75 | 21.32 | 21.37 |
| | 10b | | (9.10) ^b | 9.14 |
| | 9b | | (11.61) | 11.09 |
| | 13a | | (11.89) | 11.44 |
| | 8b | | (11.98) | 11.89 |
| | 12a | | (12.28) | ~12.2 |
| | 11a | | (12.64) | ~12.6 |
| | 7b | | (13.97) | 13.38 |
| | 6b | | (14.47) | 14.10 |
| Isobutene | 10a | | (14.82) | ~14.5 |
| | 9a | | (15.39) | |
| | 5b | | (16.35) | 15.81 |
| | 8a | | (17.01) | 17.09 |
| | 4b | | (18.70) | 18.86 |
| | 7a | | (21.41) | 20.50 |
| | 3b | | (22.51) | 22.71 |
| | 6a | | (23.19) | |
| | 2b ₂ | 9.28 | 9.38 | 9.41 |
| | 5b ₂ | 12.84 | 12.13 | 11.86 |
| | 8a ₁ | 13.82 | 12.87 | 12.84 |
| | 4b ₂ | 14.20 | 13.18 | ~13.2 |
| | 1a ₂ | 14.61 | 13.49 | ~13.6 |
| | 1b ₁ | 16.09 | 14.64 | 14.95 |
| | 7a ₁ | 16.64 | 15.06 | |
| | 3b ₂ | 16.76 | 15.15 | ~15.2 |
| | 6a ₁ | 19.39 | 17.18 | 17.32 |
| | 5a ₁ | 25.23 | 21.69 | 21.29 |
| | 2b ₂ | 25.69 | 22.05 | |

^a The data for methylenecyclopropane were included in the calculation of the correlation line and intercept. The scaled values for the other compounds are values predicted using the correlation.
^b 4-31G wave functions were not obtained for methylenecyclopentane. The scaled values are derived from the STO-3G energies.

It is well recognized that Koopmans' theorem⁴ depends on the cancellation of the reorganization energy (E_R) and the change in correlation energy (ΔE_C) on going from the neutral molecule to the doublet ion:^{13,14}

$$-\text{IP} = E_{\text{MO}} + E_R + \Delta E_C$$

The present correlation is

$$\text{IP} = AE_{\text{MO}} + B$$

Thus

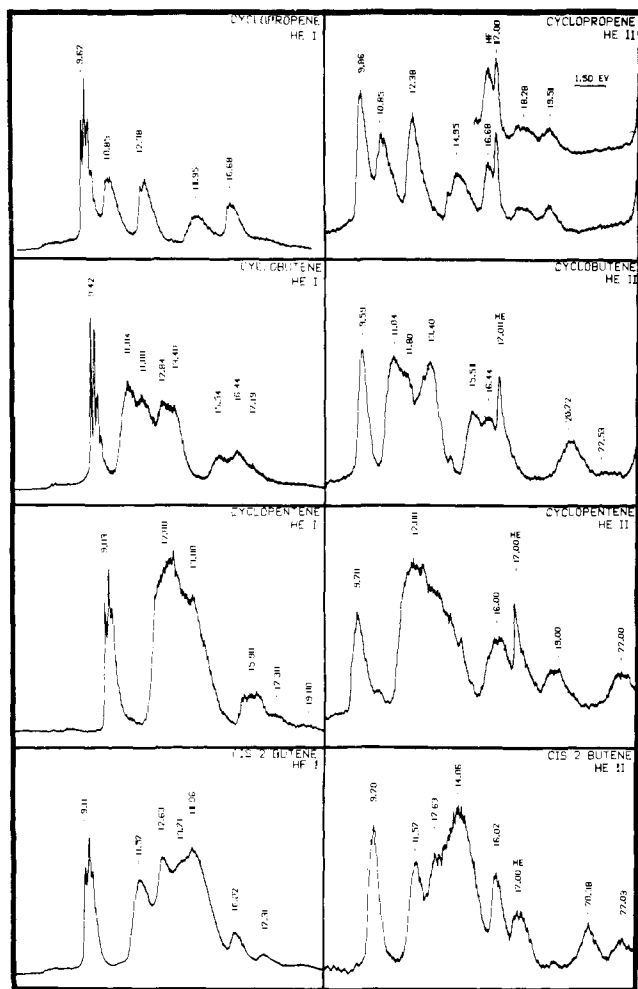


Figure 1.

$$E_{MO} = -\frac{E_R + \Delta E_C}{1 - A} + \frac{B}{1 - A}$$

The $B/(1 - A)$ term is the energy at which $E_{MO} = -IP$ (~ 9 eV for the 4-31G or larger basis sets) and $E_R + \Delta E_C = 0$. The sum of E_R and ΔE_C appears to be linearly related to E_{MO} and appears not to be markedly dependent on either the structure of the molecule or the type of orbital involved. It is likely that the correlation will change if one or more carbons are replaced by other atoms such as oxygen. This will be examined.

The reorganization energy and the change in correlation energy on going from a molecule to its ion has received some theoretical study, particularly in the case of acetylene.¹⁵ The range of ionization potentials studied thus far is not sufficient, so that a meaningful comparison can be made with the present results.

Having established these correlations, it is now possible to examine the spectra of cyclopentene, *cis*-2-butene, methylenecyclobutane, methylenecyclopentane, and isobutene. The bands in the photoelectron spectra of these compounds were predicted using the above relationships and these scaled values also are found in Tables I and II.

The scaled values are found to fit the spectra quite well. The clearly identified IP's are predicted with a root mean square error of 0.27 eV and the broad bands occur at energies corresponding to groups of predicted IP's. The approximate IP's given in the tables for the broad bands were obtained using a curve resolver and agree rather well with the calculated values.

It would be surprising if the correspondence between observed ionization potentials and calculated MO energies were

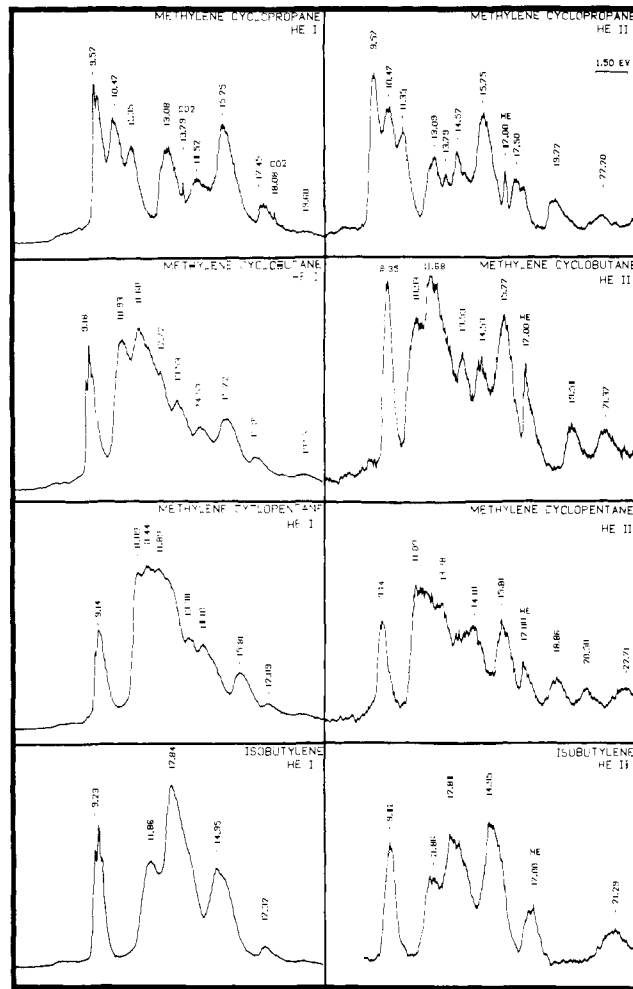


Figure 2.

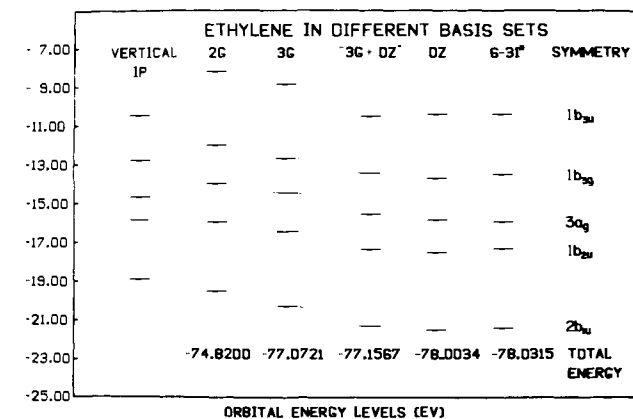


Figure 3.

coincidental and the assignments of the IP's were incorrect. However, the possibility must be recognized. The relative intensities of the photoelectron spectral bands and in intensity on going from a He(I) to a He(II) source may, in principle, be calculated from the MO wave functions.¹⁶ Agreement with the observed relative intensities would provide good confirmation of the proposed assignments. Such calculations are in progress and the results will be reported subsequently.

Experimental Section

Photoelectron Spectra. The spectrometer was a conventional high resolution instrument which has been described in detail.¹⁷ Energy

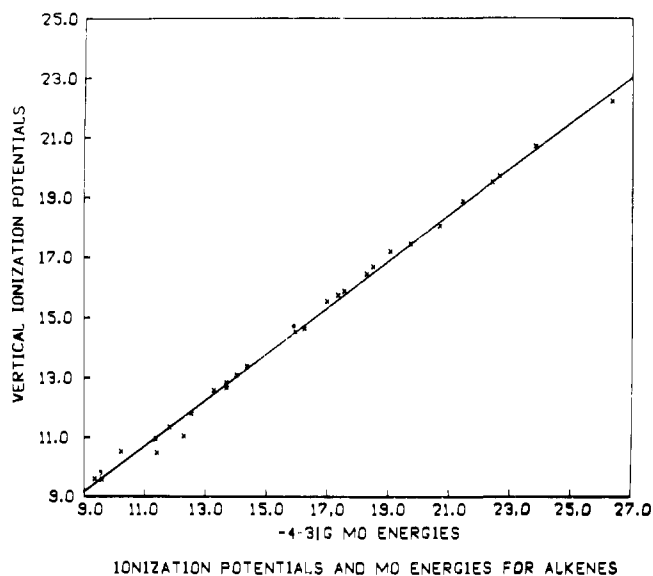


Figure 4.

resolution was measured using the Xe doublet at 12.130 and 13.436 eV and the width at half height was found to be 50 mV. The instrument was calibrated using Xe, He, and CO₂.

Compounds. All compounds were commercial samples or were prepared using standard literature methods. Final purification was effected using gas chromatography and the identity and purity of the compounds was confirmed by NMR spectroscopy.

Calculations. The MO energies were calculated using GAUSS-IAN-70¹⁸ and the experimental geometries. The atomic coordinates are listed in the Ph.D. thesis of G.B.E.

References and Notes

- (1) Research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant No. AFOSR-72-2239.
- (2) (a) Taken in part from the Ph.D. Thesis of G.B.E., 1975; (b) Yale University; (c) Bell Telephone Laboratories.

- (3) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley, New York, N.Y., 1970.
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- (5) Cf. J. J. Wendoloski and G. A. Petersson, *J. Chem. Phys.*, **62**, 1016 (1975).
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- (7) The one exception among hydrocarbons appears to be butatriene (F. Brogli, E. Heilbronner, E. Kloster-Jensen, A. Schmelzer, A. S. Manocha, J. A. Pople, and L. Radom, *J. Chem. Phys.*, **4**, 107 (1974)). Here, an extra band was found in the photoelectron spectrum, but the remainder of the IP's correlated with the MO energies.
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- (11) H. Basch, M. B. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, *J. Chem. Phys.*, **51**, 52 (1969).
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Molecular Structure of Acrolein Electronic States^{1a}

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Abstract: The ground and low-lying singlet and triplet states of acrolein, CH₂CHCHO, have been studied with ab initio SCF methods using a double ζ basis set of Gaussian orbitals. The cis and trans ground-state geometries were optimized and vertical excitation energies were determined for $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ singlet and triplet states. The separation between the cis and trans ground states was found to be 540 cm⁻¹. Optimization of major bond lengths placed the $\pi \rightarrow \pi^*$ states very close energetically to the $n \rightarrow \pi^*$ states. For all excited states, the carbon-oxygen bond length was substantially longer than in the ground state. For the $\pi \rightarrow \pi^*$ singlet and triplet, the single/double bond character of the carbon-carbon bonds is interchanged with respect to the ground state. The ground and lowest excited singlet and triplet states are planar.

Acrolein is isoelectronic with glyoxal and butadiene, but has not received as much experimental attention as glyoxal and has been the subject of fewer theoretical investigations than butadiene. Nonetheless, because of conjugation of the carbon-carbon double bond with a carbon-oxygen bond, acrolein is of unique spectroscopic and electronic structure interest.

Among the early studies of acrolein is that of Walsh, who characterized the vacuum ultraviolet spectrum, identifying a high-energy singlet state.² Inuzuka studied the $n \rightarrow \pi^*$ exci-

tation and placed the 0-0 band for the ¹A' \rightarrow ¹A'' transition³ at 25 851 cm⁻¹. From vibrational analysis of the spectrum, Inuzuka estimated the lengthening of the C=O bond in the ¹A'' state to be 0.1 Å. Brand and Williamson⁴ studied the spectrum under high resolution and derived barrier heights for internal rotation about the two carbon-carbon bonds in the ground state and the excited singlet state and concluded that there was increased π -electron density in the central carbon bond in the excited state. They also determined that the C=O