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Far-Infrared Spectra and Two-Dimensional Potential Energy Surfaces Involving the Ring-Puckering Vibration of 2,5-Dihydrothiophene

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The far-infrared spectra of 2,5-dihydrothiophene not only show the principal ring-puckering series in the 87−127 cm^{-1} region but also possess two sideband series arising from the ring-twisting first and second excited states. A third series arises from puckering transitions in the excited state of the $\upsilon_9(A_g)$ in-plane ring angle bending vibration, which occurs at 509.9 cm^{-1}. The ring-puckering levels in the υ_9 excited state are also confirmed by observed sum, difference, and hot bands. Observed double-quantum transitions confirm many of these assignments. Each of the four series can be fit well with a one-dimensional single minimum potential function possessing positive quartic and quadratic terms. Two-dimensional potential energy surfaces were also calculated to assess the interaction of the ring-puckering with the ring-twisting and in-plane ring bending modes. The twisting is anticooperative, raising the energy of the puckering process, while the in-plane ring bending is cooperative, facilitating the puckering motion.

Introduction

The far-infrared spectra of four-membered rings and "pseudo-four-membered rings" such as cyclopentene have been used for more than 3 decades to determine the vibrational potential energy functions governing the ring-puckering motions for these molecules.[1−4] Among the first group of molecules to be studied was 2,5-dihydrothiophene, $\overline{\mathrm{SCH_2CH{=}CHCH_2}}$. In 1968 Green and Harvey[5] reported the far-infrared spectrum and one-dimensional ring-puckering potential energy function for this molecule. The function has a single minimum, characteristic of a planar ring system. Earlier, Ueda and Shimanouchi[6] had analyzed the difference bands arising from a C−H stretching mode and had obtained similar puckering frequencies and potential energy function. However, both potential functions were based on a reduced mass value[6] that was calculated using a computer program[7] that was later found[8] to incorrectly describe the puckering motion.

The original far-infrared spectrum[5] of 2,5-dihydrothiophene was recorded at relatively poor resolution. Hence, only the principal puckering series in the 87−127 cm^{-1} region was observed. For the analogous oxygen compound 2,5-dihydrofuran, however, sidebands have been observed,[9,10] and these have been used to calculate a two-dimensional potential energy surface in terms of the ring-puckering and ring-twisting coordinates.[9] Since the sidebands originate from the ring-twisting excited state, there were sufficient data to evaluate the interaction between the two out-of-plane ring modes.

In this work we present far-infrared spectra showing the ring-puckering sequence of single quantum jump transitions recorded under higher resolution and with better signal-to-noise ratio. The spectra contain the expected sidebands from two ring-twisting excited states and also double quantum jump transitions. These data were then used to calculate the two-dimensional puckering/twisting potential energy surface to determine the interaction between these modes. The results were then compared to those for 2,5-dihydrofuran. For the latter compound, the two-dimensional calculation was refined using a corrected kinetic energy (reciprocal reduced mass) expression. In addition, we have observed far-infrared sidebands and mid-infrared sum and difference bands associated with the in-plane ring-bending vibration. These allowed us to determine the two-dimensional potential energy surface for the interaction between this mode and the ring puckering.

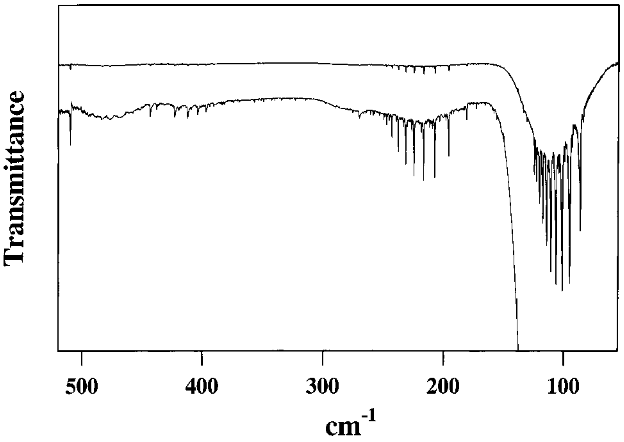

Figure 1. Far-infrared spectrum of 1.5 Torr of 2,5-dihydrothiophene at a path length of 3.75 m with a resolution of 0.25 cm^{-1} (500 scans).

Experimental Section

The sample of 2,5-dihydrothiophene was prepared and purified by the method of Birch and McAllen.[11] Far-infrared spectra were recorded using a Digilab FTS-20E spectrometer with a helium-cooled bolometer detector. Resolutions of 0.1 and 0.25 cm^{-1} were used and 500−1000 scans were collected.

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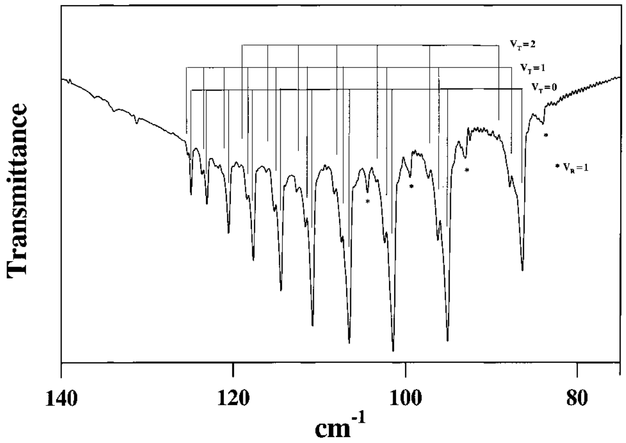

Figure 2. Far-infrared spectrum of 2,5-dihydrothiophene (expanded) in the 80−140 cm^{-1} region.

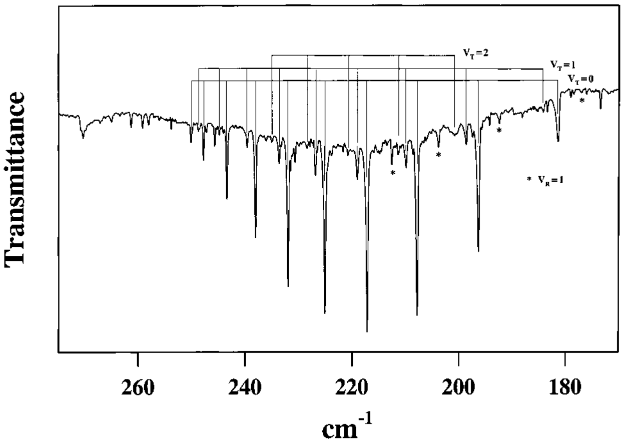

Figure 3. Far-infrared spectrum of 2,5-dihydrothiophene in the double quantum jump region.

TABLE 1: Ring-Puckering Transitions (cm^{-1}) of 2,5-Dihydrothiophene

	principal series		twisting side bands		ring-bending
transition	this work	GH[a]	$v_T = 1$	$v_T = 2$	sidebands $v_P = 1$
0−1	86.49	87.0	87.98	89.46	84.17
1−2	95.15	95.5	96.26	97.44	93.13
2−3	101.48	102.0	102.49	103.47	99.70
3−4	106.58	107.0	107.42	108.32	104.50
4−5	110.83	111.3	111.68	112.67	[107.5]
5−6	114.50	114.8	115.28	116.21	
6−7	117.71	118.1	118.46	119.4	
7−8	120.58	120.7	121.19		
8−9	123.06	123.2	123.61		
9−10	124.88	125.2	125.25		
10−11	[125.29]	127.0			

[a] Reference 5.

Samples were contained in a Wilkes variable long-path cell with variable path lengths of 4−20 m. Raman spectra of the vapor were recorded using a model 5 Ramalog 14018 SPEX spectrometer and a Coherent argon ion laser.

Results and Discussion

Analysis of Spectra. Figure 1 shows the far-infrared spectrum of 2,5-dihydrothiophene vapor in the 50−520 cm^{-1} region. Figure 2 presents the spectrum expanded in the 80−140 cm^{-1} region showing more detail, including several observed ring-puckering series. The strongest bands arise from the principal series ($\Delta v_P = +1$) when no other vibrations are excited. In addition, two weaker sideband series on the high-frequency sides of the principal bands can be observed, and these arise from the ring-twisting $v_{14}(A_2)$ excited states with $v_T = 1$ and 2. The vapor-phase Raman spectrum shows the v_{14} fundamental band to be at 377.5 cm^{-1}. A fourth series on the low-frequency side of each principal band results from molecules in the $v_9(A_1)$ in-plane ring-bending excited state ($\Delta v_R = 1$), which has a frequency of 509.9 cm^{-1}. Table 1 lists all of these observed frequencies and compares the values for the principal series to those reported by Green and Harvey.[5] The latter can be seen to be approximately 0.3−0.5 cm^{-1} too high. Our values should conservatively be accurate to ±0.05 cm^{-1}. Figure 3 shows the 170−270 cm^{-1} region for this molecule. The double quantum jump transitions ($\Delta v_P = +2$) corresponding to each of the four observed $\Delta v_P = +1$ series are evident. Table 2 lists these frequencies and compares the observed values to those inferred from adding up single quantum transition frequencies. The excellent agreement confirms the assignments for each of the series in Table 1.

Because the v_{14} ring-twisting has A_2 symmetry, no combinations between this mode and the $v_{27}(B_2)$ ring puckering can be observed. Transitions from puckering levels to the twisting excited state have A_2 (infrared forbidden) symmetry when the excited-state puckering levels have the same symmetry (even or odd). Odd-to-even or even-to-odd transitions should produce B_1 transitions with type B band contours, which have no Q branches and hence also cannot be readily observed. Combinations with $v_9(A_1)$, the in-plane ring bending, however, have been observed. The sum and difference bands ($\Delta v_P = +1$) have type C contours, while the hot bands are of type A. The weak v_9 band at 509.9 cm^{-1} can be seen in Figure 1 along with six difference bands in the 383−424 cm^{-1} region. Figure 4 shows the sum bands in the 570−655 cm^{-1} region. At first glance these appear to be difference bands off the strong $v_{26}(B_2)$ band at 669.6 cm^{-1}, but the frequencies clearly match as a combination of v_{27} and v_9. Figure 5 shows the transitions associated with v_9 including the sidebands, sum bands, and difference bands. Table 3 lists these observed frequencies, and the agreement with the values calculated for the sidebands listed

TABLE 2: Double-Quantum Transitions (cm^{-1}) for the Ring Puckering of 2,5-Dihydrothiophene

	principal series		$v_T = 1$		$v_T = 2$		$v_R = 1$	
transition	observed	inferred	observed	inferred	observed	inferred	observed	inferred
0−2	181.46	181.64	184.23	184.24		186.90	177.23	177.30
1−3	196.41	196.63	198.75	198.75	200.91	200.91	192.50	192.83
2−4	207.83	208.06	209.95	209.91	211.43	211.79	203.91	204.20
3−5	217.17	217.41	219.08	219.10	220.84	220.99	212.57	[212.0]
4−6	225.11	225.33	226.95	226.96	228.47	228.88		
5−7	232.00	232.21	233.69	233.74	234.90	235.6		
6−8	238.10	238.29	239.65	239.65				
7−9	243.45	243.64	244.89	244.80				
8−10	247.80	247.94	248.9	248.86				
9−11	250.17							

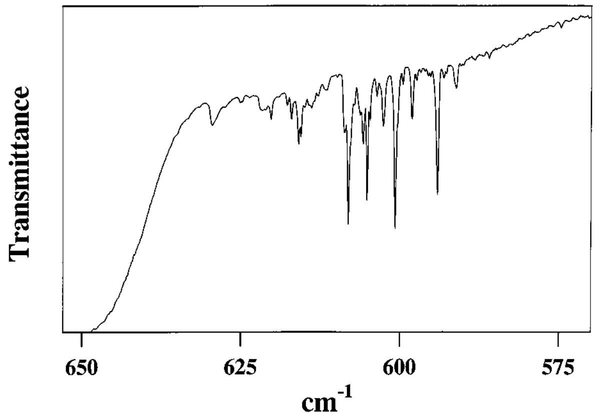

Figure 4. Infrared spectrum of 2,5-dihydrothiophene in the 550−750 cm^{-1} region showing the sum bands.

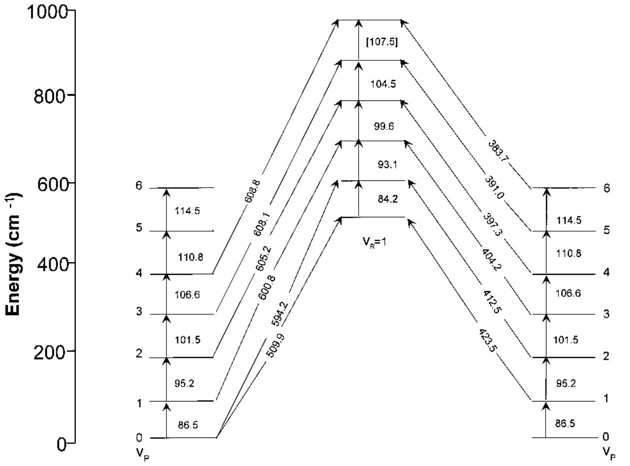

Figure 5. Transitions observed between the puckering levels and the υ_9 excited state.

TABLE 3: Sum, Difference, and Hot Bands Involving the $\upsilon_9(A_g)$ Ring-Bending Vibration

	frequency (cm^{-1})	
transition	observed	calculated[a]
	Sum Bands ($\Delta\upsilon_P = +1$)	
0−1	594.2	594.1
1−2	600.8	600.7
2−3	605.2	605.1
3−4	608.1	608.1
4−5	608.8	
	Difference Bands ($\Delta\upsilon_P = -1$)	
1−0	423.5	423.4
2−1	412.5	412.4
3−2	404.2	404.0
4−3	397.3	397.0
5−4	391.0	390.7
6−5	383.7	
	Fundamental and Hot Bands ($\Delta\upsilon_P = 0$)	
0−0	509.9	[509.9]
1−1	507.7	507.6
2−2	505.4?	505.5

[a] From ring-puckering bands in the far-infrared.

in Table 1 can be seen to be excellent. Observation of these bands was most helpful in confirming that the far-infrared sidebands, which are shifted to lower frequencies, do indeed result from transitions occurring within the υ_9 excited state ($\Delta\upsilon_R = +1$).

TABLE 4: Observed and Calculated Ring-Puckering Frequencies (cm^{-1}) for Different Ring-Twisting States

		calculated[a]	
transition	observed	2-DIM	1-DIM
	Principal Series ($\upsilon_T = 0$, $\upsilon_R = 0$)		
0−1	86.5	87.3	87.7
1−2	95.2	94.8	94.9
2−3	101.5	100.8	100.8
3−4	106.6	105.9	105.8
4−5	110.8	110.3	110.1
5−6	114.5	114.2	113.9
6−7	117.7	117.8	117.4
7−8	120.6	121.0	120.6
8−9	123.1	124.0	123.5
9−10	124.9	126.8	126.2
10−11	125.3	127.8	128.7
	Ring-Twisting Excited State ($\upsilon_T = 1$, $\upsilon_R = 0$)		
0−1	88.0	88.8	89.2
1−2	96.3	96.1	96.2
2−3	102.5	101.9	101.9
3−4	107.4	106.9	106.7
4−5	111.7	111.3	110.9
5−6	115.3	115.2	114.7
6−7	118.5	118.9	118.1
7−8	121.2	121.9	121.2
8−9	123.6	124.9	124.1
9−10	125.3	127.6	126.7
	Second Twisting Excited State ($\upsilon_T = 2$, $\upsilon_R = 0$)		
0−1	89.5	90.3	89.9
1−2	97.4	97.3	97.2
2−3	103.5	103.1	103.1
3−4	108.3	108.0	108.1
4−5	112.7	112.3	112.5
5−6	116.2	116.2	116.3
6−7	119.1	119.5	119.9

[a] From potential functions in Table 6.

Calculation of Potential Energy Surfaces. The data in Table 1 and confirmed by Tables 2 and 3 provide the information required to not only calculate the ring-puckering potential energy function in the one-dimensional approximation but also make it possible to calculate two-dimensional potential energy surfaces reflecting the interaction between the ring-puckering and the ring-twisting and ring-bending modes. To carry out these calculations, we utilized computational methods described previously.[2−4] For the one-dimensional calculation, we first determined the kinetic energy (reciprocal reduced mass) expansion using our previously described computer program.[11,12] The calculation was based on a structure from a microwave study[14] and confirmed by molecular mechanics calculations in our laboratory. The calculated expansion is given by

$$g_{44}(x_1) = (8.5674 \times 10^{-3}) - (2.6532 \times 10^{-2})x^2 - (1.1589 \times 10^{-1})x^4 + 0.7510{x_1}^6 \quad (1)$$

where $g_{44}(x_1)$ is the reciprocal reduced mass expressed in terms of the puckering coordinate x_1 given in angstroms. The one-dimensional Hamiltonian that was utilized is

$$H = (\hbar^2/2)\ \partial/\partial x_1\ g_{44}(x_1)\ \partial/\partial x_1 + V(x_1) \quad (2)$$

where the potential energy is given by

$$V(x_1) = a{x_1}^4 + b{x_1}^2 \quad (3)$$

By use of the kinetic energy function of eq 1, the one-dimensional potential function calculated for the 2,5-dihydrothiophene principal series is

$$V(\mathrm{cm}^{-1}) = (2.894 \times 10^5){x_1}^4 + (1.075 \times 10^4){x_1}^2 \quad (4)$$

TABLE 5: Observed and Calculated Ring-Puckering Frequencies (cm^{-1}) for Different Ring-Bending States

transition	observed	calculated[a] 2-DIM	1-DIM
Principal Series ($v_T = 0$, $v_R = 0$)			
0−1	86.5	87.5	87.7
1−2	95.2	94.9	94.9
2−3	101.5	100.8	100.8
3−4	106.6	105.9	105.8
4−5	110.8	110.3	110.1
5−6	114.5	114.1	113.9
6−7	117.7	117.7	117.4
7−8	120.6	120.9	120.6
8−9	123.1	123.9	123.5
9−10	124.9	126.7	126.2
10−11	125.3	127.3	128.7
Ring-Bending Excited State ($v_T = 0$, $v_R = 1$)			
0−1	84.2	84.9	84.8
1−2	93.1	92.7	92.6
2−3	99.6	98.8	98.8
3−4	104.5	104.0	104.0
4−5	107.5	108.5	108.5

[a] From potential functions in Table 6.

The frequency values calculated for this function are compared to the observed ones in Table 4, and the fit can be seen to be excellent. Similar one-dimensional calculations were carried out for the three sideband series. The potential energy parameters for these are given in Table 6 and the calculated frequencies in Tables 4 and 5. Again, the agreement is excellent.

To better assess the interaction of the puckering with the ring-twisting or the in-plane ring-bending, a two-dimensional Hamiltonian was used:

$$H = (-\hbar^2/2)[\partial/\partial x_1\, g_{44}(x_1)\, \partial/\partial x_1 + \partial/\partial x_2\, g_{55}\, \partial/\partial x_2] + V(x_1,x_2) \quad (5)$$

where x_1 and x_2 are coordinates for the ring puckering and the second vibration, respectively. The g_{55} term is the reciprocal reduced mass for the second vibration. The potential energy surface is given by

$$V(x_1,x_2) = a_1 x_1^4 + b_1 x_1^2 + b_2 x_2^2 + c x_1^2 x_2^2 \quad (6)$$

Thus, the second vibration (ring-twisting or in-plane ring bending) is assumed to be harmonic, and the parameter c reflects the degree of interaction between the two modes. Since we have no data on the interaction between the ring-twisting and in-plane ring bending, a three-dimensional calculation was not carried out.

We first examined the interaction between the puckering and twisting (x_2 = twisting) coordinate. The reduced mass value ($\mu = 1/g_{55}$) for the twisting was calculated using the program previously described.[12,13] This was found to be 24.710 au. Since the two vibrations have different symmetry species, the cross kinetic energy term g_{45} equals zero.

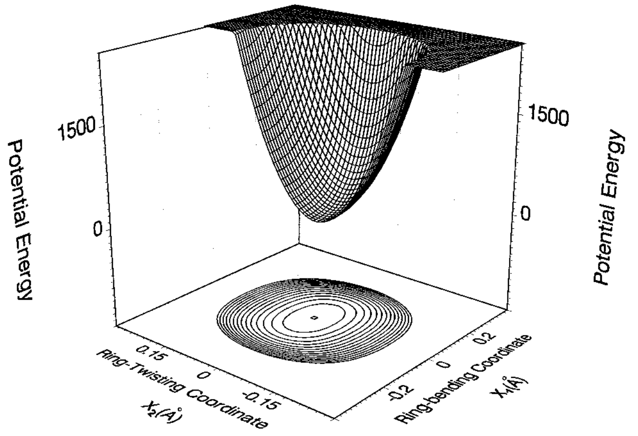

Figure 6. Potential energy surface for the ring-puckering (x_1) and ring-twisting (x_2) vibrations of 2,5-dihydrothiophene.

The two-dimensional potential energy surface calculated for the puckering/twisting is

$$V = (2.967 \times 10^5)x_1^4 + (1.029 \times 10^4)x_1^2 + (5.201 \times 10^4)x_2^2 + (1.394 \times 10^5)x_1^2x_2^2 \quad (7)$$

The frequencies calculated for this surface are given in Table 4 as the 2-DIM calculation. Figure 6 presents this surface for the planar molecule with the minima for both x_1 and x_2 at zero. As can be seen in Table 4, the increase in the puckering frequencies of approximately 1 cm^{-1} for $v_T = 1$ and of 2 cm^{-1} for $v_T = 2$ is well represented by the positive interaction term. The interaction is anticooperative, indicating that the puckering motion requires higher energy in the twisting excited states.

We also examined the interaction between the puckering and the in-plane ring angle bending (x_2 = ring bending coordinate). Since the potential energy for the puckering arises primarily from the bending of the ring angles and since the same is true for the in-plane ring angle bending v_9, a greater interaction between the modes is anticipated even though they are of different symmetry species. To carry out the two-dimensional calculation, it was first necessary to calculate the reduced mass for the ring-bending vibration. A computer program was written to do this, and its description will be presented elsewhere.[15] The kinetic energy term was calculated to be $g_{55} = 1/\mu_R = 0.132\,38$ au^{-1}. By use of this value, the two-dimensional surface was calculated to be

$$V(\mathrm{cm}^{-1}) = (2.930 \times 10^5)x_1^4 + (1.109 \times 10^4)x_1^2 + (2.925 \times 10^4)x_2^2 - (9.660 \times 10^4)x_1^2x_2^2 \quad (8)$$

The frequencies calculated for this surface are compared to the observed values in Table 5. The negative interaction term nicely

TABLE 6: Potential Energy Parameters for One- and Two-Dimensional Surfaces of 2,5-Dihydrothiophene

		$V = a_1x_1^4 + b_2x_1^2 + b_2x_1^2 + cx_1^2x_2^2$			
dimension	series	a_1 (cm^{-1}/Å^4)	b_1 (cm^{-1}/Å^2)	b_2 (cm^{-1}/Å^2)	c (cm^{-1}/Å^4)
1	$v_T = 0$, $v_R = 0$	2.894×10^5	1.075×10^4		
1	$v_T = 1$, $v_R = 0$	2.865×10^5	1.126×10^4		
1	$v_T = 2$, $v_R = 0$	3.033×10^5	1.137×10^4		
1	$v_T = 0$, $v_R = 1$	2.957×10^5	0.973×10^4		
2	v_P with v_T	2.967×10^5	1.029×10^4	5.201×10^4	1.394×10^5
2	v_P with v_R	2.930×10^5	1.109×10^4	2.925×10^4	-9.660×10^4 [a]

[a] In cm^{-1} Å^{-2} rad^{-2} units.

accounts for the approximate 2 cm^{-1} decrease in each puckering transition in the bending ($\upsilon_R = 1$) excited state. Thus, these two motions are cooperative, since the in-plane ring-bending facilitates the puckering process.

We also thought that it would be valuable to compare our puckering/twisting surface to that of the oxygen analogue, 2,5-dihydrofuran. Although this surfaces has already been calculated,[9] it was previously obtained using reduced coordinates rather than with a reduced mass expansion.[15] We have utilized the structure of 2,5-dihydrofuran[16] to first calculate new values for the kinetic energy constants:

$$g_{44}(x_1) = (1.024 \times 10^{-2}) - (2.346 \times 10^{-2})x_1^{\,2} - (4.822 \times 10^{-1})x^4 + 2.094x^6 \quad (9)$$

and

$$g_{55}(x_2) = 0.03969 \quad (10)$$

These were then used to determine the surface

$$V(\mathrm{cm}^{-1}) = (5.792 \times 10^5)x_1^{\,4} + (9.075 \times 10^3)x_1^{\,2} + (5.643 \times 10^4)x_2^{\,2} + (2.225 \times 10^5)x_1^{\,2}x_2^{\,2} \quad (11)$$

which can be compared to the corresponding 2,5-dihydrothiophene surface in eq 7. Comparison of the coefficients shows that the overall ring-puckering (x_1) motion requires greater energy for the oxygen compound, reflecting the higher angle-bending force constant for the C−O−C angle bending compared to the C−S−C angle. As expected, the ring-twisting constants, 5.643×10^4 cm^{-1}/rad^2 for the oxygen compound and 5.201×10^4 cm^{-1}/rad^2 for 2,5-dihydrothiophene, are very similar. The interaction between the puckering and twisting motions does differ somewhat between the two molecules, however. The $x_1^2x_2^2$ term for the furan is about 60% higher in magnitude.

Conclusions

2,5-Dihydrothihphene has a rich far-infrared spectrum with four ring-puckering series clearly evident, arising not only from the principal series but also from three different vibrational excited states. Examination of the frequency shifts shows that the ring-puckering and ring-twisting motions are anticooperative, while the puckering and in-plane ring-angle bending motion are cooperative.

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