2256 J. Phys. Chem. A **1999,** *103,* 2256−2261

Determination of the Structure of the Argon Cyclobutanone van der Waals Complex

Michaeleen R. Munrow, Wallace C. Pringle,* and Stewart E. Novick

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06459

Received: September 9, 1998; In Final Form: January 20, 1999

The microwave spectra of the argon cyclobutanone van der Waals complex and its three ^{13}C isotopomers have been assigned in the ground state of the ring puckering vibration. The rotational constants and centrifugal distortion constants for the ^{12}C species are determined to be $A = 3598.5200(4)$ MHz, $B = 1388.4449(1)$ MHz, $C = 1195.5254(2)$MHz, $\Delta_J = 4.846(2)$ kHz, $\Delta_{JK} = 36.11(2)$ kHz, $\Delta_K = -38.10(8)$ kHz, $\delta_J = 0.6415(6)$ kHz, $\delta_K = 20.62(4)$ kHz, $H_k = 0.067(4)$ kHz. The dipole moments have also been measured: $\mu_a = 0.29$ D, $\mu_b = 2.83$ D. The cyclobutanone ring was found to remain planar after complexation with argon. The coordinates of the argon in the monomer's principal axis system are $a = 0.23$, $b = 0.55$ (across the ring due to large amplitude bending), and $c = 3.48$ Å (above the ring). The equilibrium position of argon is in the C_s plane of the complex, 3.48 Å above the ring and shifted 0.23 Å from the $C_2-C_{2'}$ ring diagonal toward the carbonyl.

Introduction

Four-membered rings were extensively studied in the 1960s and 1970s in both the infrared and microwave regions.[1−3] The rings were found to undergo a low-frequency, large-amplitude, and very anharmonic "butterfly-like" inversion motion. This ring puckering vibration is represented by a one-dimensional double minimum or anharmonic single minimum potential function. The potential minima occur where the ring is puckered, and the potential maximum occurs where the ring is planar. This is analogous to the inversion of ammonia, where the nitrogen is on one side of the hydrogens at the minima and is coplanar with the hydrogens at the barrier.[4]

The ring puckering vibration is a delicate balance between two opposing forces in the molecule, the ring strain of the ring and the torsional strain of the bonds. Ring strain is a planar driving force, since puckering the ring decreases the already highly strained ring angles and hence increases the potential energy of the molecule. Opposing the ring strain is a torsional force about the bonds that favors a puckered ring, since the planar conformation has eclipsed torsional bonds. Molecules with higher ring strain and lower torsional strain have a single minimum potential and are best described as "planar". On the other hand, molecules with higher torsional strain and lower ring strain may have a double minimum potential. Depending on the reduced mass of the ring oscillator and the difference in the two strains, the ring is better described as nonplanar if the lowest energy level lies under the barrier. Cyclobutanone (CBO)[5,6] and oxetane,[7−9] shown in Figure 1, are described as planar since the lowest vibrational level lies above the potential barrier and the wave function for the ground state has a maximum at the planar configuration. The ground states of cyclobutane[10] and thietane[11,12] lie well below the barriers, and the wave functions have their maxima in the two wells and thus are best described as "puckered". Ring strain dominates in oxetane and cyclobutanone, especially the sp^3 carbonyl in the latter, and torsion dominates in cyclobutane and thietane. The C−S−C bond is 90° even in nonring molecules, thus reducing the ring strain in thietane. Pringle and Meinzer[13] have quantified the reduction of the barrier to planarity upon electronegative substitution on four-membered rings. They also showed that carbonyl substitution in a number of four-membered ring compounds reduces the torsional repulsion significantly.[14]

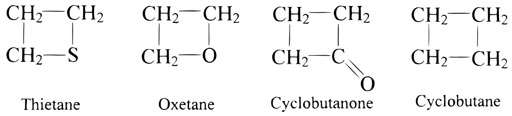

Figure 1. Four-membered ring compounds.

The microwave spectrum of CBO was first studied by Scharpen and Laurie[5] in 1968. They assigned the spectrum of the ground state and first 10 excited states of the ring puckering vibration. In addition, the ring puckering potential function is a symmetric double minimum with a barrier to inversion of 7.6 ± 2 cm^{-1} and the ground vibrational level is 9.2 cm^{-1} above the barrier. A subsequent study of the ^{18}O and 2,2,2′,2′-tetradeuterated cyclobutanone microwave spectra in the same laboratory[6] and an analysis of the electron diffraction of CBO[15] results in an excellent structure for the monomer.

Since ring puckering is a low-frequency, large-amplitude vibration and results from a delicate balance of two opposing effects, it should be sensitive to an external perturbation. One such perturbation is the formation of a van der Waals bond with another atom such as argon. Since the argon will almost certainly bind to one side of the ring, this interaction will remove that plane of symmetry which contains the four carbons (the a^m, b^m plane in Figure 2a). Thus, the puckering potential in the complex may no longer be a symmetric double minimum. The van der Waals (vdW) stretching and two bending oscillations also match the ring puckering vibration in terms of force constants and reduced masses and thus should couple strongly. As described below, if the complex has C_s symmetry, the vdW stretch and that bend which is symmetric with respect to the C_s plane may couple with the ring puckering vibration, which is also symmetric. The vdW bend that is antisymmetric with respect to the C_s plane will not couple to any of these three symmetric large-amplitude, low-frequency modes. It is well-known that small perturbations to symmetrical double minimum potential functions lead to large structural changes such as isolation of the wave function of the ground state into the lower well in the complex. The ground-state wave function is symmetric with respect to ring inversion in the unperturbed monomer.

10.1021/jp9836527 CCC: $18.00

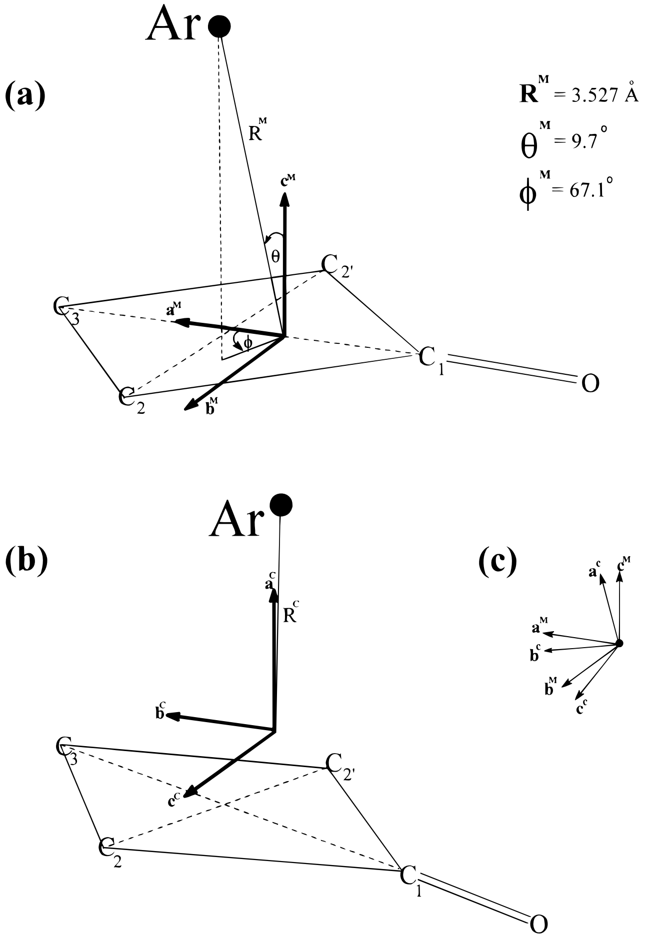

Figure 2. (a) Carbon numbering system and the polar spherical coordinates of argon in the cyclobutanone PAS, a^m, b^m, c^m. (b) PAS of argon−cyclobutanone complex, a^c, b^c, c^c. (c) Relative orientation of the axes of part a to part b.

In this paper, we report the assignment and structural analysis of the argon−CBO van der Waals complex measured with a pulsed-jet Fourier transform microwave (FTM) spectrometer. Transitions of ^{13}C substitutions at the 1, 2, and 3 carbon positions of the CBO ring were observed in natural abundance and assigned to aid in the structural determination of the complex. See Figure 2 for the numbering scheme for CBO. The dipole moment of the normal species was also measured.

Experiment

The pulsed-jet FTM spectrometer has been described elsewhere.[16] Briefly, a pulsed jet of gas with a low rotational temperature (∼4 K) is produced by a standard pulsed supersonic expansion and passes through a high-*Q* Fabry−Perot microwave cavity tunable between 5 and 26.5 GHz. A microwave pulse, coupled into the cavity by a small L-shaped antenna, is timed to coincide with the arrival of the gas pulse with a temporal width of about 1 μs and tuned to the cavity frequency. If a molecular absorption line lies within the ∼500 kHz bandwidth of the microwave pulse and Fabry−Perot cavity combination, a macroscopic polarization is induced in the molecules. The free induction decay (FID) of this polarization is collected and averaged over multiple pulses, and the Fourier transform of the FID is the frequency spectrum of the transition.

In this experiment, the sample is a 1% mixture of CBO (Aldrich Chemical) in an argon carrier gas. The gas mixture is expanded through a 0.5 mm diameter General Valve nozzle which expands through a small hole in one of the mirrors of the Fabry−Perot cavity, coaxial to the cavity axis. In this configuration, line widths (fwhm) are typically 5−10 kHz, allowing for the determination of transition frequencies to better than 1 kHz. An example of a Doppler doubled rotational transition for the argon−CBO van der Waals complex is shown in Figure 3.

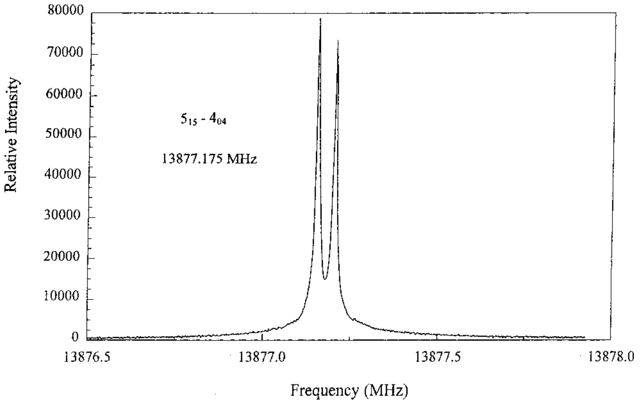

Figure 3. Doppler-doubled spectral line for the 5_{15}−4_{04} rotational transition of the ^{12}C Ar−CBO complex.

To aid in the assignment of the argon−CBO complex, we only consider transitions that are found in *Ar*−CBO but not found in a neon−CBO sample. Stark analysis is done with a 0.5 mm diameter nozzle perpendicular to the cavity axis and with Stark plates outside the cavity separated by 24.4 cm.

The spectrometer is automated to scan unattended over a broad frequency region which allows for the expeditious coverage of 5−26.5 GHz. The high sensitivity of the spectrometer allows for the observation, in natural abundance, of the ^{13}C isotopomers in the ring of the complex.

Results and Analysis

Transition Frequencies and Assignments. The transition frequencies and assignments for the normal complex are listed in Table 1. Transitions are predominantly b-type with very weak a-type lines. Using an asymmetric rotor fitting program written by A. Maki,[17] the transitions listed in Table 1 are fit to a Hamiltonian in an $\mathbf{I}^r$ representation, Watson *A* reduction, using three rotational constants, five quartic centrifugal distortion constants, and a single sextic centrifugal distortion constant, H_K. This results in a 26 line fit with a standard deviation of less than 1 kHz. Spectroscopic constants for the normal complex are given in the first column of Table 2.

The b-type transitions for ^{13}C isotopomers substituted at the 1, 2, and 3 positions in the argon complex (see Figure 2b) are observed in natural abundance and are also listed in Table 1. Table 2 also contains the spectroscopic constants for the substituted isotopic species. Transitions for the complex with a ^{13}C substitution at the 2 position are roughly twice as intense as the comparable transitions for the two complexes with ^{13}C substitutions at the 1 and 3 positions. This is evidence that the two β-substituted ^{13}C isotopomers are equivalent. Figure 4 is a plot of the Doppler-doubled 5_{15}-4_{04} transitions for the three ^{13}C isotopomers clearly showing that the intensity of the $^{13}C_2$ isotopomer is twice that of $^{13}C_1$ and $^{13}C_3$. The latter two lines are approximately 1% of the intensity of this transition from the all-^{12}C complex. Intensities are difficult to measure in FTMW, and we were careful to maintain the same cavity mode for these lines that are also reasonably close in frequency. A similar intensity pattern of approximately 2/1 was observed for the other transitions of the ^{13}C complexes listed in the last three columns of Table 1.

TABLE 1: Spectral Assignment and Frequencies for ^{12}C and ^{13}C Isotopomers of Ar−Cyclobutanone[a]

							frequency (MHz)			
J'	K_a'	K_c'		J''	K_a''	K_c''	all-^{12}C	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$
5	2	3	−	5	1	4	5932.177			
2	1	2	−	1	0	1	7184.907	7159.251	7133.271	7093.756
2	2	1	−	2	1	2	7208.759			
3	2	2	−	3	1	3	7504.590			
4	2	3	−	4	1	4	7902.620			
5	2	4	−	5	1	5	8404.602			
4	0	4	−	3	1	3	8436.346	8394.861	8386.951	8416.906
6	2	5	−	6	1	6	9011.324			
3	1	3	−	2	0	2	9483.875	9447.668	9424.013	9368.261
7	2	6	−	7	1	7	9721.900			
9	3	6	−	9	2	7	9795.440			
4	0	4	−	3	0	3	10216.770			
4	2	3	−	3	2	2	10324.158			
6	1	5	−	5	2	4	10441.059			
8	2	7	−	8	1	8	10533.289			
4	1	3	−	3	1	2	10694.330			
8	2	6	−	7	3	5	10713.396			
5	0	5	−	4	1	4	11199.527	11146.578	11131.294	11158.261
4	1	4	−	3	0	3	11706.559	11659.965	11640.396	11565.606
2	2	1	−	1	1	0	11990.752	11956.764	11879.492	11806.968
8	3	6	−	8	2	7	12134.787			
2	2	0	−	1	1	1	12195.647	12161.217	12077.977	12017.555
5	1	5	−	4	1	4	12387.387			
5	1	5	−	4	0	4	13877.175	13820.284	13805.490	13711.678
6	0	6	−	5	1	5	13933.576	13869.264	13848.824	13866.127
6	1	6	−	5	0	5	16025.293	15958.127	15947.610	15837.690
7	0	7	−	6	1	6		16541.440	16518.271	16519.615
7	1	7	−	6	0	6		18102.415	18094.781	

[a] Lines for each molecule are fit within 1 kHz standard deviation.

TABLE 2: Spectroscopic Constants for ^{12}C and ^{13}C Isotopomers of Ar−Cyclobutanone

	^{12}C	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$
A (MHz)	3598.5200(4)	3588.977(2)	3563.247(3)	3540.994(3)
B (MHz)	1388.4449(1)	1382.647(6)	1377.151(8)	1382.044(13)
C (MHz)	1195.5254(2)	1190.162(6)	1190.073(8)	1184.317(12)
Δ_J (kHz)	4.846(2)	4.70(6)	4.67(7)	4.8(1)
Δ_{JK} (kHz)	36.11(2)	35.9(5)	34.9(6)	36(1)
Δ_K (kHz)	−38.10(8)	−38(1)	−37(1)	−38(2)
δ_J (kHz)	0.6415(6)	0.61(1)	0.59(1)	0.66(2)
δ_K (kHz)	20.62(4)	16(3)	17(4)	20(5)
H_K (kHz)	0.067(4)			

Substitution Analysis. The changes in the moments of inertia from the monomer to corresponding argon−monomer complex allow calculation of the squares of the positions of the argon in the complex expressed in the principal axis system (PAS) of the monomer. This axis system is labeled as a^m, b^m, and c^m in Figures 2a and 5. The Kraitchman equations[18] are used in a novel manner to calculate this position in all four complexes. We use an argon mass of 0.0 amu for the monomer's moments of inertia and a $\Delta M = 40.0$ amu for the complex moments. As shown in Figure 2a for the planar monomer, the a^m axis passes through the carbonyl and C_3, the b^m axis is in the plane of the ring, and the c^m axis is perpendicular to the ring plane. In this PAS coordinate system of the all-^{12}C monomer, the argon substitution position is $a^m = 0.231$, $b^m = 0.547$, $c^m = 3.476$ Å. The argon is 4/5 of the distance from the carbonyl carbon to the diagonal across the ring from C_2 to $C_{2'}$. The numbering system for the ring and the structure of the complex are shown in Figure 5. Repeating the Kraitchman analysis for each ^{13}C monomer and the corresponding ^{13}C−argon complex leads to consistent coordinates for the argon in PAS coordinates of the corresponding monomers as given in Table 3. The PAS of the argon complex, which is shown in Figure 2b and labeled throughout the text as a^c, b^c, c^c, has its a^c axis rotated out of the ring plane passing almost through the argon, and the complex b^c axis is now nearly parallel to the carbonyl bond moment. Thus b-type transitions dominate the microwave spectrum of the complex.

The argon is located 0.55 Å from the plane of symmetry of the monomer that contains the carbonyl group and C_3 and is perpendicular to the ring plane (a^m, c^m plane, see Figures 2a and 5). We have strong evidence that this displacement from that plane is the result of a large-amplitude motion of the argon across the ring which is parallel to the b axis of the monomer and shown as "b^m_{Ar}" in Figure 5. We have already mentioned that only three ^{13}C-substituted structures are observed and the transitions for the substitution at position 2 are approximately twice as strong as the analogous transitions in the other two substituted species reflecting the 2% natural abundance of two equivalent carbons, $^{13}C_2$ and $^{13}C_{2'}$. Thus, the equilibrium coordinate for the argon, $b^m_{(Ar)e}$, is zero and lies in the a^m, c^m plane.

However, if the argon in the complex were actually closer to C_2 or $C_{2'}$ and *not* undergoing a large amplitude motion, then the $^{13}C_2$ isotopomer with the argon closer must have different moments of inertia from the $^{13}C_{2'}$ with the argon further away. In that case, we would have found spectra from four different ^{13}C isotopomers with equal intensities (1% of the all-^{12}C). In fact, we could predict the spectrum for this other isotopomer and were unable to find transitions attributable to it. Since the square of the position of the argon relative to the PAS of the monomer is determined in a Kraitchman analysis, two structures with $b^m = +0.55$ and $b^m = -0.55$ Å will have exactly the same changes in moments of inertia from the monomer to the complex (^{13}C) and in one the argon is closer to ^{12}C while the other is closer to ^{13}C.

The rotational constants of all four isotopomers of the complex were used to determine the structural positions of each substituted carbon utilizing two methods: Kraitchman analysis

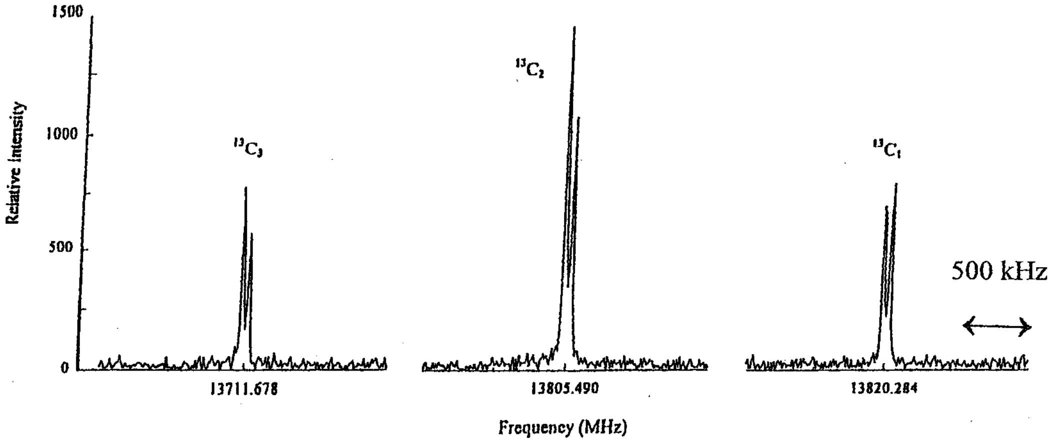

Figure 4. Spectral lines for the $5_{15}-4_{04}$ rotation transition for a single ^{13}C substitution in natural abundance, clearly showing the approximate 2:1 intensity ratio of C_2 to C_1 and C_3.

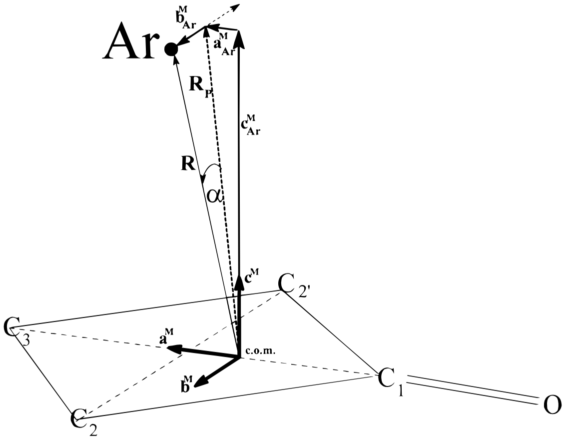

Figure 5. Parameters for the cross ring, large-amplitude argon bending oscillation.

TABLE 3: Kraitchman Substitution Coordinates, Given in Angstroms, for the Argon in the all-^{12}C and the Single-Substituted ^{13}C Complexes in the PAS Coordinates of the Corresponding Monomer[a]

	all-^{12}C	$^{13}C_2$	$^{13}C_1$	$^{13}C_3$
$\|a\|$	0.2312	0.2237	0.2389	0.2427
$\|b\|$	0.5469	0.5507	0.5388	0.5547
$\|c\|$	3.4762	3.4849	3.4867	3.4832

[a] Calculated by assuming the cyclobutanone is an isotope of the complex with argon mass = 0.

(giving an r_s structure) and a version of Schwendeman's STRFTQ program updated by K. Hillig[19] (giving an r_o structure). The positions of the substituted atoms are determined in the Kraitchman analysis. Substitution coordinates for all nuclei in the monomer except the C_3 hydrogens are taken from the results of Laurie et al.[5,6] and assumed to remain constant in the argon complex. We modified Laurie's coordinates[5,6] slightly by refitting them with the program STRFTQ to the all-^{12}C, three ^{13}C isotopomers, ^{18}O, and D_4 isotopic rotational constants[5,6] simultaneously. These r_o coordinates and uncertainties are listed in Table 4a and are very close to those in refs 5 and 6. We fit seven independent coordinates for the isotopomers of the monomer maintaining C_{2v} symmetry to the 18 observed moments of inertia due to Laurie et al.[5,6] with an rms deviation of 0.074 amu Å^2.

Using the STRFTQ program, more structural parameters of the complex may be fit using the three rotational constants and first moment conditions from the ^{12}C complex as well as the nine rotational constants of the three ^{13}C complexes. However, we found a satisfactory fit to all 15 observed moments keeping the monomer structure constant and only varying the three coordinates of the argon. The r_o structural constants for argon are given in the last row of Table 4a. As shown in Figure 2a, the polar spherical coordinates of the argon are $R^m = 3.527$ Å, $\theta^m = 9.7°$, and $\phi^m = 67.1°$. Transferring these cyclobutanone coordinates to the center of mass coordinates of the complex

TABLE 4: (a) r_o Coordinates of the Argon Calculated from All the Isotopomers of the Argon−Cyclobutanone Complex Given in Table 2;[a] (b) Coordinates of Part a in the PAS of the Complex (see Figure 2b); (c) Internal Coordinates of the Complex Calculated Directly from Part b[b]

(a) Coordinate System: PAS of CBO Monomer

	a^m	b^m	c^m
C_1	−0.593(15)	0^c	0^c
$C_2,C_{2'}$	0.460(25)	±1.111(1)	0^c
C_3	1.549	0^c	0^c
O	−1.800(11)	0^c	0^c
C_2H	0.405(20)	±1.741(4)	±0.905(2)
C_3H	2.1791^d	0^c	$\pm 0.9100^d$
Ar	0.2312	±0.5469	3.4762

(b) Coordinate System: PAS of Ar−CBO Complex

	a^c	b^c	c^c
C_1	−1.336	−0.551	0.022
C_2	−1.431	0.523	−1.065
$C_{2'}$	−1.043	0.471	1.123
C_3	−1.134	1.581	0.037
O	−1.450	−1.752	0.013
C_2H	−0.659	0.401	−1.844
C_2H'	−2.432	0.566	−1.526
$C_{2'}H$	−0.051	0.318	1.583
$C_{2'}H'$	−1.825	0.484	1.902
C_3H	−0.182	2.125	−0.118
C_3H'	−1.966	2.292	0.202
Ar	2.244 (5)	−0.068(17)	−0.051(23)

(c) Internal Coordinates

$r(C{=}O)$	1.206(18)	$\angle HC_2H$	110.1(5)	$\angle C_{2'}C_1C_2$	93.1(9)
$r(C_1-C_2)$	1.531(29)	$\angle HC_3H$	110.6	$\angle C_1C_2C_3$	87.9(8)
$r(C_2-C_3)$	1.556(25)	$\angle C_1C_2H$	112.3(20)	$\angle C_2C_3C_{2'}$	91.1(8)
$r(C_2-H)$	1.104(32)	$\angle C_2C_3H$	113.5(2)	$\angle C_3C_1Ar$	76.9(15)
$r(C_3-H)$	1.107	α	8.9(1)		
$\tau(C_{2'}C_1C_2H)$	117.6	$\tau(C_1C_2C_3H)$	116.3	$\tau(C_2C_3C_1Ar)$	98.9
$r(Ar-C_1)$	3.614	$r(Ar-H(C_2))$	3.444	$r(Ar-H(C_3))$	3.271
$r(Ar-O)$	4.061	$r(Ar-H(C_{2'}))$	2.844		

[a] The r_o coordinates of cyclobutanone are refit from the moments of all isotopomers measured by Laurie[5,6] (see Figure 2a). [b] The uncertainties reported are statistical errors resulting from the fits. [c] Maintains C_{2v} symmetry and planarity of ring. [d] Not fit.

TABLE 5: Coordinates of Substituted Atoms in Complex Given in PAS Coordinates of the all-^{12}C Complex, Figure 2b (Å)

	r_s^c	r_o^c
C_1	$a = 1.24^a$	$a = -1.34$
	$b = 0.62$	$b = -0.55$
	$c = 0.05i^b$	$c = 0.02$
C_2	$a = 1.33$	$a = -1.43$
	$b = 0.41$	$b = 0.52$
	$c = 1.11$	$c = -1.06$
C_3	$a = 1.30$	$a = -1.13$
	$b = 1.53$	$b = 1.58$
	$c = 0.13i^b$	$c = 0.04$
Ar	$a = 2.24^c$	$a = 2.24$
	$b = 0.06$	$b = -0.07$
	$c = 0.05$	$c = -0.05$

[a] Substitution coordinates are listed without sign since only the squares of the values are determined. [b] Imaginary coordinates result from atoms very close to an axis such that small errors in effective moments cause negative squares of coordinates. [c] The argon substitution coordinates do not result from an isotopic substitution but by using $\Delta M = 40$ for a Kraitchman analysis in which the monomer is treated as an isotope of argon with a mass of 0.00 amu.

and diagonalizing the moment of inertia tensor while fitting only the argon coordinates to the isotopomers listed in Table 2 results in the coordinates given in Table 4b. The moments of inertia calculated from this structure match the observed moments within 0.1%. The rms deviation of the 15 calculated from the observed moments of inertia fit to the three coordinates of the argon is 0.19 amu Å^2. The internal coordinates reported in Table 4c were calculated directly from the Cartesian coordinates.

The coordinates of the carbon atoms in the r_s and r_o structures may be found in Table 5. Imaginary substitution coordinates are an indication of the error of this method for atoms very close to an axis. There are differences of 0.1 Å between the r_s and r_o coordinates of the carbon atoms listed in Table 5. Since there are four large amplitude motions in this complex, one of which we know has an rms position of 0.55 Å from equilibrium reflecting at least 1.1 Å motion, we think these small differences are a reflection of the large amplitude averaging processes in this complex. These could be sensitive to isotopic masses.

If the complex were rigid, the r_o fits of the isotopomers would be consistent with only one of the substitution coordinates of the argon on the a^m axis as reported in Table 3, i.e., either +0.23 or −0.23 Å. However, the fits for both of these coordinates are within the 0.1 Å uncertainties shown in Table 5. The difference in these two structures is primarily that the argon has a coordinate, $b^c{}_{Ar}$, that is −0.06 in the former and +0.06 in the latter. The coordinates in Table 4 represent the structure in which the argon is closer to the $C_2-C_{2'}$ diagonal. The projections of the monomer bond moment onto the complex axis system for these two structures are identical except for the signs of the *a* and *c* moments.

Dipole Moment. Stark effect measurements have been made on nine components of the $4_{04}-3_{13}$, $4_{23}-4_{14}$, and $3_{13}-2_{02}$ transitions for the ^{12}C argon−CBO complex. The applied electric field was calibrated using measurements of the Stark effect for the 1−0 transition of OCS and its dipole moment of 0.7124 D.[20] The values determined for the *a* and *b* dipole components of the complex are 0.291(3) D and 2.83(2) D, respectively. If we project the 2.89 D dipole moment of the CBO monomer,[5] μ_0, onto the Ar−all^{12}C complex PAS, the result is $\mu = (0.263\mathbf{a} + 2.878\mathbf{b} + 0.024\mathbf{c})$ D, which is within 2 σ of our measured values for μ_a and μ_b and **a**, **b**, **c** are unit vectors in the complex PAS. The nonzero value of μ_c results from the position of the argon 0.55 Å from the a^m, c^m plane (see Figure 2a). Thus, the dipole moments of the complex are a simple projection of the monomer dipole moment on the complex PAS. Strenuous efforts to observe c type transitions were not successful and the calculated contributions of a *c* component of the dipole to the stark shifts were insignificant and therefore μ_c was constrained to zero.

Large-Amplitude Argon Cross Ring Bending. We assume that the nonzero b^m coordinate of the argon, $b^m{}_{(Ar)}$, shown in Figure 5 is the result of averaging of a large-amplitude bending mode of the argon across the ring. The complex thus belongs to the C_s symmetry group and the equilibrium coordinate of the argon is $b^m{}_{(Ar)e} = 0.0$ Å. The cross ring bend is antisymmetric with respect to the plane containing the carbonyl, C_3, and the equilibrium position of the argon (i.e., the a^m, c^m plane). Thus, this vibration does not couple to the argon stretching mode, the other bending mode, or the ring puckering vibration. The latter three vibrations may couple with each other and belong to the totally symmetric representation. Since the bending mode is also uncoupled by the low-frequency approximation[21] from the other antisymmetric modes of the molecule, the internal coordinate, α, is also very close to the normal coordinate for this vibration. A one-dimensional Hamiltonian for the argon cross ring bending vibration is approximated using an internal coordinate, α, shown in Figure 5.

$$H = -h^2/8\pi^2(1/m_{Ar}R_p{}^2 + 1/I_{aa})\,d^2/d\alpha^2 + {}^1/_2k\alpha^2$$

where m_{Ar} is the mass of argon; R_p is the distance of the argon from the center of mass of CBO when the argon is in the a^m, c^m plane; $R_p = (a^m{}_{(Ar)}{}^2 + c^m{}_{(Ar)}{}^2)^{1/2} = 3.483$ Å; I_{aa} is the moment of inertia of the ring about the *a* axis that includes the carbonyl and C_3 , 46.84 amu Å^2; α is the bending coordinate; and *k* is the harmonic bending force constant in units of energy. Referring to Figure 5, $\tan\alpha \approx \alpha - \alpha^3/3! \approx \alpha = b^m{}_{(Ar)}/R_p$ and the reduced moment of inertia for the vibration is

$$I_\mu = I_{aa}m_{Ar}R_p{}^2/(I_{aa} + m_{Ar}R_p{}^2)$$

The approximate range of the angle, α, is ±8.9° as shown in the structural parameters in Table 4c. The energies of this oscillator are $E_v = h\nu(v + 1/2)$ and $\nu = 1/2\pi(k/I_\mu)^{1/2}$. The expectation value of α^2 is $\langle v|\alpha^2|v\rangle = h(v + 1/2)/[2\pi(kI_\mu)^{1/2}]$. The value of α^2 at the classical turning point in a harmonic oscillator is equal to its expectation value in that vibrational level. If we assume that the coordinate of the argon along the b^m axis is due to an averaging caused by this bending, then $\langle v|\alpha^2|v\rangle \approx \langle v|(b^m{}_{(Ar)}/R_p)^2|v\rangle$ and we have measured

$$[\langle 0|(b^m{}_{(Ar)}/R_p)^2|0\rangle]^{1/2} = 0.547\text{ Å}/3.483\text{ Å}$$

We now can determine the value of the force constant and predict the frequency of the argon cross ring bending motion. The reduced moment of inertia using $R_p = 3.483$ Å and $I_{aa} = 46.859$ amu Å^2 is 7.093×10^{-46} kg m^2, and thus $k = 6.25 \times 10^{-21}$ J. This corresponds to a traditional bending force constant of $k/R^2 = 0.052$ J/m^2 which in turn is 5.2×10^{-4} mdyn/Å which is a factor of 1000 times smaller than a normal valence bending force constant.[21] The predicted bending frequency is thus $\nu = 1/2\pi(k/I_\mu)^{1/2} = 4.7 \times 10^{11}$ Hz or 15 cm^{-1}. Since our vibrational temperature in the beam is approximately 4 K, we are unable to observe vibrationally excited rotational transitions associated with this vibration.

An alternative method to analyze large-amplitude motions of argon-ring complexes due to Spycher et al.[22] was pointed out to us by a reviewer. This involves averaging the moment of inertia tensor along the bending coordinate, α, described above. We carried out this analysis for our complex and obtained a value of $\alpha = 8.4°$, which is very close to our result. The values of their polar spherical coordinates, Θ and *R*, are 2.1° and 3.524 Å. Our method allows us to predict the vibrational frequency of this mode and does not mix coordinates of different symmetries.

The van der Waals stretching frequency is approximated using the pseudodiatomic approximation, $D_J = 4\ B_o{}^3/\nu^2$, where D_J is the centrifugal distortion constant, Δ_J; B_o is approximated as $(B + C)/2$, and ν is the stretching frequency of the weak van der Waals bond. Using a reduced mass of the argon and CBO, we calculate the frequency to be 1.33×10^{12} Hz or 44.5 cm^{-1}. The stretching force constant is $k_s = 0.030$ mdyn/Å. We have no observables that yield information concerning the remaining totally symmetric van der Waals bending vibration.

Discussion

The argon−CBO complex is the third in a series of four-membered rings (Figure 1) complexed with argon that have been studied using our FTM spectrometer. The other two complexes are argon trimethylene sulfide (Ar−thietane)[22] and argon trimethylene oxide (Ar−oxetane).[23] Since the three complexes have internal dynamics controlled by the balancing between torsional forces and angle strain, a comparison between the structure of the three complexes is useful to the discussion of argon−CBO.

In the microwave study of the monomer, thietane, by Harris et al.,[11] the ring puckering potential function has been determined to be a symmetric double minimum with a barrier to inversion of 274.2 ± 2 cm^{-1}. The ground state is well below this inversion barrier. Thus, the thietane molecule takes on a distinctly puckered structure in its ground state and the inversion levels are nearly degenerate. In addition to the pure rotational a-type transitions where $\Delta v = 0$, c-type rotation−inversion transitions, $\Delta v = +1$, are observed leading to an accurate measure of the inversion separation, 8.232 GHz. There are also large coriolis couplings between rotational levels in different inversion states.

In our microwave study of the argon−thietane complex, transitions are observed for only a single vibrational state, namely the ground state. The inversion dipole in the monomer has become a permanent dipole component in the complex, and the inversion is quenched by the formation of the van der Waals bond. The substitution position of the argon was determined in the a^m, b^m, c^m coordinates of the thietane momomer using the Kraitchman analysis discussed above; $a^m = 0.0(1)$ Å, $b^m = 0.567(12)$ Å, $c^m = \pm 3.789(1)$ Å.

Similar to the thietane monomer, the ring puckering potential function for the oxetane monomer is a symmetric double minimum. Unlike thietane, the oxetane potential barrier is much smaller, 35 ± 5 cm^{-1}, and the ground vibrational state lies 8 ± 4 cm^{-1} above the barrier as determined by Chan, Zinn, Fernandez, and Gwinn.[7] Therefore, the oxetane ring is best described as having a planar geometry in the ground vibrational state.

The spectrum of the argon−oxetane complex was observed and the structure determined. The argon in this complex lies in the a^m, c^m plane with coordinates $a^m = 0.671$ Å, $b^m = 0.142$ Å, $c^m = 3.500$ Å.

As stated earlier, the CBO monomer is planar in its ground puckering vibrational state. The potential function, as determined by Sharpen and Laurie,[5] is a symmetric double minimum with an even smaller barrier to inversion, 7.6 ± 2 cm^{-1}, than thietane and oxetane. As in oxetane, the CBO ground state lies well above the inversion barrier.

After our extensive analysis on the normal ^{12}C and ^{13}C isotopomers for the argon CBO complex, we have found that the structure of the ring does not vary significantly from planarity upon formation of the van der Waals bond. This is not surprising due to the dominance of the ring strain in the monomer.[14] In acetone, the C−C−C angle is $117.2(4)^{o}$ [25] whereas it is 93.1 ± 0.3° in the cyclobutanone monomer. Hence, there is an enormous amount of ring strain involved. Decreasing this angle further by puckering the ring would only add additional strain to the ring. As a result, the ring remains planar in the complex.

There is also evidence in the argon−CBO complex of a wide-amplitude motion of the argon across the 1−3 carbon diagonal, as indicated by the ^{13}C data. The distance of the argon from the ring was determined to be 3.476 Å above the ring (Figure 2). This is comparable to the 3.50 Å for argon−oxetane, which has a slight van der Waals induced bend in the ring. It is also slightly smaller than the 3.79 Å argon-ring distance for the argon−thietane complex, where the ring is dominated by torsional forces and therefore puckered.

Acknowledgment. We thank David W. McCamant and Dr. W. D. R. Premasiri for their work on the argon−thietane and argon−oxetane complexes and the National Science Foundation and Hughes Foundation for support.

References and Notes

(1) Blackwell, C. S.; Lord, R. C. *Far Infrared Spectra of four-membered-ring compounds; Vibrational spectra and structure*; Durig, J. R., Ed.; Marcel Dekker: New York, 1972; Vol. 1, pp 1−24.

(2) Carriera, L. A.; Lord, R. C.; Malloy, T. B., Jr. *Fortschr. Chem. Forsch.* **1979**, *82*, 1−95.

(3) Gwinn, W. D.; Gaylord, A. S. *Spectroscopic Studies of Ring Puckering Motions in MTP International Review of Science*; Ramsey, D. A., Ed.; Physical Chemistry Series 3; Buttersworth and University Park Press: London, 1976.

(4) G. Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*; D. Van Nostrand Company: New York, 1945; pp 221−227.

(5) Sharpen, L. H.; Laurie, V. W. *J. Chem. Phys.* **1968**, *49*, 221−228.

(6) Stigliani, W. M.; Laurie, V. W.; Sharpen, L. H. *J. Mol. Spectrosc.* **1976**, *62*, 85−89.

(7) Chan, S. I.; Zinn, J.; Fernandez, J.; Gwinn, W. D. *J. Chem. Phys.* **1960**, *33*, 1643−1655.

(8) Chan, S. I.; Zinn, J.; Gwinn, W. D. *J. Chem. Phys.* **1961**, *34*, 1319−1329.

(9) Chan, S. I.; Borgers, T. R.; Russell, J. W.; Strauss, H. L.; Gwinn, W. D. *J. Chem. Phys.* **1966**, *44*, 1103.

(10) Stone, J. M. R.; Mills, I. M. *Mol. Phys.* **1970** , *18*, 631−652.

(11) Harris, D. O.; Harrington, H. W.; Luntz, A. C.; Gwinn, W. D. *J. Chem. Phys.* **1966**, *44*, 3467−3480.

(12) Borgers, T. R.; Strauss, H. L. *J. Chem. Phys.* **1966**, *45*, 947.

(13) Pringle, W. C.; Meinzer, A. L. *J. Chem. Phys.* **1974**, *61*, 2071−76.

(14) Meinzer, A. L.; Pringle, W. C. *J. Phys. Chem.* **1976**, *11*, 1178−80.

(15) Tamagawa, K.; Hilderbrandt, R. L. *J. Phys. Chem.* **1983**, *87*, 5508−5516.

(16) Hight Walker, A. R.; Chen, W.; Novick, S. E.; Bean, B. D.; Marshall, M. D. *J. Chem. Phys.* **1995**, *102*, 7298−7305.

(17) Maki, A. G. Private communication.

(18) Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17−24.

(19) Hillig, K.; Schwendeman, R. Private communication.

(20) Meunter, J. S. *J. Chem. Phys.* **1968**, *48*, 4544.

(21) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; McGraw-Hill: New York, 1955.

(22) Spycher, R. M.; Petitprez, D.; Bettens, F. L.; Bauder, A. *J. Phys. Chem.* **1994**, *98*, 11863−11869.

(23) Premasiri, W. D. R.; McCamant, D. W.; Novick, S. E.; Pringle, W. C. Presented at Ohio State Molecular Spectroscopy Symposium, Columbus, OH, 1995; Talk RI07.

(24) McCamant, D. W.; Munrow, M. R.; Novick, S. N.; Premasiri, W. D. R.; Chen, W.; Pringle, W. C. Presented at Ohio State Molecular Spectroscopy Symposium, Columbus, OH, 1997; Talk TI12.

(25) Nelson, R.; Pierce, L. *J. Mol. Spectrosc.* **1965**, *18*, 344−352.