

# The Vibrational Spectra of Cyclopropenone and Cyclopropenone- $d_2$ <sup>1</sup>

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**Abstract:** Pure cyclopropenone and cyclopropenone- $d_2$  have been prepared and their vibrational spectra obtained for the first time. Complete infrared and Raman data are given for the solid and liquid phases, and partial infrared data for the vapor. The spectra are strongly influenced by the physical state of the sample. Assignments are made for all the fundamentals of both molecules except for the one  $a_2$  mode. They are based on Raman polarizations, a few infrared band contours, and the Teller-Redlich product rule. They are believed to be reliable. The most interesting feature of the spectra is the appearance of the "C=C stretching mode" at an extremely low frequency, 1483  $\text{cm}^{-1}$  in cyclopropenone and 1409  $\text{cm}^{-1}$  in cyclopropenone- $d_2$ . This is the lowest C=C stretch of which we know. It is in sharp contrast with disubstituted cyclopropenones, all of which have a strong band near 1650  $\text{cm}^{-1}$ .

Cyclopropenone (Figure 1a) is of considerable interest because of its remarkable structure. It was first prepared (in solution only) by Breslow and Ryan.<sup>2a</sup> In 1972 Breslow and Oda isolated pure cyclopropenone.<sup>2b</sup> An excellent microwave study by Flygare and coworkers<sup>3</sup> has established beyond doubt that the structure is that represented in Figure 1a. They found  $r(\text{C}=\text{C})$  to be 1.302 Å, in close agreement with the cyclopropene value of 1.300 Å.<sup>4</sup> The  $r(\text{C}=\text{O})$  distance is 1.212 Å, which is in the normal range for ketones and aldehydes of  $1.215 \pm 0.005$  Å.<sup>5</sup> However, the  $r(\text{C}-\text{C})$  distance of 1.412 Å is considerably shorter than that for cyclopropene (1.515 Å) and cyclopropane (1.524 Å). This implies substantial conjugation between the carbonyl and olefinic bonds.

Cyclopropenone is a colorless liquid, mp  $-28^\circ$ . At Dry Ice temperature and in the absence of air it is stable for many months, but at room temperature it polymerizes noticeably within an hour. In solution in organic solvents at room temperature it is much more stable, especially if the solvent is polar.

The existence of this highly strained small ring compound with reasonable stability is surprising. The three-membered ring restricts the internal ring angles to an average of  $60^\circ$ , whereas for a normal  $sp^2$  carbon atom these angles would be expected to be  $120^\circ$ . We cannot think of a molecule which has a higher amount of bond angle strain than cyclopropenone. Another remarkable property is its vapor pressure, which is only 0.45 Torr at  $30^\circ\text{C}$ .<sup>2b</sup> This is surprisingly low for a molecule with a molecular weight of only 54 and with no obvious possibilities for strong hydrogen bonding. (Acetone, for example, has 280 Torr at  $30^\circ$ .) It must be due to its exceptionally large dipole moment of 4.39 D,<sup>3</sup> and is further evidence for substantial conjugation.

Naturally these unusual properties give cyclopropenone considerable theoretical interest. There has been discussion, for example, about the importance of the dipolar, pseudoaromatic form represented in Figure 1b. The photoelectron and electron impact spectra have recently been reported.<sup>6</sup> They provide evidence for "an unusually large interaction between both the  $\pi$  and lone pair orbitals on the carbonyl portion of the molecule with the  $\pi$  and  $\sigma$  orbitals of the olefin portion." This, of course, must be the cause of the unexpected stability of the molecule.

One of the physical properties which should be investigated is the vibrational spectrum. The only infrared data which have been reported are two bands in the carbonyl region for each of four isotopic molecules.<sup>7a</sup> There are no Raman results. We have therefore prepared both cyclopropenone and cyclopropenone- $d_2$  and obtained their infrared

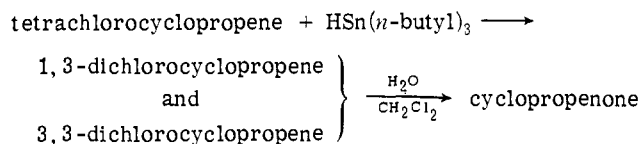
and Raman spectra in both the solid and liquid states. There are also limited gas-phase infrared results for both molecules.

For the sake of brevity, cyclopropenone and cyclopropenone- $d_2$  will hereafter be referred to as  $d_0$  and  $d_2$ , respectively.

The most interesting finding is that there is no "C=C stretching" band at 1600–1660  $\text{cm}^{-1}$ . Instead it is at the abnormally low value of 1483  $\text{cm}^{-1}$  in  $d_0$  and 1409  $\text{cm}^{-1}$  in  $d_2$ . This is in sharp contrast to the findings for several disubstituted cyclopropenones, and will be discussed later.

## Experimental Section

**1. Preparation of Cyclopropenone.** The method of Breslow and Oda<sup>2b</sup> was followed. The reaction sequence was



The tri- $n$ -butyltin hydride was prepared by treating tri- $n$ -butyltin chloride with lithium aluminum hydride as described by van der Kerk, *et al.*<sup>8</sup> The crude cyclopropenone reaction product was vacuum distilled and then further purified by recrystallization from dry ether at  $-78^\circ$  under argon as described by Breslow and Oda. The progress of the purification was followed by noting changes in the infrared and Raman spectra. Attempts to purify the sample by vacuum transfers at various temperatures were ineffective because of the similar volatility of the compound and of troublesome impurities.

The sample was identified as authentic cyclopropenone by agreement of the melting point, vapor pressure, nmr spectrum, and mass spectrum with reported values.<sup>2</sup>

**2. Preparation of Cyclopropenone- $d_2$ .** This was accomplished with a high percentage of deuteration by using lithium aluminum deuteride to give  $\text{DSn}(n\text{-butyl})_3$ , and then using this in the above reaction sequence as was first done by Breslow, Ryan, and Groves.<sup>7</sup> The spectra of the product gave no obvious evidence of incomplete deuteration.

**3. Infrared Spectra.** These were obtained from 400 to 4000  $\text{cm}^{-1}$  on a Beckman IR-12 spectrophotometer. The frequency scale was calibrated with standard reference bands at or near the time the spectra were run.<sup>9</sup> Frequencies are believed to be accurate to better than  $\pm 1$   $\text{cm}^{-1}$  throughout except for weak or broad bands. The cell windows and cold plates were of KBr.

Solid samples were examined at about 100°K by condensing the gas onto a window cooled with liquid nitrogen in a cold cell of conventional design.<sup>10</sup> Liquid spectra were obtained by placing a drop of the liquid between KBr plates in an argon atmosphere, wrapping the edges of the plates with "Parafilm," and running the spectrum immediately. The liquid decomposed noticeably in 20–40 min in

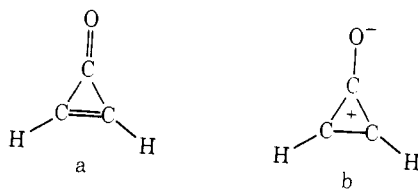


Figure 1. (a) Cyclopropenone; (b) possible dipolar form.

the instrument to a brown, highly insoluble polymer, so several fresh preparations were used to cover the complete spectrum. The decomposition was more rapid with impure samples. Time-dependence studies of the spectrum helped to distinguish between sample and polymer bands.

Gas-phase spectra were obtained in a 10-cm cell at the vapor pressure of the sample, about 0.4 Torr. The only bands clearly evident were in the region of 1700–2000  $\text{cm}^{-1}$ . An attempt was made to use a 10 m folded path gas cell, but the sample disappeared too rapidly to give a useable spectrum. The rate of disappearance could easily be monitored. Polymer bands did not appear in the spectrum, so we believe that the sample was adsorbed or polymerized on the inside metal surface of the cell rather than on the windows and mirrors.

Later, when the need for band contours became urgent, the gas was examined on a Digilab FTS-14 interferometer through the courtesy of Dr. G. L. Carlson of Mellon Institute, Carnegie-Mellon University. A 20-cm glass-walled cell was used, and scans were made at 0.5- and 1.0- $\text{cm}^{-1}$  resolution. The intensity scale was expanded to enhance weak features. Only one new gas-phase band was found with certainty in each compound: at 742  $\text{cm}^{-1}$  in  $d_0$  and at 679  $\text{cm}^{-1}$  in  $d_2$ . Both are clearly type C bands; in fact all that was observed was the sharp, needle-like Q branch. Although these results were limited, they proved to be important.

**4. Raman Spectra.** Raman spectra were obtained with a Spex Ramalog instrument which has been described elsewhere.<sup>11</sup> The source was a Spectra Physics Model 164 argon ion laser. Both the 4880- and 5145-Å lines were used, with powers of 200–300 mW at the sample. At these power levels there was no problem with sample decomposition. The frequency scale was calibrated with discharge lines of argon and krypton<sup>12</sup> at or near the time the sample spectra were recorded. Raman frequencies are believed to be accurate to  $\pm 2 \text{ cm}^{-1}$  for all but weak or broad bands.

The Raman samples were vacuum transferred into thin-walled Pyrex capillaries and sealed *in vacuo*. All Raman spectra were obtained at reduced temperatures in a cold cell which has been described previously.<sup>13</sup> The liquid samples were run at approximately  $-10^\circ$ , and the solids from  $-35$  to  $-100^\circ$ .

**5. Nmr and Mass Spectra.** Nmr spectra were run in  $\text{D}_2\text{O}$  solution on a Varian A-60 spectrometer, using acetone as an internal

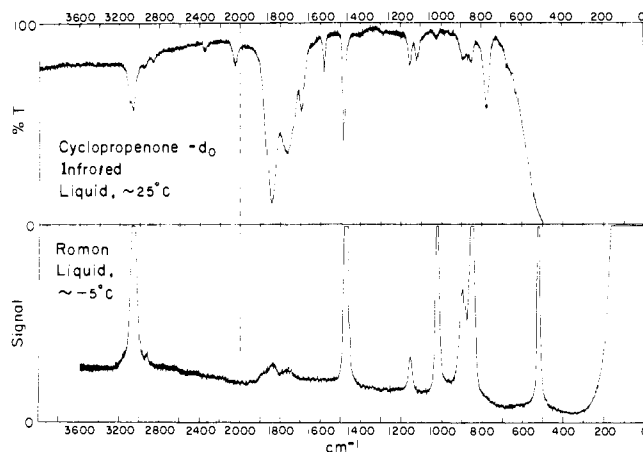


Figure 2. Infrared and Raman spectra of liquid cyclopropenone- $d_0$ . For this particular infrared experiment, NaCl windows were used.

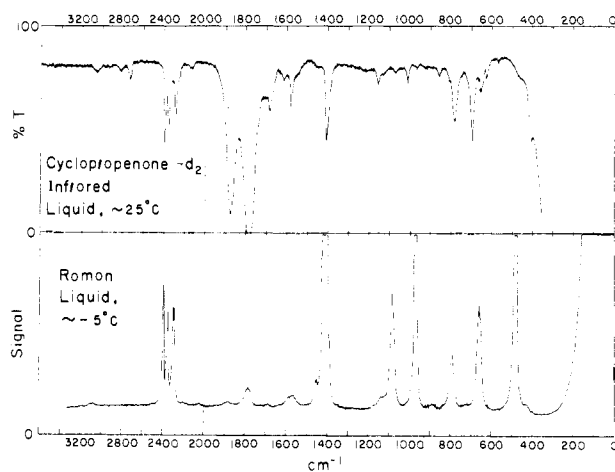


Figure 3. Infrared and Raman spectra of liquid cyclopropenone- $d_2$ .

standard. The mass spectra were obtained on an LKB 9000 mass spectrometer. The sample was introduced as a gas, with the inlet system at room temperature to minimize thermal decomposition.

## Results

The measured frequencies, together with our assignments, are given in Tables I and II for  $d_0$  and  $d_2$ , respectively. Table III gives the vapor-phase data for both compounds. The spectra are shown in Figures 2–6.

Table I. Raman and Infrared Spectra ( $\text{cm}^{-1}$ ) of Cyclopropenone- $d_0$ <sup>a</sup>

Solid	Raman			Infrared			Assignment
	Liquid	Liquid	$\rho$	Solid	Liquid (25°)	Int	
	Int <sup>b</sup>						
529	528	230	0.77	500	493	m	$\nu_3$
				536	531	w	$\nu_{12}$
				788	788 <sup>d</sup>	s	$\nu_7$
871	855	240	0.47	886	851	m	$\nu_5$
911	~900 <sup>e</sup>	50	0.80	904	892	m, b	$\nu_{11}$
1043	1026	180	0.04	1046	1025	w, b	$\nu_4$
1180	1163	27, b		1178	1160	m	$\nu_{10}$
1450	1460	10, sh					?
1467	1480	1000	0.04	1467	1485	s	$\nu_3$
1760	1770	5, b		1774	1770	s, b	$2 \times 892 = 1784$
				(1786)	(1792) <sup>e</sup>	s	Imp
	1840	10, b		1856	1840 <sup>f</sup>	vs	$\nu_2$
	2950	5					$2 \times 1480 = 2960$
3065	3069	80, sh	dp ?	3062	3068	s	$\nu_{11}$
3094	3100	160, b	0.17	3088	3096	s	$\nu_1$

<sup>a</sup> w, m, s = weak, medium, strong; v = very; b = broad; ~ = approximate; sh = shoulder; dp = depolarized; Imp = impurity; FR = Fermi resonance;  $\rho$  = depolarization ratio. For depolarized lines,  $\rho = 0.75 \pm 0.05$ . <sup>b</sup> Peak intensity for liquid on a scale of 1–1000, uncorrected for instrument response. <sup>c</sup> 900  $\text{cm}^{-1}$ . Raman value not measured accurately. <sup>d</sup> 752  $\text{cm}^{-1}$  in gas. Type C band. <sup>e</sup> 1792  $\text{cm}^{-1}$ . See text concerning impurity. <sup>f</sup> 1840  $\text{cm}^{-1}$ . See Figure 6 for gas values.

**Table II.** Raman and Infrared Spectra ( $\text{cm}^{-1}$ ) of Cyclopropenone- $d_2$ 

Raman				Infrared			Assignment
Solid		Liquid Int <sup>a</sup>	$\rho$	Solid	Liquid (25°)	Int	
				418	409	w	$\nu_8$
478	478	400	0.76				$\nu_{12}$
500		vw		486		m	$\nu_{12}?$
							?
				570	570	vw	?
					651	w, sh	?
670	656	130	0.63	669	658	m	$\nu_5$
				697	697 <sup>b</sup>	s	$\nu_7$
795	788	65	0.79	791	786	s	$\nu_{11}$
971	967	1000	0.07	971	969	w	$\nu_1$
990		vw, sh					?
1090	1078	130	0.80	1088	1074	w, b	$\nu_{10}$
	1130	6, b					$478 + 657 = 1135$
				1150	1158	w	?
				1240		m, b	?
				1270		m, b	$486 + 793 = 1279$
1380		vw, sh		1375		vw	?
1396	1409	950	0.02	1395	1409	s	$\nu_3$
1410		w, sh		1406		w	
1430	1440	13					$478 + 967 = 1445$
1445							$657 + 787 = 1444$
1580	1582	11, b		1589	1580	m	Imp
				1627		vw, b	
				1701	1685	m	Imp
				1740		vw, sh	
1760	1780	19, b	0.80	1776	1780 <sup>c</sup>	vs	$\nu_2$
	1880	4, b		1887	1878	vs	$478 + 1409 = 1887$
				2180		w	$2 \times 1089 = 2178$
2291	2292	90	0.77	2289	2288	s	$\nu_3$
2355	2350	70	0.06	2342	2355	m	$967 + 1409 = 2376$ in FR <sup>d</sup> with $\nu_1$
2388	2392	130	0.08	2385	2392	s	
				2622		w, b	
				2730	2730	m	
				2850	2820	vw	
				2919		vvw	
	3100	vvw, b		3079	3050	vw, b	$697 + 2392 = 3089$
							$787 + 2280 = 3067$

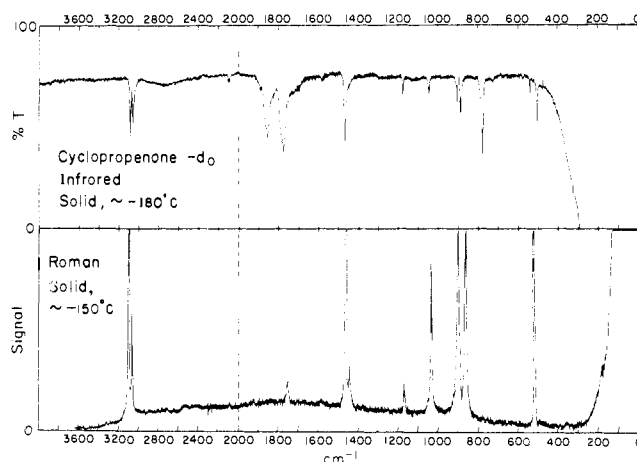
<sup>a</sup> See Table I, footnote b. <sup>b</sup> 679  $\text{cm}^{-1}$  in gas. Type C band. <sup>c</sup> 1886  $\text{cm}^{-1}$  in gas. Type A band. <sup>d</sup> Table I, footnote a.

**Table III.** Gas-Phase Infrared Bands ( $\text{cm}^{-1}$ ) of Cyclopropenone- $d_0$  and - $d_2$ 

	Band type	Assignment
Cyclopropenone- $d_0$		
742	C	$\nu_7(b_1)$
1840	C	?
~1855	A	?
1859		
~1866	A	$\nu_2(a_1)$
~1866		
1883	A	$\nu_2(a_1)$
1890		
1959	B	?
(1967) min.		
~1976		
Cyclopropenone- $d_2$		
679	C	$\nu_7(b_1)$
~1738	B	$787 + 968 = 1755^a$
(~1747) min.		
~1758		
1874	A	$\nu_2(a_1)$
1886		
1898		

<sup>a</sup> Liquid-state frequencies.

The bands attributed to impurities in the tables are only the ones which were most difficult to remove. Other impurity bands were evident in the Raman spectrum of  $d_0$  at 400, 460, 642, 678, 768, 1129, 1392, 1587, 1635, and 1698  $\text{cm}^{-1}$ . It was possible, after careful purification, to obtain spectra in which all the above bands were absent. In the in-

**Figure 4.** Infrared and Raman spectra of solid cyclopropenone- $d_0$ .

frared spectrum of  $d_0$  the impurity bands at 1587 and 1698  $\text{cm}^{-1}$  were clearly evident and difficult to remove completely. It also appears that in the infrared spectrum there is an impurity band at approximately 1790  $\text{cm}^{-1}$  which overlaps the sample absorption at 1770  $\text{cm}^{-1}$ . Two bands were not actually resolved in this region, but as the sample was purified the peak absorption in this region shifted from about 1790 to about 1770  $\text{cm}^{-1}$  in the sample of best purity.

Similarly in  $d_2$  several weak bands due to impurities were eliminated on purification. The most bothersome of these occurred at 861, 1585, and 1685  $\text{cm}^{-1}$ .

In the solid state, annealing of the sample in the infrared

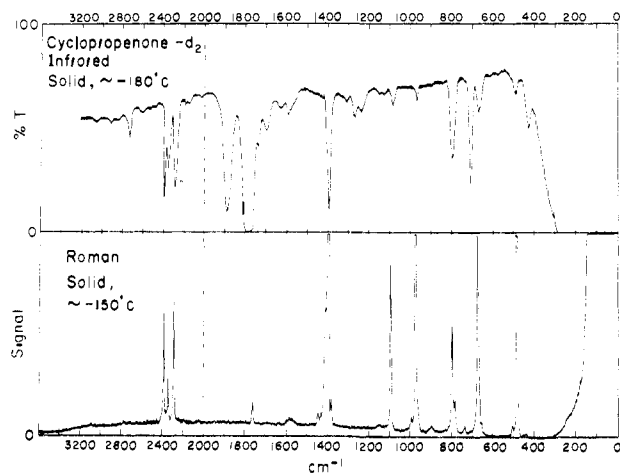


Figure 5. Infrared and Raman spectra of solid cyclopropanone- $d_2$ .

cold cell had a marked influence on the positions, shapes, and relative intensities of some of the infrared bands. The tabulated frequencies are for annealed samples. This complication was far less bothersome in the Raman spectrum, probably because the solid was prepared by much slower cooling of a liquid rather than by deposition of the vapor onto a cold plate held near  $100^\circ\text{K}$ .

The measured infrared and Raman frequencies for the same transition in the same physical state should agree within  $\pm 3\text{ cm}^{-1}$  if our estimates of the experimental errors are correct. For several bands this criterion is not met. It does not bother us if the discrepancies are for the solid, because the differences may be due to annealing problems. However, even for the liquid state there are three bands in both  $d_0$  and  $d_2$  with discrepancies of 4 or  $5\text{ cm}^{-1}$ . This occurred even though both instruments were calibrated at the time the spectra were being run. After noting these differences the spectra were rerun, and the results verified. The reason for these discrepancies is unknown, but we believe that they are due to the sample and not to the instruments because we have not had such a problem with any other sample either before or since this work.

### Assignments

Table IV summarizes the symmetries, selection rules, band contours, schematic descriptions, and assignments of the normal vibrations. The molecular symmetry was assumed to be  $C_{2v}$  as found in the microwave study by Flygare and coworkers.<sup>3</sup> Our spectroscopic results are completely compatible with it. The normal modes of cyclopropanone then have the symmetry classification  $5a_1 + 1a_2 +$

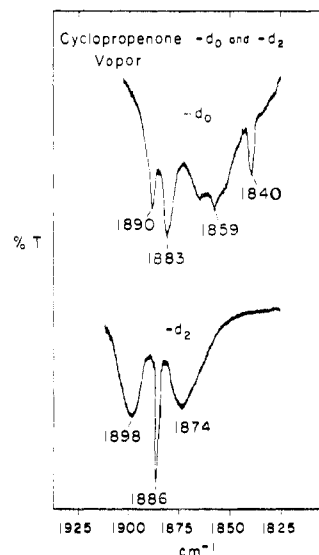


Figure 6. Infrared spectrum of cyclopropanone- $d_0$  and - $d_2$  vapor,  $1825\text{--}1925\text{ cm}^{-1}$ .

$2b_1 + 4b_2$ . All are allowed in the Raman spectrum, and all but the one  $a_2$  mode are allowed in the infrared. In discussing the assignments we shall use liquid state frequencies, taking the average of the infrared and Raman values unless there is an obvious reason for doing otherwise; e.g., in one of the two spectra the band is broad, weak, or overlapped.

The accurate values of the moments of inertia<sup>3</sup> were used to calculate the Teller-Redlich product rule ratios<sup>14a</sup> and the P-R separations of the gas-phase infrared bands.<sup>15</sup> The results are given in Table V. Type A infrared bands will have distinct P, Q, and R branches, type B bands will have no Q branch, and for type C bands the Q branch will be the dominant feature and the P and R branches will be very weak (ref 16, case 7).

**1.  $a_1$  Modes.** The five  $a_1$  fundamentals are assigned at  $3098, 1840, 1483, 1026,$  and  $853\text{ cm}^{-1}$  for  $d_0$  and at  $[2370], 1780, 1409, 968,$  and  $657\text{ cm}^{-1}$  for  $d_2$ . All are polarized in the Raman spectrum except  $1840$  and  $1780\text{ cm}^{-1}$  and are identified with certainty. The two exceptions are too weak for an accurate determination of their depolarization ratio, but the frequency region and the high infrared intensity surely establish them as  $a_1$  fundamentals. The very low Raman intensity is noteworthy. For the  $1840\text{-cm}^{-1}$  band of  $d_0$  this, together with the occurrence of broad, troublesome impurity bands in this region, made the detection of this Raman band difficult. It was only after careful purification that it was possible to conclusively locate it.

Table IV. Assignments of the Fundamentals for Cyclopropanone- $d_0$  and - $d_2$

$C_{2v}$ species	Activity	No.	Schematic description	Assignments					
				Liquid <sup>a</sup>		Solid <sup>b</sup>		Gas	
				$d_0$	$d_2$	$d_0$	$d_2$	$d_0$	$d_2$
$a_1$	R(p), ir (Type A)	1	C—H stretch	3098	[2370] <sup>c</sup>	3094	[2370] <sup>c</sup>		
		2	C=O stretch	1840	1780	1856	1776	1883	1886
		3	C=C stretch	1483	1409	1467	1396		
		4	C—C stretch	1026	968	1043	971		
		5	C—H wag in-plane	853	657	871	670		
$a_2$	R(dp)	6	C—H wag out-of-plane						
$b_1$	R(dp), ir (Type C)	7	C—H wag out-of-plane	788	697	788	697	742	679
		8	C=O wag out-of-plane	493	409	500	418		
$b_2$	R(dp), ir (Type B)	9	C—H stretch	3068	2290	3065	2291		
		10	C—C stretch	1161	1078	1180	1090		
		11	C—H wag in plane	892	787	911	795		
		12	C=O wag in plane	529	478	529	478		

<sup>a</sup> Average of Raman and infrared values where both observed. <sup>b</sup> Raman values where observed. <sup>c</sup> Fermi resonance between  $\nu_1$  and  $1409 + 967 = 2376\text{ cm}^{-1}$  (see text).

**Table V.** (a) Theoretical *vs.* Observed Product Rule Ratios and (b) Calculated PR Separations for Infrared Bands

		(a)	
Species		$\tau_{\text{theor}}$	$\tau_{\text{obsd}}$
$a_1$		1.964	1.951
$a_2$		1.238	
$b_1$		1.337	1.363
$b_2$		1.853	1.810

		(b)	
Band type	Species	$-\Delta\nu(\text{PR}), \text{cm}^{-1}$	
		$d_0$	$d_2$
A	$a_1$	23.5	22.5
B	$b_2$	19.6	18.7
C	$b_1$	35.3	33.8

**a.  $\nu_1$  (C-H Stretch).** The  $a_1$  C-H stretch in  $d_0$  is easily assigned to the band at  $3098 \text{ cm}^{-1}$ . In  $d_2$  there are two polarized bands of good intensity in the C-D stretching region, 2352 and  $2392 \text{ cm}^{-1}$ . They are reasonably explained by Fermi resonance between the  $a_1$  C-D stretch and the combination of two strong polarized Raman bands  $1409 + 968 = 2377 \text{ cm}^{-1}$ . The unperturbed C-D stretch is then estimated to be about  $2370 \text{ cm}^{-1}$ .

**b.  $\nu_2$  ("C=O Stretch").** The next lower mode,  $\nu_2$ , will be termed the "carbonyl stretch" for convenience. (It is emphasized that these schematic names are useful for purposes of discussion but are not necessarily realistic. A later paper will deal with the actual form of these vibrations.<sup>17</sup>) Candidates for  $\nu_2$  in liquid  $d_0$  are the bands at 1840 and  $1770 \text{ cm}^{-1}$ , and in  $d_2$  the ones at 1879 and  $1780 \text{ cm}^{-1}$ . The  $d_2$  band at 1879 can be eliminated because it is higher than either band in  $d_0$ . Similarly the  $d_0$  band at 1770 can probably be eliminated because it is lower than either band in  $d_2$ . This means that  $\nu_2$  in  $d_0$  is 1840, and in  $d_2$  it is  $1780 \text{ cm}^{-1}$ . This is confirmed by the infrared intensities, because these bands are the stronger of the two in each molecule.

The next question is how to explain the second strong infrared band in this region. We believe that it cannot be the C=C stretch; that must be below  $1500 \text{ cm}^{-1}$  for reasons to be discussed shortly. Therefore  $1770 \text{ cm}^{-1}$  in  $d_0$  and  $1879 \text{ cm}^{-1}$  in  $d_2$  must be combination tones. It was our original expectation that their considerable intensity is due to Fermi resonance with the fundamental, but we have been unable to make a reasonable case for it. It is suggested that 1770 is the overtone of  $892 \text{ cm}^{-1}$  ( $2 \times 892 = 1784$ ). Although this has  $a_1$  symmetry, it is rather far from  $\nu_2$  at 1840, and Fermi resonance is therefore questionable. In view of this the intensity of the overtone is remarkably large. The  $1879\text{-cm}^{-1}$  band of  $d_2$  is explained as the sum tone  $1409 + 478 = 1887 \text{ cm}^{-1}$ . This requires that 1879 is not  $a_1$ , so no Fermi resonance is possible between 1879 and  $1780 \text{ cm}^{-1}$ . Therefore the large intensity of the sum tone is also remarkable.

It was hoped that the gas-phase infrared spectrum would provide further aid in assigning  $\nu_2$ . Figure 6 shows the bands observed for the gas in this region. In  $d_2$  there is a band at  $1886 \text{ cm}^{-1}$  with the well-defined P-Q-R structure of a Type A band. The observed PR separation is  $24 \text{ cm}^{-1}$ , in adequate agreement with our calculated value of  $22.5 \text{ cm}^{-1}$  (Table V). This is surely an  $a_1$  fundamental. Note that the band has shifted from 1780 in the liquid to 1886 in the gas, an upward shift of  $106 \text{ cm}^{-1}$ , which is unusually large. The gas spectrum of  $d_0$  is more complicated. There appear to be two or three overlapping bands. Our guess is that there are three, with Q branches at 1883, 1859, and  $1840 \text{ cm}^{-1}$ . The 1883 band is slightly more intense than the others. We believe that 1883 is the gas-phase value of  $\nu_2$ . It is unfortunate that the gas-phase values of the lower fundamentals are not known. The combination  $1026 + 853 =$

$1879 \text{ cm}^{-1}$  (liquid values) falls in this region, has  $a_1$  symmetry, and therefore may be in Fermi resonance with  $\nu_2$ . It may account for one of the other components. We have no suggestion to make for the third band, if there is one.

Note that if  $\nu_2$  in the gas phase is  $1883 \text{ cm}^{-1}$  in  $d_0$  and  $1886 \text{ cm}^{-1}$  in  $d_2$ , there is a small upward shift on deuteration. We do not know how to explain this, for it appears that there is no mechanism which could have forced 1883 down nor 1886 up from an unperturbed value.

Another awkward feature is that the shift of frequency between gas and liquid is very different for the two molecules, being  $1883 - 1840 = 43 \text{ cm}^{-1}$  for  $d_0$  and  $1886 - 1780 = 106 \text{ cm}^{-1}$  for  $d_2$ . We have no explanation for this difference.

**c.  $\nu_3$  ("C=C Stretch").** This mode is expected somewhere in the (generous) range  $1500\text{--}1750 \text{ cm}^{-1}$ . To our great surprise there is nothing significant in either  $d_0$  or  $d_2$  in this range. The next lower frequency is at  $1483 \text{ cm}^{-1}$  in  $d_0$  and at  $1409 \text{ cm}^{-1}$  in  $d_2$ . In the Raman spectra both are highly polarized, and are the first or second most intense bands. They are also strong in the infrared. We shall for convenience call them the "C=C stretch." They fit this designation in that the C=C stretch is usually intense in the Raman spectrum, and the deuteration shift of  $72 \text{ cm}^{-1}$  is comparable to the shift of  $84 \text{ cm}^{-1}$  observed in cyclopropene.<sup>18</sup> However, 1483 and  $1409 \text{ cm}^{-1}$  are remarkably low in comparison with other compounds. Typical C=C stretches occur between  $1620$  and  $1680 \text{ cm}^{-1}$ .<sup>19</sup> It is  $1656 \text{ cm}^{-1}$  in cyclopropene and  $1572 \text{ cm}^{-1}$  in cyclopropene-1,2- $d_2$ .<sup>18</sup> The lowest values of which we are aware are  $1512 \text{ cm}^{-1}$  in 3,3-dichlorocyclopropene- $d_2$ <sup>7b</sup> and  $1515 \text{ cm}^{-1}$  in ethylene- $d_4$ .<sup>14b</sup>

Other possible assignments for the  $1483\text{-cm}^{-1}$  band of  $d_0$  are the  $a_1$  C-H in-plane bend and the  $a_1$  C-C stretch. The C-H bend can be eliminated because it would have a much larger shift on deuteration than from 1483 to 1409. For the C-C stretch, we believe that  $1026$  and  $968 \text{ cm}^{-1}$  are much more acceptable choices. The  $1483\text{-}$  and  $1409\text{-cm}^{-1}$  bands *must* be fundamentals, and  $\nu_3$  seems to be the clear choice. The matter of the schematic description will have to be considered further.

We conclude that 1483 is the C=C stretch. However, it is clearly not a conventional one. This is the most unusual and interesting feature of the entire spectrum, and it will be discussed more later.

**d.  $\nu_4$  and  $\nu_5$ .** These are easily assigned to the two remaining polarized bands in each molecule:  $1026$  and  $853 \text{ cm}^{-1}$  in  $d_0$  and  $968$  and  $657 \text{ cm}^{-1}$  in  $d_2$ . On the basis of isotope shifts the  $1026\text{--}968$  pair must be the C-C stretch, and the  $853\text{--}657$  pair the C-H deformation.

**e. Product Rule.** The theoretical and observed Teller-Redlich product rule ratios for each of the species are given in Table V. We have used the reciprocal of Herzberg's equation<sup>14a</sup> in order to make the ratios greater than one. The observed ratios should therefore be slightly smaller than the theoretical ones because of anharmonicity. Liquid state frequencies were employed. The good agreement for  $a_1$  supports the assignments.

**2.  $a_2$  Mode.** This species contains only one vibration, an out-of-plane C-H wag, which is only Raman active. In cyclopropene the analogous band was assigned to  $920 \text{ cm}^{-1}$ .<sup>18</sup> No candidate was observed for either  $d_0$  or  $d_2$ , so  $\nu_6$  must be left unassigned.

**3.  $b_1$  and  $b_2$  Modes.** There are two  $b_1$  and four  $b_2$  fundamentals. It is reasonably obvious that they are to be chosen from 493, 529, 788, 892, 1161, and  $3068 \text{ cm}^{-1}$  in  $d_0$ , and from 409, 478, 697, 787, 1078, and  $2290 \text{ cm}^{-1}$  in  $d_2$ . Note that 788 and 697 are both observed in the infrared only, which suggests that they should be paired. The same thing

is true of 493 and 409  $\text{cm}^{-1}$ .

The proper number of bands is thus available (six for each molecule), and the problem is to attribute them to the correct species. Some criterion for doing this reliably is much needed. Group frequencies are of some help. It is certain, for example, that the C-H stretch ( $\nu_9$  of  $b_2$ ) is 3068  $\text{cm}^{-1}$  in  $d_0$  and 2290  $\text{cm}^{-1}$  in  $d_2$ . The second-highest available frequency (1161 in  $d_0$  and 1078  $\text{cm}^{-1}$  in  $d_2$ ) will surely be a  $b_2$  mode because it is too high for the out-of-plane  $b_1$  modes. It is therefore assigned to  $\nu_{10}$ .

The only experimental criterion for distinguishing between  $b_1$  and  $b_2$  bands is the infrared band contour. It has been mentioned that one C-type band was observed for each molecule in the range being considered: 742  $\text{cm}^{-1}$  in  $d_0$  and 679  $\text{cm}^{-1}$  in  $d_2$ . These must therefore be  $b_1$  modes. The question is to identify the corresponding liquid-phase band. In  $d_0$  742 cannot be the counterpart of any liquid frequency except 788, yet this means that the frequency has *increased* by 46  $\text{cm}^{-1}$  in going from the gas to the liquid. This is very unusual because the magnitude of the shift is exceptionally large, and the sign is opposite that usually found. It is another indication of the powerful influence of physical state on the vibrational spectrum of this molecule. In  $d_2$  the type C gas band at 679  $\text{cm}^{-1}$  falls between liquid-phase bands at 658 and 697  $\text{cm}^{-1}$ . It cannot be the counterpart of 658 because that is polarized and therefore an  $a_1$  mode, whereas 679 has a type C contour and is therefore a  $b_1$  mode. Consequently it must be the counterpart of 697  $\text{cm}^{-1}$ . Again there has been an upward shift in going from the gas to the liquid, this time by 18  $\text{cm}^{-1}$ . Thus the liquid frequencies 788 ( $d_0$ ) and 697 ( $d_2$ ) have been placed in species  $b_1$ . They are surely the highest modes in this species, *viz.*,  $\nu_7$ .

The next criterion for identifying the  $b_1$  and  $b_2$  fundamentals was the product rule. The C-H and C-D stretches ( $\nu_9$  of  $b_2$ ) were fixed at 3068 and 2290  $\text{cm}^{-1}$ , and the 788 and 697 modes were placed in  $b_1$  as just described. This leaves only four ways of distributing the other four pairs of bands between  $b_1$  and  $b_2$ . For three of these the observed product rule ratio is in poor agreement with the theoretical one. The best agreement is obtained for the set of assignments given in Table IV. The observed ratio for  $b_1$  is slightly too high (Table Va). Presumably there is some experimental error or some perturbation of one of the four  $b_1$  frequencies which causes this. Nonetheless this set of assignments seems to be the best one.

The values for the in-plane and out-of-plane carbonyl wags (529 and 493  $\text{cm}^{-1}$ ) are reasonable when compared with assignments for other compounds. For cyclopentanone they are 471 and 451  $\text{cm}^{-1}$ ,<sup>20</sup> for cyclobutanone 461 and 403  $\text{cm}^{-1}$ ,<sup>21</sup> and for oxetan-3-one 456 and 403  $\text{cm}^{-1}$ ,<sup>22</sup> respectively.

**4. Other Comments.** This completes the assignment of the fundamentals. Frequencies have been attributed to all but the one  $a_2$  mode. It is our belief that the assignments are reasonably reliable.

Explanations for a number of left-over bands as binary combinations are included in Tables I and II. For  $d_0$  the situation is good, but for  $d_2$  there are quite a number of weak bands for which we have no explanation. Some of them may belong to the half-deuterated molecule.

## Discussion

The most remarkable feature of the spectrum is the lack of the expected "C=C stretching" band somewhere between 1500 and 1750  $\text{cm}^{-1}$ , and instead a very strong band at 1483 ( $d_0$ ) or 1409 ( $d_2$ ). This is even more striking when compared with the results for substituted cyclopropenones. The infrared spectra of several of these have been studied, for example, dichloro-,<sup>23</sup> dimethyl-,<sup>24</sup> and diphenylcyclo-

**Table VI.** Bands in the "Double Bond" Region for Some Cyclopropenones

R	R'	State	$\nu_a$	$\nu_b$	Ref
H	H	Liq	1840 (1770) <sup>a</sup>	1483	This work
D	D	Liq	(1878) <sup>a</sup> 1780	1409	This work
CH <sub>3</sub>	CH <sub>3</sub>	CCl <sub>4</sub> soln	1869 1851	1656	22
Ph	Ph	CCl <sub>4</sub> soln	1861 (1845) <sup>a</sup>	1637	22
Cl	Cl	CS <sub>2</sub> soln	1886	1615	21

<sup>a</sup> Not a fundamental.

propenone.<sup>24,25</sup> Some data for these three are given in Table VI. In every case there are one or two bands (but only one fundamental) between 1845 and 1890  $\text{cm}^{-1}$ , and one band between 1610 and 1660  $\text{cm}^{-1}$ . Similar results have been reported for some unsymmetrical disubstituted cyclopropenones.<sup>26</sup> There has been vigorous discussion in the literature about the form of the vibration corresponding to these two fundamental frequencies.<sup>24</sup> It now seems to be established that they are out-of-phase and in-phase mixtures of the C=O and C=C stretches,<sup>24,25</sup> with some contribution also from the symmetric C-C stretch.<sup>27</sup>

One would like to know whether these substituted compounds have a band just below 1500  $\text{cm}^{-1}$  analogous to 1483 in  $d_0$ . It is impossible to say for dimethyl- and diphenylcyclopropenone because these two substituents have bands of their own there. The dichloro derivative provides a clear answer; however, it has nothing between 1615 and 1120  $\text{cm}^{-1}$ .

Clearly, then, the 1650 band of the substituted compounds is replaced by the much lower 1483 in  $d_0$  and 1409 in  $d_2$ . Two questions immediately present themselves. Why is there this difference? What is the form of the corresponding vibration? We have considered the following "explanations."

1. There is a possibility that  $\nu_2$  and  $\nu_3$  were nearly the same in zero approximation, and underwent a first-order interaction. This is assumed to have separated the two levels symmetrically about the mean of the observed values, which is near 1660  $\text{cm}^{-1}$ . To have such a large splitting, the unperturbed levels must have been nearly coincident at 1660  $\text{cm}^{-1}$ . This is a reasonable value for the unperturbed C=C stretch, for it is 1656  $\text{cm}^{-1}$  in cyclopropene. However, 1660 is far too low for the unperturbed C=O stretch. For example  $\nu(\text{C=O})$  is 1905  $\text{cm}^{-1}$  in cyclopropanone<sup>28</sup> and 1815  $\text{cm}^{-1}$  in cyclobutanone.<sup>21</sup> Therefore this is an unlikely explanation.

2. If the molecule were in the dipolar form shown in Figure 1b, the 1483- $\text{cm}^{-1}$  band could be interpreted as one of the totally symmetric ring modes of the cyclopropenium ring. However, there are convincing arguments against this. The band at 1840  $\text{cm}^{-1}$  is in the range expected for a localized carbonyl, but not for one containing a great deal of C-O<sup>-</sup> character. Furthermore, Flygare and coworkers found the C=O distance to be 1.212 Å.<sup>3</sup> This is in the normal range for both saturated and conjugated ketones and aldehydes,  $1.215 \pm 0.005$  Å,<sup>5</sup> and contrary to an appreciable amount of C-O<sup>-</sup> character. We therefore reject this explanation.

3. The 1483- $\text{cm}^{-1}$  vibration is still mainly a C=C stretch, but is abnormally low because of a low force constant or a mass effect (or both). This is apparently the correct explanation. In a later paper we shall present a normal coordinate calculation which shows that both effects are operative.<sup>17</sup> It is shown that the 1483- $\text{cm}^{-1}$  band is due to a

fairly pure C=C stretch (78% of the potential energy is this). The force constant is somewhat low, 8.0 mdyn/Å, compared with 9.5 for  $k_{\text{C=C}}$  in cyclopropene,<sup>29</sup> and with 9.5–10 for most C=C groups.<sup>30</sup> However, values have been reported for H<sub>2</sub>C=CX<sub>2</sub> molecules ranging from 7.6 to 8.5,<sup>31</sup> so there is precedent for this magnitude.

In substituted cyclopropenones the force constant may still be low, but the increased mass has the effect of placing a frequency near 1650 cm<sup>-1</sup>. At the same time the C=O, C=C, and C—C symmetric stretches become badly mixed. The interested reader is referred to the later paper for details. It gives the potential energy distributions for all the observed fundamentals of  $d_0$  and  $d_2$ .

The 1483-cm<sup>-1</sup> band has the lowest value for the stretch of a localized C=C group of which we are aware. It is one more aspect of the unusual nature of cyclopropenone.

Several puzzling or anomalous features have been mentioned in this paper, *viz.*: (1) the poor agreement between some infrared and Raman frequencies, even for the liquid state; (2) some unusual frequency shifts accompanying the change from liquid to gas for the only two fundamentals measured in both; and (3) the difficulty in explaining the extra bands in the vicinity of 1800 cm<sup>-1</sup>. We suspect that very strong intermolecular interactions in the condensed states may be the cause of these, especially of the first two. This could produce molecular aggregates in the liquid and solid that are probably broken upon vaporization, thus causing the large frequency shifts. Suppose further that a high concentration of dimers exists in the liquid, and that they have a center of symmetry. Then in the Raman effect the g modes will be observed, and in the infrared the u ones. This is analogous to the situation for carboxylic acid dimers, and leads one to expect frequency differences between infrared and Raman bands.

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## References and Notes

- (1) Taken in part from a thesis submitted by Dennis H. Finseth for the degree of Doctor of Philosophy at the University of Pittsburgh, 1973.
- (2) (a) R. Breslow and G. Ryan, *J. Amer. Chem. Soc.*, **89**, 3073 (1967); (b) R. Breslow and M. Oda, *ibid.*, **94**, 4787 (1972).
- (3) R. C. Benson, W. H. Flygare, M. Oda, and R. Breslow, *J. Amer. Chem. Soc.*, **95**, 2772 (1973).
- (4) P. H. Kasai, R. J. Myers, D. F. Eggers, and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959).
- (5) "Interatomic Distances. Supplement." *Chem. Soc. Spec. Publ.*, No. 18, 21s (1965).
- (6) W. R. Harshbarger, N. A. Kuebler, and M. B. Robin, *J. Chem. Phys.*, **60**, 345 (1974).
- (7) R. Breslow, G. Ryan, and J. T. Groves, *J. Amer. Chem. Soc.*, **92**, 988 (1970); (a) p 991; (b) Table I.
- (8) G. J. M. van der Kerk, J. G. Noites, and J. G. A. Luitjen, *J. Appl. Chem.*, **7**, 366 (1957).
- (9) IUPAC, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworths, Washington, D.C., 1961.
- (10) R. C. Lord, R. S. McDonald, and F. A. Miller, *J. Opt. Soc. Amer.*, **42**, 149 (1952).
- (11) F. A. Miller, B. M. Harney, and J. Tyrrell, *Spectrochim. Acta, Part A*, **27**, 1003 (1971).
- (12) "MIT Wavelength Tables," MIT Press, Cambridge, Mass., 1969.
- (13) F. A. Miller and B. M. Harney, *Appl. Spectrosc.*, **24**, 291 (1970).
- (14) G. Herzberg, "Infrared and Raman Spectra," Van Nostrand, Princeton, N.J., 1945: (a) p 231; (b) p 326.
- (15) W. A. Seth-Paul and G. Dijkstra, *Spectrochim. Acta, Part A*, 2861 (1967).
- (16) T. Ueda and t. Shimanouchi, *J. Mol. Spectrosc.*, **28**, 350 (1968).
- (17) E. C. Tuazon, D. H. Finseth, and F. A. Miller, *Spectrochim. Acta, Part A*, in press.
- (18) R. W. Mitchell, E. A. Dorko, and J. A. Merritt, *J. Mol. Spectrosc.*, **26**, 197 (1968).
- (19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N.Y., 1958, pp 35–41.
- (20) V. B. Kartha, H. H. Mantsch, and R. N. Jones, *Can. J. Chem.*, **51**, 1749 (1973).
- (21) K. Frei and H. Günthard, *J. Mol. Spectrosc.*, **5**, 218 (1960).
- (22) J. R. Durig, A. C. Morrissy, and W. C. Harris, *J. Mol. Struct.*, **6**, 375 (1970).
- (23) R. W. Mitchell and J. A. Merritt, *Spectrochim. Acta, Part A*, **27**, 1643 (1971).
- (24) A. Krebs and B. Schrader, *Justus Liebigs Ann. Chem.*, **709**, 46 (1967).
- (25) J. J. Chang and R. C. Lord, B.S. Honors Thesis of J.J.C., Department of Chemistry, Massachusetts Institute of Technology, 1965, private communication.
- (26) E. M. Briggs, C. W. Bird, and A. F. Harmer, *Spectrochim. Acta, Part A*, **25**, 1319 (1969).
- (27) F. Höfler, B. Schrader, and A. Krebs, *Z. Naturforsch. A*, **24**, 1617 (1969).
- (28) W. J. M. Van Tilborg, *Tetrahedron Lett.*, **7**, 523 (1973).
- (29) G. Hagen, *Acta Chem. Scand.*, **23**, 2311 (1969).
- (30) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N.Y., 1955, p 175.
- (31) K. Ramaswamy and V. Devarajan, *J. Mol. Struct.*, **8**, 325 (1971).