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Far-Infrared and Raman Spectra and Vibrational Potential Energy Surface for the Ring-Puckering and Ring-Flapping of Coumaran

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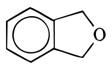
The far-infrared and Raman spectra of coumaran vapor have been recorded and analyzed. Single, double, and triple quantum jump transitions ($\Delta v_P = 1, 2, 3$) were observed in the 60−270 cm^{-1} region for the ring-puckering vibration in both the ground and first excited states of the ring-flapping vibration. These were utilized to assign the ring-puckering quantum states for both flapping states, allowing both one- and two-dimensional potential energy functions to be determined. The one-dimensional function in terms of the ring-puckering coordinate (x_1) has the form V (cm^{-1}) $= (7.92 \times 10^5)x_1^4 - (2.99 \times 10^4)x_1^2$ and has a barrier to planarity of 279 cm^{-1} (3.32 kJ/mol) with energy minima corresponding to dihedral angles of ±30°. The two-dimensional surface in terms of the puckering and flapping coordinates shows that there is extensive interaction between these two vibrations. The barrier for the two-dimensional surface is 275 cm^{-1}, and the dihedral angle is 37°. The coumaran barrier is considerably higher than that for 2,3-dihydrofuran (83 cm^{-1}), which does not have the attached benzene ring.

I. Introduction

We have recently reported the far-infrared and Raman spectra of phthalan[1,2] (**I**) and 1,3-benzodioxole[3] (**II**) and used the data to determine the vibrational potential energy surfaces for the ring-puckering and ring-flapping motions of these molecules.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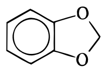
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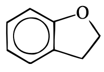
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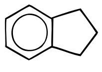
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In the present paper we extend our studies to coumaran (**III**), and in future work we will examine indan (**IV**).

Our work on phthalan[1,2] showed that this molecule has a barrier to planarity of 35 cm^{-1} but is essentially planar since the zero-point energy for the puckering is comparable to the barrier. For phthalan the ring-puckering and ring-flapping motions, which are defined elsewhere,[1,2] are very strongly coupled through the cross kinetic energy term, and this gives rise to a very irregular pattern of energy states. 1,3-Benzodioxole[3] is puckered, and probably slightly "flapped", because of the presence of the anomeric effect, which is present for molecules with oxygen atoms in the 1,3 positions. The barrier to planarity of 1,3-benzodioxole is 164 cm^{-1}.

Coumaran (**III**) has been studied previously by electronic absorption spectroscopy,[4,5] infrared and Raman spectroscopy,[6] and laser-induced fluorescence spectroscopy.[7] None of the studies provided any structural conclusions or reported data on the ring-puckering or flapping, although the last paper found evidence for dimer formation and reported band progressions in the excitation spectra.

II. Experimental Section

Coumaran was purchased from Aldrich Chemical Co. and purified by vacuum distillation. Far-infrared spectra were recorded at the National Institute of Petroleum and Energy Research (NIPER) using a Digilab FTS-20E spectrometer with a liquid-helium-cooled bolometer detector. Samples were contained in a Wilkes variable long-path cell with variable path lengths of 17.25−20.25 m. Two Mylar beam splitters (12.5 and 6.25 μm) were used to acquire spectra from 50 to 500 cm^{-1} at resolutions of 0.25 and 0.5 cm^{-1}.

Vapor-phase Raman spectra were recorded using an ISA U-1000 double monochromator with a slit width of 3 cm^{-1}. The high-temperature cells described elsewhere[8] were used to record spectra at 225 °C. The 532 nm line of a Coherent Radiation DPSS-400 Nd:YAG laser served as the excitation source. Scattered light was collected using either a liquid-nitrogen-cooled charge-coupled detector (CCD) or a photomultiplier tube (PMT).

III. Results and Discussion

Figure 1 shows the far-infrared spectrum of coumaran vapor in the 60−162 cm^{-1} region. The quantum numbers for many of the ring-puckering transitions are also shown on the diagram. Figure 2 shows the far-infrared and Raman spectra in the 150−450 cm^{-1} region. The strong band in both spectra at 192 cm^{-1} is from the ring-twisting mode. This is confirmed by the calculated Raman band contour for this vibration, which is also shown on the diagram. The spectral region between 200 and 300 cm^{-1} in the infrared is rich with weak bands due to the ring-flapping vibration in combination with the ring-puckering vibration.

Figure 3 shows an energy diagram for the puckering levels in the flapping ground ($v_F = 0$) and excited states ($v_F = 1$). Also shown are many of the transitions observed in the far-infrared spectra. Table 1 lists the assignments for the observed transitions in both states. The observation of many puckering double and triple quantum jumps helps to confirm essentially all of the assignments, as can be seen by comparison of the observed and inferred frequencies for the transitions.

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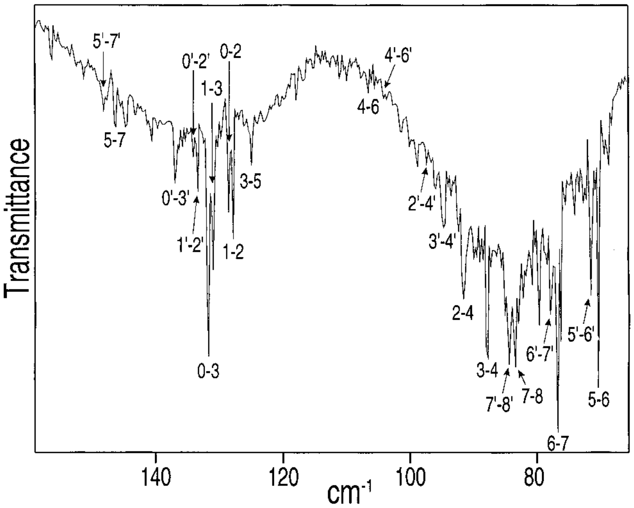

Figure 1. Far-infrared spectrum of coumaran vapor: 18.75 m path, 0.5 Torr pressure, 0.25 cm^{-1} resolution. The transitions for many of the ring-puckering transitions are indicated. Primes refer to the $\upsilon_F = 1$ ring-flapping state.

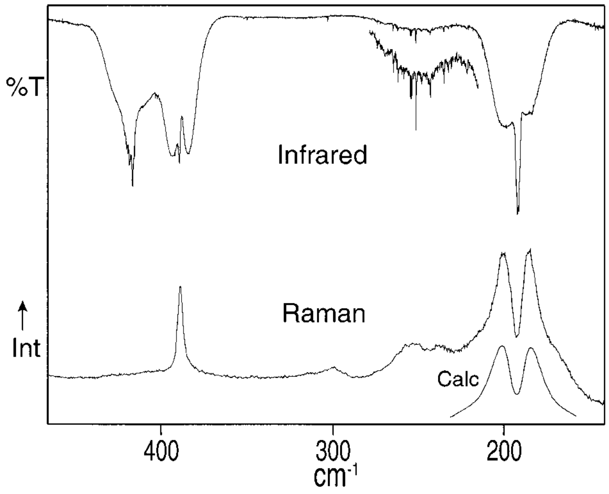

Figure 2. Far-infrared and Raman spectra of coumaran vapor in the 150−450 cm^{-1} region.

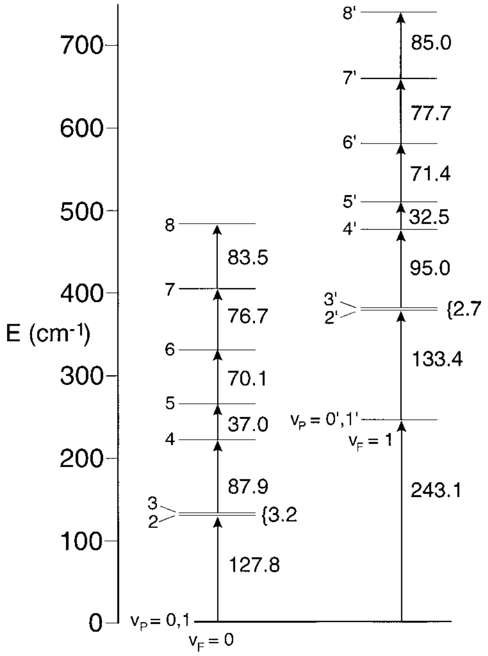

Figure 3. Energy level diagram for the ring-puckering levels in the $\upsilon_F = 0$ and 1 flapping states. The primes indicate puckering levels in the $\Delta\upsilon_F = 1$ state.

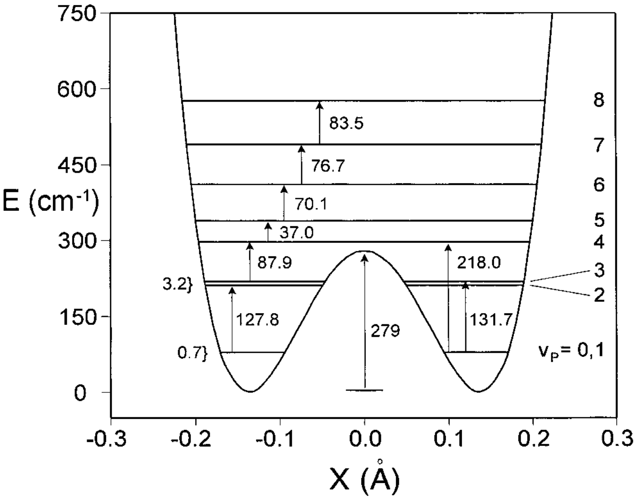

Figure 4. One-dimensional ring-puckering potential energy function of coumaran.

The ring-twisting vibration at 191.8 cm^{-1} is expected to interact considerably less with the ring-puckering vibration than does the flapping vibration but will nonetheless give rise to spectral features in the far-infrared region. There are a number of weak unassigned bands throughout this region that are most likely due to puckering/twisting combinations, but these were not easily assigned with any confidence.

IV. Potential Energy Functions

We have previously outlined the procedures for the calculation of kinetic energy and potential energy functions for these types of molecules.[1−3] Unlike phthalan and 1,3-benzodioxole, coumaran is asymmetric and possesses C_s rather than C_{2v} symmetry for the planar structure. Hence, the kinetic energy function for the puckering had to be calculated using a modified version of the program previously described[9] for asymmetric five-membered-ring calculations. The modified program produced the one-dimensional kinetic energy expansion in terms of the ring-puckering coordinate (x_1):

$$g_{44}(x_1) = 0.00646 - 0.03676x_1^2 + 0.03281x_1^4 + 0.02173x_1^6 \quad (1)$$

This function was then used to calculate the one-dimensional potential energy function:

$$V(\mathrm{cm}^{-1}) = (7.92 \times 10^5)x_1^4 - (2.99 \times 10^4)x_1^2 \quad (2)$$

This potential function, shown in Figure 4, has a barrier of 279 cm^{-1} and minima at $x_1 = \pm 0.14$ Å, which correspond to dihedral angles of bending of ±30°. A one-dimensional calculation for the $\upsilon_F = 1$ flapping excited state gives

$$V(\mathrm{cm}^{-1}) = (8.45 \times 10^5)x_1^4 - (3.21 \times 10^4)x_1^2 \quad (3)$$

which has a barrier of 305 cm^{-1}. The calculated frequencies for these functions are compared to the observed values in Table 2. The frequency agreement is moderately good but poorer than what we have typically obtained for simpler systems.[10−13] The calculated intensities are also not as good as usual, indicating that the one-dimensional wave functions from the calculation are only fair approximations. Both the strong interaction between

TABLE 1: Ring-Puckering Transitions ($\Delta v_{\mathrm{P}} = 1, 2, 3$) in the Far-Infrared Spectrum of Coumaran

	transition	frequency (cm^{-1})	inferred	relative intensity
$v_{\mathrm{F}} = 0$, $\Delta v_{\mathrm{P}} = 1$	0−1	(0.7)[a]	0.7	
	1−2	127.8	127.8	0.6
	2−3	(3.2)[a]	3.2	
	3−4	87.9	87.9	0.6
	4−5	(37.0)[a]	37.0	
	5−6	70.1	70.1	1.2
	6−7	76.7	76.7	1.0
	7−8	83.5	83.5	0.5
$\Delta v_{\mathrm{P}} = 2$	0−2	128.5	128.5	0.4
	1−3	130.9	131.0	0.5
	2−4	91.7	91.1	0.4
	3−5	124.9	124.9	0.2
	4−6	106.7	107.1	0.1
	5−7	146.3	146.8	0.2
	6−8	160.1	160.2	0.1
$\Delta v_{\mathrm{P}} = 3$	0−3	131.7	131.7	1.0
	1−4	218.0	218.9	0.08
	2−5	∼128.1	128.1	0.4
	3−6	obscured	195.0	
	4−7	obscured	183.8	
	5−8	230.7	230.3	0.1
$v_{\mathrm{F}} = 1$, $\Delta v_{\mathrm{P}} = 1$	0−1	(0.7)[a]	0.7	
	1−2	133.4	133.4	0.3
	2−3	(2.7)[a]	2.7	
	3−4	95.0	95.0	0.3
	4−5	(32.5)[a]	32.5	
	5−6	71.4	71.4	0.7
	6−7	77.7	77.7	0.5
	7−8	85.0	85.0	0.2
$\Delta v_{\mathrm{P}} = 2$	0−2	134.1	134.1	0.1
	1−3	136.3	136.1	0.2
	2−4	97.7	97.7	0.03
	3−5	127.5	127.5	0.06
	4−6	104.2	103.9	0.03
	5−7	148.3	149.1	0.2
	6−8	163.8	162.7	0.1
$\Delta v_{\mathrm{P}} = 3$	0−3	136.3	136.8	0.2
	1−4	230.7	231.1	0.1
	2−5	130.1	130.2	0.1
	3−6	obscured	198.9	
	4−7	obscured	181.6	
	5−8	233.4	234.1	0.1
$\Delta v_{\mathrm{F}} = 1$, $\Delta v_{\mathrm{P}} = 0$	0−0	243.1	243.1	0.3
	1−1	243.1	243.1	0.3
	3−3	248.2	248.2	0.1
	4−4	254.8	255.3	0.2
	5−5	251.5	250.8	0.8
	6−6	252.2	252.1	0.1

[a] Calculated from $\Delta v_{\mathrm{P}} = 2$ or 3 transitions.

TABLE 2: Comparison of Observed and Calculated Ring-Puckering Frequencies

		frequency (cm^{-1})			relative intensity		
	transition	obsvd	calc I[a]	calc II[b]	obsvd	calc I[a]	calc II[b]
$v_{\mathrm{F}} = 0$	0−1	0.7	0.1	0.1			
	1−2	127.8	131.4	132.9	0.6	1.0	1.0
	2−3	3.2	4.7	4.6			
	3−4	87.9	86.8	86.3	0.6	0.8	0.8
	4−5	37.0	40.4	41.1		0.4	0.3
	5−6	70.1	70.0	70.2	1.2	0.8	0.8
	6−7	76.7	72.8	74.2	1.0	0.8	0.7
	7−8	83.5	80.8	82.4	0.5	0.7	0.7
	0−3	131.7	136.2	137.6	(1.0)	(1.0)	(1.0)
$v_{\mathrm{F}} = 1$	0−1	0.7	0.1	0.1			
	1−2	133.4	137.8	137.2	0.3	0.5	0.3
	2−3	2.7	3.6	3.2			
	3−4	95.0	93.6	92.2	0.3	0.4	0.2
	4−5	32.5	36.9	35.8		0.1	0.1
	5−6	71.4	71.4	69.9	0.7	0.1	0.2
	6−7	77.7	72.8	72.0	0.5	(0.5)	0.2
	7−8	85.0	81.6	81.1	0.5	0.2	0.2
	0−3	136.3	141.5	140.4	0.2	0.2	0.3

[a] One-dimensional calculations: $V\,(\mathrm{cm}^{-1}) = (7.92 \times 10^5)x_1^4 - (2.99 \times 10^4)x_1^2$ for $v_{\mathrm{F}} = 0$ $V\,(\mathrm{cm}^{-1}) = (8.45 \times 10^5)x_1^4 - (3.21 \times 10^4)x_1^2$ for $v_{\mathrm{F}} = 1$. [b] Two-dimensional calculations: $V\,(\mathrm{cm}^{-1}) = (3.31 \times 10^5)x_1^4 - (1.91 \times 10^4)x_1^2 + (8.16 \times 10^3)x_2^2 - (3.95 \times 10^4)x_1^2x_2^2$.

the puckering and flapping vibrations as well as the asymmetry of the molecule, which allows additional interactions with other vibrational modes, contribute to the larger deviations in the calculations. On the other hand, the agreement is good enough that the barrier height should be accurate to ±10 cm^{-1}.

To better understand the interaction between the puckering and flapping motions, a two-dimensional calculation was also carried out in a manner similar to that used for the phthalan[1,2] and 1,3-benzodioxole[3] analyses. Because the asymmetry of the coumaran molecule makes it virtually impossible to simultaneously and definitively define the puckering and flapping motions, we did not undertake writing a computer program that would calculate the kinetic energy functions in terms of both x_1 and x_2. Instead, we carried out these computations on 1,3-benzodioxole and indan using our program[2] for these symmetric molecules. Coumaran (**III**), with its single oxygen atom, can be thought of as the average of these two molecules. Hence, we approximated the magnitudes of g_{44}, g_{55}, and g_{45} at each x_1 and x_2 by averaging the corresponding 1,3-benzodoxole and indan values. The validity of this method was tested by comparing this type of approximation to the computed one-dimensional kinetic energy function for coumaran in eq 1, and the agreement was found to be entirely satisfactory. The two-dimensional kinetic energy functions thus found for coumaran are

$$g_{44}(x_1,x_2) = 0.009297 - 0.079746x_1^2 + 0.220533x_1^4 - 1.006769x_1^6 - 0.000392x_2^2 + 0.000290x_2^4 - 0.000754x_2^6 + 0.005923x_1^2x_2^2 + 0.014856x_1^3x_2 + 0.041195x_1x_2^3 \quad (4)$$

$$g_{55}(x_1,x_2) = 0.124240 - 0.109598x_1^2 + 0.036131x_1^4 - 0.014996x_1^6 - 0.039725x_2^2 + 0.213203x_2^4 + 1.224073x_2^6 + 0.055513x_1^2x_2^2 + 0.000142x_1^3x_2 + 0.476078x_1x_2^3 \quad (5)$$

$$g_{45}(x_1,x_2) = 0.016877 + 0.103428x_1^2 - 0.143663x_1^4 + 1.324173x_1^6 + 0.009191x_2^2 - 0.001801x_2^4 + 0.001634x_2^6 - 0.039635x_1^2x_2^2 - 0.410915x_1^3x_2 - 0.101312x_1x_2^3 \quad (6)$$

Our previous two-dimensional potential energy calculations on phthalan[2] and 1,3-benzodioxole[3] using their calculated kinetic energy expressions very successfully reproduced the observed frequencies. An attempt to duplicate this for coumaran proved to be disappointing since several computed interactions were found to be much greater than those in the experimental data. Whereas experimentally the 0′ and 1′ (primes refer to the $v_{\mathrm{F}} = 1$ state) are nearly degenerate, in the calculation the $v_{\mathrm{P}} = 5$ level at 255.9 cm^{-1} and 0′ level at 243.1 cm^{-1} (both of B_2 symmetry) push each other apart, resulting in the calculated

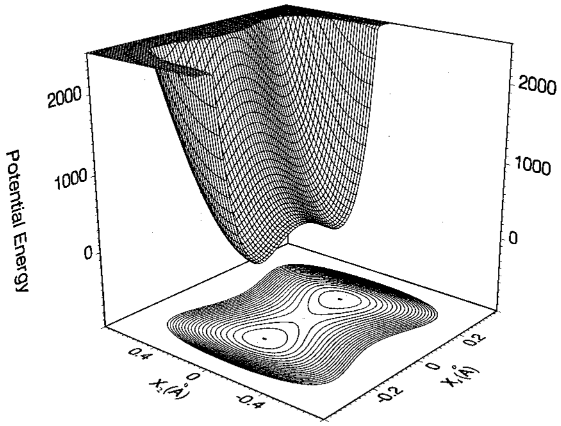

Figure 5. Two-dimensional potential energy surface for coumaran; x_1 = ring-puckering; x_2 = ring-flapping.

value for $v_P = 5$ being too high and the 0′ too low [refer to Figure 3]. Similarly, $v_P = 4$ at 218.9 cm^{-1} and 1′ at 243.8 cm^{-1}, both of A_1 symmetry, interact too much in the computation, pushing $v_P = 4$ down and 1′ up. Thus, in all the computations 0′ and 1′ show a substantial splitting that is not present in the actual molecule. To a smaller extent, $v_P = 6$ and 3′, both of A_1 symmetry, interact and push apart as do 7 and 2′, both of B_2 symmetry. This results in too large a splitting in the computation between 2′ and 3′. These computed interactions cannot be eliminated by adjusting the potential energy interaction constant between the puckering and flapping but can be minimized if the flapping frequency is computationally raised (by increasing the x_2^2 coefficient in the potential energy) to about 300 cm^{-1} or higher, separating the interacting levels in energy to a greater extent. In previous two-dimensional calculations[11] we have on occasion encountered calculated energy levels that were very sensitive to the potential energy parameters, but we were able nonetheless to obtain a satisfactory potential energy function. For coumaran we could not do this because the kinetic energy expressions in eqs 4−6 are poorer approximations than normal, since the asymmetry of the molecule makes the puckering and flapping motions very difficult to represent with much accuracy. In particular, the magnitude of g_{45} in eq 6 plays a significant role in determining the computed interactions described above.

Since we could not achieve a satisfactory result using the g_{45} in eq 6, we carried out the computation with g_{45} set to zero. In doing so, we recognized that the effect of g_{45} would have to be compensated for by the potential energy interaction term. Alternatively, we could have adjusted both g_{45} and the interaction term but felt that that approach simply added another adjustable parameter. With g_{45} set to zero we did obtain a moderately satisfactory two-dimensional surface:

$$V\,(\mathrm{cm}^{-1}) = (3.31 \times 10^5)x_1^{\,4} - (1.91 \times 10^4)x_1^{\,2} + (8.16 \times 10^3)x_2^{\,2} - (3.95 \times 10^4)x_1^{\,2}x_2^{\,2} \quad (7)$$

Again, it should be noted that the coefficient of the $x_1^2x_2^2$ term not only represents potential energy interaction but also incorporates the effect of the cross kinetic energy term. The surface in eq 7 has a barrier of 275 cm^{-1} and energy minima at $x_1 = \pm 0.17$ Å, which correspond to dihedral angles of ± 37°. This surface is shown in Figure 5. Because of the approximations used for this two-dimensional calculation, we feel that the one-dimensional approximation provides better values for the barrier height and dihedral angle. However, the two-dimensional analysis does help to corroborate what is shown in Figure 3; namely, there is substantial interaction between the puckering and flapping and this most likely involves both kinetic and potential energy effects.

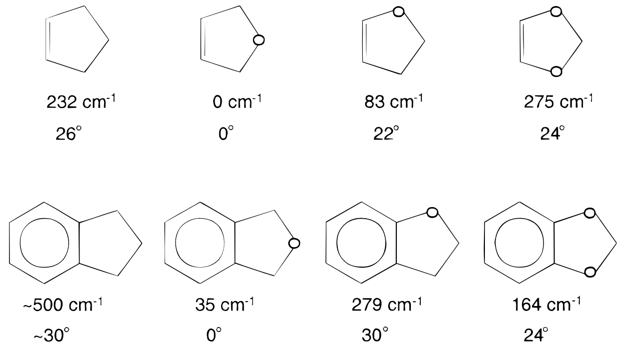

Figure 6. Barriers to planarity and dihedral angles of some five-membered-ring and fused-ring molecules.

V. Conclusions

Figure 6 compares the barriers to planarity and dihedral angles of several five-membered-ring molecules in the cyclopentene and indan families. Cyclopentene[14] has a barrier of 232 cm^{-1} resulting from the two $-CH_2-CH_2-$ torsional interactions. The barrier of 1500 cm^{-1} reported[15] for indan is clearly incorrect but appears to be about 500 cm^{-1} on the basis of preliminary data in our laboratory. 2,5-Dihydrofuran[16] has no barrier because it lacks the torsional interactions, but phthalan[1,2] with the attached benzene ring has a small barrier of 35 cm^{-1} (for no obvious reason). The single $-CH_2-CH_2-$ interaction for 2,3-dihydrofuran[17] results in a barrier of 83 cm^{-1}, while the coumaran studied here has a much higher barrier of 279 cm^{-1}. Since the benzene ring bonds have bond orders of 1.5, the angle strain of the five-membered ring in coumaran is expected to be less than that of 2,3-dihydrofuran. Since the angle strain is the primary force favoring planarity, it is not surprising that the coumaran barrier is higher. Both 1,3-dioxole and 1,3-benzodioxole are nonplanar because of the anomeric effect.[3] The benzene ring appears to supress this for the latter molecule, resulting in a lower barrier.

An ab initio calculation at the MP2/6-31G* level predicts[18] a barrier to planarity of 258 cm^{-1} for coumaran, in excellent agreement with our experimental value of 279 cm^{-1}.

For coumaran and the other molecules in the indan family, the vibrational coupling between the puckering and flapping motions is substantial because the motions are similar and of the same symmetry. Furthermore, the asymmetry of coumaran no doubt results in increased coupling with other motions such as the ring-twisting vibration. This means that the one- and two-dimensional approximations used for the analyses in the present work are not expected to be as good as for the other molecules shown in Figure 5. Indeed, this was found to be the case, especially for our two-dimensional calculations.

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