Vibrational Analysis and Ring-Puckering Inversion Barrier of Perfluorocyclopentene

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Perfluorocyclopentene, like cyclopentene, is expected to have a nonplanar structure with a low barrier to inversion. However, in contrast to cyclopentene, no cluster of bands that could be assigned to the ring-puckering vibration has been reported in the infrared and Raman spectra. To address this problem, ab initio molecular orbital calculations have been carried out to determine the structure and harmonic vibrational frequencies of the puckered molecule (C_s), and the molecule constrained to planarity (C_{2v}). The molecule is nonplanar at all levels of theory, with a dihedral angle of 24°. The calculated barrier to inversion (320 ± 50 cm^{-1}), and puckering frequency (42 cm^{-1}), have been used in a one-dimensional, quadratic, and quartic potential function to calculate the puckering spectrum. The predicted spectrum is characterized mainly by a number of close-lying transitions extending over the range 40 to 56 cm^{-1}. In light of the calculations, some assignments in the vibrational spectra have been revised.

Introduction

The role of chlorofluorocarbons in atmospheric ozone destruction and in greenhouse warming has initiated much research on replacements, and on their spectral and thermodynamic properties. Some hydrofluorocarbons have found industrial applications. In this context, the cyclic fluorocarbons and hydrofluorocarbons have received much less attention. However, as members of the class of small cyclic molecules that are characterized by low inversion barriers to ring puckering, they are of interest.[1−3]

The infrared (IR) and Raman spectra have been reported for perfluorocyclopentene (C_5F_8).[4] The assignments of the observed bands have been based on measured depolarization ratios, relative band intensities, and group frequency correlations. However, because of extensive mixing between C−F and C−C motions, the assignments are somewhat speculative.[5] No theoretical ab initio molecular orbital calculations of the equilibrium structures, vibrational frequencies, and inversion barrier have been reported.

A puzzling feature in the IR and Raman spectra of perfluorocyclobutane (C_4F_8) and perfluorocyclopentene has been the absence of any bands or structure in the spectra that could be unambiguously assigned to the puckering vibration.[4,6,7] A recent investigation of C_4F_8 has proposed an explanation for the apparent absence of puckering structure in the infrared absorption spectrum,[8] despite the fact that it is a puckered, nonplanar molecule, with a low barrier to inversion. For cyclobutane no absorption was detected in the far-IR that could be assigned to the ring-puckering vibration, but puckering transitions have been measured in the mid-IR from sum and difference tones with another fundamental.[9,10] For 1,1,2,2-tetrafluorocyclobutane a broad band observed in the IR spectra at 80−90 cm^{-1} has been assigned to the ring-puckering mode.[11] The problem of the reported absence of puckering structure in the perfluorocyclopentene spectra forms a key aspect of this paper.

A number of review articles have appeared on the ring-puckering vibrations of small ring molecules.[1−3] In all cases the conformations and vibrational potential energy surfaces have been determined through study of the spectra. As the most representative example of pseudo-four-membered-ring molecules with relatively low barriers to inversion, cyclopentene (C_5H_8) has been at the center of numerous spectroscopic investigations.[12−15] Theoretical studies addressing the large-amplitude puckering motion have also been reported, as well as ab initio computational work,[15] one at high level.[14] These studies have yielded the dihedral puckering angle, the inversion barrier, and the puckering vibrational frequency. However, some uncertainty remains in the values of the two former quantities. It is suggested that an investigation of the vibrational spectra of C_5F_8, and a consideration of its double-minimum potential function for the low-frequency ring-puckering vibration in the context of other perfluorocyclocarbons, will provide an answer for the apparent absence of puckering structure in the spectra, and will contribute to a better understanding of the vibrational spectra of the class of perfluorocyclocarbons and partially fluorinated cyclocarbons, and of four-membered and pseudo-four-membered-ring compounds in general.

The relative ease of carrying out high-level ab initio molecular orbital calculations for the determination of the potential energy surfaces has made possible the prediction of the vibrational spectra. In this work we report on ab initio molecular orbital calculations of the molecular structures of C_5F_8, puckered and planar, and the vibrational frequencies and transition intensities. For comparison similar calculations have been carried out for C_5H_8. In light of the calculations some of the vibrational assignments have been revised. A treatment is presented which allows prediction of the puckering vibration and the associated vibrational structure that should be present in the IR spectrum.

Calculations

Standard ab initio molecular orbital calculations were carried out on C_5F_8 and C_5H_8 using the GAUSSIAN 94 suite of programs.[16] The C_5H_8 calculations were for purposes of comparison, both with the C_5F_8 results and with the previously reported[14] C_5H_8 calculations. Uncorrelated wave functions were obtained by Hartree−Fock (HF) theory. Electron correlation was

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TABLE 1: Optimized Structures of C_5F_8 (Å (1 Å = 0.1 nm), and deg)

	C_s			C_{2v}		
	HF	B3LYP	MP2	HF	B3LYP	MP2
r(1,2)	1.310	1.334	1.340	1.309	1.334	1.338
r(2,3)	1.495	1.499	1.493	1.492	1.497	1.490
r(3,4)	1.543	1.563	1.545	1.551	1.568	1.557
r(1,6)	1.304	1.324	1.330	1.304	1.324	1.330
r(3,8)	1.326	1.354	1.356	1.329	1.357	1.360
r(3,9)	1.331	1.359	1.363	1.329	1.357	1.360
r(10,4)	1.325	1.351	1.356	1.321	1.347	1.350
r(11,4)	1.319	1.344	1.347	1.321	1.347	1.350
C3C4C5	105.1	105.4	104.8	105.9	106.0	106.1
C2C3C4	103.0	103.4	102.9	104.0	104.0	104.3
C1C2C3	112.4	112.6	111.8	113.0	113.0	112.7
C1C2F7	127.6	127.0	127.4	127.4	126.8	127.1
C3C4F11	112.3	111.7	112.4	110.5	110.4	110.3
C3C4F10	109.0	109.2	108.7	110.5	110.4	110.3
C4C3F9	110.5	110.4	110.1	111.2	110.9	111.0
C4C3F8	111.9	111.5	111.9	111.2	110.9	111.0
C2C3F9	111.6	111.8	111.7	111.5	111.7	111.5
C2C3F8	112.2	112.1	112.3	111.5	111.7	111.5

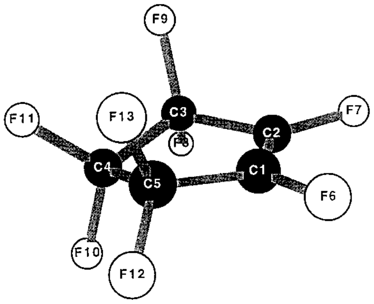

Figure 1. Perfluorocyclopentene.

treated with second-order (MP2-frozen core) and fourth-order (MP4-frozen core), perturbation expansions, and density functional theory (DFT). The DFT technique employed the Becke3 (B3)[17] exchange functional which was supplemented with the Lee, Yang, Parr (LYP)[18] correlation functional.

The majority of the calculations were performed with the 6-31G(d) basis set. This basis set is of double-ζ type with polarization functions on all heavy atoms. To ascertain the importance of diffuse functions in the basis on the energies and geometries, the HF and MP2 optimizations were also carried out with the 6-31+G(d) basis. The MP4 energies were calculated at the MP2/6-31G(d) and MP2/6-31+G(d) optimized geometries, but only for C_5H_8. The geometry was also optimized with the carbon ring of the molecule constrained to planarity (C_{2v} symmetry). However, the nonplanar structure (C_s symmetry) is the more stable at all levels of theory.

The optimized ground-state structures at various levels of theory are listed in Table 1. Apart from the dihedral angles there are no significant differences (greater than 2.5%) in the structures for the different levels of theory, and constraining the molecule to planarity has had only very minor impact on the bond lengths and angles. Furthermore, the calculated C−C bond lengths are only marginally different from those measured in a gas-phase electron diffraction study of cyclopentene.[20] In all the calculations the largest discrepancy involves the C−C bond length, r(2,3) (Figure 1) which in C_5F_8 is about 1.5% smaller than the measured and calculated length for the same bond in C_5H_8.[14,20] Use of the larger basis has resulted in only slight changes in the optimized structures of both C_5F_8 and C_5H_8. The dihedral angles have experienced the largest change. For C_5F_8 they have changed from 20.3° and 23.9°, to 20.0° and 24.3° for the HF and MP2 calculations respectively (Table 2). The good agreement obtained for the dihedral angle of C_5H_8 between the MP2 calculations and experiment suggests that a similar good agreement may hold for C_5F_8, and that its dihedral angle is therefore 24°.

Force constants and harmonic vibrational frequencies were obtained by analytic second differentiation of the energy with respect to nuclear displacements. The frequency calculations were applied to the computed minima. No frequency calculations were undertaken at the MP2 level of theory for C_5F_8 but were undertaken for C_5H_8. For molecules as large as C_5F_8, MP2 frequency calculations are very costly and the resulting frequencies are frequently not better than those calculated at lower theoretical levels.[19] This was shown to be the case for perfluorocyclobutane[8] where the deviations of the scaled HF/6-31G(d) calculated frequencies were less than the deviations of the scaled MP2/6-31G(d) frequencies for the majority of the experimentally measured frequencies. The theoretical frequencies calculated at the HF/6-31G(d) and B3LYP/6-31G(d) levels have been scaled by the factors 0.895 and 0.9614, respectively, and for the puckering mode in the DFT and MP2 calculations the recommended scaling factors of 1.0013 and 1.0485 were used.[19]

The barrier heights, dihedral puckering angles, and puckering frequencies are given in Table 2. It is seen that the barrier heights and dihedral angles are roughly comparable for C_5F_8 and C_5H_8, but the puckering frequencies are much smaller for the heavier molecule. On the other hand, relative to C_4F_8 the puckering frequencies are comparable, but the dihedral puckering angle is significantly larger for C_5F_8.[8] Furthermore, much better agreement is obtained between the scaled HF/6-31G(d) and B3LYP/6-31G(d) calculated puckering frequencies and the experimental frequency for C_5H_8 than for the MP2/6-31G(d) calculation. This supports the point made above on the relative values of HF and MP2 frequency calculations. Finally, in these comparisons an important difference in the characterization of the ring-puckering dynamics concerns the ratio of the barrier height to puckering vibration frequency. The ratio is much larger for the fluorinated molecules.

It remains a feature of ab initio molecular orbital calculations that they are still unable to provide precise estimates (i.e., within a few cm^{-1}) of the barrier heights of the four- and pseudo-

TABLE 2: Barrier Heights (cm^{-1}), Dihedral Puckering Angles (deg), and Puckering Frequencies (cm^{-1}) for C_5F_8 and C_5H_8

C_5F_8	HF 6-31G(d)	B3LYP	MP2	HF 6-31+G(d)	MP2
barrier height	159	89	266	183	396
dihedral angle	20.3	16.5	23.9	20.0	24.3
puckering freq	42	32			

C_5H_8	HF 6-31G(d)	B3LYP	MP2	MP4	HF 6-31+G(d)	MP2	MP4	exp[a]
barrier height	113	97	288	225	134	340	273	232
dihedral angle	21.7	20.0	26.1		21.1	26.7		26.0
puckering freq	135	137						127

[a] Reference 1.

four-membered ring molecules. This is illustrated by the extensive series of calculations on C_5H_8 carried out by Allen and co-workers.[14] They pointed out the difficulty of predicting the barrier height, and although they proposed a value of 235 $\pm$ 20 cm^{-1}, which is within experimental range, it must be recognized that prior knowledge of the expected value must have influenced their final choice of calculations. Furthermore, the convergence of their MP4 and MP∞ energies to the experimentally deduced value must be considered partly fortuitous since the energies were not calculated at the optimized structures but for the geometry determined at a lower level of theory. We have repeated the MP4 calculations for C_5H_8. The barrier heights calculated at the MP2/6-31G(d) and MP2/6-31+G(d) optimized geometries are 225 and 273 cm^{-1} for the two basis sets, respectively. When zero-point vibrational effects[14] are included they are reduced to 200 and 250 cm^{-1}, compared to an experimentally deduced value of 232 cm^{-1}. So the value determined with the larger basis is in marginally better agreement with experiment.

The inclusion of electron correlation and a larger basis, clearly, have both increased the barrier height substantially. The inclusion of diffuse functions is more of relevance for C_5F_8 than C_5H_8 and is reflected in the differences in the MP2/6-31G(d) and MP2/6-31+G(d) energies. The fluorines possess lone pair electrons. Because of the better agreement achieved for C_5H_8 between the MP4 single point calculations and the experimentally deduced barrier height than the MP2 calculations, similar MP4 calculations were seen as useful for C_5F_8. However, the number of "heavy" atoms precluded them being carried out. Nevertheless, inspection of Table 2 allows an estimate to be made for the barrier height of C_5F_8. The upper and lower bounds are given by the MP2/6-31+G(d) and HF/6-31+G(d) values of 396 and 183 cm^{-1}, respectively. For C_5H_8, the MP2/6-31+G(d) value is too large by about 80 cm^{-1} when allowance is made for the zero-point effect (see below). Assuming that the error for C_5F_8 is similar, or less since the 6-31+G(d) basis is more relevant for C_5F_8, a value for the barrier height in the vicinity of 320 $\pm$ 50 cm^{-1} is arrived at.

For cyclopentene, high-level ab initio calculations have shown that apart from the puckering mode, nine of the remaining 32 vibrational frequencies change by more than 10 cm^{-1} in going from the puckered to the planar geometries.[14] Despite cancellations resulting from both positive and negative changes, an overall change of 25 cm^{-1} remains in the total zero-point vibrational energy. This must be considered a contribution to the empirically derived puckering inversion barrier.[14] According to our HF and B3LYP calculations for C_5F_8, seven and three frequencies respectively are changed by more than 10 cm^{-1} in going from the puckered to the planar geometries, but in contrast the largest change is only 18 cm^{-1} compared to a largest change of 79 cm^{-1} for the same calculations on C_5H_8. The total change in the zero-point vibrational energy is much smaller for C_5F_8 than for C_5H_8, -7 and $+1$ cm^{-1} in the HF and B3LYP calculations, respectively. Thus, the contribution of the zero-point vibrational energy to the puckering inversion barrier is similarly much smaller.

Vibrational Assignments for C_5F_8

The fundamental vibrations divide into two groups of 18 a′ and 15 a″ symmetries for the puckered C_s structure, which correlate with 11 a_1 and 7 b_1, and 6 a_2 and 9 b_2, respectively, for the planar C_{2v} form (a_1 and b_2 vibrations are defined to occur in the molecular plane). The vibrational frequencies and transition intensities (Raman and IR) have been calculated for the planar (C_{2v}) and puckered (C_s) structures of C_5F_8, Table 3. As indicated above, most vibrational frequencies are little changed (less than 5%), in going from the puckered to planar structures and a good correlation can be established. This shows the lack of sensitivity of the vibrational frequencies to the puckered structure, and in particular confirms that the large-amplitude puckering vibration can be separated from the other vibrational modes.

Also included in the table are the experimental values obtained from the IR and Raman spectra.[4] Overall good agreement is established between the observed and calculated frequencies. Most vibrations are heavily mixed and the descriptions in terms of bond stretching, angle bending, and so on, previously reported,[4] are in broad agreement with the forms of the calculated normal coordinates. However, some assignments proposed by Harris and Longshore[4] have been revised in light of the calculations. The most important of the revisions to the proposed assignments concerns the puckering vibration.

Perfluorocyclopentene is a pseudo-four-membered ring, with an expected low barrier to inversion. A line centered at 100 cm^{-1} in the Raman spectrum was assigned to the ring-puckering fundamental.[4] For a number of reasons this assignment is considered by us to be unsatisfactory. First, no multiline spectrum or broad band that could be attributed to the ring-puckering vibration was observed, in contrast to cyclopentene[12] and 1,1,2,2-tetrafluorocyclobutane.[11] Second, in light of the vibrational frequencies for the puckering modes of cyclopentene and perdeuteriocyclopentene, 127 and 108 cm^{-1}, respectively,[12,13] a frequency of 100 cm^{-1} seems too large for the much more massive perfluorocyclopentene. Third, a comparison with cyclobutane[9,10] and perfluorocyclobutane[4] suggests a frequency less than 50 cm^{-1}. Finally, a compelling argument against assigning the puckering mode to the 100 cm^{-1} band is the large discrepancy with the calculated frequencies of the puckering mode (ν_p about 40 cm^{-1}). The close similarity of the calculated frequencies for C_4F_8 (45 cm^{-1}) and C_5F_8 (42 cm^{-1}) should be noted.

In the low-temperature far-infrared spectrum recorded down to 33 cm^{-1}, Harris and Longshore[4] detected no absorption below 188 cm^{-1}. The fact that they did not observe the band at 100 cm^{-1}, which was however observed in their Raman spectrum, suggests that an assignment for the 100 cm^{-1} band to an a″ mode (C═C torsion), which correlates with an a_2 mode (IR inactive) in the planar (C_{2v}) conformation, may be more appropriate. The absence of a band at about 40 cm^{-1} in the far-IR spectrum measured down to 33 cm^{-1} can be attributed to its predicted very low intensity. Thus the band seen at 100 cm^{-1} should not be assigned to the puckering mode, but rather to the lowest frequency a″ mode, for which the calculated results, 101 cm^{-1} in HF calculation for C_s structure, are in much better agreement.

Other bands that are particularly prominent in the IR spectra of the cyclic fluorocarbons and hydrofluorocarbons are the bands at about 980 cm^{-1}, largely ring stretching.[4,6,7,8,21−23] For C_5F_8 they must be assigned to the two intense bands at 1008 a′ (a_1 in C_{2v}), and 985 a″ (b_2 in C_{2v}) cm^{-1}, in close agreement with the calculations, where very strong bands at 996 and 980 cm^{-1} are obtained in the HF calculations. The calculations provide confirmation for the assignment of the C═C stretch to the band at 1770 cm^{-1}. It is of the order of 150 cm^{-1} higher than in cyclopentene where it is assigned to the band observed at 1617 cm^{-1}. This parallels the calculations which also yield a 150 cm^{-1} difference for the C═C stretching vibration frequencies in the two molecules. For the vibrations with frequencies less than

TABLE 3: Calculated (C_s and C_{2v}) and Observed Vibrational Frequencies (cm^{-1}), and IR and Raman Intensities for C_5F_8[a]

	puckered C_s						planar C_{2v}				exp[b] C_s
	HF			B3LYP			HF		B3LYP		
	IR ν	IR int	R int	IR ν	IR int		IR ν	IR int	IR ν	IR int	IR ν or R, int
a′	1809	15	100	1748	26	a_1	1812	14	1750	21	1770, s
	1391	2	30	1340	<1		1393	<1	1342	<1	1386, R
	1368	18	10	1287	29		1358	15	1278	21	1327, s
	1152	13	4	1120	28		1153	1	1120	5	1144, sh
	996	75	2	978	86		997	68	978	68	1008, s
	656	1	34	639	2		646	1	632	1	663, m
	616	1	3	600	1		609	3	595	2	603, ms
	418	2	15	410	2		420	2	412	2	430, m
	340	<1	7	326	<1		322	<1	314	<1	347, vw
	304	1	1	296	1		311	1	302	1	312, m
	240	<1	2	235	<1		238	<1	234	<1	252, ss, mw
	1255	19	6	1192	43	b_1	1258	19	1194	34	1219, s
	1226	100	3	1153	100		1219	100	1146	100	1180, s
	603	2	5	589	2		618	<1	598	<1	617, R
	497	<1	7	480	<1		497	<1	478	<1	499, R
	214	<1	<1	213	<1		236	1	228	1	234, ss, mw
	171	1	1	164	1		172	1	163	1	187, s
	42	<1	<1	32	<1						
a″	1206	1	21	1132	1	a_2	1208	0	1130	0	1211, ss, sh
	696	<1	21	655	<1		690	0	651	0	721, vw
	403	1	12	394	1		417	0	402	0	419, ss, sh
	258	<1	<1	255	<1		274	0	267	0	274, ss, mw
	238	<1	<1	230	<1		241	0	231	0	234, ss, mw
	101	<1	2	94	<1		94	0	88	0	100, R
	1396	69	<1	1360	85	b_2	1395	66	1359	70	1389, s
	1338	37	24	1255	46		1329	29	1248	34	1300, s
	1116	1	<1	1073	4		1113	2	1072	6	1106, sh
	980	68	<1	955	78		979	63	952	63	985, s
	839	<1	<1	825	<1		841	<1	826	<1	889, mw
	584	7	2	570	7		582	7	568	6	627, sh
	436	1	10	423	1		424	1	415	1	444, ss, s
	307	<1	1	300	<1		318	1	308	<1	312, m
	252	<1	<1	250	<1		255	<1	252	<1	252, ss, mw

[a] The IR and Raman intensities have been arbitrarily scaled such that the strongest intensity for each is 100. [b] W. C. Harris and C. T. Longshore, ref 4. All entries are IR of gas, unless IR solid state (ss) or Raman gas (R).

400 cm^{-1}, many of which are characterized by very low intensities, considerable ambiguity remains in the assignments.

Ring Puckering

The ring-puckering mode is of a′ symmetry, correlating with b_1 symmetry for the planar structure. As such it is allowed in the IR and Raman spectra as a fundamental. However, both its IR absorption intensity and Raman activity are calculated to be very small (Table 3). The ring-puckering mode may also appear in the spectra as a combination band. In this context it has been observed in the IR spectrum of cyclobutane where the fundamental is IR inactive.[9,10] Although it is argued that for C_5F_8 the ring-puckering fundamental and its associated vibrational structure have not yet been correctly identified, it must be active in some weak bands that may be assigned to combination bands involving the puckering mode. Comparison with C_4F_8 (weak, broad band removed about 60 cm^{-1} from the associated fundamental), and 1,1,2,2-tetrafluorocyclobutane (80−90 cm^{-1}) suggests that weak bands removed some 30−80 cm^{-1} may be representative of puckering sideband structure. The weak bands in the IR absorption spectrum at 1057 and 1820 cm^{-1} are possible candidates. They are removed 49 and 50 cm^{-1}, respectively, from the strong bands at 1008 (ring stretch) and 1770 cm^{-1} (C═C stretch), and are of the predicted relative intensity, 0.01−0.03, of the fundamental. Furthermore, the combination band assignments proposed by Harris and Longshore[4] do not fit at all well, even if significant anharmonicity is allowed for, according to their analyses: 1076 (631 + 445) and 1850 (631 + 1219) cm^{-1}.

The same approach that was employed for C_4F_8 in the treatment of the puckering structure expected in the infrared spectrum is adopted here.[8] Briefly, the puckering energy levels and wave functions are determined from a one-dimensional Hamiltonian, eq 1, for which the puckering potential is represented by quadratic and quartic terms in the mass-weighted ring-puckering coordinate, $Q = m_z^{1/2}Z$. The effective mass is given by m_z, and Z is the puckering coordinate.

$$H = -(\hbar^2/2)(\partial^2/\partial Q^2) - (A/m_z)Q^2 + (B/m_z^2)Q^4 \qquad (1)$$

A two-parameter expression of this form has proved quite satisfactory in interpreting the ring-puckering spectra of many four-membered and pseudo-four-membered ring[2,3] compounds. The lack of an observed ring-puckering spectrum for C_5F_8 precludes the use of a more sophisticated form for the potential with additional parameters. However, the applicability of an analytical quadratic/quartic form for the potential is supported by the good match found with the potential energy determined by a number of single-point calculations (HF/6-31G(d)), along the puckering coordinate, Figure 2. In this point-calculated potential the barrier is believed to be too small, but the form is clearly correct, and in the absence of observed puckering vibrational structure, cannot be easily improved upon.

For a potential of the form of eq 1 the relationship between the coefficients and the barrier height, b, is given by eq 2.

$$B = A^2/4b \qquad (2)$$

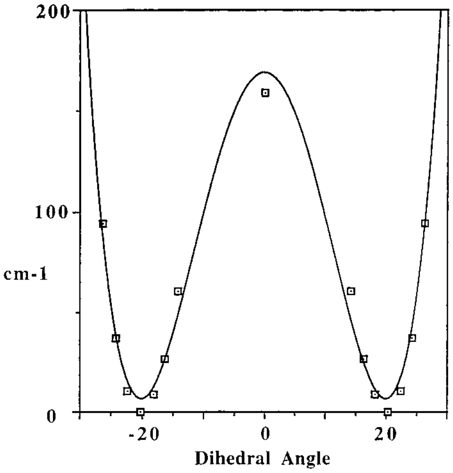

Figure 2. Puckering potential determined from single point HF/6-31G(d) energies.

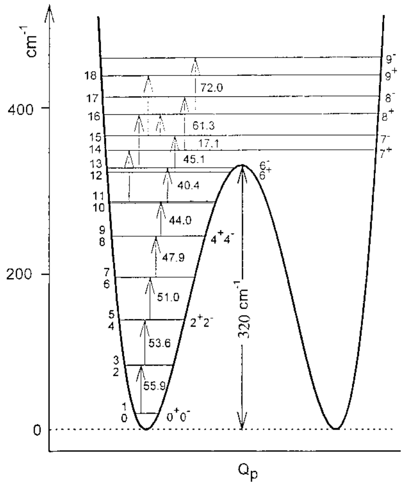

Figure 3. Potential energy curve for the ring-puckering vibration. Transitions with intensities greater than 10% of the transition with maximum intensity are indicated.

The choice of values for the two coefficients, A/m_z and B/m_z^2 of Q^2 and Q^4, respectively, are constrained by the value of the barrier height (eq 2). The choice of the former coefficient, A/m_z, has been determined by the value of the puckering vibrational frequency (ν_p), and by the requirement to achieve matching with the experimentally assigned spectrum, that is, with the broad sidebands at 1057 and 1820 cm^{-1} removed some 50 cm^{-1} from the fundamentals.

The final values adopted for the barrier height and puckering vibration frequency are $b = 320$ and $\nu_p = 42$ cm^{-1}. Justification for the choice of b has been given above, and the scaled HF/6-31G(d) calculated frequency has been adopted on the grounds of the good agreement found for C_5H_8 (Table 2) and the similarly good agreement found between the HF calculated and experimentally deduced frequency for cyclobutane.[8]

The potential well and the associated energy levels are depicted in Figure 3. Only transitions with intensities greater than 10% of the maximum are depicted. It is seen that the levels 6^+ (12) and 6^- (13) are still below the barrier, and are only split by 5.3 cm^{-1}. This contrasts the behavior of cyclopentene where only the levels 0^+ (0) and 0^- (1) are below the barrier, and the levels 1^+ (2) and 1^- (3) are approximately at the height of the barrier. The limited spread in the transition frequencies is evident in that most lie in the range from about 56 to 40 cm^{-1} with the maximum transition intensity centered at about 49 cm^{-1}. Transitions starting from levels higher than $6^\pm$ are associated with much smaller intensities due both to rapidly decreasing Boltzmann factors and decreasing transition intensities. With $A/\gamma m_z = 20$ cm^{-1} and accordingly $B/(\gamma m_z)^2 = 0.307$ cm^{-1}, where $\gamma = 4\pi^2\nu_p/h$, a cluster of transitions is obtained over an approximately 16 cm^{-1} range with maximum at about 49 cm^{-1}, in accordance with the proposed interpretations of the bands at 1057 and 1820 cm^{-1}.

The extent of wavelength dispersion of the vibrational structure is largely governed by the magnitude of the ratio of barrier height to puckering frequency. This ratio is similar for C_4F_8 and C_5F_8 but much larger than the corresponding ratio for C_4H_8 and C_5H_8. For the case of the large ratio, that is, a small frequency for the puckering mode relative to the barrier height, many vibrational levels occur below the barrier height. For C_5F_8 the level spacings, although decreasing, nevertheless only vary over a range of some 16 cm^{-1}. For the room temperature molecule it is these levels that are associated with the maximum intensities, so that only a limited spread of transition frequencies is obtained. In parallel with C_4F_8, where the sideband structure for a combination band involving the puckering mode, was shown to be largely concentrated in a narrow range displaced some 60 cm^{-1} from the fundamental, so for C_5F_8 the vibrational structure associated with the puckering vibration is expected to be found predominantly in a narrow frequency range. This finds support in the broad band observed at 80−90 cm^{-1} in the IR spectrum of 1,1,2,2-tetrafluorocyclobutane assigned to the ring-puckering mode.[11] No distinct Q branches could be resolved.

For the puckering vibration which is a′ (b_1 in the C_{2v}), the rotational contours are of type C, which in the case of the planar structure corresponds to a transition polarized normal to the molecular plane. Using the ground state rotational constants determined in the MP2 calculation, and for the vibrationally excited state incorporating small decreases in the rotational constants in accordance with the MP2 calculated constants for the planar form, a type C rotational contour has been calculated. It is marked by an intense Q branch with half width of about 2 cm^{-1}, and weak P and R like wings.

Without the participation of other vibrations as hot bands, vibrational structure due to the puckering vibration should be marked by resolved, relatively narrow lines. This is the case for many of the four-membered and pseudo-four-membered ring compounds possessing low inversion barriers. However, for C_5F_8 in addition to the puckering mode, there are calculated to be nine vibrations with frequencies less than 400 cm^{-1}. At room temperature, all of these can be expected to have relatively large populations in their first excited vibrational states. The excitations of these vibrations slightly alter the potential function for the puckering vibration. As a consequence, each line in the "pure" puckering vibration spectrum will be accompanied by a host of near-lying lines. This is exactly what is seen in the cyclopentene spectrum, with the exception that only one vibration is of sufficiently low frequency to participate; thus, in the far-infrared spectrum of cyclopentene a weak side peak occurs within 1−2 cm^{-1} of each strong absorption peak.

The relatively limited spread of the vibrational puckering structure (16 cm^{-1}), taken together with both the occurrence of numerous hot bands due to excitation of the low-frequency vibrations, and a Q branch peak half-width of about 2 cm^{-1}, can readily account for the absence of discrete peaks in the measured spectra. Rather, the puckering vibrational structure should appear as a broad band. This has been seen to be the case for 1,1,2,2-tetrafluorocyclobutane, where a half-width of some 40 cm^{-1} has been obtained in the gas-phase far-IR spectrum.[11]

Conclusion

From a series of ab initio molecular orbital calculations carried out for C_5F_8 and C_5H_8 an inversion barrier height of 320 ± 50 cm^{-1} and puckering frequency of 42 cm^{-1} have been established for the puckering mode of C_5F_8, and a dihedral angle of 24°. The barrier height and puckering frequency have been used in a quadratic/quartic potential to predict the appearance of combination bands involving the puckering mode, as broad bands extending over the range 40 to 56 cm^{-1} from the associated fundamental. This interpretation has been proposed for the weak bands in the infrared absorption spectrum at 1820 and 1057 cm^{-1}. The IR and Raman absorption spectra have been calculated and shown to be in good agreement with the observed spectra. The calculations have suggested some revision of previous vibrational assignments. In particular, the band at 100 cm^{-1} in the Raman spectrum has been assigned a torsion and not the ring puckering mode.

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References and Notes

(1) Rosas, R. L.; Cooper, C.; Laane, J. *J. Phys. Chem*. **1990**, *94*, 1830.
(2) Laane, J. *Pure Appl. Chem*. **1987**, *59*, 1307.
(3) Carreira, L. A.; Lord, R. C.; Malloy, T. B. *Top. Curr. Chem*. **1979**, *82*, 1.
(4) Harris, W. C.; Longshore, C. T. *J. Mol. Struct*. **1973**, *16*, 187.
(5) Tuazon, E. C.; Fateley, W. G.; Bentley, F. F. *Appl. Spectrosc*. **1971**, *25*, 374.
(6) Miller, F. A.; Capwell, R. J. *Spectrochim. Acta* **1971**, *27A*, 1113.
(7) Claasen, H. H. *J. Chem. Phys*. **1950**, *18*, 543.
(8) Fischer, G.; Purchase, R. L.; Smith, D. M. *J. Mol. Struct*. **1997**, *405*, 159.
(9) Stone, J. M. R.; Mills, I. M. *Mol. Phys*. **1970**, *18*, 631.
(10) Miller, F. A.; Capwell, R. J. *Spectrochim. Acta* **1971**, *27A*, 947.
(11) Durig, J. P.; Harris, N. C. *Spectrochim. Acta* **1971**, *27A*, 649.
(12) Laane, J.; Lord, R. C. *J. Chem. Phys*. **1967**, *47*, 4941.
(13) Villerreal, J. R.; Bauman, L. E.; Laane, J.; Harris, W. C.; Bush, S. F. *J. Chem. Phys*. **1975**, *63*, 3727.
(14) Allen, W. D.; Csaszar, A. G.; Horner, D. A. *J. Am. Chem. Soc*. **1992**, *114*, 6834.
(15) Champion, R.; Godfrey, P. D.; Bettens, F. L. *J. Mol. Spectrosc*. **1991**, *147*, 488.
(16) *Gaussian 94*, Revision E.2; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head- Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.
(17) Becke, A. D. *J. Chem. Phys*. **1992**, *97*, 9173.
(18) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(19) Scott, A. P.; Radom, L. *J. Phys. Chem*. **1996**, *100*, 16502.
(20) Davis, M. I.; Muecke, T. W. *J. Phys. Chem*. **1970**, *74*, 1104.
(21) Mao, C.; Nie, C.; Zhu, Z. *Spectrochim. Acta* **1988**, *44A*, 1093.
(22) Miller, F. A.; Harney, B. M. *Spectrochim. Acta* **1972**, *28A*, 1059.
(23) Bauman, R. P.; Bulkin, B. J. *J. Chem. Phys*. **1966**, *45*, 496.