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Far-Infrared Spectra, ab Initio Calculations, and the Ring-Puckering Potential Energy Function of 2,3-Dihydrofuran

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The far-infrared spectrum resulting from the ring-puckering vibration of 2,3-dihydrofuran (23DHF) has been re-examined, and 11 single-quantum jump transitions and nine triple-quantum jump transitions were observed. High-level ab initio calculations were used to predict the structure which was then used to calculate the kinetic energy (reciprocal reduced mass) as a function of the puckering coordinate. The experimental data along with the kinetic energy expression produced the potential energy function $V(x) = 1.019 \times 10^6 x^4 - 1.946 \times 10^4 x^2$ which has a barrier to planarity of 93 cm^{-1} and energy minima at dihedral angles of ±22°. The values agree well with the ab initio values of 96 cm^{-1} and ±23°. Quantum transitions to the 11th and 12th puckering states are fit less well with the potential function, and this apparently reflects the fact that higher-order (x^6) potential energy terms become more important due to steric effects at larger values of x. The interaction between the ring-puckering and ring-twisting modes was analyzed by examining the hot bands near 446 cm^{-1}. A two-dimensional potential energy surface, which fits the puckering data well in both the twisting ground and excited states, was determined. The interaction cross term was somewhat smaller than those for cyclopentene and related molecules.

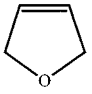
Introduction

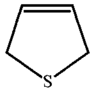
Over the past four decades, far-infrared and Raman spectra have been utilized to determine the ring-puckering potential energy functions of several dozen cyclic molecules.[1−5] R. P. Bell[6] first predicted in 1945 that four-membered ring molecules such as cyclobutane should possess quartic potential energy functions for their ring-puckering vibrations. When sufficiently good far-infrared instrumentation became available in the 1960s, the spectra of molecules such as trimethylene oxide,[7] trimethylene sulfide,[8] cyclobutanone,[8] and silacyclobutane[9] demonstrated that indeed the quartic term was the dominant one in the potential function. However, these molecules also typically possessed barriers to planarity due to CH_2-CH_2 torsional interactions, and these gave rise to negative quadratic terms in the potential functions, yielding

$$V(x) = ax^4 - bx^2 \qquad (1)$$

where x is the ring-puckering coordinate as previously defined[1−5] and a and b are potential energy parameters. This type of potential function has proved to work exceptionally well for four-membered ring molecules whenever the ring-puckering vibration can be separated from the other vibration molecules according to the high−low frequency separation.

In 1967 Laane and Lord[10] studied the far-infrared spectra of cyclopentene (CP) and recognized that a five-membered ring with a double bond would possess a ring-puckering vibration that behaved like that in a four-membered ring and could be described by the potential energy function given in eq 1. Hence, they termed these molecules “pseudo-four-membered rings” to indicate that the two atoms joined by a double bond moved together like a single atom during the puckering vibration. Analysis of the spectra showed that the molecule had a barrier to planarity of 232 cm^{-1} (0.66 kcal/mol). Further, far-infrared and Raman work on cyclopentene and its isotompomers has been published by the Laane group[11] since that first initial investigation. In addition, a number of cyclopentene-like molecules have also been investigated, and these are shown below.


25DHF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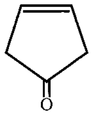
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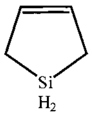
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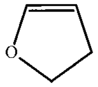
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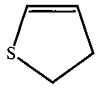
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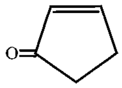
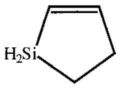

2CP


2SCP

The first group of molecules, 2,5-dihydrofuran (25DHF),[12] 2,5-dihydrothiophene (25DHT),[13] 3-cyclopentenone (3CP),[14] and 3-silacyclopentene (3SCP),[15] were all found to be planar molecules since none of these have any CH_2-CH_2 torsional interactions. In the second group, however, each molecule has a single CH_2-CH_2 interaction. We have recently analyzed the far-infrared spectra of 2,3-dihydrothiophene (23DHT)[16] and showed earlier work to be erroneous. This molecule has a barrier to planarity of 435 cm^{-1}. 2-Cyclopentenone (2CP)[17] does have a CH_2-CH_2 interaction, but this is not sufficient to overcome the substantial conjugation between the C═O and C═C groups. Hence, the molecule is planar. Similarly, 2-silacyclopentene (2SCP)[18] is also planar and rigid, apparently due to interactions between the carbon−carbon double bond and the silicon atoms. The far-infrared spectra of 2,3-dihydrofuran (23DHF) were reported by Green[19] in 1969, and a barrier to planarity of 83 cm^{-1} using the potential energy function of eq 1 was calculated.

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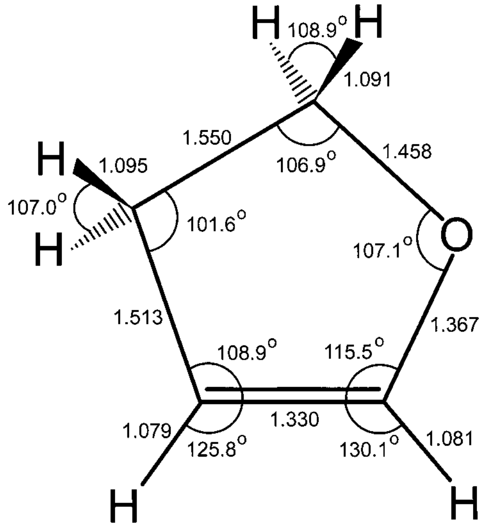

Figure 1. Calculated structure for 2,3-dihydrofuran (23DHF).

However, the calculations were done in reduced form, and no attempt was made to calculate a reduced mass for the molecule. Consequently, it has not been possible to ascribe the energy minima of the potential energy function to any particular structures with specified dihedral angles of puckering.

In our present study we undertook a reinvestigation of the far-infrared spectra of 23DHF. Instrumentation has greatly improved in the past thirty years, and we now have the tools with which to calculate reliable bond lengths and angles for the molecule from ab initio calculations. This then allowed us to calculate the variable kinetic energy (reciprocal reduced mass) expansion as a function of the ring-puckering coordinate and then determine a reliable potential energy function in terms of this coordinate.

In our recent investigation of 23DHT[16] we were also able to analyze the interaction between the ring-puckering and ring-twisting modes since puckering sidebands originating from the twisting excited state were observed. Therefore, we hoped to find similar data for 23DHF. Finally, we were also interested in seeing whether we could observe the rotational fine structure for this near-symmetric-top molecule and then see how this correlated with recent microwave work.[20] For 25DHF, which is also a near-symmetric top, we did resolve such fine structure.[21]

Experimental Section

2,3-Dihydrofuran (99%) was purchased from Sigma Aldrich Chemical Co. and transferred by trap-to-trap distillation to a sample tube containing a molecular sieve as the drying agent. Spectra of samples in a 20 m multipass cell equipped with polyethylene windows (pounded to remove interference fringes) were recorded using a Bomem DA8.02 instrument. Mylar beam splitters (6.25 and 12.5 μm) and DTGS detection were used. Typically a resolution of 0.25 or 0.1 cm^{-1} was selected, and 4000 scans were averaged. Sample pressures from 1 to 100 Torr were used.

Ab Initio Calculations

Ab initio calculations were performed utilizing the Gaussian 98 program[22] and carried out at the MP2 and B3LYP level of theory with a 6-311++G** basis set. The resulting structure shown in Figure 1 was calculated. A dihedral angle of puckering of 23° was predicted along with a barrier to planarity of 96 cm^{-1}. A small twisting angle of 3.5° was also predicted. The 23DHF bond lengths and angles thus calculated for this basis set were utilized for the computation of the kinetic energy function.

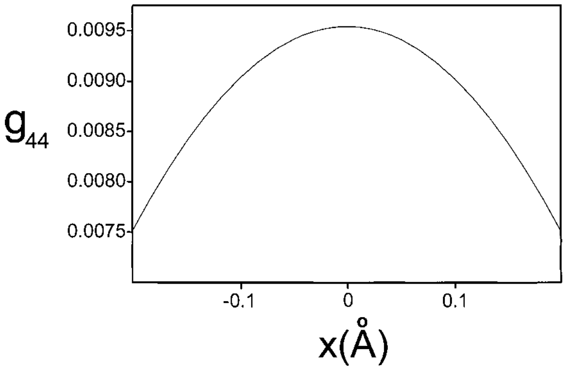

Figure 2. Coordinate dependence of $g_{44}(x)$, the reciprocal reduced mass of 23DHF.

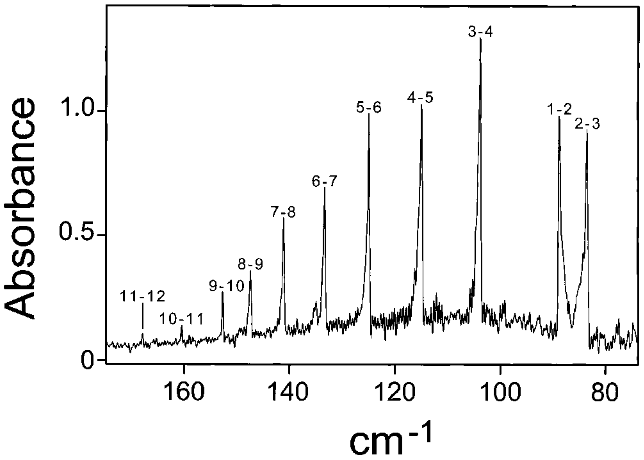

Figure 3. Far-infrared spectrum of 23DHF, at 3 Torr, with a 20 m path length and 0.25 cm^{-1} resolution.

Kinetic and Potential Energy Functions

Using the computational methodology previously described[23] and the structure in Figure 1, the kinetic energy expansion was calculated to be

$$g_{44}(x) = 0.009541 - 0.05071x^2 - 0.02059x^4 + 0.5554x^6 \quad (2)$$

where g_{44} is the reciprocal reduced mass for the ring puckering as a function of the puckering coordinate x. The coordinate dependence of g_{44} is shown in Figure 2.

For the potential energy calculation, the Hamiltonian

$$H(x) = \frac{-\hbar^2}{2}\frac{\partial}{\partial x} g_{44}(x) \frac{\partial}{\partial x} + V(x) \quad (3)$$

was used where $V(x)$ is given in eq 1. In the original work by Green,[19] the calculation was done in reduced coordinates with a fixed reduced mass, as described by Laane.[24]

Results and Discussion

Figure 3 shows the far-infrared spectrum of 23DHF, and Figure 4 shows an expanded segment in the 112−128 cm^{-1} region. Figure 5 shows the ring-twisting region which is infrared active due to the asymmetry of the molecule (for cyclopentene, this is a forbidden A_2 mode in the C_{2v} approximation). Each of the spectra shows resolved fine structure, and the average

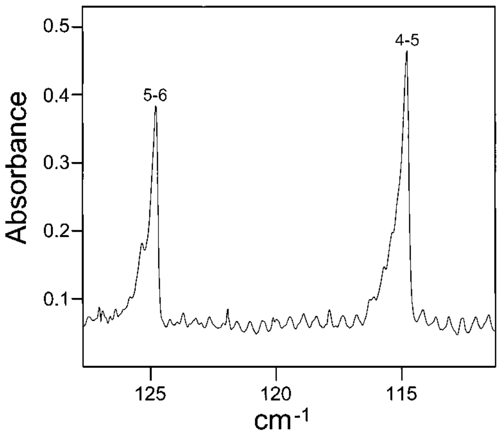

Figure 4. Far-infrared spectrum of 23DHF in the 112−128 cm^{-1} region, at 100 Torr, with a 20 cm path length and 0.1 cm^{-1} resolution.

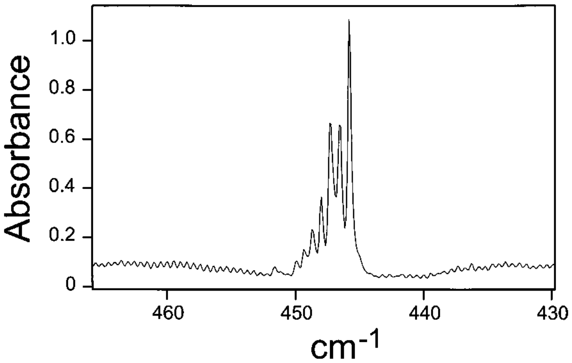

Figure 5. Far-infrared spectrum of the ring-twisting region of 23DHF, at 2 Torr, with a 20 cm path length and 0.25 cm^{-1} resolution.

TABLE 1: Observed and Calculated Far-Infrared Frequencies for the Ring Puckering of 2,3-Dihydrofuran

	frequency (cm^{-1})				relative intensity	
transition	lit.[a]	obsd	calcd[b]	Δ	obsd	calcd[b]
$v_T = 0$						
0−1	[19.1][c]	[18.9][c]	19.1	−0.2	−	0.11
1−2	88.5	88.8	88.6	0.2	0.80	0.90
2−3	84.2	83.5	83.5	0.0	0.76	0.87
3−4	103.9	103.8	103.6	0.2	(1.00)	(1.00)
4−5	115.1	114.9	114.8	0.1	0.77	0.83
5−6	125.3	124.9	124.8	0.1	0.75	0.61
6−7	132.6	133.3	133.4	−0.1	0.50	0.41
7−8	140.6	141.1	140.9	0.2	0.40	0.26
8−9	147.0	147.4	147.7	−0.3	0.22	0.15
9−10	−	152.7	153.9	−1.2	0.17	0.09
10−11	−	160.4	159.9	0.9	0.06	0.05
11−12	−	167.9	164.7	3.2	0.04	0.02
0−3	191.8	191.2	191.1	0.1	0.15	0.27
1−4	276.2	275.9	275.6	0.3	0.20	0.11
2−5	302.7	301.8	301.8	0.0	0.06	0.08
3−6	343.7	343.2	343.2	0.0	0.06	0.05
4−7	−	372.2	372.9	−0.2	0.05	0.03
5−8	−	398.9	398.1	−0.2	0.04	0.02
6−9	−	422.1	422.0	0.1	0.02	0.01
7−10	−	−[d]	442.5	−	−	0.005
8−11	−	460.6	461.1	−1.1	0.01	0.003
9−12	−	480.8	478.1	2.7	0.01	0.001
$v_T = 1$						
0−1	−	[20.4][e]	19.5	0.9	−	0.01
1−2	−	~88.1 sh[f]	86.9	1.2	w[f]	0.09
2−3	−	84.2	84.1	0.1	~0.1	0.09
3−4	−	104.3	104.0	0.3	~0.1	0.10
4−5	−	~115.6 sh[f]	115.9	−0.3	~0.1	0.08
5−6	−	125.4	126.5	−1.1	~0.1	0.06
6−7	−	~133.8 sh[f]	135.8	−2.0	w[f]	0.04

[a] From ref 19. [b] $V = 1.019 \times 10^6x^4 - 1.946 \times 10^4x^2$ when $v_T = 0$, and $V = 9.089 \times 10^5x^4 - 1.802 \times 10^4x^2$ when $v_T = 1$. [c] Calculated from 1 → 2, 2 → 3, and 0 → 3 transition frequencies. The reported microwave value[20] is 18.684 cm^{-1}. [d] Observed by ring-twisting band. [e] Frequency not observed directly; calculated from ring-twisting hot bands. [f] sh, shoulder; w, weak.

spacing between rotational levels is 0.52 cm^{-1}. The microwave work[20] reports the following rotational constants: $A = 0.269$ cm^{-1}, $B = 0.260$ cm^{-1}, and $C = 0.140$ cm^{-1}. Utilizing the near-symmetric-top model[21]

$$B^* = \frac{\bar{A} + \bar{B}}{2} = 0.264\ \text{cm}^{-1} \tag{4}$$

the energy spacing $2B^*$ is predicted to be 0.529 cm^{-1}, consistent with our observations. The rotational fine structure results, of course, from the overlap of bands from the different puckering Q branches, but in each region there is typically one series that dominates the spectra. This was also the case for 25DHF.[21]

Table 1 lists the frequencies and intensities observed for the ring-puckering bands and compares the frequencies to those of Green.[19] The agreement is good, but in our spectra we observe three additional puckering levels with a Δv_P of 1 and five additional $\Delta v_P = 3$ transitions. The frequencies can be nicely fitted with the potential function

$$V = 1.019 \times 10^6 x^4 - 1.946 \times 10^4 x^2 \tag{5}$$

which has a barrier to planarity of 93 cm^{-1} and energy minima at ±0.098 Å, which correspond to dihedral angles of ±22°. Figure 6 shows this potential energy function. Table 1 compares both the observed frequencies and relative intensities to those calculated from the potential function. The agreement between observed and calculated values is outstanding except for the three highest frequencies. Although these higher-frequency spectral bands are weak, they are still clearly part of the puckering sequence as confirmed by the triple-quantum jump transitions. Table 2 shows that there is excellent agreement between the observed triple-jump frequencies and the values inferred by adding together the corresponding single-quantum jump transitions.

Examination of the puckering frequencies shows the expected decrease in separation between the individual bands. After the 103.8 cm^{-1} band the separations are 11.1, 10.0, 8.6, 7.8, 6.3, and 5.3 cm^{-1}. However, the next two separations have increased to 7.7 and 7.5 cm^{-1}. This is the first case where this type of divergence between the quantum states has been observed. As shown in Table 1, the calculated frequencies for these bands agree much more poorly than for any other transitions. A plausible explanation for one shifted band is to invoke Fermi resonance, and indeed, such interactions have been documented in the past. However, significant Fermi interactions for both the $v_P = 11$ and 12 levels, where both levels are pushed up substantially, seem improbable. We feel it is more likely that these levels, which are more than 1200 cm^{-1} above the energy minima, more likely reflect the fact that at higher values of the puckering coordinate x, where the potential energy is quite large, $V(x)$ can no longer be quite as well represented by the two-term function of eq 1. For the $v_P = 11$ and 12 states, the amplitude of the vibration is approximately $x = \pm 0.2$ or ±45° for the dihedral angle. At these high coordinate values, it is not surprising if the potential energy begins to become a bit stiffer (requiring an x^6 term) due to steric repulsions.

Examination of the spectra for sidebands resulting from transitions in the ring-twisting excited state proved to be

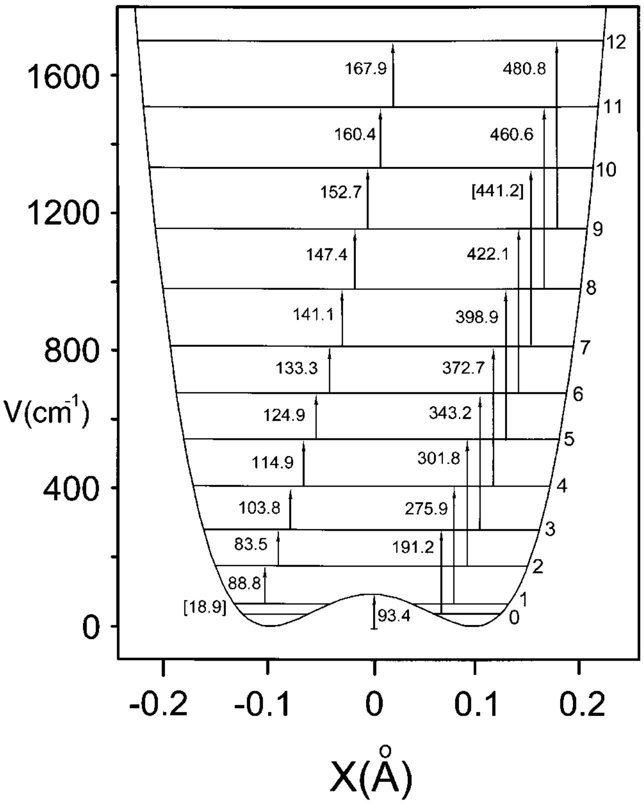

Figure 6. Potential energy function for the ring puckering of 23DHF.

TABLE 2: Comparison of Observed and Infrared Triple-Jump Transitions of 2,3-Dihydrofuran

	frequency (cm^{-1})				frequency (cm^{-1})		
transition	obsd	inferred[a]	Δ	transition	obsd	inferred[a]	Δ
0−3	191.2	191.2	0.0	5−8	398.9	399.3	−0.4
1−4	275.9	276.1	−0.2	6−9	422.1	421.8	0.3
2−5	301.8	302.2	−0.4	7−10	−[b]	441.2	−
3−6	343.2	343.6	−0.4	8−11	460.6	460.5	0.1
4−7	372.7	373.1	−0.4	9−12	480.8	481.0	−0.2

[a] Inferred from $\Delta v_P = 1$ transitions. [b] Obscured by ring-twisting bands.

disappointing as only a few weak bands can be detected. Most of the main bands show only an asymmetry on the high-frequency side, suggesting approximately where the sidebands are located. Searching for these bands is also complicated by the rich rotational−vibrational bands produced by each of the puckering bands. However, in a few cases, such as the 5 → 6 sideband at 125.4 cm^{-1} shown in Figure 4, the band can be resolved and the frequency determined.

Nonetheless, the puckering states in the first excited twisting state can be ascertained accurately from the hot band spectra shown in Figure 5. These bands result from the $\Delta v_P = 0$ bands arising from the different puckering levels ($v_P = 1, 2, 3, ...$) to the twisting state with $v_T = 1$. Figure 7 shows the hot band transitions and the energy separations calculated for the $v_T = 1$ state. Several of these are confirmed by weak sidebands. The two strongest bands in the spectrum arise from the most populated $v_P = 0$ and 1 states as expected. The other bands show a progression toward higher frequencies resulting from increased energy separations. The $v_P = 1 \rightarrow 1$ transition is higher than the 0 → 0 band since the 0−1 splitting has increased in the $v_T = 1$ state. However, the 2 → 2 band is lower than the 1 → 1 band as the 1 → 2 separation in the $v_T = 1$ state is smaller than for the twisting ground state. When $v_P \geq 3$, the energy separations for $v_T = 1$ are greater than for $v_T = 0$. The asymmetry of the puckering levels confirms this view as the hot band shoulders are on the high-frequency side for all bands except the 1 → 2 transition. The assignment shown in Figure 7 assumes that the strong 1 → 1 and weaker 3 → 3 transitions are coincident, and this is consistent with the potential energy calculation. The puckering levels for the $v_T = 1$ state can be nicely fit using the one-dimensional function

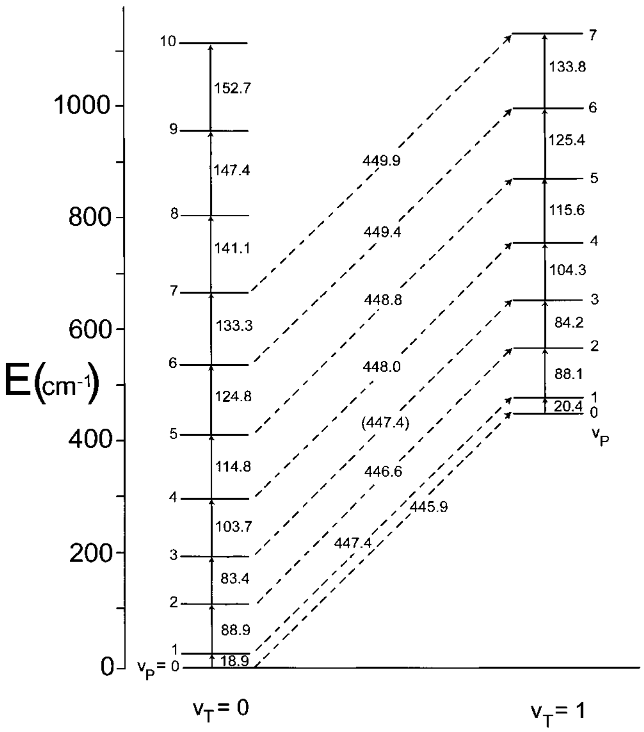

Figure 7. Ring-puckering energy levels of 23DHF in the ground ($v_T = 0$) and first excited ($v_T = 1$) ring-twisting states.

$$V = 0.909 \times 10^6 x^4 - 1.802 \times 10^4 x^2 \tag{6}$$

This has an energy barrier of 88 cm^{-1}. The frequencies calculated for this function are also shown in Table 1. However, a two-dimensional calculation in terms of both puckering (x_1) and twisting (x_2) is more meaningful. For these purposes we used the computational methods previously described.[1−5] The $g_{44}(x_1)$ in eq 2 was retained, and g_{45}, the kinetic cross term, was assumed to be negligible. Since the molecule is asymmetric, this is not totally correct, but the similarity of the masses of the oxygen atom and the CH_2 group makes this a reasonable approximation. For g_{55} the reciprocal reduced mass for the ring twisting, a value of 21.61 amu was used. This is the average of values computed for cyclopentene and 1,3-dioxole. The uncertainty in this value (approximately ±5%) only affects the magnitude of the harmonic potential energy parameter for the ring-twisting motion. The two-dimensional potential energy surface calculated in this manner is

$$V(x_1,x_2) = 1.024 \times 10^6 x_1^4 - 1.986 \times 10^4 x_1^2 + 6.266 \times 10^4 x_2^2 + 1.302 \times 10^5 x_1^2 x_2^2 \tag{7}$$

This has an energy barrier of 96 cm^{-1} and energy minima at ±22°, very similar to the one-dimensional results. Table 3 also compares the frequencies calculated for this surface to the observed values, and the agreement can be seen to be very good for both the $v_T = 0$ and 1 states. Figure 8 shows this potential energy surface.

TABLE 3: Observed and Calculated Frequencies of 2,3-Dihydrofuran for the Two-Dimensional Model

	frequency (cm^{-1})			relative intensity	
transition (υ_T, υ_P)	obsd	calcd[a]	Δ	obsd	calcd[a]
$\upsilon_T = 0, \Delta\upsilon_P = 1$					
(0,0) → (0,1)	[18.9]	18.9	0.0	–	0.11
(0,1) → (0,2)	88.9	88.7	0.2	0.80	0.89
(0,2) → (0,3)	83.4	83.3	0.1	0.76	0.86
(0,3) → (0,4)	103.7	103.6	0.1	(1.00)	(1.00)
(0,4) → (0,5)	114.8	114.8	0.0	0.77	0.83
(0,5) → (0,6)	124.8	124.8	0.0	0.75	0.61
(0,6) → (0,7)	133.3	133.4	−0.1	0.50	0.41
(0,7) → (0,8)	141.1	140.9	0.2	0.40	0.26
(0,8) → (0,9)	147.4	147.7	−0.3	0.22	0.15
(0,9) → (0,10)	152.7	153.9	−1.2	0.17	0.09
(0,10) → (0,11)	160.4	159.5	0.9	0.06	0.05
(0,11) → (0,12)	167.9	164.7	3.2	0.04	0.02
$\upsilon_T = 0, \Delta\upsilon_P = 3$					
(0,0) → (0,3)	191.2	191.0	0.2	0.15	0.28
(0,1) → (0,4)	275.9	275.6	0.3	0.20	0.11
(0,2) → (0,5)	301.8	301.6	0.2	0.06	0.08
(0,3) → (0,6)	343.2	343.1	0.1	0.06	0.05
(0,4) → (0,7)	372.2	372.9	−0.7	0.05	0.03
(0,5) → (0,8)	398.9	399.1	−0.2	0.04	0.02
(0,6) → (0,9)	422.1	422.0	0.1	0.02	0.01
(0,7) → (0,10)	–[b]	442.6	–	–	0.01
(0,8) → (0,11)	460.6	461.2	−0.6	0.01	0.00
(0,9) → (0,12)	480.8	478.2	2.6	0.01	0.00
$\upsilon_T = 1, \Delta\upsilon_P = 1$					
(1,0) → (1,1)	[20.4]	20.1	0.3	–	0.01
(1,1) → (1,2)	~88.1 sh[d]	88.2	−0.1	w[d]	0.11
(1,2) → (1,3)	84.2	84.6	−0.4	~0.1	0.10
(1,3) → (1,4)	104.3	104.2	0.1	~0.1	0.12
(1,4) → (1,5)	~115.6 sh[d]	115.4	0.2	~0.1	0.10
(1,5) → (1,6)	125.4	125.4	0.0	~0.1	0.07
(1,6) → (1,7)	~133.8 sh[d]	133.9	−0.1	w[d]	0.05
$\Delta\upsilon_T = 1, \Delta\upsilon_P = 0$					
(0,0) → (0,1)	445.9	445.9	0.0	51	(51)
(0,1) → (1,1)	447.4	447.1	0.3	27	47
(0,2) → (1,2)	446.6	446.6	0.0	18	31
(0,3) → (1,3)	(447.4)[c]	447.8	–	–	21
(0,4) → (1,4)	448.0	448.5	−0.5	14	13
(0,5) → (1,5)	448.8	449.2	−0.4	7	7
(0,6) → (1,6)	449.4	449.8	−0.4	4	4
(0,7) → (1,7)	449.9	450.3	−0.4	2	2

[a] $V = 1.024 \times 10^6 x_1^4 - 1.986 \times 10^4 x_1^2 + 6.266 \times 10^4 x_2^2 + 1.302 \times 10^5 x_1^2 x_2^2$. [b] Obscured by ring-twisting bands. [c] Obscured by the (0,1) → (1,1) transition. [d] sh, shoulder; w, weak.

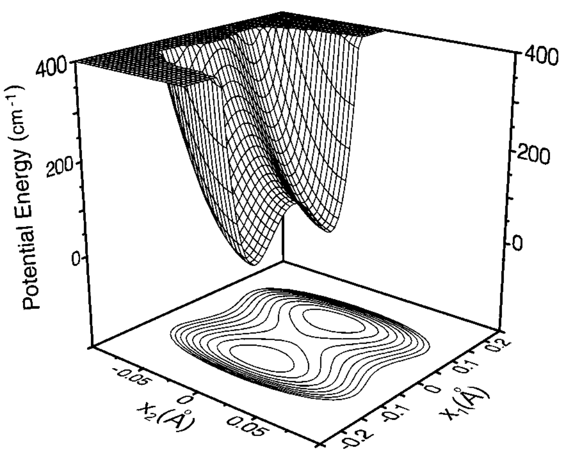

Figure 8. Two-dimensional potential energy surface for the ring puckering (x_1) and ring twisting (x_2) of 23DHF.

The potential energy cross term, which is a measure of vibrational interaction, of 1.302×10^5 cm^{-1}/Å^4 is compared to cross terms for related molecules[16] in Table 4. As can be seen, the value for 23DHF is in the expected range, although it is the lowest of the values that were measured.

TABLE 4: Comparison of Pucker−Twist Interaction Terms

molecule	interaction term (cm^{-1}/Å^4)
CP	1.90×10^5
3SCP	1.70×10^5
25DHF	2.23×10^5
25DHT	1.39×10^5
23DHT	1.71×10^5
23DHF	1.30×10^5

TABLE 5: Vibrational Frequencies (cm^{-1}) for 2,3-Dihydrofuran

			this work		lit.[a]
υ	description	obsd[a]	MP2	B3LYP	AM1
A′					
1	CH stretch	3122	3246	3290	3122
2	CH stretch	3110	3222	3264	3110
3	CH$_2$ stretch	2905	3036	3080	2894
4	CH$_2$ stretch	2875	3007	3067	2886
5	C=C stretch	1625	1666	1645	1623
6	CH$_2$ def.	1482	1518	1539	1476
7	CH$_2$ def.	1459	1497	1507	1465
8	CH wag	1378	1400	1421	1376
9	CH$_2$ wag	1305	1320	1345	1306
10	CH$_2$ wag	1282	1303	1313	1282
11	CH wag	1141	1158	1169	1143
12	ring stretch	1066	1084	1104	1069
13	ring stretch	995	1001	1026	1007
14	ring stretch	929	930	965	929
15	ring stretch	918	926	955	908
16	ring bend	828	835	836	791
17	ring bend	674	687	655	711
A″					
18	CH$_2$ stretch	2977	3110	3185	2966
19	CH$_2$ stretch	2935	3059	3143	2935
20	CH$_2$ twist	1220	1244	1258	1235
21	CH$_2$ twist	1192	1207	1224	1172
22	CH$_2$ rock	1061	1070	1081	1080
23	CH wag	885	920	906	890
24	CH$_2$ rock	842	843	865	823
25	CH wag	705	718	710	702
26	ring twisting	448	458	454	446
27	ring puckering	89[b]	109	201	213

[a] From ref 25. [b] The 1 → 2 transition.

Since we carried out the ab initio calculations at both the MP2 and B3LYP levels, we obtained predicted frequencies for all of the vibrations of the molecule. In Table 5 these are compared to the observed values and to calculated semiempirical AM1 values previously reported.[25] As can be seen, the agreement is fairly good, although scaling factors in the range of 0.95−1.00 would be needed to give better agreement.

Conclusion

Utilizing improved spectra and computations, we have determined the barrier to planarity for 23DHF to be 93 cm^{-1} as compared to the value of 83 cm^{-1} reported by Green.[19] The energy minima correspond to dihedral angles of ±22°. These were not previously determined. Ab initio calculations predict a barrier of 96 cm^{-1} and dihedral angles of ±23°, in excellent agreement with the experiment. The barrier for 23DHF is considerably lower than for the analogous sulfur compound 23DHT, which has a barrier of 435 cm^{-1}. This result is consistent with the expectation[1−18] that increased angle strain tends to favor the planar structure and thus reduce the barrier to planarity. The COC angle bending force constant in 23DHF is greater than the CSC angle bending constant in 23DHT, and thus, the oxygen-containing molecule has the greater angle strain.

The highest ring-puckering transitions suggest the puckering potential energy may be taking on a more complicated form at higher energies. The level of the puckering−twisting interaction is similar but somewhat lower than that for related molecules.

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