Mass spectroscopic Knudsen cell studies of the vapor over $P_4O_{10}(H)$ at 150, 315, and 400 °C have shown that P_4O_{10} undergoes a phase transition which lowers the vapor pressure at 300 °C and that the vapor is composed of P_4O_{10} , P_4O_9 , and P_4O_8 molecules with an approximate ratio of 10:3:1; furthermore, the decomposition products P_4O_8 and P_4O_7 showed increased concentration with higher Knudsen cell temperatures.¹⁹ While species such as $P_3O_{4-7}^+$ were produced by 40-eV electron impact, they showed no temperature dependence and were unique to mass spectroscopic studies. The $P_2O_{2-5}^+$ ions were also produced by the electron impact process, as indicated by their high appearance potentials, but they showed increased intensities at higher temperatures, corroborating the present matrix infrared observation that P_4O_8 and P_4O_7 are more prone to unimolecular cage decomposition than P_4O_{10} .

Conclusions

The YAG laser evaporation of hexagonal (molecular) P_4O_{10} produced mainly P_4O_{10} with small yields of the P_2O_5 and PO_2 decomposition products. The depolymerization of orthorhombic (covalent network) P_4O_{10} with laser ablation gave a randomized distribution of PO, PO₂, P₂O, P₂O₄, and P₂O₅ fragmentation products, where the smaller fragments had high intensities, and little P_4O_{10} . The HOPO and HOPO₂ molecules were observed as hydrolysis intermediates. Thermolysis of P_4O_{10} at 900–950 °C produced a nonrandomized distribution of depolymerization products, which favored P_4O_9 and PO_2 , and to a lesser extent P_4O_8 , P_2O_5 , and P_2O_4 .

Reactive laser ablation of red phosphorus and oxygen produced the same species as the depolymerization reactions of orthorhombic P_4O_{10} and earlier reactions of P_2 with O_2 and O_3 .⁵⁻⁷ The reaction was confined to the plume produced by the laser owing to the production of excited phosphorus fragment species. This work shows that PO_2 is a particularly stable gaseous species²⁰ and suggests that molecular P_2O_5 can also be observed in the gas phase.

Laser ablation has been used for a number of years with great success in combination with matrix-isolation fluorescence spectroscopy by Bondybey and co-workers²¹ and for matrix-isolation ESR studies by Knight.¹¹ This work exploits the combination of laser ablation of polymerized substrates and reactive laser ablation with matrix infrared spectroscopy.

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Vibrational Spectra and Assignments for 1-Fluoro- and 1-Chlorocyclobutenes. Revised Assignment for Cyclobutene

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Gas-phase infrared spectra and liquid-phase Raman spectra are presented for 1-chlorocyclobutene and 1-fluorocyclobutene. Complete assignments of vibrational fundamentals are proposed for these molecules of C_s symmetry. For 1-chlorocyclobutene (cm⁻¹): (a') 3090, 2947, 2940, 1595, 1452, 1434, 1250, 1197, 1165, 1120, 916, 891, 869, 493, 299; (a'') 2980, 2966, 1140, 1070, 1016, 854, 751, 395, 211. For 1-fluorocyclobutene (cm⁻¹): (a') 3111, 2954, 2948, 1667, 1464, 1437, 1306, 1214, 1189, 1154, 972, 911, 866, 651, 412; (a'') 2982, 2969, 1142, 1076, 1020, 855, 764, 436, 264. Frequencies of CH-rich modes correlate closely for these isotopomer-like molecules. These results along with a Raman spectrum of liquid cyclobutene near -100 °C have provided evidence for assigning five unsettled vibrational fundamentals of cyclobutene. These modes in cm⁻¹ are (a₂) $\nu_9 = 2944$, $\nu_{11} = 1011$, and $\nu_{12} = 846$ and (b₁) $\nu_{19} = 903$ and $\nu_{20} = 888$. Ring-puckering frequencies for a variety of halogen-substituted cyclobutenes are compared and found to follow an understandable pattern.

Introduction

This investigation of the vibrational spectra of 1-chlorocyclobutene (ClCB) and 1-fluorocyclobutene (FCB) was begun with the goal of achieving the first characterization of the vibrational fundamentals of singly halogen-substituted cyclobutenes. The vibrational assignment of cyclobutene (CB) itself, a well-studied molecule, promised to be a guide to the assignment of the fundamentals of ClCB and FCB. Nevertheless, the structural variety and the low symmetry of the two 1-halocyclobutenes as well as the near-isotopomer relationship between them led to a more secure assignment of all the fundamentals of these two molecules than was available for CB. Encouraged by these implications for extending the assignment of CB, we reinvestigated the laser Raman spectra of liquid CB, this time near -100 °C, and of the solid. The investigation of the vibrational fundamentals of CB began in 1957. Lord and Rea observed the infrared and prelaser Raman spectra of CB and its fully deuterated isotopomer and proposed an assignment of 20 of the 24 fundamentals of CB.¹ Estimates were given of the remaining four modes, which were of the a_2 symmetry species. From an investigation of the laser Raman spectrum of CB in 1976, Aleksanyan and Garkusha reassigned seven of the fundamentals and added two of the missing a_2 modes.² The 1962 normal-coordinate analysis of Sverdlov and Krainov,³ which had been keyed to the experimental results of Lord and Rea, anticipated some of the new observations but was not an unerring guide. In 1986, as part of a Fourier transform infrared study, at 0.1-cm⁻¹ resolution, of the local-mode approximation

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in CB, Baggott, Clase, and Mills reevaluated the accumulated experimental evidence for the assignment of fundamentals of CB.⁴ They proposed one more a2 assignment, revised one b1 assignment, and left the lowest frequency b₁ mode unassigned.⁵ Experimental evidence for the infrared-inactive a_2 modes remained meager, however. We now propose a complete, experimentally based assignment for the fundamentals of CB that correlates closely with the assignments for ClCB and FCB.

FCB is a new substance. Its synthesis and characterization are described here. CICB has been reported as the product of isomerization of cyclopropylchlorocarbene, but there has been some disagreement about the outcome of this reaction.⁶ Chloromethylenecyclopropane has been proposed as an alternative product.⁷ We describe a less ambiguous synthesis for ClCB and review the substantial evidence in support of the CICB structure. For CB itself, we have found that a little-known, one-step synthesis of CB⁸ is preferable to the multistep methods commonly used.

Vibrational assignments for two other partly halogen-substituted cyclobutenes and for two fully halogenated cyclobutenes are given in the literature. The partly halogenated ones are cis-3,4-dichlorocyclobutene⁹ and 1,4,4-trifluorocyclobutene.¹⁰ The fully halogenated ones are perfluorocyclobutene and 1,2-dichlorotetrafluorocyclobutene.¹¹ A sufficient number of ring-puckering frequencies of substituted cyclobutenes is now available to make the relationship between these frequencies and halogen substitution interesting and interpretable.

Experimental Section

Syntheses. 1-Chlorocyclobutene. The reaction scheme for preparing ClCB was



The mixture of various dichlorocyclobutanes was the product of the cautious, visible-light photolysis of 8 mmol of chlorocyclobutane (Fairfield Chemical) and 8 of mmol chlorine (Matheson Gas Products) in a 2-L flask.¹² Coproduct HCl was vacuumdistilled from the mixture at pentane-slush temperature.

A mixture of the two isomers of monochlorocyclobutene was prepared by distilling a mixture of dichlorocyclobutanes bulbto-bulb through a 30-cm column packed with Ascarite (NaOH on asbestos) coated (11% w/w) with 3:3:2 mixture of tetraglyme, 18-crown-6 ether, and 15-crown-5 ether. CICB was isolated by preparative gas chromatography on a 5 m \times 7 mm (i.d.) tricresyl phosphate (TCP) on Chromosorb column at 65 °C and dried by passage through a column containing P2O5. ClCB, the first peak of significance, had an elution time of 14 relative to air on this column. GC-MS confirmed the molar mass of ClCB with parent peaks at 88 and 90. In ppm relative to TMS, the proton NMR spectrum of ClCB in CDCl₃ showed signals at 5.82 (intensity 1, t, $(J_{HH} = 1.20 \text{ Hz})$ of t $(J_{HH} = 0.40 \text{ Hz}))$ for —CH and 2.74 (2, m), 2.39 (2, m) for CH₂'s. The proton-decoupled ¹³C NMR spectrum showed signals (ppm) at 130.6 for CCl, 127.6 for =CH, and 36.6, 26.1 for CH₂'s. Off-resonance decoupling gave the

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number of hydrogen atoms attached to each carbon atom. 1-Fluorocyclobutene. The reaction scheme for preparing FCB was



Fluorocyclobutane was made by condensing chlorocyclobutane in succession on two portions of vacuum-dried silver difluoride (Aldrich Chemical) and allowing reaction to occur at ice temperature.¹³ Byproduct SiF₄ was vacuum-distilled from the mixture at pentane-slush temperature.

1-Chloro-1-fluorocyclobutane was one product of the photolysis of a 1:1 mixture of gaseous fluorocyclobutane and chlorine. After HCl and SiF₄ were vacuum-distilled from the products at pentane-slush temperature, the mixture of five monochlorofluorocyclobutane isomers was separated by gas chromatography on the TCP column at 90 °C. 1-Chloro-1-fluorocyclobutane had an elution time of 2.4 relative to fluorocyclobutane. For 1-chloro-1-fluorocyclobutane, the gas-phase infrared spectrum showed bands (cm⁻¹) at 3020 s, 2970 s, 1425 m, 1270 s, 1225 m, 1165 s, 1110 s, 960 m, 890 m, 850 m, 790 s, 665 m, 565 m, 490 w, and 440 m. The proton NMR spectrum of 1-chloro-1-fluorocyclobutane in CFCl₃ showed signals at 2.67 (intensity 4, m) and 1.87 ppm (2, m); the ¹³C NMR spectrum, signals at 109.6 ppm (d (J_{CF} = 286 Hz)), for CFCl, 41.50 ppm (d $(J_{CF} = 22 \text{ Hz}))$ for the near CH_2 's, and 11.78 ppm (d ($J_{CF} = 10 \text{ Hz}$)) for the distant CH_2 's; and the ¹⁹F spectrum, a multiplet at -85.9 ppm.

FCB was prepared by distilling 1-chloro-1-fluorocyclobutane through the coated Ascarite column, isolated by gas chromatography on an Apiezon M on Fluoropak column at 40 °C,14 and dried with P2O5. Relative to that of unconverted 1-chloro-1fluorocyclobutane, elution times were 0.30 for FCB and 0.21 for byproduct butadiene. GC-MS of FCB gave a molar mass of 72. The proton NMR spectrum of FCB showed signals at 4.67 ppm (intensity 1, d (J_{HF} = 8.7 Hz) of m) for =-CH, 2.70 (2, d (J_{HF} = 6.4 Hz) of t ($J_{\rm HH}$ = 3.1 Hz) of m) and 1.97 ppm (2, d ($J_{\rm HF}$ = 14.6 Hz) of t (J_{HH} = 3.1 Hz) for m) for CH₂'s; the ¹³C NMR spectrum, signals at 149.8 ppm d (J_{CF} = 343.1 Hz) for CF, 102.8 ppm (d (J_{CF} = 4.5 Hz)) for ==CH, and 32.8 (d (J_{CF} = 20.5 Hz)), 18.2 ppm (d ($J_{CF} = 24.3 \text{ Hz}$)) for CH₂'s; and the ¹⁹F NMR spectrum, a signal at -81.9 ppm (t (J_{HF} = 14.6 Hz) of d (J_{HF} = 8.7 Hz) of t $(J_{\rm HF} = 6.4 \text{ Hz}))$.

Cyclobutene. CB was prepared by dripping an equal-volume mixture of bromocyclobutane (Columbia Organic) and ethanol into a refluxing mixture of 5 g of KOH and 10 mL of 95% ethanol.8 The volatile CB and byproduct butadiene were collected in a dry ice cooled trap. CB was isolated by gas chromatography on the TCP column at 0 °C with care being taken to remove all byproduct butadiene. The elution time of CB relative to butadiene was 1.25. CB was dried by passage through P2O5.

Vibrational Spectroscopy. Infrared spectra were recorded on a Perkin-Elmer 1760 Fourier transform spectrometer with 0.5-cm⁻¹ resolution and a spectral range to 370 cm⁻¹. A Perkin-Elmer 580B dispersive instrument with resolution of about 1 cm⁻¹ was used for the low-frequency region to 180 cm⁻¹ and for the survey scans displayed in this paper. The gas cell was 10 cm in length and fitted with CsI windows. Raman spectra were recorded with 514.5-nm argon ion laser excitation on a computerized Spex Ramalog 5 system. Other details of the vibrational spectroscopy were as described before.15

Other Instrumentation. Mass spectra were obtained with a Hewlett-Packard 5970 quadrupole mass-selective filter coupled

⁽⁵⁾ Our choice for the b₁ and b₂ symmetry species is opposite to that of Baggott, Clase, and Mills but is consistent with that of all other workers. The plane of the ring is taken as a "higher order" symmetry element than the plane

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lyzed on a Chromosorb support. Subsequent work has shown that Fluoropak coated with TCP is an effective column for separating halocyclobutenes.

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Figure 1. Gas-phase infrared spectrum of 1-chlorobutene at 29 Torr and saturation pressure.

to a 5890A gas chromatograph (phenyl methyl silicone OV2 capillary column). NMR spectra were recorded on an IBM/ Bruker AC 200-MHz FT spectrometer. ¹H and ¹³C spectra were referenced externally to TMS and to CFCl₃.

Results and Discussion

CICB was one of two structures proposed for the product of isomerization of cyclopropylchlorocarbene.^{6,16,17} The other structure was chloromethylenecyclopropane.7 The principal reason for preferring the CICB structure was the production of chloroprene upon further isomerization.⁶ The proton NMR spectra, including the one reported here, are for a single substance.^{6,7} Since the proton NMR spectrum does not distinguish between the two isomers of symmetry grounds, it seems well to review the evidence for the CICB structure.

The evidence for the CICB structure is now quite strong. This evidence is chemical as well as spectroscopic. The current synthesis method, dehydrohalogenation of a dichlorocyclobutane, must give a chlorocyclobutene rather than a methylenecyclopropane. The chemical shifts for the CH_2 moieties in both the proton (2.4, 2.7) ppm) and ¹³C (36.6, 26.1 ppm) spectra are not characteristic of methylenecyclopropane rings. The CH₂ proton shift in the methylenecyclopropane ring is 1.0 ppm, and the ¹³C shift is 2.8 ppm.¹⁸ The CH₂ stretching frequencies in ClCB are well below 3000 cm⁻¹ and are in good agreement with those for CB. In contrast, corresponding CH₂ stretching frequencies in methylenecyclopropane are mostly well above 3000 cm⁻¹.¹⁹ Furthermore, as developed in this paper, the overall vibrational spectra of CICB are interpreted convincingly in favor of the cyclobutene structure. Comparable spectral evidence supports the cyclobutene structure for FCB.

Cyclobutenes have planar rings, as has been shown by a detailed microwave study of cyclobutene²⁰ and by spectroscopy of halogen-substituted cyclobutenes.⁹⁻¹¹ As is shown in this paper, the vibrational spectra of CICB and FCB are fully consistent with a planar ring. In both ClCB and FCB, the plane of the ring is the single element of symmetry. CICB is a near-prolate symmetric top ($\kappa = -0.93$) with the following approximate values for the principal moments of inertia in amu Å²: $I_a = 39.9$, $I_b = 199.1$, and $I_c = 232.6$.^{20,21} The corresponding values for FCB are 39.9, 116.7, and 150.3 and $\kappa = -0.79^{20,22}$ In both molecules the axis of the least principal moment of inertia, I_a , is essentially along the carbon-halogen bond, and the axis for the greatest principal moment of inertia, I_c , is perpendicular to the plane of the ring. Thus, for these molecules of C_s symmetry, the 15 modes of the

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 1981, 37A, 847 (for the CCl bond length of 1.70 Å).
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100 (for the CF bond length of 1.335 Å).



Figure 2. Liquid-phase Raman spectrum of 1-chlorocyclobutene at -48 °C and 195 mW: solid line, analyzer polarizer parallel to laser beam; dashed line, polarizer perpendicular.



Figure 3. 1-Chlorocyclobutene spectra in the CH stretching region: (top) gas-phase infrared spectrum at 0.5-cm⁻¹ resolution and 29 Torr; (bottom) liquid-phase Raman spectrum at -37 °C, 200 mW, and 2.5-cm⁻¹ resolution

a' symmetry species have type-A/B hybrid band shapes in the gas-phase infrared spectrum and polarized Raman bands. The nine modes of a" symmetry have type-C band shapes in the gas-phase infrared spectrum.

1-Chlorocyclobutene. The gas-phase infrared spectrum of ClCB is shown in Figure 1, and the liquid-phase Raman spectrum in Figure 2. Details of the CH stretching region in both spectroscopies are shown in Figure 3. Table I gives the observed frequencies and their assignments for this molecule. In the following discussion by symmetry species, we emphasize the less certain assignments.

a' Modes. Most of the 15 totally symmetric modes are firmly supported by appropriate band shapes in the infrared spectrum and polarized bands in the Raman spectrum. The depolarization ratios for the Raman bands at 1428 and 305 cm⁻¹ are within experimental uncertainty of the depolarized ratio of 0.75. Nonetheless, the shapes of the corresponding bands in the gasphase infrared spectrum and group-frequency considerations leave no doubt about the assignment of these frequencies to v_6 and v_{15} . Distinguishing two frequencies for the nearly degenerate symmetric CH₂ stretching modes and assigning three a' modes within 60 cm⁻¹ around 900 cm⁻¹ also require some justification.

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TABLE I: Observed Vibrational Frequencies (cm⁻¹) and Assignments for 1-Chlorocyclobutene

| $\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$ | | IR, gas | | F | Raman, liq | | | |
|---|-----------|--------------------|------------------|----------|------------------|------------------|--------------------------------|-------------|
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | freqª | shape ^b | int ^c | freq | pol ^d | int ^c | assignment | sym species |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 3179 | В | m | 3164 | р | w | $3190 = 2v_4$ | Α' |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 3090 (12) | В | m | 3083 | p | m | ν_1 fund. | a' |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 2980 | С | S | 2972 | dp | m | ν_{16} fund. | a″ |
| $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ | 2966 | С | m | 2960 | dp | m | ν_{17} fund. | a″ |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 2953 | A? | s | | | | ? | |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 2947 | A ? | S | 2939 | р | S | ν_2 fund. | a' |
| $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | 2940 | A? | m | 2931 | p | s | ν_3 fund. | a' |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 2890 | Α | m | | | | $2904 = 2\nu_5$ | a' |
| $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ | | | | 2875 | р | m | $2886 = \nu_5 + \nu_6$ | A' |
| $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | 2865 | Α | m | | - | | $2868 = 2\nu_6$ | Α' |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | | | | 2840 | р | m | $2845 = \nu_4 + \nu_7$ | A' |
| 1614 A m shoulder 1613 = $\nu_{10} + \nu_{14}$ A' 1595 (13) A s 1588 p s ν_{4} fund. a' 1504 B? w 1502 = $2\nu_{22}$ A' 1452 (14) A m 1444 p m ν_{5} fund. a' 1434 B? m 1428 dp? m ν_{5} fund. a' 1499 A m 1418 p m ν_{7} fund. a' 1284 B? m 1255 p w ν_{7} fund. a' 1255 (12) A s 1255 p w ν_{7} fund. a' 1146 A? m 1197 m n 149 p m ν_{9} fund. a' 1146 A? m 1162 p w ν_{9} fund. a' 1145 ν_{14} p m ν_{16} fund. a' a' 1140 dp w ν_{16} fund. a'' a' | | | | 1633 | p | w | impurity | |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 1614 | Α | m | shoulder | | | $1613 = \nu_{10} + \nu_{14}$ | Α' |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 1595 (13) | Α | S | 1588 | р | 8 | ν_4 fund. | a' |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 1504 | B ? | w | | | | $1502 = 2\nu_{22}$ | A' |
| | 1452 (14) | Α | m | 1444 | p | m | ν_5 fund. | a' |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 1434 | B ? | m | 1428 | dp? | m | ν_6 fund. | a' |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 1409 | Α | m | | | | $1419 = v_{10} + v_{15}$ | A' |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 1284 | B ? | m | | | | $1281 = \nu_{19} + \nu_{24}$ | Α′ |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 1255 (12) | Α | s | 1255 | р | w | ν_7 fund. | a' |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 1244 (12) | Α | s | 1242 | р | w | $1248 = \nu_{21} + \nu_{23}$ | A'* |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 1197 (13) | Α | m | 1194 | р | m | ν_8 fund. | a' |
| 1146A?m1140dpw $1145 = \nu_{22} + \nu_{23}$ A'1120 (13)As1112pw ν_{18} fund.a''1070 (19)Cm1069dpw ν_{19} fund.a''1016Cw1013dpw ν_{20} fund.a''986A?w~975pw986 = $2\nu_{14}$ A'966Bm962 = $\nu_{22} + \nu_{24}$ A'916 (12)Bm914pm ν_{11} fund.a'891 (13)As882ps ν_{12} fund.a''854C?m854dpm ν_{22} fund.a''612 (11)Bw605 = $\nu_{23} + \nu_{24}$ A'493 (14)As491pvs ν_{14} fund.a'486 | 1165 (14) | В | m | 1162 | р | w | ν9 fund. | a' |
| $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ | 1146 | A? | m | | | | $1145 = \nu_{22} + \nu_{23}$ | Α' |
| 1120 (13)As1112pw ν_{10} fund.a''1070 (19)Cm1069dpw ν_{19} fund.a'''1016Cw1013dpw ν_{20} fund.a'''986A?w~975pw986 = $2\nu_{14}$ A'966Bm962 = $\nu_{22} + \nu_{24}$ A'916 (12)Bm914pm ν_{11} fund.a'916 (13)As882ps ν_{12} fund.a'869 (14)As864pm ν_{13} fund.a'854C?m854dpm ν_{22} fund.a''612 (11)Bw605 = $\nu_{23} + \nu_{24}$ A'486485ps ν_{14} fund.a'486485ps ν_{14} fund.a'395 (20)Cm399dpw ν_{23} fund.a''299 (14)Bm305dp?m ν_{15} fund.a''211C?m227dpvw ν_{24} fund.a'' | | | | 1140 | dp | w | ν_{18} fund. | a‴ |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | 1120 (13) | Α. | S | 1112 | р | w | ν_{10} fund. | a' |
| 1016Cw1013dpw ν_{20} fund.a''986A?w~975pw986 = $2\nu_{14}$ A'966Bm962 = $\nu_{22} + \nu_{24}$ A'916 (12)Bm914pm ν_{11} fund.a'891 (13)As882ps ν_{12} fund.a'869 (14)As864pm ν_{13} fund.a'854C?m854dpm ν_{21} fund.a''751 (17)Cs752dpw 022 fund.a''612 (11)Bw 025 $\nu_{23} + \nu_{24}$ A'493 (14)As491pvs ν_{14} fund.a'486 -485 ps ν_{14} fund.a'395 (20)Cm399dpw ν_{23} fund.a''299 (14)Bm305dp?m ν_{15} fund.a''211C?m227dpvw ν_{24} fund.a'' | 1070 (19) | С | m | 1069 | dp | w | ν_{19} fund. | a″ |
| 986A?w~975pw986 = $2\nu_{14}$ A'966Bm967962 = $\nu_{22} + \nu_{24}$ A'916 (12)Bm914pm ν_{11} fund.a'891 (13)As882ps ν_{12} fund.a'869 (14)As864pm ν_{13} fund.a'854C?m854dpm ν_{21} fund.a''751 (17)Cs752dpw ν_{22} fund.a''612 (11)Bw ω $605 = \nu_{23} + \nu_{24}$ A'486 485 ps ν_{14} fund.a' 486 ω $454 = 2\nu_{24}$ A' $395 (20)$ Cm 399 dpw ν_{23} fund.a'' $299 (14)$ Bm 305 dp?m ν_{15} fund.a'' 211 C?m 227 dpvw ν_{24} fund.a'' | 1016 | С | w | 1013 | dp | w | ν_{20} fund. | a‴ |
| 966Bm $962 = v_{22} + v_{24}$ A'916 (12)Bm914pm v_{11} fund.a'891 (13)As882ps v_{12} fund.a'869 (14)As864pm v_{13} fund.a'854C?m854dpm v_{21} fund.a''751 (17)Cs752dpw o_{22} fund.a''612 (11)Bw $o_{05} = v_{23} + v_{24}$ A'493 (14)As491pvs v_{14} fund.a'486 v_{450} ps v_{14} fund.a'395 (20)Cm399dpw v_{23} fund.a''299 (14)Bm305dp?m v_{15} fund.a''211C?m227dpvw v_{24} fund.a'' | 986 | A? | w | ~975 | р | w | $986 = 2\nu_{14}$ | Α' |
| 916 (12)Bm914pm ν_{11} fund.a'891 (13)As882ps ν_{12} fund.a'869 (14)As864pm ν_{13} fund.a'854C?m854dpm ν_{21} fund.a''751 (17)Cs752dpw ν_{22} fund.a''612 (11)Bw $605 = \nu_{23} + \nu_{24}$ A'493 (14)As491pvs ν_{14} fund.a'486 -450 ps ν_{14} fund.a'295 (20)Cm399dpw ν_{23} fund.a''299 (14)Bm305dp?m ν_{15} fund.a''211C?m227dpvw ν_{24} fund.a'' | 966 | В | m | | | | $962 = \nu_{22} + \nu_{24}$ | Α′ |
| 891 (13) A s 882 p s ν_{12} fund. a' 869 (14) A s 864 p m ν_{13} fund. a' 854 C? m 854 dp m ν_{21} fund. a'' 751 (17) C s 752 dp w ν_{22} fund. a'' 612 (11) B w 605 = $\nu_{23} + \nu_{24}$ A' 493 (14) A s 491 p vs ν_{14} fund. a' 486 | 916 (12) | В | m | 914 | р | m | ν ₁₁ fund. | a' |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 891 (13) | Α | S | 882 | р | S | ν_{12} fund. | a' |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 869 (14) | Α | S | 864 | р | m | ν_{13} fund. | a′ |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 854 | C? | m | 854 | dp | m | ν_{21} fund. | a″ |
| 612 (11) B w $605 = \nu_{23} + \nu_{24}$ A' 493 (14) A s 491 p vs ν_{14} fund. a' 486 485 p s ν_{14} (^{17}Cl) a' 395 (20) C m 399 dp w ν_{23} fund. a'' 299 (14) B m 305 dp? m ν_{15} fund. a'' 211 C? m 227 dp vw ν_{24} fund. a'' | 751 (17) | С | s | 752 | dp | w | ν_{22} fund. | a″ |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 612 (11) | В | w | | | | $605 = v_{23} + v_{24}$ | Α′ |
| 486485ps ν_{14} (^{37}Cl)~450psh454 = $2\nu_{24}$ A'395 (20)Cm399dpw ν_{23} fund.a''299 (14)Bm305dp?m ν_{15} fund.a''211C?m227dpvw ν_{24} fund.a'' | 493 (14) | Α | S | 491 | р | vs | ν_{14} fund. | a' |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 486 | | | 485 | р | S | ν_{14} (³⁷ Cl) | |
| 395 (20)Cm399dpw ν_{23} fund.a''299 (14)Bm305dp?m ν_{15} fund.a'211C?m227dpvw ν_{24} fund.a'' | | _ | | ~450 | P | sh | $454 = 2\nu_{24}$ | Α' |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 395 (20) | С | m | 399 | dp | w | ν_{23} fund. | a″ |
| 211 C? m 227 dp vw v ₂₄ fund. a" | 299 (14) | В | m | 305 | dp? | m | ν_{15} fund. | a' |
| | 211 | C? | m | 227 | dp | vw | ν_{24} fund. | a″ |

^a PR spacing in parentheses. ^b Band shape, dominant component for A/B hybrids. ^cAbbreviations: vs = very strong; s = strong; m = medium; w = weak; vw = very weak. ^d Abbreviations: p = polarized; dp = depolarized. Fermi resonance with v_{γ} .

In the detailed Raman spectrum of ClCB in part of the CH stretching region in Figure 3, the strongly polarized band in the CH₂ stretching region has two partly resolved peaks of comparable intensity, one at 2939 cm⁻¹ and one at 2931 cm⁻¹. Consistent with different intensity characteristics of two modes, the residual peak in the polarized trace at 2937 cm⁻¹ corresponds to only one of the maxima. Furthermore, in the infrared spectrum in Figure 3 two likely Q branches of type-A bands appear at 2947 and 2940 cm⁻¹, and no binary combination tone is predicted in this region. Thus, the cumulative evidence supports distinct assignments for ν_2 and

Four bands appear in the congested 900-cm⁻¹ region in both the infrared and Raman spectra, as shown in the survey scans in Figures 1 and 2. In the infrared spectrum a band of largely type-B shape is centered at 916 cm⁻¹. Two bands of type-A shape have distinct Q branches at 891 and 869 cm⁻¹. In the Raman spectrum, all three bands have polarized counterparts in strong support of their assignment to a' modes. The fourth infrared band with a prominent Q branch at 854 cm^{-1} appears to be a type-C band and thus to be due to a mode of a" symmetry, v_{21} . This interpretation is supported by a shoulder at 854 cm⁻¹ in the Raman spectrum, which is almost certainly depolarized. Of course, a possibility for the occurrence of bands of the same a' symmetry within a narrow spectral range is Fermi resonance. Not only are the depolarization ratios in the Raman spectrum quite different for the three bands, but on the basis of the full assignment of the fundamentals, no binary combinations occur between 792 and 962 cm⁻¹. Thus,

Fermi resonance is unlikely. We conclude that three fundamentals of a' symmetry species, ν_{11} , ν_{12} , and ν_{13} , are at 916, 891, and 869 cm⁻¹, respectively.

a'' Modes. The assignments for six of the nine modes of a''symmetry, including ν_{21} as discussed in the previous paragraph, are supported by type-C band shapes in the gas-phase infrared spectrum and by depolarized Raman bands. The three exceptions are for v_{17} , v_{18} , and v_{24} . We consider the evidence in some detail in support of these assignments.

Can the two nearly degenerate antisymmetric CH₂ stretching modes be distinguished? In Figure 3, the Q-branch at 2966 cm⁻¹ in the infrared spectrum appears to be the center of a type-C band second to the obvious one at 2980 cm⁻¹. In the Raman spectrum, the breadth of the depolarized band in the 2965-cm⁻¹ region suggests two overlapping bands. No binary combination tone of A" symmetry species is predicted in this region. In addition, the frequency shifts between the gas phase and liquid phase for these two modes are close to the shifts found for the two symmetric CH₂ stretching modes. We assign the second antisymmetric CH₂ stretching mode at 2966 cm⁻¹.

For v_{24} the type-C band shape in the infrared spectrum at 211 cm⁻¹ is in doubt because of the low intensity of this band and its location near the limit of performance of the available spectrometer. Nevertheless, the weak feature looks like a dominant Q branch of a type-C band. Though weak, the corresponding Raman band appears to be depolarized. In addition, these features cannot be due to a mode of a' symmetry species, since a sufficient



Figure 4. Gas-phase infrared spectrum of 1-fluorocyclobutene at 11 and 36 Torr.



Figure 5. Liquid-phase Raman spectrum of 1-fluorocyclobutene at -35 °C and 210 mW.

number of low-frequency modes of a' symmetry species have been assigned at higher frequencies. We assign v_{24} with confidence at 211 cm⁻¹. The unusual, marked shift to higher frequency in going from the gas phase to the liquid phase also seems to occur in CB and may be characteristic of ring-puckering modes.²³

The CH₂ torsion, ν_{18} , appears to be represented by the depolarized Raman band of weak-to-medium intensity at 1140 cm⁻¹. Though of low intensity, this depolarized band is an unlikely candidate for an alternative assignment as a combination tone. In Raman spectra, the observable bands due to combination tones are normally polarized and assignable to transitions of totally symmetric modes. In the Raman spectrum of CICB, Figure 2, the two bands nearest 1140 cm⁻¹ are definitely polarized and thus unlikely partners in Fermi resonance with the depolarized band at 1140 cm⁻¹. Unfortunately, little support for the assignment of v_{18} to 1140 cm⁻¹ comes from the infrared spectrum. A band of approximately type-B shape occurs at slightly higher frequency. Although the P branch of this band has enhanced intensity, no Q branch of a type-C band ban be discerned in the structure of the P branch. Low intensity for the infrared transition of v_{18} is not surprising, since this mode correlates with the infrared-inactive CH₂ torsion of a_2 symmetry species in CB. Reinforcing the assignment of ν_{18} at 1140 cm⁻¹ is the value of 1142 cm⁻¹ for this fundamental in CB (see below).

Summary. In conclusion, we regard the assignment of the 24 fundamentals of CICB as complete. This assignment, which is summarized in Table IV, is reinforced by good correlations with the assignments for the isotopomer-like FCB, as presented below. In addition, a number of weak features in the infrared and Raman spectra can be explained as binary combinations, as shown in Table I. The spectral evidence confirms C_s symmetry and thus a planar ring for ClCB.

1-Fluorocyclobutene. Figures 4 and 5 are the survey spectra of FCB in the infrared region and for the Raman effect. A small amount of butadiene impurity contributes to these spectra, especially to the Raman spectrum.²⁴ Figure 6 shows the details of both spectra in part of the CH stretching region at higher resolution, and Figure 7 is a detail of the Raman spectrum in the 1000-1300-cm⁻¹ region. Table II gives all the frequencies of the



Figure 6. 1-Fluorocyclobutene spectra in the CH stretching region: (top) gas-phase infrared spectrum at 11 Torr and 0.5-cm⁻¹ resolution; (bottom) liquid-phase Raman spectrum at -79 °C at 2.5-cm⁻¹ resolution and 300 mW (two scans).



Figure 7. Liquid-phase Raman spectrum of 1-fluorocyclobutene in the 1000-1300-cm⁻¹ region at -87 °C, 2.5-cm⁻¹ resolution, and 300 mW (nine scans); parallel polarization.

spectral features and their assignments. In the discussion by symmetry species that follows, we emphasize less secure assignments.

a' Modes. Fourteen of the 15 modes of the a' symmetry species are rather well supported by type-A/B band shapes in the gasphase infrared spectrum and polarized counterparts in the liquid-phase Raman spectrum. The occurrence of three of these modes of the same symmetry within 60 cm⁻¹ around 1200 cm⁻¹ raises some questions. The polarization ratio for v_{14} at 413 cm⁻¹ is close to the depolarization limit of 0.75. Nevertheless, the near type-B band shape leaves no question about this assignment. The separate assignment of the second symmetric CH₂ stretching mode at 2948 cm⁻¹ is the exception among the a' modes in that no Raman feature has been distinguished for this mode.

In Figure 6, for the CH stretching region of FCB, two distinct Q branches characteristic of type-A bands are seen at 2954 and

⁽²³⁾ In the gas-phase infrared spectrum of CB, a feature at 535 cm⁻¹ can (25) In the gas phase infrared spectrum of CB, a feature at 55 cm⁻¹, if $\nu_{13} = 314$ cm⁻¹ in the gas phase, a frequency lower than that in the liquid phase. (24) Bondybey, V. E.; Nibler, J. W. Spectrochim. Acta 1973, 29A, 645. (25) Craig, N. C.; Hawley, S. E.; Perry, C. L. Spectrochim. Acta, in press.

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TABLE II: Observed Vibrational Frequencies (cm⁻¹) and Assignments for 1-Fluorocyclobutene

| | | IIK, gas | | | Kaman, ny | | | | | |
|------|------|--------------------|------------------|------|-----------------|------------------|--------------------------------------|-------------|--|--|
| fre | eq" | shape ^b | int ^c | freq | pold | int ^c | assignment | sym species | | |
| 3111 | (15) | А | m | 3102 | p | m | ν ₁ fund. | a' | | |
| 3002 | | р | m | | | | 3002 ^e impurity butadiene | | | |
| 2982 | (17) | Ċ | s | 2973 | dp | m | v_{16} fund. | a″ | | |
| 2969 | | C? | m | | - | | ν_{17} fund. | a‴ | | |
| 2954 | (13) | Α | s | 2944 | р | vs | ν_2 fund. | a' | | |
| 2948 | (12) | Α | S | | - | | ν_3 fund. | a' | | |
| 2911 | | A ? | m | 2902 | р | w | $2928 = 2\nu_5$ | Α' | | |
| 2900 | | A? | m | 2889 | p | m | $2901 = v_5 + v_6$ | Α′ | | |
| 2875 | (17) | Α | m | 2862 | p | m | $2881 = \nu_4 + \nu_8$ | Α' | | |
| | . , | | | 2845 | р | m | $2856 = \nu_A + \nu_9$ | Α' | | |
| 1667 | (18) | A/B | vs | 1654 | p | vs | $v_{\rm A}$ fund. | a' | | |
| 1632 | · · | A? | m | 1637 | p | m | 1638 ^e impurity butadiene | | | |
| 1625 | | A? | m | 1622 | p | w | $1626 = v_8 + v_{15}$ | Α' | | |
| 1618 | | Α | m | | • | | $1623 = v_{11} + v_{14}$ | Α' | | |
| 1464 | | Â | w | 1460 | p | m | vs fund. | a' | | |
| | | | | 1451 | Ď | m | $1456 = y_{20} + y_{22}$ | Â'ſ | | |
| | | | | 1437 | r | w | 1438 ^e impurity butadiene | | | |
| 1437 | (17) | В | m | 1430 | Ð | m | ν_{ϵ} fund. | a' | | |
| 1327 | (18) | Ā | m | | r | | $1340 = v_{10} + v_{24}$ | Â' | | |
| 1306 | (18) | A/B | vs | 1293 | n | w | v_{τ} fund. | a′ | | |
| | () | , = | | 1277 | n | w | 1278 ^e impurity butadiene | u u | | |
| 1277 | | A 7 | m | | P | | $1291 = y_{01} + y_{02}$ | Δ' | | |
| 1214 | (20) | A | m | 1209 | n | m | v_0 fund | a' | | |
| | (20) | •• | | 1203 | P | w | 1203 ^e impurity butadiene | u | | |
| 1189 | (20) | Α | m | 1185 | dn ⁹ | w | v _o fund | a′ | | |
| 1154 | (18) | A | m | 1148 | up. | w | v. fund | a' | | |
| 1151 | (10) | <i>.</i> | | 1140 | dn? | w | no fund | a″ | | |
| 1076 | (28) | C | w | 1076 | dn. | w | via fund | a 9″ | | |
| 1020 | (20) | č | w | 1018 | dn | w | v ₁₀ fund | a 9″ | | |
| 1014 | | č | w | 1010 | чp | ** | impurity butadiene | a | | |
| 972 | (18) | Δ | • • | 962 | n | VE | nipurity outaclene | a' | | |
| 712 | (10) | A | 3 | 902 | P | *3 | 2 2 | a | | |
| 911 | (16) | ۸ | m | 011 | P | | . fund | a' | | |
| 908 | (10) | ô | m | 711 | Р | | ? impurity butadiene | a | | |
| 200 | | Ŷ | 111 | 877 | 9 | - | $\frac{1}{2}$ | A/ | | |
| 866 | (20) | • | m | 866 | ; n | m | $372 - 2\nu_{23}$ | ~ | | |
| 855 | (20) | A C | m | 000 | P | 111 | ν_{13} fund. | a 2// | | |
| 764 | (22) | Č | | 745 | dm | | ν_{21} fund. | a* | | |
| /04 | (22) | D D | m | 705 | ap | w | v_{22} rund. | a | | |
| 692 | (20) | <u>Б</u> | w | 703 | р | w | $v_{00} = v_{23} + v_{24}$ | A | | |
| 651 | (20) | A | m | 048 | р | s | v_{14} rund. | a | | |
| | | | | 538 | p | w | $520 = 2v_{24}$ | A' | | |
| 434 | (36) | C | | 513 | P | W | 513 impurity butadiene | . 11 | | |
| 430 | (23) | | m | 439 | ap | m | ν_{23} fund. | a'' | | |
| 412 | (20) | в | m | 413 | ap? | m | v_{15} fund. | a' | | |
| | | | | 264 | dp | w | ν_{24} fund. | a‴ | | |

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^a PR spacing in parentheses. ^b Band shape, dominant component for A/B hybrids. ^cAbbreviations: vs = very strong; s = strong; m = medium; w = weak; vw = very weak. ^dAbbreviations: p = polarized; dp = depolarized. ^cReference 24. ^fFermi resonance with ν_5 .

2948 cm⁻¹. This spectral region is similar to that of ClCB, Figure 3. We take the two Q branches to be due to the two symmetric CH₂ stretching modes, since no binary combination tone is predicted in this region. The single strong and polarized Raman feature does not distinguish between these two modes, in contrast to the Raman spectrum of ClCB.

The overall evidence supports assignments as fundamentals for each of the three infrared bands of type-A shape that overlap in the 1200-cm⁻¹ region. As shown in Figure 7, the Raman counterpart at 1185 cm⁻¹ of the middle band is much weaker than the Raman counterparts of the other two. Were the middle due to a combination tone gaining intensity by Fermi resonance mixing, the relative intensities of the two neighboring components would be expected to be comparable in both spectroscopies. Thus, we rule out the possibility that the combination tone, $\nu_{22} + \nu_{23}$, predicted at 1200 cm⁻¹ is contributing to this cluster and assign all three bands to fundamentals.

a" Modes. Assignments of five of the modes of a" symmetry are reported by gas-phase infrared bands of type-C shape and by corresponding depolarized bands in the Raman spectrum. For the other four modes, evidence is largely absent from one of the spectroscopies.

For the second antisymmetric CH_2 stretching mode, Figure 6 shows a likely Q-branch of a second type-C band at 2969 cm⁻¹

in the infrared spectrum. In addition, the Raman spectrum has a broad band in this region that suggests the overlap of two bands. The correlation with both spectra of ClCB, Figure 3, is close. Thus, we assign ν_{17} at 2969 cm⁻¹.

In Figure 7, we take the shoulder at 1142 cm^{-1} to be ν_{18} . The infrared spectrum of this region is dominated by rather intense bands due to modes of a' symmetry. Furthermore, ν_{18} , which correlates with the torsion of the a_2 symmetry species in CB, is expected to have low intensity in the infrared spectrum. Were it not for the more secure assignments of the corresponding mode in CB and in ClCB, we would hesitate to make this assignment.

In the gas-phase infrared spectrum the prominent type-C shape at 855 cm⁻¹ directs the assignment of ν_{21} even though the Raman spectrum of this region is dominated by the polarized band due to ν_{13} of the a' symmetry species. For the ring-puckering mode, ν_{24} , observed as a weak depolarized band at 264 cm⁻¹ in the Raman spectrum, no counterpart was found in the gas-phase infrared spectrum at the maximum pressure of our sample. Despite the single-spectrum evidence for these two modes, we have no doubt about the assignments.

Summary. With the exception of some residual questions about the assignment of ν_{18} (a") and about distinguishing two CH₂ stretching frequencies of each symmetry species, the assignments of the 24 fundamentals of FCB seem secure. Table II includes

TABLE III: Revised Vibrational Assignment for Cyclobutene in Comparison with Previous Assignments⁴

| | | I | R, gas | Ram | an, liq | | | | | |
|--------------------|---------------------------|------|-------------------|------|----------|------------------|--------------|---------------------|-----------|--|
| mode a | nd approx descripn | freq | int, shape | freq | int, pol | BCM ^b | AG | LR ^d | SK, calcd | |
| a, (IR | type A; R, pol) | | | | | | | | | |
| , vi | sym =CH str | 3067 | m, A | 3053 | s, p | \checkmark | \checkmark | 3058 | 3050 | |
| ν ₂ | sym CH ₂ str | 2943 | s, A | 2930 | vs, p | \checkmark | \checkmark | 2933 | 2939 | |
| ν ₃ | C=C str | 1570 | w, A | 1563 | vs, p | \checkmark | \checkmark | 1566 | 1575 | |
| νA | sym CH ₂ bend | 1449 | vw, A | 1441 | m, p | \checkmark | \checkmark | 1444 | 1433 | |
| vs | sym —CH bend | 1185 | w, A | 1180 | m, p | \checkmark | 1182 | 1276 | 1241 | |
| ¥6 | ĆC str | 1116 | vw, A | 1112 | vs, p | \checkmark | 1112 | 1182 | 1148 | |
| ν ₇ | sym CC str | 980 | vw, A | 984 | m, p | \checkmark | 984 | 1113 | 1071 | |
| ν ₈ | sym CH ₂ wag | 875? | w, ? | 875 | m, p | \checkmark | 874 | 986 | 941 | |
| a ₂ (IR | inactive; R, dp) | | | | | | | | | |
| <i>v</i> 9 | sym CH ₂ str | | | 2944 | m, dp | \checkmark | | (2950)8 | 2970 | |
| P10 | sym CH ₂ tors | 1145 | vw, Q | 1142 | w, dp | \checkmark | 1144 | (1100) ^g | 1267 | |
| V11 | sym CH ₂ rock | 1015 | vw, Q | 1011 | w, dp | 906 | 909 | (800) | 1094 | |
| V12 | HC=CH tors | | | 846 | m | 689 | | (640)\$ | 813 | |
| ν_{13} | ring pucker | | | 328 | w, dp | \checkmark | \checkmark | 325 | 286 | |
| b ₁ (IR | , type B; R, dp) | | | | | | | | | |
| V14 | asym ==CH str | 3058 | m, B * | 3044 | m, dp? | \checkmark | 3046 | 3126 | 3019 | |
| V15 | asym CH ₂ str | 2937 | s, B ^h | | • | \checkmark | 2934 | 2916 | 2929 | |
| P16 | asym CH ₂ bend | 1432 | w, B* | 1424 | m, dp? | \checkmark | \checkmark | 1426 | 1405 | |
| V17 | asym —CH bend | 1296 | m, B * | 1290 | vw, dp? | \checkmark | \checkmark | 1288 | 1278 | |
| V18 | asym CH ₂ wag | 1214 | w, B* | 1209 | vw, dp? | \checkmark | \checkmark | 1210 | 1198 | |
| V19 | CCCC ring bend | 906 | w, B? | 903 | w, dp | 888 | 1009 | 875 | 929 | |
| ^ν 20 | asym CC str | 888 | m, B * | ~886 | sh, dp? | | 885 | 850 | 747 | |
| b ₂ (IR | type C; R, dp) | | | | | | | | | |
| P21 | asym CH ₂ str | 2963 | s, C ^h | 2953 | w, dp? | \checkmark | \checkmark | 2955 | 2982 | |
| v22 | asym CH_2 tors | 1075 | m, C [*] | 1073 | w, dp | \checkmark | \checkmark | 1074 | 1111 | |
| V23 | asym CH ₂ rock | 848 | s, C ^h | 847 | m, dp | \checkmark | \checkmark | 846 | 885 | |
| V24 | —CH flap | 635 | s, C ^k | 639 | vw, dp | \checkmark | \checkmark | 635 | 617 | |

^a Frequencies are in cm⁻¹. Check marks indicate that the referenced authors agree within experimental error with the earlier work of authors listed to the right and with the present assignments. ^bReference 4. ^cReference 2. ^dReference 1. ^cReference 3. ^JFrom crystal-phase measurements. ^sFrequencies in parentheses are estimates. ^hRotational spacing of $\sim 0.8 \text{ cm}^{-1}$ for the more intense Q branches of subbands confirms these band shapes. The predicted spacing is $\sim 0.4 \text{ cm}^{-1}$ with a 1:3 intensity ratio, as seen in ref 4.



Figure 8. Liquid-phase Raman spectrum of cyclobutene at -98 °C and 420 mW.

the assignments for the stronger binary combination tones. Others have been omitted for brevity. The assignment of fundamentals is summarized in Table IV in comparison with the assignment for ClCB. The good correlation of most of the frequencies for these two isotopomer-like molecules, as discussed below, is further support for the assignments for both molecules.

Cyclobutene. Our principal contribution to the vibrational spectroscopy of cyclobutene is a Raman spectrum of the liquid at low temperature. Previous liquid-phase spectra were observed at room temperature. Lord and Rea (herafter LR) did a study in prelaser days with photographic detection.¹ Aleksanyan and Garkusha (hereafter AG) did laser Raman spectroscopy of the liquid at room temperature and of the solid at liquid nitrogen temperature.² They reported their results only in tabular form. Figure 8 is a survey spectrum of liquid cyclobutene at -98 °C, which agrees in general with the report of AG but which gives much better evidence for weaker features due to band sharpening at the lower temperature. We also examined the spectrum of the frozen material in a capillary at -146 °C. Our spectrum of the solid confirms the published report of AG, including the splittings of various bands, except for differences of a few wavenumbers for most of the bands.



Figure 9. Gas-phase infrared spectrum of cyclobutene in the 850-cm⁻¹ region at 53 Torr and 0.5-cm⁻¹ resolution.

We also reexamined the gas-phase infrared spectrum at somewhat lower resolution than that used by Baggott, Clase, and Mills (hereafter BCM).⁴ Our spectrum agrees closely with the published spectrum, thereby confirming that both samples were free of the troubelesome butadiene impurity and thus suitable for use in interpreting weak features. In addition, the somewhat lower resolution, 0.5 cm⁻¹ versus 0.1 cm⁻¹, revealed a feature in the congested 850-cm⁻¹ region that bears on the assignment of fundamentals. This portion of the spectrum at 0.5-cm⁻¹ resolution is shown in Figure 9. Missing from the spectra reported by BCM was the region below 700 cm⁻¹, which contains a type-C band centered at 635 cm⁻¹ and flanked by well developed rotational structure in both the R and P branches. A second, significant Q branch at 640 cm⁻¹ is probably due to Fermi resonance with the $2\nu_{13} = 656$ cm⁻¹ (liquid phase) combination tone. The overall band also appears to have some hot-band structure. For other regions in the gas-phase spectrum, we refer the reader to the published figures.⁴

Table III summarizes the history of assignments of vibrational fundamentals of cyclobutene along with our proposed revisions in the assignment. Check marks in the table indicate that the referenced authors agree with experimental error with the earlier work of authors listed to the right and with the present assignment on the left. This table summarizes the present infrared and Raman evidence. Contributing to the difficulty in assigning the vibrational fundamentals of CB is the occurrence of a number of instances of near-mutual exclusion between the infrared and Raman spectra despite the C_{2v} symmetry of this molecule. As seen in Table III for the a₁ symmetry species, six of the eight fundamentals are represented by weak or very weak bands in the infrared spectrum. For the b_2 modes, three of the four modes have weak or very weak Raman bands. For the b_1 symmetry species, four of the six modes have weak or very weak Raman bands, and one of the remaining ones has a weak infrared band. For the a2 modes, only Raman activity is expected.

As Table III shows, general agreement has been reached on the assignments for the modes of the a_1 and b_2 symmetry species. Eight polarized Raman bands of significant intensity leave no doubt about the a_1 assignments. Type-C bands, confirmed by the resolved rotational spacing, in the gas-phase infrared spectrum settle the assignments of the b_2 modes. The discrepancies in the published assignments for CB are in the b_1 and a_2 symmetry species. For the first four of the six b_1 modes, all workers agree within experimental error with the original assignments of LR. All agree that one of the two remaining b_1 modes is at 888 cm⁻¹.

BCM and AG have assigned the mode near 900 cm⁻¹ to v_{11} , the CH_2 torsion of a_2 symmetry. We conclude, however, that this frequency belongs to another mode, most likely of b₁ symmetry. In part, the reason is that there is a better candidate for v_{11} . New evidence from the low-temperature Raman spectrum, shown in Figure 8, is the depolarized feature at 1011 cm⁻¹ that we assign to v_{11} (a₂). This band has a very weak counterpart in the gas-phase infrared spectrum that could be a consequence of some intensity due to Coriolis coupling. BCM assigned this infrared feature to a combination tone, $\nu_{12} + \nu_{13}$, and thereby placed ν_{12} at 689 cm⁻¹. Given our results for CICB and FCB, their derived frequency for v_{12} is too low for the HC=CH torsion. The intensity of the Raman band at 1011 cm⁻¹ is too high for a combination tone in the absence of Fermi resonance, and no credible binary tone explains a frequency of 1011 cm⁻¹. Furthermore, assignments for six binary combination tones $(2A_1, 1B_1, 3B_2)$ support this assignment for v_{11} at 1011 cm⁻¹.

We turn to the revised assignment of the mode near 900 cm⁻¹. As Figure 10 shows, a depolarized Raman feature at 903 cm⁻¹ is more distinct in the liquid phase at low temperature and unmistakable in the crystal phase. This band must represent a fundamental, either v_{12} (a₂) or the remaining b₁ mode. We favor assigning this mode as v_{19} of b_1 symmetry for two reasons. As seen in Figure 9, a distinct feature appears near 900 cm⁻¹ on the R branch of the type-B band in this region. In the higher resolution spectrum of BCM, this feature seems to have a mate at slightly higher frequency that could be the partner Q branch of a type-B band. Also, this band has sufficient intensity in the gas-phase infrared spectrum to appear on top of the R branch, an unlikely outcome for a mode of a_2 symmetry, which should be infrared inactive. The second reason is that the assignments for CICB and FCB imply a somewhat lower frequency than 900 cm⁻¹ for the HC=CH torsion. A residual concern about assigning v_{19} at 903 cm⁻¹ and, thus, v_{20} at 888 cm⁻¹ is the nearness of these two modes of the same symmetry species. If one is mostly antisymmetric CC stretching and the other mostly in-plane bending of the CCCC framework, each carbon atom is moving in largely orthogonal directions in the two modes. Thus, little mixing should occur, and similar frequencies are acceptable.

Left to be considered are assignments for v_9 and v_{12} of the a_2 symmetry species. All previous workers agree in predicting the a_2 antisymmetric CH₂ stretching mode around 2950 cm⁻¹. The



Figure 10. Liquid-phase and solid-phase Raman spectra of cyclobutene in the 850-cm⁻¹ region: (top) liquid-phase spectrum at -94 °C and 420 mW (16 scans), (bottom) solid-phase spectrum at -146 °C and 310 mW (25 scans). The resolution is 2.5 cm⁻¹ for all spectra.

new, low-temperature Raman spectrum of the liquid has partly resolved features at 2953 and 2943 cm⁻¹, which appear to be depolarized. The solid-phase Raman spectrum has well-defined features at comparable frequencies. Consequently, we assign the lower frequency to v_9 . An alternative is to assign these Raman features to v_{15} (b₁). Such an assignment would, however, involve a shift to higher frequency in going from the gas phase to the condensed phase. Less certain experimental evidence points to an assignment of v_{12} in the 850-cm⁻¹ region. As seen in Figure 9, a Q-branch feature appears at 815 cm⁻¹ in the gas-phase spectrum. A difference tone, $v_4 - v_{24} = 814 \text{ cm}^{-1}$ (b₂), can explain this band, however. The 635-cm⁻¹ frequency of v_{24} is rather high to contribute a difference tone at room temperature. Nevertheless, a weak feature at 550 cm⁻¹ appears to be another difference tone involving v_{24} , $v_5 - v_{24} = 550 \text{ cm}^{-1}$ (B₂). In addition, the 815-cm⁻¹ feature has no counterpart in the Raman spectrum in Figure 10, unless it is a weak feature observed in the solid-phase spectrum at 837 cm⁻¹. A frequency increase of 22 cm⁻¹ in going from gas to solid would be exceptional. We prefer to assign the 815-cm⁻¹ feature in the gas-phase spectrum to a difference tone and to take the band at 846 cm⁻¹ in the solid-phase Raman spectrum, Figure 10, as v_{12} . This choice is questionable because the two components in the solid-phase Raman spectrum near 850 cm⁻¹ may be due to crystal splitting of the ν_{23} mode. Although two or three bands in the solid phase spectrum are clearly split by crystal effects, most of the modes are represented by single bands. Unfortunately, no binary combination tones provide additional support for the assignment of v_{12} to 846 cm⁻¹. As remarked above, BCM derived a value of 689 cm⁻¹ for ν_{12} from combination tones. One was a combination with v_{13} to give 1015 cm⁻¹, which is better interpreted as v_{11} (a₂). The other combination tone was 1538 cm⁻¹ formed with ν_{23} to have B₁ symmetry and give a band of type-B shape. However, the evidence for this band shape is meager, and a band of type-C shape is clearly present at 1540 cm⁻¹. In the Raman spectrum, a polarized band, probably due to v_3 of the ¹³C molecular species, is the only feature near 1540 cm⁻¹. Given all the experimental evidence and a good correlation of the average of ν_{12}

TABLE IV: Vibrational Assignments, Characterizations, and Frequencies (cm⁻¹) for 1-Chlorocyclobutene, 1-Fluorocyclobutene, and Cyclobutene

| approx descripn" | | | |
|--|--------|-------|---------------------------|
| | a' Moo | ies | |
| ν_1 , ==CH str | 3090 | 3111 | $3067 (a_1)/3058 (b_1)$ |
| ν_2 , sym CH ₂ str (a ₁) | 2947 | 2954 | 2943 |
| ν_3 , sym CH ₂ str (b ₁) | 2940 | 2948 | 2937 |
| ν_4 , C=C str | 1595 | 1667 | 1570 |
| ν_5 , sym CH ₂ bend (a ₁) | 1452 | 1464 | 1449 |
| ν_6 , sym CH ₂ bend (b ₁) | 1434 | 1437 | 1432 |
| ν_7 , —CH bend | 1250 | 1214 | $1185 (a_1)/1296 (b_1)$ |
| ν_8 , CH ₂ wag (b ₁) | 1197 | 1189 | 1214 |
| ν9, CC str (a1) | 1165 | 1154 | 1116 |
| ν_{10} , sym CC str (a ₁) | 1120 | 972 | 980 |
| ν_{11} , CCCC ring bend | 916 | 911 | 906 |
| $\nu_{12}, CH_2 wag (a_1)$ | 891 | 866 | 875° |
| ν_{13} , asym CC str (b ₁) | 869 | 651 | 888 |
| ν_{14} , CCl(F) str | 493 | 1306 | |
| ν_{15} , CCl(F) bend | 299 | 412 | |
| | a″ Mo | des | |
| v ₁₆ , asym CH ₂ str (b ₂) | 2980 | 2982 | 2963 |
| ν_{17} , asym CH ₂ str (a ₂) | 2966 | 2969 | 2944 ^c |
| ν_{18} , CH ₂ tors (a ₂) | 1140° | 1142° | 1145 |
| ν_{19} , CH ₂ tors (b ₂) | 1070 | 1076 | 1075 |
| ν_{20} , sym CH ₂ rock (a ₂) | 1016 | 1020 | 1015 |
| ν_{21} , asym CH ₂ rock (b ₂) | 854 | 855 | 848 |
| ν_{22} , —CH flap | 751 | 764 | $846^{c} (a_2)/635 (b_2)$ |
| ν_{23} , =CCl(F) flap | 395 | 436 | |
| v24, ring pucker | 211 | 264° | 328° |

^aSymmetry designations refer to the $C_{2\nu}$ symmetry of unsubstituted cyclobutene and are approximate for the two halocyclobutenes. The numbering is appropriate to 1-chlorocyclobutene. See Table II for the proper numbering for 1-fluorocyclobutane. ^bAverage of a Fermi resonance doublet. ^cCondensed-phase values. All others from the gas phase.

 (a_2) and ν_{24} (b₂) with the frequency of the ==CH flapping mode in CICB and FCB, however, we conclude that ν_{12} lies somewhere in the 850-cm⁻¹ region and regard 846 cm⁻¹ as a reasonable assignment.

The whole set of fundamental frequencies of CB agree reasonably well with the normal-coordinate calculations of Sverdlov and Krainov shown in the last column of Table III,³ even though these calculations were fitted to the original assignment of fundamentals by LR. For the most part, the approximate characterizations of the modes of CB in terms of symmetry coordinates in Table III are fixed by symmetry considerations as well as the calculations of SK. The greatest area of doubt about these characterizations is deciding between the CCCC in-plane ring bend and the antisymmetry CC stretch, which belong to the same b_1 symmetry species and have closely similar frequencies. Although the normal-coordinate calculations of SK give a lower frequency to the CCCC bending mode, we have given the higher frequency to this mode. We have done so because the 906-cm⁻¹ frequency correlates closely with assignments for ClCB and FCB. This frequency is thus little dependent on halogen substitution on the vinyl carbon, a reasonable outcome for the in-plane ring-bending mode.

Summary. The assignments of the vibrational fundamentals of CB now seem secure for 23 of the 24 modes. Before the current work, five assignments were in doubt. These disputed assignments are in the a_2 and b_1 symmetry species. Prior agreement had been reached on two of the five a_2 modes and four of the six b_1 modes. One of the previously unobserved a_2 modes was ν_9 , the antisymmetric CH₂ stretching mode, which was estimated at 2950 cm⁻¹. This mode has been observed at 2944 cm⁻¹ in the present work. Most agree that another fundamentals is near 900 cm⁻¹. We find that the evidence supports assigning this mode to ν_{19} (b_1) and using the accepted frequency for a b_1 mode of 888 cm⁻¹ for ν_{20} . Strong experimental evidence now supports assigning ν_{11} (a_2) at 1011 cm⁻¹ in the liquid phase. Though more tentative, the accumulated evidence suggests that the remaining fundamental of the a_2 sym-

TABLE V: Ring-Puckering Modes for Cyclobutenes

| compound | freq, cm ⁻¹ | ref |
|------------------------------------|------------------------|-----|
| cyclobutene | 328 | a |
| 1-fluorocyclobutene | 264 | а |
| 1-chlorocyclobutene | 211 | а |
| 3-fluorocyclobutene | 222 | Ь |
| 3-chlorocyclobutene | 1 97 | Ь |
| cis-3,4-dichlorocyclobutene | 145 | с |
| trans-3,4-dichlorocyclobutene | 134 | Ь |
| 3,3,4,4-tetrafluorocyclobutene | 132 | b |
| perfluorocyclobutene | 98 | d |
| 1,2-dichlorotetrafluorocyclobutene | 78 | d |

^a Present work. ^b Reference 25. ^c Reference 9 gives 381 cm⁻¹. This frequency is revised to 145 cm⁻¹ on the basis of our assignment for the trans isomer and correlation with other halocyclobutenes. ^d Reference 11.

metry species, ν_{12} , is near 845 cm⁻¹. The overall assignment of fundamentals agrees reasonably well with the normal-coordinate calculations of SK and correlates strongly with the assignments for ClCB and FCB, as discussed below.

Correlation of the Fundamentals of 1-Chlorocyclobutene, 1-Fluorocyclobutene, and Cyclobutene. Table IV summarizes the assignments of fundamentals of ClCB and FCB and correlates them with the fundamentals of CB. The approximate characterizations in symmetry coordinates for the 1-halocyclobutenes are reinforced by the greater symmetry constraints on the assignments for CB. For each of the =CH modes, the two related modes of CB are given. The C_{2v} symmetry species of CB are used to distinguish similar modes due to the CH₂ groupings in the 1-halocyclobutenes.

The modes that are due largely to =CH and CH₂ groupings in ClCB and FCB correlate closely. For the modes of a' symmetry above 1400 cm⁻¹ and for all the modes of a'' symmetry, in which mixing with other modes is small, the frequencies for FCB are slightly higher than those for ClCB. The remaining =CH and CH₂ modes of a' symmetry below 1400 cm⁻¹ also correlate closely between ClCB and FCB. Between CB and the two 1-halocyclobutenes, the CH₂ modes also correlate well. Average values for each pair of =CH modes in CB correlate with each single value in the halocyclobutenes after some allowances for an increase in frequency with halogen substitution.

Though more varied due to the difference between the effects of chlorine and fluorine, the skeletal modes of ClCB and FCB also make sense. Through effects on both the G and F matrix elements, halogen substitution on the double bond raises the "C==C stretching" frequency. A similar effect has been noted in cyclopropenes.²² The effect is larger with fluorine substitution. The substantial frequency decrease in the antisymmetric CC stretching mode (b_1) in FCB likely reflects mixing of this symmetry coordinate with the higher frequency CF stretching coordinate. In the CICB molecule, it is probable that the symmetric CC stretching frequency is raised by mixing with the CCl stretching coordinate. The higher frequencies for CF bending modes in FCB in comparison with the CCl bending modes in ClCB are as expected. The ring-stretching and ring-bending frequencies of CB also correlate rather well with those of the two halogen-substituted species after allowance for the effects of halogenation described above.

The close correlation between the frequencies of the fundamentals of ClCB, FCB, and CB reinforces the assignments for each of these molecules. In particular, the revisions in the assignments of CB are given added weight.

With our recently published assignment of the vibrational spectra of 1,4,4-trifluorocyclobutene, we included a correlation of the fundamentals of this molecule with those of CB.¹⁰ At that time, our work on the 1-halocyclobutenes and CB was in progress. With two exceptions, the characterizations of modes that we cited for CB were the same as the ones we give now. The exceptions were interchanging the characterizations of two of the b₁ modes, ν_{18} and ν_{20} , which followed the designations of BCM.⁴ In our present work we have been guided by the SK calculations³ and

correlations with the assignments for CICB and FCB in exchanging the characterizations of these modes.

Ring-Puckering Mode. Both 1-halocyclobutenes have appreciably lower ring-puckering frequencies than CB due to the anchoring effect of the halogen substituent. With the heavier halogen atom substituent, CICB has the lower ring-puckering frequency. Table V shows the relationships between ring-puckering frequencies and halogen substitution on cyclobutene. Included in Table V is our revision of the assignment for cis-3,4-dichlorocyclobutene as well as some other ring-puckering frequencies for halocyclobutenes from work in our laboratory. Halogen substitution on the methylene carbon causes a larger frequency decrease than does substitution on the vinyl carbon. The greater effect is surely due to inhibition of the motion of the singly bonded methylene carbon atoms, which have greater excursions than the vinyl carbon atoms in unsubstituted cyclobutene. Substituting chlorine atoms on each of the methylene carbons causes about twice the frequency lowering as adding a chlorine atom to one. Substituting two fluorine atoms on each of the methylene carbons has the same effect as substituting one chlorine on each carbon. Thus, the effect seems largely a mass effect. Simplicity of the pattern of changes in ring-puckering frequencies due to halogen substitution is consistent with this out-of-plane mode being rather free of mixing with other modes.

Conclusions

Gas-phase infrared spectra and liquid-phase Raman spectra have provided complete assignments of the 24 vibrational fundamentals of 1-chlorocyclobutene and 1-fluorocyclobutene and have confirmed the previously disputed cyclobutene structure for the chloro compound. A close correlation exists between the CH-rich modes of these isotopomer-like molecules. The relationship between the skeletal modes of the two molecules has also been interpreted qualitatively in terms of mixing of symmetry coordinates.

Despite several detailed studies in the past, the fundamentals of cyclobutene itself remained unsettled. The Raman spectrum of liquid cyclobutene near -100 °C and correlation with the fundamental frequencies of two 1-halocyclobutenes have provided good evidence for the five unsettled a_2 and b_1 fundamentals. New assignments in cm⁻¹ are as follows: (a₂) $v_9 = 2944$, $v_{11} = 1011$, and $v_{12} = 846$; (b₁) $v_{19} = 903$ and $v_{20} = 888$.

The ring-puckering frequencies for halogen-substituted cyclobutenes fit into an understandable pattern. Chlorine substitution has a larger effect than fluorine substitution. Substitution on a methylene carbon atom has a larger effect than substitution on the vinylic carbon atom. Due to two single bonds, the methylene carbon atoms in cyclobutene undergo greater out-of-plane motion than do the vinylic carbon atoms. Thus, anchoring a methylene carbon atom with a halogen atom has a larger frequency-lowering effect than anchoring a vinylic carbon atom.

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Thermodynamics of Gas-Phase Mixed-Solvent Cluster Ions: Water and Methanol on K⁺ and Cl⁻ and Comparison to Liquid Solutions

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The enthalpy, entropy, and Gibbs free energy values for the gas-phase ion-molecule association reactions $Q^{\pm}(CH_{3}OH)_{n-1}(H_{2}O)_{m}$ + CH₃OH \rightleftharpoons Q[±](CH₃OH)_n(H₂O)_m and Q[±](CH₃OH)_n(H₂O)_{m-1} + H₂O \rightleftharpoons Q[±](CH₃OH)_n(H₂O)_m for Q[±] = Cl⁻ and K⁺ were determined. The thermodynamic values of the association reactions were used to calculate the thermodynamic values of the switching reactions, $Q^{\pm}(CH_{3}OH)_{n-1}(H_{2}O)_{m} + (CH_{3}OH) \Rightarrow Q^{\pm}(CH_{3}OH)_{n}(H_{2}O)_{m-1} + (H_{2}O)$. Results for reactions with up to a total, n + m, of four ligands are presented; these data are used to determine the preferential clustering of solvent molecules onto the ions as a function of the composition of the gas phase. The difference of the free energies of clustering of a solvent onto the two separate ions shows a good correlation with the corresponding bulk-phase reaction. This correlation does not hold for the enthalpy and entropy changes.

Introduction

The study of ion-molecule complexes in the gas phase has revealed much about the nature of ion-solvent interactions.^{1,2} Gas-phase studies provide data on the forces operating in individual complexes without the interferences arising from the presence of the bulk solvent or counter ions. Thermodynamic data for the clustering of a few molecules onto an ion have been particularly useful in evaluating single-ion heats of solvation.^{3,4} The success

of gas-phase results for single-component solvents suggests a natural extension to examine the utility of gas-phase data for binary solvents.

The properties of alcohol-water solutions have received considerable scrutiny,⁵⁻⁹ and methanol is the simplest of the alcohols.

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