Microwave Spectrum and Structure of Cyclopropanone

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Abstract: The microwave spectra of $^{13}C_1$, $^{13}C_2$, and 2,2-dideuteriocyclopropanone have been observed in the ground vibrational state. The ground-state rotational constants for the $^{13}C_1$ species are $A = 20155 \pm 10$ MHz, $B = 7457.3 \pm 0.3$ MHz, and $C = 5866.2 \pm 0.2$ MHz. The ground-state rotational constants for the $^{13}C_2$ species are $A = 19685 \pm 5$ MHz, $B = 7370.60 \pm 0.05$ MHz, and $C = 5772.29 \pm 0.04$ MHz. The ground-state rotational constants for the 2,2-dideuterio species are $A = 17005.0 \pm 6$ MHz, $B = 6960.8 \pm 0.1$ MHz, and $C = 5477.91 \pm 0.09$ MHz. The structural parameters obtained from the spectral data for the isotopically normal cyclopropanone and the three isotopically labeled species are: C–H = 1.086 ± 0.025 Å, C_1–C_2 = 1.475 ± 0.017 Å, C_2–C_3 = 1.575 ± 0.012 Å, C–O = 1.191 ± 0.021 Å, $C_1C_2C_3$ angle = 57° 42′ ± 25′, HCH angle = 114 ± 2°, and HCH plane angle with C_2–C_3 axis = 29 ± 2°.

Previous work in our laboratory on cyclopropanone established that the molecule could exist in the gas phase in the ring-closed form.[2] This conclusion contrasts with the results of extended Hückel calculations which predict the ring-opened form of cyclopropanone to be more stable, and that cyclopropanone would have no stability with respect to conversion to oxyallyl.[3]

In our previous paper we reported a dominant isotope rotational assignment, molecular electric dipole moment ($(2.67 \pm 0.1) \times 10^{-18}$ esu cm), and an approximate molecular structure. We concluded that the C–C bond which is perpendicular to the CO bond is unusually long. We now report on the microwave spectra of several more isotopic species of cyclopropanone which we have observed in order to obtain a complete molecular structure for this interesting molecule.

Experimental Section

Microwave transitions of the normal and three isotopically substituted cyclopropanones were observed in several microwave absorption cells. The microwave spectrograph has been described elsewhere.[4] Considerable difficulty was experienced in maintaining the quality of the spectra above Dry Ice temperatures. However, the absorption signals were maintained 5 or 6 hr at Dry Ice temperatures. To improve signal to noise in all spectra taken in the 8–18-Gc region, a backward diode detection system, incorporating a Philco 1454-L backward diode, was used.[5]

Cyclopropanone was prepared from ketene and diazomethane in fluorotrichloromethane by the method of Hammond and Turro.[6] The 2,2-dideuterio isotopic species was prepared with dideuterioketene synthesized from perdeuterioacetone. No difficulty was experienced in obtaining a rotational assignment in 2,2-dideuteriocyclopropanone, and the results are listed in Tables I and II. The transitions were identified on the basis of their Stark effect as in the case of the normal isotopic species. The transitions and rotational constants of the isotopically normal cyclopropanone are also listed in Tables I and II.

Both ^{13}C isotopes were observed in natural abundance from samples prepared from ketene generated from diketene. $^{13}C_1$ refers to the carbon atom which is bonded to the oxygen atom. As the $^{13}C_2$ isotopic species has two equivalent carbon positions, the spectra will exhibit 2% of the intensity of the normal species. An approximate molecular structure was used to compute the spectra of both the $^{13}C_1$ and $^{13}C_2$ isotopic species. The more abundant $^{13}C_2$ species was easily identified by the Stark effect and the relative intensity was about the expected 2% of the normal species. These results are listed in Tables I and II. The structure was refined to fit the new moments of inertia and then the $^{13}C_1$ spectra was predicted. Careful frequency-locked scans in the region of the predicted $^{13}C_1$ spectra revealed a weak set of lines which had the correct Stark effect. We have assigned these to the $^{13}C_1$ spectrum, and the results are also listed in Tables I and II. As the C_1 atom lies on the symmetry *a* axis, the *A* rotational constant must be identical in the normal and $^{13}C_1$ species. Also listed in Table II are the $I_a + I_b - I_c$ differences in the moments. These differences lead to numbers which are due only to the four out-of-plane hydrogen atoms.[2] Therefore, the values of $I_a + I_b - I_c$ should be constant for an in-plane substitution. This difference is remarkably constant in the three isotopically distinct cyclopropanones, as may be seen in Table II. The constant value of $I_a + I_b - I_c$ in the normal, $^{13}C_2$, and $^{13}C_1$ isotopic species is strong evidence that our ^{13}C assignments are correct. The only other origin of lines which have intensities nearly equal to the ^{13}C spectra are the out-of-plane vibrations. However, these out-of-plane vibrations would lead to moments that give $I_a + I_b - I_c$ differences substantially different that the ground vibrational state values. These arguments were recently used by Scharpen and Laurie[7] to assign the ground vibrational state ^{13}C spectra of cyclobutanone.

Molecular Structure

Substitutional coordinates of all atoms in cyclopropanone are given in Table III. Bond lengths and angles determined from these coordinates ae given in Table IV. The carbon skeleton and the in-plane proton coordinates were first determined by the method of Kraitchman.[8] A mass scale with $M_{^{16}O} = 16.0$ was used in all calculations.

The proton out-of-plane distance was determined in two ways. First, z_H was determined from all isotopic species by using $8m_Hz_H^2 = I_a^0 + I_b^0 - I_c^0$. The resultant average value of 0.911 ± 0.001 is reasonable. Second, z_H was determined by the method of Laurie,[9] incorporating a pseudo-inertial defect (Δ). Our small value of Δ = 0.0674 compares well with other small ring compounds such as ethylene oxide (Δ = 0.042)[9] and ethylene sulfide (Δ = 0.070).[9] However, because of the large uncertainty in the out-of-plane determination by this method ($z_H = 0.916 \pm 0.004$), it was decided to use the value of 0.911 ± 0.001 given above.

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Table I. Microwave Transitions (MHz) of Normal Cyclopropanone and Several Isotopic Species[a]

Transition	Normal species		$^{13}C_2$		$^{13}C_1$		2,2-Dideuterio	
	Obsd	Obsd − calcd	Obsd	Obsd − calcd	Obsd	Obsd − calcd	Obsd	Obsd − calcd
0(0,0)-1(0,1)	13338.6	0.3						
1(1,1)-2(1,2)	25082.1	0.1	24687.4	−0.1	25055.4	−0.4	23394.7	0.2
1(1,0)-2(1,1)	28271.6	0.2	27884.2	+0.1			26360.8	0.5
1(0,1)-2(0,2)	26535.8	0.1	26140.1	0.0			24724.6	−0.5
2(0,2)-3(0,3)	39458.0	−0.1	38853.7	0.0	39416.6	0.0	36717.1	0.1
2(2,1)-3(2,2)	40014.8	−0.3	39428.5	−0.2	39970.5	0.0	37315.8	−0.3
2(1,2)-3(1,3)	37538.7	0.1	36944.1	+0.1	37500.1	0.2	35001.2	0.2
2(2,0)-3(2,1)	...	...					37915.2	0.0
3(1,3)-3(1,2)	9560.4	0.3						
5(1,5)-5(1,4)	23703.4	0.0						
6(2,5)-6(2,4)	8623.6	1.1						
6(1,6)-6(1,5)	32847.6	−0.6						
7(2,6)-7(2,5)	14329.8	0.9						
8(2,7)-8(2,6)	21719.0	0.5						
9(2,8)-9(2,7)	30697.0	0.2						
12(3,10)-12(3,9)	25017.8	−0.9						

[a] Experimental errors estimated to be 0.1 MHz.

Table II. Rotational Constants[a] and Moments of Inertia[b] for Several Isotopic Species of Cyclopropanone

	Normal species	$^{13}C_1$	$^{13}C_2$	2,2-Dideuterio
A	20155.11 ± 0.39	20155 ± 10	19684.93 ± 4.65	17004.98 ± 6.00
B	7466.52 ± 0.04	7457.3 ± 0.3	7370.60 ± 0.05	6960.80 ± 0.11
C	5871.85 ± 0.04	5866.2 ± 0.2	5772.29 ± 0.04	5477.91 ± 0.09
I_a^0	25.082 ± 0.002	25.082 ± 0.012	25.681 ± 0.008	29.728 ± 0.012
I_b^0	67.706 ± 0.004	67.790 ± 0.003	68.588 ± 0.005	72.625 ± 0.005
I_c^0	86.094 ± 0.006	86.177 ± 0.003	87.579 ± 0.006	92.285 ± 0.008
$I_a + I_b - I_c$	6.694	6.680	6.690	10.068

[a] Units = MHz/sec. [b] Units = amu Å², and conversion factor is 505531.0 MHz amu Å².

Table III. Coordinates of Atoms in Cyclopropanone from Center of Mass[a]

Atom	x	y	z
C_1	0.3080 ± 0.011	0.0	0.0
C_2	−0.9386 ± 0.0047	−0.7876 ± 0.0064	0.0
C_3	−0.9386 ± 0.0047	0.7876 ± 0.0064	0.0
O	1.4986 ± 0.0102	0.0	0.0
H_1	−1.2255 ± 0.0040	1.3027 ± 0.0236	0.9114 ± 0.0011
H_2	−1.2255 ± 0.0040	1.3027 ± 0.0236	−0.9114 ± 0.0011
H_3	−1.2255 ± 0.0040	−1.3027 ± 0.0236	0.9114 ± 0.0011
H_4	−1.2255 ± 0.0040	−1.3027 ± 0.0236	−0.9114 ± 0.0011

[a] C_1 is bonded to the oxygen atom.

Because the in-plane proton distance from the molecular symmetry axis is dependent on the A rotational constant to a large extent, it was decided to use the most accurately determined rotational constants to reevaluate this position for the proton. The parent species rotational constants and the equation

$$I_{zz} + I_{xx} - I_{yy} = 2\sum m_i y_i^2 = 4m_c y_c^2 + 8m_p y_p^2$$

were used.

The value for y_c was determined by Kraitchman's equation. The position of the oxygen atom in the molecule was determined by the first-moment equations,[10] after the position of all other atoms in the molecule had been determined. The C_1 atom is very close to the center of mass. Therefore, the bond distances associated with this atom have larger experimental uncertainties than the other bond distances.

Table IV. Structure of Cyclopropanone

C_1–O, Å	1.191 ± 0.020
C_1–C_2, C_1–C_3, Å	1.475 ± 0.017
C_2–C_3, Å	1.575 ± 0.012
$C_{2,3}$–$H_{1,2,3,4}$, Å	1.086 ± 0.025
$C_1C_2C_3$	57° 42′ ± 25′
∠HCH	114° 8′ ± 2°
∠$C_2C_1C_3$	64° 36′ ± 50′
HCH plane angle with C_2–C_3 axis	29° 7′ ± 2°

Discussion and Conclusion

The structure of cyclopropanone is significant in that it contains one of the longest carbon–carbon single bonds every measured spectroscopically. There are several examples of long C–C bonds observed in X-ray crystallography.[11,12]

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In chlorocyclopropane[13] the carbon skeletal structure is an equilateral triangle with C–C bond lengths of 1.514 Å. In cyclopropanone the C_1–C_2 and C_1–C_3 bond length of 1.475 Å is smaller than the other cyclopropanes previously measured, but agrees well with the C–C bond lengths of the strained-ring compounds ethylene oxide (C–C = 1.472 Å) and ethylene sulfide (C–C = 1.492 Å).[14] The C–O bond length of 1.191 Å is approximately the same as formaldehyde.[15] The long C_2–C_3 bond length coupled with the shorter C_1–C_2 and C_1–C_3 bonds lengths (1.475 Å) would seem to suggest that cyclopropanone contains one especially weak carbon–carbon bond. This long bond is the one which is broken in reactions between cyclopropanone or substituted cyclopropanones with dienes such as furan to give cycloadducts.[16-23] The lengthening of the C_2–C_3 bond is also in agreement with the work of Scharpen and Laurie on cyclobutanone.[7] In cyclobutanone, the $C_2C_1C_4$ angle (C_1 bonding to the oxygen atom) of 93.1 ± 0.3° might indicate that the carbonyl bonding in the molecule is tending to enlarge the $C_2C_1C_4$ angle, making the C_2–C_4 distance larger than expected. This would be analogous to cyclopropanone, where the C_2–C_1–C_3 angle is 64° 36′, but the effect is not as acute. It is also interesting to note the angle of 29 ± 2° for the HCH plane angle with the C_2–C_3 axis.

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The Molecular Structure of Cyclohexene

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Abstract: The molecular structure of cyclohexene in the vapor phase has been determined by electron diffraction. The molecule has C_2 symmetry, in the half-chair conformation, in agreement with other studies of cyclohexene and of its derivatives. The geometrical parameters, obtained by least-squares analysis of the reduced molecular intensity pattern, are: $C_1{=}C_2 = 1.335 \pm 0.003$ Å, $C_2{-}C_3 = 1.504 \pm 0.006$ Å, $C_3{-}C_4 = 1.515 \pm 0.020$ Å, $C_4{-}C_5 = 1.550 \pm 0.040$ Å, $C{-}H = 1.093 \pm 0.015$ Å; $\angle C_2C_1C_6 = 123.5°$, $\angle C_1C_6C_5 = 121.1°$, $\angle C_3C_4C_5 = 111.0°$.

More than a quarter of a century ago Lister[1] proposed a half-chair conformation for cyclohexene on the basis of his measurements of the heats of bromination of cyclic olefins. Later Pitzer, *et al.*,[2] calculated the energy for different conformations and concluded that the most stable conformation was indeed the half-chair form (C_2 symmetry), to the extent of 2.7 kcal/mol lower than the half-boat configuration. Subsequently other theoretical calculations on the conformation of cyclohexene[3-5] were published; all of them concluded that the lower energy form has C_2 symmetry and the energy difference is about twice the above value. Since there has been no experimental determination of the molecular structure of cyclohexene, this investigation was deemed necessary.

Experimental Section

The purified sample of cyclohexene was kept at −30°. Sectored electron diffraction patterns were taken with our new apparatus under the following conditions: high-voltage beams (70 kV) at sample-to-plate distances of 262.4 and 129.4 mm. An additional set was obtained at low voltage (25 kV), with $L = 262.4$ mm. Diffraction patterns were recorded using several exposure times on 4 × 5 in. Kodak process plates; magnesium oxide patterns were recorded concurrently to establish the scale factor. The gas patterns were microphotometered with a double-beam Jarrell-Ash microdensitomer interfaced with a digital recorder. The procedure for data reduction has been described previously.[6]

Analysis and Results

The total experimental intensity curves for the three sets of data along with the refined background are plotted in Figure 1. The reduced experimental molecular intensity curve and that calculated for the best model are compared in Figure 2; the difference curve is also shown. The refined radial distribution curve and the difference

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