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The $S_1(n,\pi^*)$ states of cyclopentanone and cyclobutanone in a supersonic nozzle beam

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Fluorescence excitation spectra of cyclopentanone and cyclobutanone have been observed for their (n,π^*) transition in a pulsed supersonic nozzle beam using a high power tunable laser. A drastic reduction of hot bands has been attained, making it possible to discuss the vibronic assignments in more detail than the previous works. The C=O out-of-plane wagging mode was found to be active for both molecules. The ring twisting and flapping in cyclopentanone and the ring puckering in cyclobutanone were also active. The molecules are pyramidally distorted in the excited states with double minimum potentials in the out-of-plane displacement coordinates. The barrier to inversion (V) and the C=O out-of-plane angle at the potential minimum (θ_m) have been determined for the $S_1(n,\pi^*)$ state; $V = 680 \pm 17 \text{ cm}^{-1}$ and $\theta_m = 34^\circ$ for cyclopentanone, and $V = 1850 \pm 50 \text{ cm}^{-1}$ and $\theta_m = 42^\circ$ for cyclobutanone. The puckering mode ($\nu_{20'}$) of cyclobutanone was also found to have a double minimum potential with $V = 16.9 \text{ cm}^{-1}$. The rotational envelope of each vibronic band has been analyzed on the basis of a computer simulation for an asymmetric top molecule. In contrast with formaldehyde, the A -type (parallel) component, as well as the B -type, was shown to be important in these cyclic ketones. The mechanism of the vibronic intensity borrowing is discussed on the basis of the band-type considerations.

I. INTRODUCTION

The photochemical properties of aliphatic carbonyl compounds have been the subject of a number of investigations, which have been reviewed by Lee and Lewis.¹ As predicted by Walsh² this type of molecules are pyramidally distorted in the carbonyl region in the $S_1(n,\pi^*)$ state in contrast with the ground state where they are approximately planar. The geometrical change upon excitation will play an important role in photochemical processes such as intramolecular energy transfer and photochemical dissociation. It is therefore of great interest to investigate the vibrational structure of the S_1 state in connection with the geometrical change. The vibrational-rotational analysis has been completed on the gas phase absorption spectra of formaldehyde, a prototype molecule of aliphatic carbonyl compounds.³⁻⁵ However, the analyses are quite insufficient for larger carbonyl compounds, mainly because of the band congestion due to hot bands in the room-temperature spectra.

The beautiful technique of combined laser spectroscopy and supersonic nozzle beam⁶ has been developed and applied to polyatomic molecules in the last decade. Molecules are supercooled upon free expansion to simplify the spectrum drastically. Furthermore, high power tunable lasers have made it possible to observe very weak (n,π^*) transitions in carbonyl compounds such as acetaldehyde⁷ and acetone.⁸

In view of the success in obtaining well resolved supersonic jet fluorescence excitation spectra for acetone and acetone- d_6 ,⁸ we decided to extend the work to the simple aliphatic ketones, cyclopentanone and cyclobutanone. The room-temperature absorption spectrum of cyclobutanone vapor has been analyzed by Moule.⁹ The fluorescence excitation spectrum has been measured by Lee *et al.*¹⁰ The absorption spectra of cyclopentanone have also been measured and analyzed by Howard-Lock and King.¹¹ The phosphores-

cence excitation spectra have also been measured at 77 K by Chandler and Goodman for these molecules.¹² However these spectra are heavily congested by overlapping hot bands, making the assignments more or less unreliable. In the present work, the supersonic molecular beam technique has been applied to the fluorescence excitation spectra of cyclopentanone and cyclobutanone for the purpose of re-investigating the vibronic assignments in greater detail.

The intensity of the forbidden (n,π^*) transition ($A_2 \leftarrow A_1$ in the case of the C_{2v} symmetry) is borrowed from higher excited states through Herzberg-Teller vibronic coupling. Rotational analysis will provide some useful information on the mechanism. In formaldehyde, the B -type band dominates in the absorption spectrum, which can be understood as the result of the coupling with the $B_2(n,\sigma^*)$ state. On the other hand, the importance of the coupling with the $A_1(\pi,\pi^*)$ state has been postulated for cyclopentanone and cyclobutanone,¹² and the coupling with the $B_1(\sigma,\pi^*)$ state has been suggested to be important in acetone.⁸ It is one of the purposes of this paper to analyze the rotational envelopes of vibronic bands and to elucidate the mechanism of vibronic intensity borrowing in the case of aliphatic cyclic ketones.

The active vibrational modes in the absorption spectrum of the formaldehyde (n,π^*) transition are the C=O out-of-plane wagging (ν_4 ; 124.6 cm^{-1}) and the C=O stretching (ν_2 ; 1173 cm^{-1}).²⁻⁴ Active in cyclic ketones are the C=O out-of-plane wagging and the ring puckering modes. The activity of the former has been related to the pyramidal structure in the (n,π^*) state. This distortion was predicted for formaldehyde by Walsh² in 1953. He showed that the mixing of $\pi^*(b_1)$ and $\sigma(a_1)$ orbitals would stabilize the pyramidal configuration in the (n,π^*) state. In other words, sp^3 hybridization of the carbon atom would be more stable than sp^2 when an electron occupies the π^* antibonding orbital. This prediction was confirmed by Brand,³ who determined the

potential curve by a detailed analysis of the absorption spectrum. We shall discuss this valence-induced distortion in the case of cyclic ketones.

II. EXPERIMENTAL

The apparatus for the measurement of a fluorescence excitation spectrum in a supersonic nozzle beam will be given briefly. A detailed description has been given in the literature.⁶ We employed an automobile engine electric fuel injector for the pulsed nozzle: orifice diameter, 0.3 mm driven by a pulse generator at 5 Hz, duration about 1 ms. This nozzle was mounted in a stainless steel chamber evacuated by a turbo molecular pump (Sargent–Welch, 1500 ℓ/s). The sample reservoir was a stainless steel tube (20 cm³) through which argon gas was flowed. The gas flow line and the nozzle were heated by a wire heater in order to increase the vapor pressure of the sample.

A Nd–YAG pumped dye laser (Quantel, pulse duration 15 ns) was used as an exciting light source. UV light was produced by frequency doubling the output of Exciton DCM dye (FWHM 0.1 cm⁻¹) with a KDP crystal. This crystal and the grating of the dye laser could be continuously scanned by stepping motors which were synchronously driven by a microcomputer. The wavelength was calibrated against a Ne discharge lamp and a 25 cm monochromator (Nikon P-250). The laser light was mildly focused with a quartz lens ($f = 500$ cm) into the molecular beam through a Brewster window and a light baffle train. The distance between the nozzle and the crossing point was about 1 cm. Fluorescence was focused using a quartz lens (diameter 8 cm, $f = 10$ cm) and detected by a photomultiplier (Hamamatsu, R1104). A glass filter (Hoya B390 and L38) was used to block the scattered laser light. The signal output of the photomultiplier was fed to a box-car integrator (Princeton Applied Research model 162 and 165) and normalized against the laser power (detected by a photodiode). Spectra were recorded on a strip chart recorder.

Commercially obtained cyclobutanone (Aldrich) was used without further purification. Cyclopentanone (Tokyo Kasei) was purified by repeated vacuum distillations.

III. RESULTS AND DISCUSSION

A. Selection rule

For the convenience of later discussion, symmetry relations in the vibronic intensity borrowing mechanism are summarized in Table I, including the second-order intensity borrowing as well as the usual first order case. In the latter, the induced transition moment is

$$\mu \sim \langle G | \mu | U \rangle \langle A_2 | \partial H / \partial Q | U \rangle f(Q) f'(Q), \quad (1)$$

where G , A_2 and U are the electronic ground, (n, π^*) and upper allowed states, respectively, and Q is the normal coordinate active in the intensity borrowing. The vibrational integrals $f(Q)$ and $f'(Q)$ are defined by

$$f(Q) \equiv \langle 0, 0, \dots, 0 | Q_r | v_1, v_2, \dots, v_m \rangle \quad (2)$$

and

$$f'(Q) \equiv \langle 0, 0, \dots, 0 | v'_1, v'_2, \dots, v'_n \rangle, \quad (3)$$

TABLE I. Symmetry relations in the vibronic intensity borrowing mechanism.^a

Upper state symmetry ^b	Active modes	Band type ^c
	(1st order)	
A_1	a_2	A
B_1	b_2	C
B_2	b_1	B
	(2nd order)	
A_1	a_1, a_2	A
	b_1, b_2	
B_1	a_1, b_2	C
	a_2, b_1	
B_2	a_1, b_1	B
	a_2, b_2	

^a C_{2v} symmetry is assumed.

^b Symmetry of the upper state from which intensity is borrowed.

^c Band type of rotational contour. A , B , and C correspond to the polarization z (parallel to C=O bond), y (perpendicular to C=O, in plane), and x (perpendicular to the plane), respectively.

where v_1, v_2, \dots, v_m are vibrational quantum numbers for the modes belonging to the same symmetry Γ as Q_r , and v'_1, v'_2, \dots, v'_n are those belonging to the representations other than Γ .

Besides the selection rule due to the symmetry properties of electronic wave functions, the “vibrational” selection rules for polyatomic molecules are

$$f(Q) \neq 0 \quad \text{for} \quad \sum_{j=1}^m \Delta v_j = \text{odd} \quad (4)$$

and

$$f'(Q) \neq 0 \quad \text{for} \quad \sum_{j=1}^n \Delta v_j = \text{even}. \quad (5)$$

Normally the totally symmetric modes give rise to long progressions according to Eq. (5), because of displacement of the excited state potential minimum with respect to the ground state. Nontotally symmetric modes generally give $\Delta v = 1$ for Eq. (4) and $\Delta v = 0$ for Eq. (5), with the other components negligibly small. This is because there is no displacement of potential by symmetry reasons. An exception to this rule is met when the mode has a double minimum potential. In this case the selection rule (4) or (5) would give a long progression.

The second order intensity is induced through either

$$\mu \sim \langle G | \mu | U \rangle \langle A_2 | \partial H / \partial Q_1 | U' \rangle \langle U' | \partial H / \partial Q_2 | U \rangle \times f(Q_1) f(Q_2) f'(Q_1, Q_2), \quad (6)$$

$$\mu \sim \langle G | \mu | U' \rangle \langle A_2 | \partial H / \partial Q_1 | U' \rangle \langle G | \partial H / \partial Q_2 | U' \rangle \times f(Q_1) f(Q_2) f'(Q_1, Q_2), \quad (7)$$

or

$$\mu \sim \langle G | \mu | U \rangle \langle A_2 | \partial^2 H / \partial Q_1 \partial Q_2 | U \rangle \times f(Q_1) f(Q_2) f'(Q_1, Q_2). \quad (8)$$

The first two equations represent the second order perturbation arising from the first order expansion of Hamiltonian in normal coordinates. The last equation comes from the second order expansion of Hamiltonian. As far as symmetry is concerned, all three terms give rise to the same result as summarized in Table I. In the table are also indicated the rotational band type, where the A , B , and C type components polarize along the z (parallel with the C=O bond), y (in

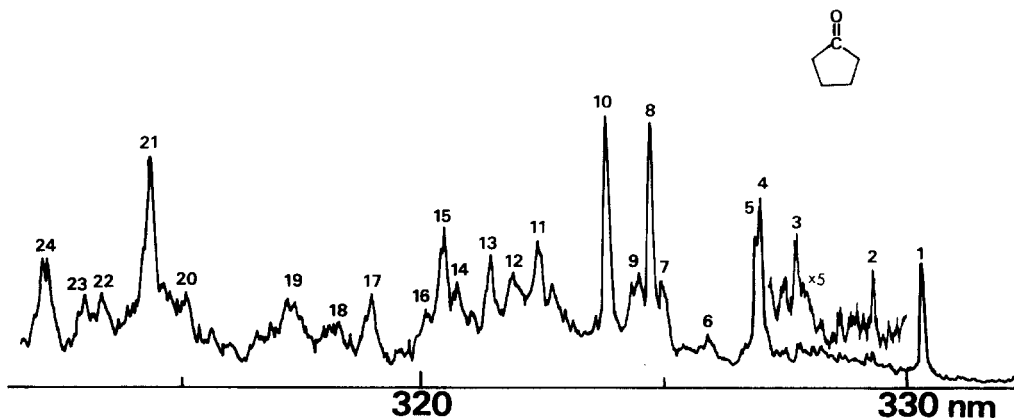


FIG. 1. Fluorescence excitation spectrum of cyclopentanone in an Ar supersonic nozzle beam with the stagnation pressure of 4 atm. The temperature of the nozzle and the sample reservoir is 130 °C.

plane, perpendicular to C=O) and x (out-of-plane) coordinates, respectively.

B. Cyclopentanone

The fluorescence excitation spectrum of cyclopentanone in an Ar supersonic nozzle beam with the stagnation pressure of 4 atm (405 kPa) is shown in Fig. 1. The spectral feature was affected neither by sample purification nor by changing stagnation pressure. Therefore we can exclude the contributions of impurities, clusters, and hot bands. The measured frequencies and assignments are summarized in Table II and Fig. 2. The band at 30 264 cm^{-1} was assigned to the origin since we could not find any peak at lower energy. The active vibrational modes are the C=O out-of-plane wagging ($\nu_{25'}$), ring twisting ($\nu_{18'}$), and ring flapping ($\nu_{26'}$). It is well known that $\nu_{25'}$ (b_1) has a double minimum potential. Similarly it is reasonable to assume that $\nu_{18'}$ (a_2) and $\nu_{26'}$ (b_1) have also double minimum potentials with relatively high and low barriers, respectively. Thus the selection rule given in Table I and Eqs. (4) and (5) leads us to present assignments in which the overlap of type- A and B polarizations is predicted.

Howard-Lock and King have analyzed the absorption spectrum of cyclopentanone.¹¹ Although their room-temperature spectrum was obscured by hot bands, they analyzed progressions starting at several pseudo-origins to determine $\nu_{25'}$, $\nu_{18'}$, and the potential for the out-of-plane wagging. Besides inaccuracy due to band congestion, they have assigned the 30 278 cm^{-1} band (corresponding to our 30 264 cm^{-1} origin) to a pseudo "hot" origin; i.e., the transition $\nu_{18'} = 1 \rightarrow \nu_{18'} = 0$. We assign the band to the true origin because it does not change intensity upon varying the stagnation pressure.

In order to determine the potential curve for the C=O out-of-plane wagging motion, the observed energy levels in the progressions 25_0^{0-} and $18_0^{0-} 25_0^{0+}$ were fitted to a quartic-quadratic potential $V(\theta) = a\theta^4 - b\theta^2$, where θ denotes the angle of the C=O bond to the C-C-C plane. The one-dimensional wave function is

$$-(\hbar^2/2\mu)(d^2\psi/dx^2) + (V - E)\psi = 0, \quad (9)$$

where $x = r_{\text{C=O}} \times \theta$ and μ is the reduced mass for the wagging vibration ($\mu = 2.09 \times 10^{-24}$ g) which is obtained by the method of Wilson's G matrix.¹³ Equation (9) can be transformed into the following dimensionless eigenvalue problem:

$$d^2\psi/dz^2 + (\lambda - z^4 + Bz^2)\psi = 0, \quad (10)$$

where

$$z = (2\mu/\hbar^2)^{1/6} a^{1/6} x, \quad (11)$$

$$B = -(2\mu/\hbar^2)^{1/3} a^{-2/3} b, \quad (12)$$

$$\lambda = (2\mu/\hbar^2)^{2/3} a^{-1/3} E. \quad (13)$$

The eigenvalues of Eq. (10) have been tabulated by Laane.¹⁴ The best fit values for the barrier height V and the angle of the C=O bond to the C-C-C plane at the potential minimum θ_m are $V = 680 \pm 17 \text{ cm}^{-1}$ and $\theta_m = 34^\circ$ for $a = 1.27 \times 10^{-4} \text{ cm}^{-1} \text{ deg}^{-4}$ and $b = 2.94 \times 10^{-1} \text{ cm}^{-1} \text{ deg}^{-2}$. These values may be compared with the litera-

TABLE II. Vibrational analysis of cyclopentanone.

Number ^a	Wave number	Δ/cm^{-1}	Assignment ^b
1	30 264	0	$18_0^{0-}, 25_0^{0-}$
2	30 356	92	26_0^{0-}
3	30 501	237	$18_1^{1-}, 18_1^{1+} 25_0^{0-}$
4	30 572	308	$18_0^{0-} 25_1^{1+}$
5	30 578	314	25_1^{1-}
6	30 676	412	$26_0^{0-} 25_1^{1+}$
7	30 760	496	$26_1^{1+} 25_1^{1-}$
8	30 791	527	$18_0^{0-} 25_2^{2+}$
9	30 817	553	$18_1^{1-} 25_1^{1+}, 18_1^{1+} 25_1^{1-}$
10	30 871	607	25_2^{2-}
11	31 005	741	$18_0^{0-} 25_3^{3+}$
12	31 055	791	$26_1^{1+} 25_2^{2-}$
13	31 099	835	$18_1^{1+} 25_2^{2-}, 26_0^{0-} 25_3^{3+}$
14	31 166	902	25_3^{3-}
15	31 190	926	$18_1^{1-} 25_3^{3+}$
16	31 229	965	$18_0^{0-} 25_4^{4+}$
17	31 339	1075	$18_1^{1+} 25_3^{3-}, 26_0^{0-} 25_4^{4+}$
18	31 418	1154	$18_0^{0-} 3_1^{1-}, 25_0^{0-} 3_1^{1-}, 25_4^{4-}$
19	31 499	1235	$18_1^{1+} 25_4^{4-}, 18_0^{0-} 25_5^{5+}, 26_1^{1+} 25_4^{4-}$
20	31 723	1459	$25_1^{1-} 3_1^{1-}, 18_0^{0-} 25_6^{6+}, 18_1^{1+} 25_5^{5-}$
21	31 804	1540	$18_0^{0-} 25_7^{7+}, 18_1^{1+} 25_6^{6-}$
22	31 907	1643	
23	31 938	1674	
24	32 019	1755	$18_0^{0-} 25_8^{8+}, 18_1^{1+} 25_7^{7-}$

^a See Fig. 1.

^b Based on the C_{2v} symmetry. The ground state vibrational level is not indicated since all transitions occur from $v'' = 0$. The modes in their lowest levels are not shown explicitly; e.g., 18_0^{0-} , 25_0^{0-} , and 26_0^{0-} are $18_0^{0-} 25_0^{0+} 26_0^{0+}$, $18_0^{0+} 25_0^{0-} 26_0^{0+}$, and $18_0^{0+} 25_0^{0+} 26_0^{0-}$, respectively.

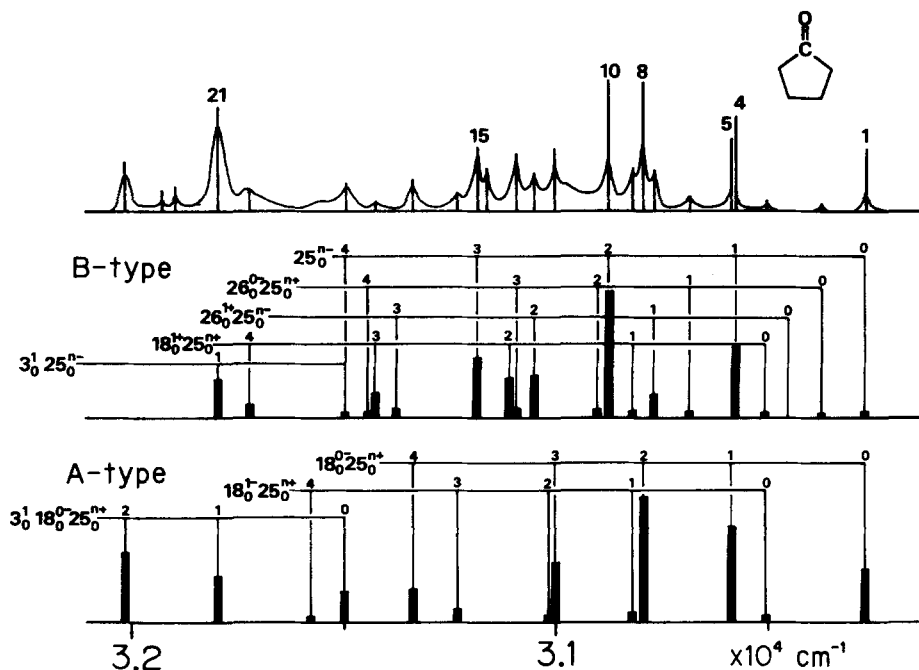


FIG. 2. Vibronic assignments of cyclopentanone. The schematic spectrum on the top is the same as that in Fig. 1. Intensities in the stick diagram are only qualitative reproductions of the observed relative intensities.

ture values $V = 706 \text{ cm}^{-1}$ and $\theta_m = 35^\circ$.¹¹ The results are schematically shown in Fig. 3. We have also fitted our data to another type of potential function, $V(\theta) = (1/2)\alpha\theta^2 + A \exp(-\beta^2\theta^2)$, using the table given by Coon *et al.*¹⁵ Assuming $\rho = 0.6$ we obtained $V = 693 \pm 15 \text{ cm}^{-1}$ and $\theta_m = 35^\circ$. The analysis is likely insensitive to the functional form of the double minimum potential.

The frequencies for $\nu_{25'}$ are $\Delta\nu(25^{1+} - 25^{0+}) = 308 \text{ cm}^{-1}$, $\Delta\nu(25^{1-} - 25^{0+}) = 314 \text{ cm}^{-1}$, and $\Delta\nu(25^{2+} - 25^{0+})$

$= 521 \text{ cm}^{-1}$ in reasonable agreement with the Howard-Lock and King's values,¹¹ 307, 314, and 528 cm^{-1} , respectively. These frequencies are much smaller than the ground state value, 446 cm^{-1} .¹⁶ The frequency for $\nu_{18'}$ is 237 cm^{-1} , which is close to the ground state value,¹⁶ 238 cm^{-1} , but in poor agreement with the literature value, 284 cm^{-1} .¹¹ The frequencies for the 26' mode have also been determined; $\Delta\nu(26^{0-} - 26^{0+}) = 92 \text{ cm}^{-1}$ and $\Delta\nu(26^{1+} - 26^{0-}) = 90 \text{ cm}^{-1}$. They are also close to the ground state value, 95 cm^{-1} .¹⁶

In Fig. 4(a) are shown the observed rotational contours of some of the C=O out-of-plane wagging progression

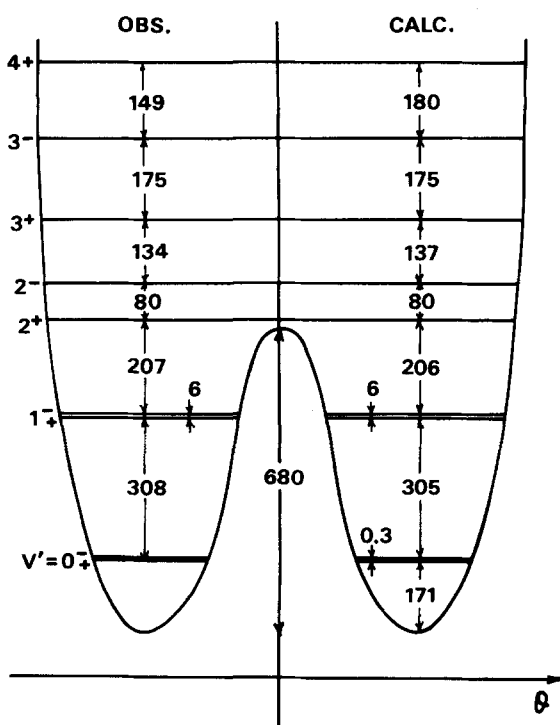


FIG. 3. Observed and calculated energy levels of the C=O out-of-plane wagging ($\nu_{25'}$) vibration in the S_1 state of cyclopentanone.

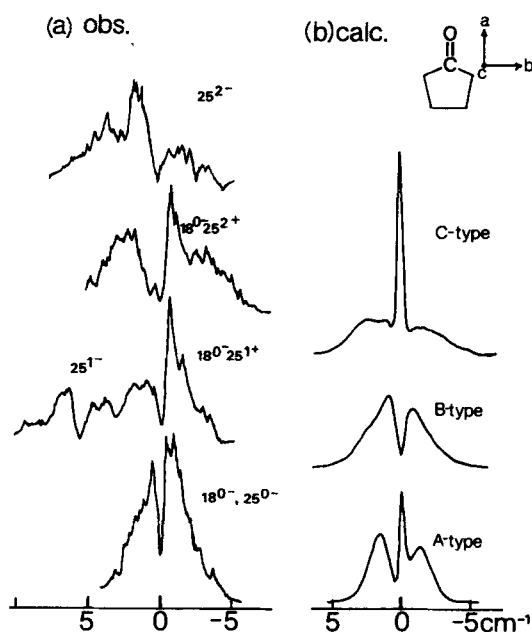


FIG. 4 (a) Observed and (b) calculated rotational envelopes of vibronic bands of cyclopentanone. See the text for details.

bands, 25_0^{n-} and $18_0^{0-} - 25_0^{n+}$. Calculated band envelopes are shown in Fig. 4(b). The calculation was made for the rotational quantum number J up to 23, assuming the rotational temperature of 10 K and the bandwidth of 0.2 cm^{-1} . The rotational constants reported by Howard-Lock and King were used¹¹, namely, $A'' = 0.220\,63$, $B'' = 0.111\,69$, $C'' = 0.080\,33$, $A' = 0.214\,18$, $B' = 0.111\,97$, and $C' = 0.081\,09 \text{ cm}^{-1}$. The observed contours of the 18_0^{0-} , $18_0^{0-} - 25_0^{1+}$, and $18_0^{0-} - 25_0^{2+}$ bands are close to the A band which has a sharp head near the center. On the other hand, the contour of the 25_0^{1-} (and possibly 25_0^{2-}) band is of B type. These results are in complete accordance with the assignments given in Fig. 2 and Table II, i.e., the progressions starting at pseudo origins vibronically induced by the b_1 vibrations (25_0^{n-} , $26_0^{0-} - 25_0^{n+}$, $26_0^{1+} - 25_0^{n-}$, and $18_0^{1+} - 25_0^{n-}$) are B polarized and those induced by the a_2 vibration ($18_0^{0-} - 25_0^{n+}$ and $18_0^{1+} - 25_0^{n+}$) are A polarized. The importance of the A -type character is consistent with the result of the excitation polarization experiment carried out by Chandler and Goodman,¹² but disagrees with Howard-Lock and King.¹¹ At first glance, the ring twisting mode, $\nu_{18}(a_2)$, seems to be less active because of its distance from the $\text{C}=\text{O}$ group in which the $n-\pi^*$ transition localizes. However this difficulty would be overcome by the existence of a low-lying, intense (π, π^*) transition in the $\text{C}=\text{O}$ group, which induces an A -polarized dipole moment. The B -polarized bands borrow their intensity either from the (n, σ^*) transitions or from higher (σ, σ^*) transitions in the ring. The former channel is relatively unfavorable because of the low intensity of the (n, σ^*) transition. The latter is also unfavorable in view of the large energy separation.

The $\text{C}=\text{O}$ stretching (ν_3'') frequency in the ground state has been determined to be 1771 cm^{-1} by the IR and Raman spectra.^{16,17} In the (n, π^*) state, it is expected to decrease down to $1200\text{--}1300 \text{ cm}^{-1}$ because of the change in the $\text{C}=\text{O}$ bond length on the analogy of formaldehyde and other carbonyl compounds.^{3,18} We assigned the weak band at 1235 cm^{-1} to $18_0^{0-} - 3_0^{1-}$. The band at 1540 cm^{-1} is then assigned to the overlap of $25_0^{1-} - 3_0^{1-}$ and $18_0^{0-} - 25_0^{1+} - 3_0^{1-}$, and the 1755 cm^{-1} band to $18_0^{0-} - 25_0^{2+} - 3_0^{1-}$. Those bands should be considered as the $\Delta v_3 = 1$ components in the totally symmetric ν_3 progressions starting at lower vibronic bands induced by ν_{18} and ν_{25} .

The present assignments are based on the C_{2v} symmetry of the molecule. Although cyclopentanone is actually skewed in its ground state with its symmetry reduced to C_s ,¹⁹ the C_{2v} selection rule is believed to hold approximately since the (n, π^*) transition is localized in the $\text{C}=\text{O}$ group and the local symmetry of $\text{C}_2\text{C}=\text{O}$ is C_{2v} .¹¹ We have confirmed that the approximate C_{2v} selection rule holds in our assignments. However the larger relative intensity of the origin band of this molecule compared with molecules of rigorous C_{2v} symmetry (formaldehyde, acetone, and cyclobutanone) may be ascribed to the deviation from the C_{2v} symmetry in the ground state. Namely, the true origin $18_0^{0+} - 25_0^{0+}$ will be forbidden under the rigorous selection rule in the C_{2v} symmetry but should locate very close to 18_0^{0-} and 25_0^{0-} at $30\,264 \text{ cm}^{-1}$ because of the high barriers in ν_{18} and ν_{25} . The reduction of C_{2v} into C_s in the actual molecule makes the 18_0^{0+}

transition allowed. Therefore the true origin may give rise additional intensity to the $30\,264 \text{ cm}^{-1}$ band.

The ring motion of cyclopentanone is understood to be a pseudorotation (or pseudotorsion). A far-infrared study has determined the barrier to pseudorotation in the ground state to be 1303 cm^{-1} .^{20,21} The pseudotorsion mode is a composite of our twisting and flapping modes. Since the main barrier to pseudotorsion corresponds to that of the twisting motion,²⁰ it seems to be reasonable that the latter has a high barrier to give completely degenerate levels for $\nu_{18} = 0_{\pm}$ and 1_{\pm} . On the other hand, the flapping mode (ν_{26}) has a shallow potential which is consistent with the ring puckering discussed below for cyclobutanone.

C. Cyclobutanone

In Fig. 5 is shown the fluorescence excitation spectrum of cyclobutanone in an Ar supersonic nozzle beam with the stagnation pressure of 4 atm. The measured frequencies and tentative assignments are summarized in Table III. The fluorescence excitation spectrum of cyclobutanone vapor has been reported by Lee.¹⁰ His assignments are based on the analysis of the absorption spectrum given by Moule.⁹ Our supersonic jet spectrum is again much simpler than the corresponding room-temperature spectrum and shows no change upon varying the stagnation pressure. Therefore the bands in Fig. 5 can be considered as transitions from $v'' = 0$. The difference of peak positions between our spectrum and the previous ones is presumably due to the overlapping hot bands in the latter.

It is clearly seen that the progressions due to the $\text{C}=\text{O}$ out-of-plane wagging (ν_{19}) and the ring puckering (ν_{20}) modes are prominent in the spectrum. Apart from the "absolute" assignment (see below), the analysis of the progressions starting at $30\,270 \text{ cm}^{-1}$ is essentially the same as that of Moule⁹ based on IR spectra.²² However there are large differences in the frequencies of these two modes; we obtained the differences: $\Delta\nu(20^1 - 20^0) = 105 \text{ cm}^{-1}$ and $\Delta\nu(20^2 - 20^1) = 166 \text{ cm}^{-1}$, compared with Moule's values: 134 and 156 cm^{-1} , respectively. Similarly, $\Delta\nu(19^1 \pm - 19^0 \pm) = 369 \text{ cm}^{-1}$ and $\Delta\nu(19^2 \pm - 19^0 \pm) = 712 \text{ cm}^{-1}$, compared with Moule's 355 and 696 cm^{-1} , respectively.

The progression of ν_{19} is rather harmonic and no splitting due to inversion doubling was found. These facts indicate that the barrier height to inversion is substantial. We fitted them to a quartic-quadratic potential $V(\theta) = a\theta^4 - b\theta^2$, to get the best fit values of $a = 1.49 \times 10^{-4} \text{ cm}^{-1} \text{ deg}^{-4}$ and $b = 5.25 \times 10^{-1} \text{ cm}^{-1} \text{ deg}^{-2}$ with $\mu = 3.04 \times 10^{-24} \text{ g}$. The calculated potential and energy levels are schematically shown in Fig. 6 together with observed level spacings. The barrier height and the out-of-plane angle are $V = 1850 \pm 50 \text{ cm}^{-1}$ and $\theta_m = 42^\circ$, compared with the literature values 1550 cm^{-1} and 39° , respectively.⁹ The barriers to inversion (1850 cm^{-1} for cyclobutanone and 680 cm^{-1} for cyclopentanone) are much higher than that for formaldehyde (356.2 cm^{-1}).²³ The appreciably increased barrier in cyclobutanone indicates that the ring tension in the four-membered ring plays an important role.

We also determined the potential for the ring puckering

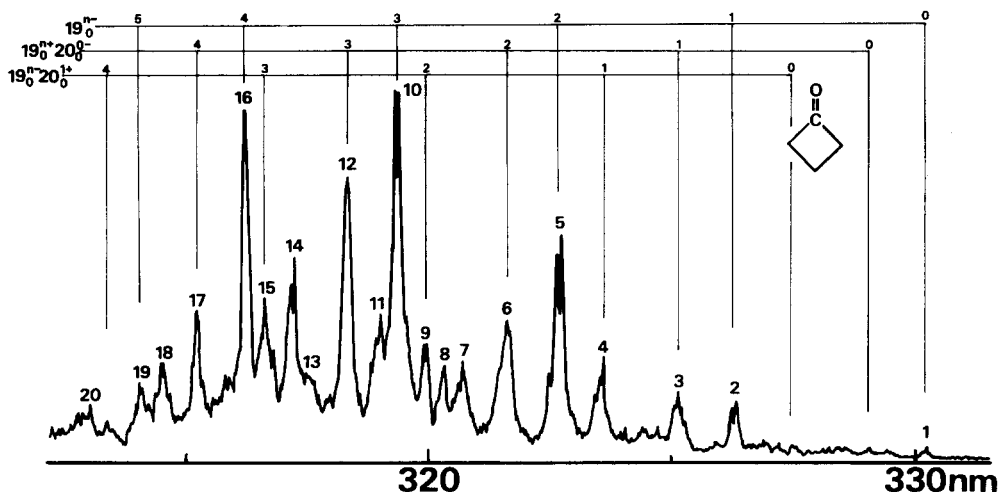


FIG. 5. Fluorescence excitation spectrum of cyclobutanone in an Ar supersonic nozzle beam with the stagnation pressures of 4 atm. The temperature of the nozzle and the sample reservoir is 100 °C.

vibration ($\nu_{20'}$) fitting the averaged energies of the combination bands with $19^0 \pm 1 \pm 2 \pm$ to the potential function similar to $\nu_{19'}$. Results are schematically shown in Fig. 7. In contrast with the single minimum potential proposed by Moule,⁹ our analysis predicts a double minimum potential with the barrier height $V = 16.9 \text{ cm}^{-1}$, compared with 7.6 cm^{-1} in the ground state.²⁴ In the Rydberg $^1B_2(n, 4s)$ state of cyclobutanone the vibrational mode of 118 cm^{-1} has been observed and assigned to ν_{20} .²⁵ This frequency, as well as the present one (105 cm^{-1}), is much larger than that of the ground state, 35.9 cm^{-1} ,²⁴ suggesting that the increase of the frequency upon electronic excitation is related to the loss of a nonbonding electron.

The observed rotational envelopes of some vibronic bands are shown in Fig. 8(a). The notations are based on the assignments shown in Fig. 5 and Table III. The calculated contours for an asymmetric top ($J \leq 23$) are shown in Fig. 8(b) for the rotational temperature of 25 K and the bandwidth of

0.2 cm^{-1} . We have used calculated rotational constants assuming the geometry determined by a microwave study²⁴ for the ground state; $A'' = 0.3598$, $B'' = 0.1603$, and $C'' = 0.1187 \text{ cm}^{-1}$, where the definition of A , B , and C is the same as that for cyclopentanone. For the excited state, we assumed rotational constants for the same geometry except for $r_{\text{C=O}} = 1.32 \text{ \AA}$ and $\theta = 40^\circ$ (the C=O out-of-plane angle); $A' = 0.3355$, $B' = 0.1626$, and $C' = 0.1233 \text{ cm}^{-1}$. Figure 8 shows that the bands 19^n- are composites of A and B types, while 19^1+20^0- and 19^1-20^1+ seem to contain an appreciable amount of C character.

A microwave study has shown that the molecule is planar with C_{2v} symmetry in its ground state.¹⁵ The $A_2 \leftarrow A_1$ transition is then rigorously forbidden with the intensity of vibronic bands attributed entirely to vibronic coupling. The assignments given in Fig. 5 seem to be reasonable in view of the vibronic activity of $\nu_{19'}$, which is spatially close to the C=O group, and of $\nu_{20'}$, which is strongly coupled with $\nu_{19'}$. However this assignment is based on the activity of the b_1 vibrations ($\nu_{19'}$ and $\nu_{20'}$) so that the resultant vibronic bands are all of B type. This brings about some difficulty in ac-

TABLE III. Vibrational analysis of cyclobutanone.

Number ^a	Wave number	Δ / cm^{-1}	Assignment ^b
1	30 270	0	19^0-
2	30 639	369	19^1-
3	30 744	474	19^1+20^0-
4	30 899	629	19^1-20^1+
5	30 892	712	19^2-
6	31 087	817	19^2+20^0-
7	31 174	904	
8	31 212	942	
9	31 249	979	19^2-20^1+
10	31 307	1037	19^3-
11	31 339	1069	
12	31 408	1138	19^3+20^0-
13	31 482	1212	
14	31 518	1248	$3^1 19^0-$
15	31 577	1306	19^3-20^1+
16	31 616	1346	19^4-
17	31 720	1450	19^4+20^0-
18	31 789	1519	
19	31 835	1565	19^5-
20	31 951	1681	

^a See Fig. 5.

^b See footnote b to Table II. A tentative assignment is given assuming the $30\,270 \text{ cm}^{-1}$ band is close to the true origin; see the text for details.

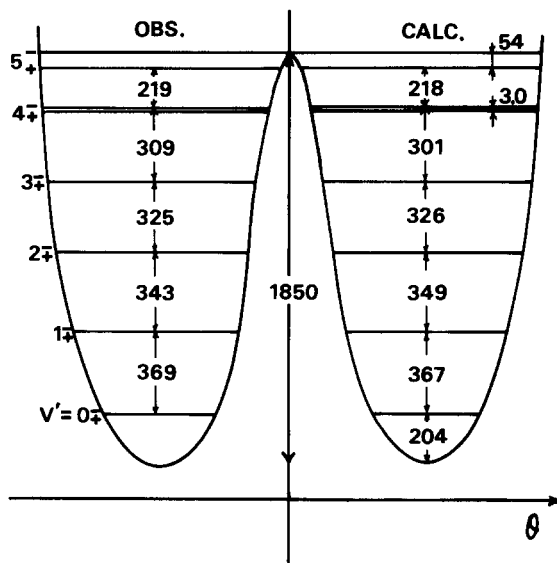


FIG. 6. Observed and calculated energy levels of the C=O out-of-plane wagging ($\nu_{19'}$) vibration in the S_1 state of cyclobutanone.

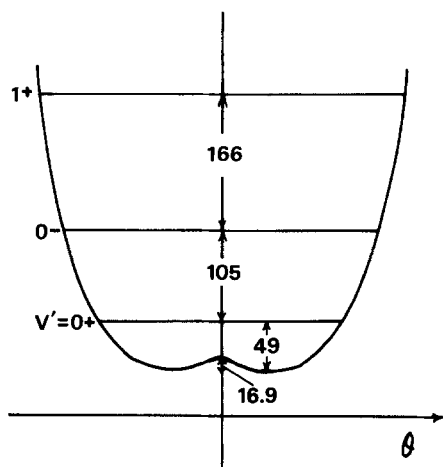


FIG. 7. Energy levels of the ring puckering ($\nu_{20'}$) vibration of cyclobutanone in the S_1 state.

counting for the observed rotational envelopes. One could overcome this difficulty by assuming a b_2 vibration to be active. If we assume that the frequency of the C=O in-plane deformation ($\nu_{27'}$) is $\sim 340 \text{ cm}^{-1}$ (the corresponding frequency in the ground state is 454 cm^{-1} ²⁰), there should be the type-C progressions $27_0^1 19_0^+$, $27_0^1 19_0^- 20_0^0$, and $27_0^1 19_0^+ 20_0^1$ starting at $30\,610 \text{ cm}^{-1}$ ($= 30\,270 + 340$). Similarly type-A progressions could be expected to arise from second order intensity borrowing in which $\nu_{27'}$ and $\nu_{19'}$ are active. Therefore the type A series, $27_0^1 19_0^-$, $27_0^1 19_0^+ 20_0^0$, and $27_0^1 19_0^- 20_0^1$ also start at $30\,610 \text{ cm}^{-1}$ completely degenerate with the type-C progressions. However, this model does not completely explain the observed rotational contours; the bands 19_0^- (type B) should not degenerate completely with type-C and type-A series because of the anharmonicity in $\nu_{19'}$, whereas no indication of splitting of the overlapping bands is observed for 19_0^- ($n = 0, 1, 2$).

The second possibility to explain the observed band shape is to assume an active a_2 vibration. The $\alpha\text{-CH}_2$ rocking $\nu_{13'}$ is the most probable candidate since this is the a_2 mode nearest to the C=O group and has the lowest frequency (902 cm^{-1}) in the ground state.²² If the mode is not of double-

minimum character, it is necessary to take the $30\,240 \text{ cm}^{-1}$ band to be a pseudo origin where the progression $13_0^1 19_0^+$ starts and to assume the true origin at some 1000 cm^{-1} lower energy. This is what is assumed by Moule.⁹ In this assignment, two sets of progressions are predicted, starting at the pseudo origin at $30\,270 \text{ cm}^{-1}$; namely, $13_0^1 19_0^+$, $13_0^1 19_0^- 20_0^0$, and $13_0^1 19_0^+ 20_0^1$, which give rise to the A-type bands, and $13_0^1 19_0^-$, $13_0^1 19_0^+ 20_0^0$, and $13_0^1 19_0^- 20_0^1$, which are induced by the second order interaction in which the a_2 and b_1 modes are active and give rise to C-type bands. The difficulty in this assignment is that the 19_0^- , $19_0^+ 20_0^0$, and $19_0^- 20_0^1$ series were not observed in the lower energy region than $30\,270 \text{ cm}^{-1}$. This should be observed as B-type progressions. Hence this assignment can hardly explain the B character of the observed rotational contours.

The third possibility is to take the $30\,270 \text{ cm}^{-1}$ band as the true origin and to assume the a_2 mode also has a double minimum character. Under this assumption, the situation is similar to cyclopentanone and the type-A progressions, 13_0^0 , 19_0^+ , $13_0^0 19_0^- 20_0^0$ and $13_0^0 19_0^+ 20_0^1$, and the type B progressions, $13_0^0 19_0^-$, $13_0^0 19_0^+ 20_0^0$, and $13_0^0 19_0^- 20_0^1$, are expected to be nearly degenerate. The second order interaction (both the b_1 and a_2 modes are active) also results in the C-type progressions, $13_0^0 19_0^-$, $13_0^0 19_0^+ 20_0^0$, and $13_0^0 19_0^- 20_0^1$. This scheme seems to be the most attractive one in view of the present experimental results. It also accounts for the phosphorescence polarization experiment¹² which shows the transitions to be predominantly of A type with a minor contribution from the other components. A difficulty lies, however, in assuming a double minimum potential in the $\alpha\text{-CH}_2$ antisymmetric rocking mode ($\nu_{13'}$). It is unfortunate that the intensity borrowing mechanism cannot be determined uniquely from these discussions. A search for the true origin in the lower energy region and a higher resolution study of the rotational band structure would clarify this point.

SUMMARY

In the fluorescence excitation spectra of the $S_1(n, \pi^*)$ states of cyclobutanone, the active vibrational modes are shown to be the C=O out-of-plane wagging, the ring twisting, and the ring flapping. The activity of these modes may be related to pyramidal distortion of the molecule in the excited state. The observed vibronic structure is unambiguously analyzed on the basis of the double minimum character of these modes, assuming local C_{2v} symmetry. The assignments rationalize the rotational band types. The functional form of the potentials for these modes have been determined with reasonable accuracy. Although the absolute assignment for cyclobutanone is still questionable, the frequencies and the potential curves for the C=O wagging and ring puckering modes were determined unambiguously by analyzing the relative energies in the progression bands of these modes.

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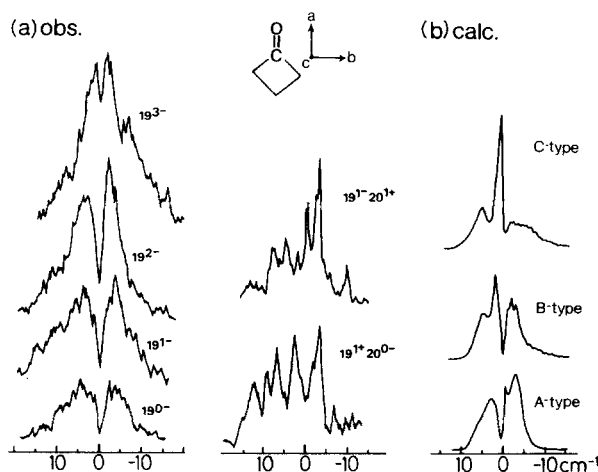


FIG. 8. (a) Observed and (b) calculated rotational envelopes of vibronic bands of cyclobutanone. See the text for details.

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