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The Vacuum Ultraviolet Spectrum of Tetramethyl-1,3-cyclobutanedione

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An experimental and theoretical investigation of the higher-lying electronic states of the cyclic diketone, tetramethyl-1,3-cyclobutanedione, has been performed. Vapor phase vacuum ultraviolet spectra have been recorded to 65 000 cm^{-1}. Single crystal polarized spectral results are presented for a band at 43 500 cm^{-1}. Vibrational analyses have been carried out and band assignments made. Transitions to $\sigma\pi^*$, $n\sigma^*$, and mixed $n\sigma^*$, $\pi\pi^*$ states have been observed. Molecular orbital calculations including configuration interaction have been done on the parent molecule, cyclobutanedione, in the CNDO/S, CNDO/2, and INDO approximations. The results from the CNDO/S computation are shown to fit the experimental results reasonably well.

I. INTRODUCTION

Although the electronic structure and spectra of nonconjugated monocarbonyl compounds such as formaldehyde have been much studied and are now well characterized, a similar situation does not exist for dicarbonyl compounds. The primary interest in these systems and also their major complication is the magnitude and mechanism of the electronic interaction between the two carbonyl moieties. Because of this current interest we have initiated a spectroscopic and photochemical investigation of one particular diketone, tetramethyl-1,3-cyclobutanedione, Fig. 1. This molecule has a number of desirable characteristics which should, in principle, be helpful in understanding the mechanism and magnitude of its transannular interaction. Its chromophoric groups are spatially close enough to expect a readily observable interaction, its molecular framework is planar and symmetrical in its ground electronic state, its crystal structure is known and simple, and its vapor pressure at room temperature is sufficient for vapor studies. In the present paper, we report on our experimental and theoretical study of the higher-lying excited electronic states of tetramethyl-1,3-cyclobutanedione (TMCBD). Discussion of the low-lying energy region (*i.e.*, including $n\pi^*$ transitions) will be presented in another paper.

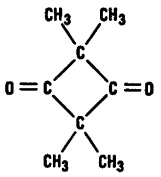

Fig. 1. Tetramethylcyclobutane-1,3-dione.

In order to elucidate the nature of the higher-lying electronic states of TMCBD we have investigated its vacuum ultraviolet spectrum to 65 000 cm^{-1} in the vapor phase and have also studied the polarized single crystal absorption spectrum for the band at 43 500 cm^{-1}. Additionally we have calculated the transition energies of the parent molecule, cyclobutanedione, in the CNDO/S, and CNDO/2, and INDO approximations. The experimental details are presented in Section II and the computational

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procedures in Section III; the results are given in Section IV, discussed in Section V, and compared to the theoretical molecular orbital predictions in Section VI.

II. EXPERIMENTAL

The TMCBD was obtained from Aldrich Chemical Company as a white solid with a vapor pressure of about 0.5 torr at room temperature[1]; recrystallization was carried out from benzene or toluene solvent. The vacuum UV spectra were obtained from the gas phase on a McPherson Model 240 Two Meter UV spectrograph and scanning monochromator equipped with a modified Model 630 Hinteregger type discharge lamp filled with either hydrogen or xenon gas. Each spectrum was recorded at least twice photographically to check for sharp lines and twice photoelectrically, using a double beam technique, to detect broad bands and to insure that photoproducts, if produced, were not responsible for the observed bands. Except for small changes, possibly due to temperature fluctuations or deposits on the cell windows, the spectra were reproducible. The temperature of the cell was 297 K.

The single crystal spectrum was run on a Cary 14 spectrophotometer, at room temperature. The crystal was mounted over a hole in a copper square which was in turn held in the beam by a sample holder.

III. COMPUTATIONAL PROCEDURES

In our calculations, it has been assumed that the neglect of the methyl groups will play no major role, other than possibly shifting the energy levels slightly. The geometry of the parent molecule, cyclobutanedione, was assumed to coincide with that of TMCBD, as given by an X-ray crystallographic study.[2] The C – C bond distances were taken as 1.56 Å, the C – O distances 1.20 Å, the C – H distances 1.10 Å, the C – C – C ring angles as 90°, and the HCH angles [3] as 116°. The CNDO/2, CNDO/S, and INDO calculations were performed with a

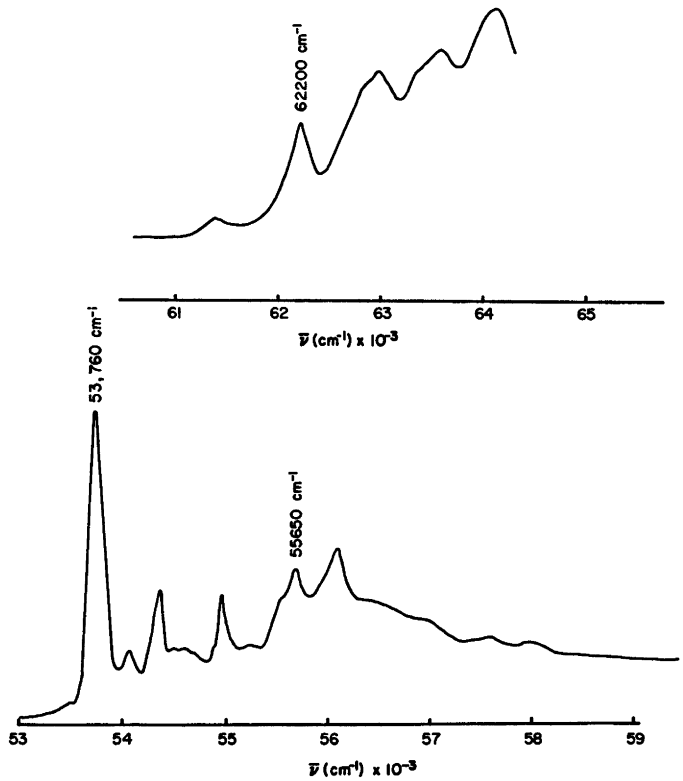

Fig. 2. Vapor phase vacuum ultraviolet spectrum of tetramethyl-1,3-cyclobutanedione.

revised version of QCPE program 141. Further details on the computation procedures employed are provided elsewhere.[4-6]

IV. RESULTS

The vapor vacuum UV spectrum is shown in Fig. 2 and the band positions given in Table 1.

In addition, we have measured the room temperature polarized absorption spectrum of the 43 500 cm^{-1} band on a single crystal. TMCBD belongs to the monoclinic space group $C2/m(C_{2h}^3)$. In the primative unit cell, there is only one molecule which is aligned such that the planar molecular skeleton (excluding the methyls) is perpendicular to the b crystallographic axis.[2] Transitions polarized parallel-to-b are therefore out-of-plane with respect to the molecular framework and transitions polarized perpendicular-to-b are in-plane. The band at 43 500 cm^{-1} is broad and structureless with a predominant out-of-plane polarization, although some intensity in the in-plane polarization was observed. Crystals thin enough to observe the band maximum of the former polarization could not be successfully grown.

Table 2 gives the results of our molecular orbital computations. The symmetry of the upper state and the nature of the transition are also given. The $n\pi^*$ transition energies have been included for comparison, although a complete study of them, utilizing low temperature (4.2 K) single crystal polarized absorption techniques, will be the subject of a separate report.[7]

V. DISCUSSION OF SPECTRAL RESULTS

a. The 43 500 cm^{-1} transition

Ballard and Park [8] have reported the solution spectrum of the 43 500 cm^{-1} region (as well as the lower energy $n\pi^*$ region) in TMCBD and assigned the broad band observed there to the $n\sigma^*$ transition, in analogy with the 53 000 cm^{-1} band in acetone. Whitlock and Duncan [9] in their study of cyclobutanone observed a transi-

Table 1. Observed electronic transitions in tetramethyl-1,3-cyclobutanedione.

State Symmetry	Energy (cm^{-1})	Interval (cm^{-1})	Vibrational assignment (cm^{-1})	Ground state vibration
$^1B_{1u}$	43500	–	–	–
$^1B_{3u}$	53500	−260	−260	270(R)
	53560	−200	−200	217(R)
	53760	0	0−0	–
	54050	+290	+290	298(R)
	54350	+590	+590	584(R)
	54500	+740	+740	760(IR)
	54560	+800	+800	820(IR)
	54650?	+890	+290+590	–
	54880	+1120	?	?
	54950	+1190	+2×590	–
	55250	+1490	+2×590+290	–
	55560	+1800	+3×590	–
$^1B_{2u}$,$^1B_{1g}$	55650	0	0−0	–
	56030	+380	+380	?
	56120	+470	+470	?
	56500	+850	+470+380	–
	56880	+1230	+470+2×380	–
	57410	+1760	+2×470+2×380?	–
	57970	+2320	?	?
^1A_g	61385	0	0−0	–
	62200	+815	+815	820(IR)
	62800	+1415	+815+600	632 or 584(R)
	62900	+1515	+815+700	?
	63350	+1965	+815+1150	1851(R)
	63600	+2215	+815+600+700	–
	64100	+2715	+815+1150+700	–

Table 2. Energies of electronic states in tetramethyl-1,3-cyclobutanedione.

Observed energies (eV)		Calculated energies (eV) CNDO/S		CNDO/2		INDO	
		$^1B_{3g}(n\pi^*)$	3.16	$^1B_{3g}(n\pi^*)$	4.27	$^1B_{3g}(n\pi^*)$	4.24
		$^1A_u(n\pi^*)$	3.16	$^1A_u(n\pi^*)$	4.44	$^1A_u(n\pi^*)$	4.39
$^1B_{1u}$	5.46	$^1B_{1u}(\sigma\pi^*)$	6.00	$^1B_{2g}(\sigma\pi^*)$	9.04	$^1B_{2g}(\sigma\pi^*)$	8.69
		$^1B_{2g}(\sigma\pi^*)$	6.04	$^1B_{1g}(n\sigma^*)$	9.24	$^1B_{1g}(n\sigma^*)$	8.96
				$^1B_{1u}(\sigma\pi^*)$	9.35	$^1B_{1u}(\sigma\pi^*)$	9.04
		$^1B_{3g}(n\pi^*)$	6.20				
		$^1A_u(n\pi^*)$	6.22				
$^1B_{3u}$	6.67	$^1B_{3u}(n\sigma^*)$	7.08	$^1B_{3g}(n\pi^*)$	9.81	$^1B_{3g}(n\pi^*)$	9.44
$^1B_{2u}$	6.90	$^1B_{2u}(n\sigma^*)$	7.23	$^1B_{2u}(n\sigma^*)$	10.34	$^1B_{2u}(n\sigma^*)$	9.66
$^1B_{1g}$		$^1B_{1g}(n\sigma^*)$	7.26	$^1A_u(n\pi^*)$	10.38	$^1A_u(n\pi^*)$	9.96
^1Ag	7.71	$^1A_g(n\sigma^*,\pi\pi^*)$	7.63	$^1A_g(n\sigma^*)$	10.55	$^1B_{3u}(n\sigma^*)$	10.32
				$^1B_{3u}(n\sigma^*)$	10.88	$^1A_g(\pi\pi^*)$	10.59

tion at 49 281 cm^{-1} which they assigned to an $n'\pi^*$ transition, the n' orbital being essentially a $2p$ orbital extending along the carbonyl axis.[10]

In theory, an unambiguous assignment of this electronic band to either a $n\sigma^*$ or $\sigma\pi^*$ (*i.e.*, $n'\pi^*$-like) transition should be possible by investigation of the polarized crystal spectrum. Because of the presence of the two carbonyl groups, each of these transitions could be split into a maximum of four separate transitions, the exact number depending upon the magnitude of the splittings of the MO's involved in the transition. From our MO computations, it can be seen (in Table 2) that four $n\sigma^*$ transitions with symmetries $^1B_{2u}$, $^1B_{3u}$, $^1B_{1g}$, and ^1A_g and two $\sigma\pi^*$ transitions (for the energy range under consideration) with symmetries $^1B_{1u}$ and $^1B_{2g}$ are predicted. Optical transitions to the $^1B_{3u}$ and $^1B_{2u}$ $n\sigma^*$ states are allowed with x and y (in-plane) polarizations, respectively, while the transition to the $^1B_{1u}$ $\sigma\pi^*$ state is allowed only in a z (out-of-plane) polarization.

The observed absorption spectrum shows a band whose polarization is predominantly out-of-plane, thus lending very strong support to its characterization as a $\sigma\pi^*$ transition. The observed in-plane component could possibly be the $^1B_{2g}$ transition whose appearance is made allowed by vibronic coupling *via* a b_{1u} vibration (such as the out-of-plane ring puckering mode [1]). Alternatively, the in-plane component could be ascribed to a transition between n and π^* or σ^* orbitals, both of which should be in-plane polarized. This possibility exists because of the strong mixing between n and σ type orbitals in this molecule (*vide infra*). However, in the absence of vibrational structure on the band both these explanations must be regarded as speculative at present.

The interpretation of the 43 500 cm^{-1} band as a $\sigma\pi^*$ transition is consistent with the $n'\pi^*$ assignment of Whitlock and Duncan,[9] since the n' orbital is mixed strongly with a number of different σ orbitals. It is also consistent with previous assignments of a similarly-positioned transition in other cyclic ketones,[4] *e.g.* cyclopentanone and cyclohexanone.

b. The 54 000 and 55 600 cm^{-1} transitions

In the region between 53 500 cm^{-1} and 58 000 cm^{-1}, the spectrum of TMCBD shows some vibrational structure. Due to the irregularity of the absorption envelope (see Fig. 2), the presence of two electronic transitions in this region is indicated. If we assign the band at 53 760 cm^{-1} to the 0 – 0 band of the first electronic transition, a reasonable and consistent vibrational analysis is possible. Table 1 gives the analysis of the band structure.

A progression of at least three members in a 590 cm^{-1} mode built on the 0 – 0 transition is prominent in the region from 53 500 cm^{-1} to

55 560 cm^{-1}. Built upon each of these modes is one quantum of a 290 cm^{-1} vibration. The ground state counterparts of these two vibrations have been observed in the single crystal Raman spectrum:[1] one at 584 cm^{-1} has been identified as the totally symmetric ring breathing mode and the other at 298 cm^{-1} as one of the carbonyl wagging modes. The bands at 53 500 cm^{-1} (0 – 0 minus 260 cm^{-1}) and 53 560 cm^{-1} (0 – 0 minus 200 cm^{-1}) can be assigned to vibrational hot bands. An attempt was made to substantiate the latter tentative assignment by varying the temperature of the cell, but the results was inconclusive due to the overlapping tail of the intense 0 – 0 absorption band. However, two vibrational modes, one at 270 cm^{-1} and the other at 217 cm^{-1}, have been observed [1] in the Raman spectrum of a polycrystalline TMCBD sample and are likely the vibrations involved.

Two factors point toward the symmetry-allowed nature of this transition: (1) the shape of the Franck-Condon envelope with the 0 – 0 band most intense, and (2) the proximity in energy of the ground and excited state vibrational frequencies. One expects that for an allowed transition with little or no geometry change in the excited state that the 0 – 0 band will be most intense and, furthermore, that the excited state vibrational force constants (and therefore frequencies) will be similar to those in the ground state. The appearance of a progression in the ring breathing mode plus the carbonyl wagging activity is indicative of the presence of an electronic transition originating from either a σ and/or an n type orbital. Since the σ and n orbitals are substantially mixed in TMCBD and since the 43 500 cm^{-1} transition has previously been characterized as a predominantly $\sigma\pi^*$ transition, we interpret this band as an allowed $n\sigma^*$ transition. Using a symmetry argument it is possible to choose between the two allowed orbital designations for the excited state, $^1B_{2u}$ or $^1B_{3u}$. With two types of carbonyl wagging vibrations in TMCBD, an in-phase b_{1u} mode and an out-of-phase b_{2g} mode, the most probable vibronic symmetry of the 54 050 cm^{-1} band can be determined from the direct product of the electronic symmetries, B_{2u} and B_{3u}, with the possible vibrational ones, b_{1u} and b_{2g}. Only in the case of a b_{2g} vibration built on a B_{3u} electronic origin is a state of allowed vibronic symmetry generated (B_{1u}). Thus it can be concluded that the 53 760 cm^{-1} band is an allowed $n\sigma^*$ transition of $^1B_{3u}$ symmetry.

An alternate analysis of the vibrational structure in this region is possible, though much less preferable. With the one dominant vibrational mode frequency half the other, to whithin experimental error (590 cm^{-1} *vs.* 290 cm^{-1}) the observed structure could be due to a *single* multimembered progression in a 290 cm^{-1} mode. Since there are two carbonyl wags in TMCBD, neither of which is totally symmetric, the observation of an every-member progression dictates that the geometry of the excited state must be distorted, such that either or both of these modes become totally symmetric. In such a case the intensity alternation could then be the result of inversion doubling. However, the shape of the Franck-Condon envelope with the 0 – 0 band most intense mitigates against this interpretation, since this is an observation one does not expect in a transition to a distorted excited state.

A second electronic transition is indicated in the region from 55 650 cm^{-1} to 58 000 cm^{-1} with its origin most probably at 55 650 cm^{-1}. Because of the diffuseness of the bands a precise vibrational analysis in this region is difficult, although a tentative one is given in Table 1. Average vibrational intervals of 380 cm^{-1} and 470 cm^{-1} are apparent in this region. Identification of these vibrations has not been possible, other than to conclude that they most likely involve skeletal bending modes. Thus, with the present data, the assignment of this electronic transition is very difficult; however, taken together with our MO computations the data lead to its assignment as one (or more) of the remaining $n\sigma^*$ transitions (*i.e.*, ^1A_g, $^1B_{1g}$, or $^1B_{2u}$) (*vide infra*).

c. The 63 000 cm^{-1} transition

The absorption in this region is characterized by several broad vibrational bands built on a rising background (see Fig. 1). With the 61 385 cm^{-1} band assigned as the 0 – 0 transition the vibrational analysis for this electronic transition is straightforward (see Table 1). The 62 200 cm^{-1} band is assigned to the 815 cm^{-1} non-totally symmetric carbon-carbon stretching

mode, correlating well with the solution 820 cm^{-1} mode (of b_{1u} or b_{3u} symmetry [1]) in the ground state. This assignment is consistent with the fact that the shape of the spectral envelope indicates the transition is a symmetry forbidden one; it is vibronically induced *via* the 815 cm^{-1} non-totally symmetric vibration. The 62 800 cm^{-1} band is assigned to a combination of the 815 cm^{-1} mode and a 600 cm^{-1} mode. The latter vibration is probably a totally symmetric mode involving skeletal bending. Two such vibrations are found in this frequency range in the solution Raman spectrum (632 and 584 cm^{-1}). The 63 350 cm^{-1} band is assigned to a combination of the 815 cm^{-1} mode and an 1150 cm^{-1} vibration, the latter of which is believed to be the in-phase totally symmetric carbonyl stretching mode, which in the ground state occurs at 1851 cm^{-1}. In the corresponding electronic transition in cyclobutanone the carbonyl stretching frequency appears at 1040 cm^{-1} in the $\pi\pi^*$ state and at 1816 cm^{-1} in the electronic ground state.[9]

The nature of this electronic transition and its symmetry assigment cannot conclusively be made with the present data. Interestingly however, neither the 54 000 cm^{-1} band nor the 56 000 cm^{-1} band(s) show any carbonyl stretching frequencies, whereas the present band appears to do so, in addition to displaying several skeletal frequencies. This vibrational activity indicates an electronic transition to a state of mixed origin, probably involving σ (and/or n) orbitals and π orbitals. By analogy with cyclobutanone [9] and other alkyl ketones,[4] it could be argued that this transition should be characterized as a $\pi\pi^*$ transition. However, a complicating factor with this assignment in the present dione is the possibility of a finite transannular interaction between the two chromophoric carbonyl groups. Such an interaction would result in a splitting of the π and π^* orbitals as well as any n, σ, or σ^* orbitals involved in the transition. Mixing between such electronic states with similar symmetries is possible (*e.g.* between $\pi\pi^*$ and $n\sigma^*$ ^1A_g states) provided the energy separation of the zeroth order states is not too great. Given the symmetry-forbidden nature of this band, its unique vibrational activity, and the molecular orbital calculational results (*vide infra*), the most probable assignment for this state is ^1A_g. The major *calculated* contributions to this state are from $n\sigma^*$ and $\pi\pi^*$ transitions, a result consistent with the experimental observations.

Finally, it is of interest to determine whether any of the bands thus far discussed could be assigned to a Rydberg transition. The first ionization potential of TMCBD, as determined by photoelectron spectroscopy, is 8.80 eV.[11] Assuming a Rydberg defect of 1.05 (the cyclobutanone value [9]), Rydberg transitions, if present, should appear at approximately 59 200 cm^{-1} ($n=4$), 64 300 cm^{-1} ($n=5$), and 66 700 cm^{-1} ($n=6$). The first transition falls in a transparent region and the latter two to higher energies than our last observed band, beyond which a continuum appears to be setting in. Thus, it seems unlikely that any of the bands discussed above are Rydberg transitions.

VI. DISCUSSION OF MOLECULAR ORBITAL CALCULATIONS

Three different MO approximations [5,8] were used in calculating the transition energies of cyclobutanedione. Table 2 outlines the overall findings of the three calculations and compares them to the experimental data. As determined in our previous work [4] on the cycloalkanones, the CNDO/2 and INDO approximations give energies which are too high by 3 to 4 eV, whereas the CNDO/S scheme more closely fits the observed energy pattern. In the following discussion we thus concentrate exclusively on the CNDO/S results.

Table 3 gives the CNDO/S results again but in somewhat greater detail: the specific MO's involved in the transitions and the contribution of each to the particular band are described explicitly. Because of the inclusion of configuration interaction, many of the transitions are composite ones made up of several electronic transitions of the same symmetry. The shapes of the most important molecular orbitals as determined by this calculation are sketched in Fig. 3.

The first calculated transition to higher energy of the $n\pi^*$ transitions is to the allowed $^1B_{1u}$ ($\sigma\pi_-^*$) state with the forbidden $^1B_{2g}$ ($\sigma\pi_+^*$) to slightly higher energy. This is in excellent agreement with the polarized single crystal results (see Sec. VA). That the $^1B_{1u}$ state lies lower than the $^1B_{2g}$ one (*i.e.*, the π_-^* orbital

Table 3. Calculational results on cyclobutanedione using the CNDO/S method.

Symmetry	Energy(eV)	Orbitals [a]
$^1B_{3g}$	3.16	$n_+ \rightarrow \pi_+^*(.71)$ $n_- \rightarrow \pi_-^*(.68)$
^1A_u	3.16	$n_+ \rightarrow \pi_-^*(.72)$ $n_- \rightarrow \pi_+^*(.67)$
$^1B_{1u}$	6.00	$\sigma_1(n') \rightarrow \pi_-^*(.90)$ $\sigma_2(n') \rightarrow \pi_+^*(.42)$
$^1B_{2g}$	6.04	$\sigma_2(n') \rightarrow \pi_+^*(.90)$ $\sigma_1(n') \rightarrow \pi_-^*(.43)$
$^1B_{3g}$	6.20	$n_+ \rightarrow \pi_+^*(.70)$ $n_- \rightarrow \pi_-^*(.68)$ $\sigma_3 \rightarrow \pi_+^*(.21)$
^1A_u	6.22	$n_+ \rightarrow \pi_-^*(.69)$ $n_- \rightarrow \pi_+^*(.69)$ $\sigma_3 \rightarrow \pi_-^*(.21)$
$^1B_{3u}$	7.08	$n_+ \rightarrow \sigma_1^*(.96)$
$^1B_{2u}$	7.23	$n_+ \rightarrow \sigma_2^*(.81)$ $n_- \rightarrow \sigma_3^*(.53)$
$^1B_{1g}$	7.26	$n_+ \rightarrow \sigma_3^*(.84)$ $n_- \rightarrow \sigma_2^*(.49)$
^1A_g	7.63	$n_- \rightarrow \sigma_1^*(.91)$ $\pi_+ \rightarrow \pi_+^*(.30)$ $\pi_- \rightarrow \pi_-^*(.20)$

[a] The orbital designations are shown pictorially in Fig. 3. The numbers in parenthesis after the orbital descriptions denote the percentage of configuration mixing. Only the major contributors are listed.

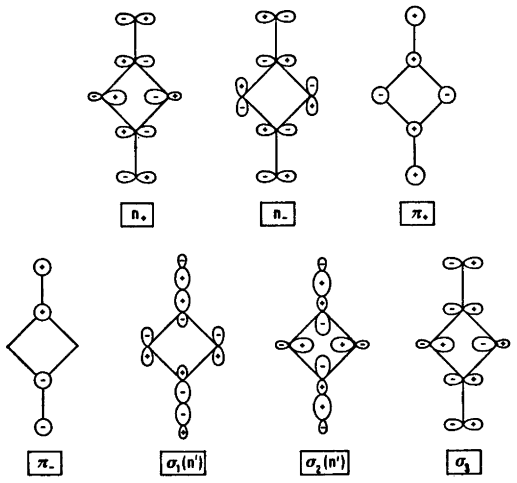

Fig. 3. Several molecular orbitals of cyclobutanedione as determined by a CNDO/S-CI calculation. The orbitals involving the ring hydrogens are omitted for the sake of clarity.

lying lower than the π_+^* orbital (see Table 3)) is also in agreement with the results deduced from the bands in the $n\pi^*$ region.[7] It is also of interest to note here that the σ orbitals from which the electronic transition originates are clearly n'-like, (see Fig. 3) as first proposed by Barnes and Simpson,[10] although they are substantially mixed with the σ framework of the cyclobutane ring.

Transitions to two symmetry-forbidden $n\pi^*$ states are predicted to occur next, at an energy slightly higher than the $\sigma\pi^*$ transitions. Because of their intrinsically lower intensity it is expected that such transitions would be difficult, if not impossible, to identify if they were to occur in a region close to a symmetry-allowed band, such as the $^1B_{1u}$ $\sigma\pi^*$ transition. Indeed, we have been unable to uncover any evidence for or against their appearance in this region and therefore comment no further on them here.

The next group of calculated transitions are to several $n\sigma^*$ states, the lowest of which is a $^1B_{3u}$ state. Again, this prediction is in excellent agreement with the observations (see Sec. VB). From the spectrum it is obvious that the band at 54 000 cm^{-1} is an allowed transition and our analysis shows it to be of $^1B_{3u}$ symmetry. Moreover, the fact that the $^1B_{3u}$ band, whose electron transition originates from the n_+ orbital, lies at lower energy than any of the bands of n_- origin is in accordance with our results in the $n\pi^*$ region.[7] As has been noted, the observed bands in the 55 600 cm^{-1} region are difficult to assign. From their overall shape one would expect them to be symmetry forbidden, however, if two electronic origins are present within the spectral envelope and are close-lying, the relative heights of the sharper 55 560 cm^{-1} and 56 120 cm^{-1} bands could be the result of an under-lying broad band. If this were true, then one could assign the sharper bands to the $^1B_{2u}$ transition and the under-lying broader ones to the $^1B_{1g}$ transition. We note, but put no particular stress on, the fact that the observed energy interval between the origin of the 54 000 cm^{-1} band and the origin of 55 600 cm^{-1} band is 0.23 eV, a value not very different from the calculated splitting between the $^1B_{3u}$ and $^1B_{2u}$ states of 0.15 eV. With the present data, the assignment of the 55 560 cm^{-1} and 56 120 cm^{-1} bands to the $^1B_{2u}$ transition and the higher energy,

broader ones to the $^1B_{1g}$ transition is regarded as tentative at present.

The final calculated transition before the observed onset of the continuum is to a mixed $n\sigma^*$, $\pi\pi^*$ state of ^1A_g symmetry. Although the data are not conclusive enough for an unambiguous identification, this assignment is consistent with both experiment and theory.

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