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S_0 Ring-Puckering Potential Energy Function for Coumaran

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With the aid of a reported inversion splitting value, the far-infrared spectrum resulting from the ring-puckering vibration of coumaran has been reassigned and the one-dimensional potential energy function has been determined. The barrier to planarity is 155 ± 4 cm^{-1} and the dihedral angle is 25°. These results agree well with the millimeter wave spectra values of 152 cm^{-1} and 23°, which utilized different data and a different type of potential function for the calculations. The MP2/cc-pvtz ab initio values of 238 cm^{-1} and 26.5° agree more poorly. If the benzene ring is assumed to remain rigid, the calculated barrier drops to 204 cm^{-1}. The puckering potential functions for the ring-flapping and ring-twisting vibrationally excited states were also determined and the barriers were found to be 149 and 156 cm^{-1}, respectively.

Introduction

In recent years we have used spectroscopic methods to investigate the potential energy surfaces of various molecules in their ground and excited electronic states.[1] These have included the bicyclic molecules in the indan family. In 2000 we reported[2] our analysis of the far-infrared and Raman spectra of coumaran along with a one-dimensional analysis of the ring-puckering potential energy function. We then proceeded to investigate the jet-cooled laser induced fluorescence (LIF) spectra of this molecule as well as its ultraviolet absorption spectra. The single vibrational level fluorescence (SVLF or dispersed fluorescence) spectra recorded at that time clearly showed that there was a vibrational level near 95 cm^{-1}, and this was inconsistent with our assignments that placed the first level ($v = 2$) above the nearly degenerate ground-state levels ($v = 0$ and 1) at 127.8 cm^{-1}. Consequently, when this was discussed with Professors W. Caminati (Bologna) and J. Alonso (Valladolid) at a molecular spectroscopy conference, they agreed that one of them would examine the microwave and/or millimeter wave spectra of the molecule to help resolve the problem. Ottoviani and Caminati[3] have now reported their results and indeed have shown that our original assignment needed revision. They determined that the ground-state splitting between $v = 0$ and 1 was 3.12 cm^{-1}. We had previously assigned this to the splitting between $v = 2$ and 3. In this paper we present our revised assignment of the far-infrared spectrum of coumaran along with the one-dimensional ring-puckering potential energy function that does a very good job of fitting the data.

Experimental Section

The far-infrared and the ultraviolet absorption spectra were recorded on a Bomem DA3.02 instrument using sampling techniques previously described.[1,2] The recording of the dispersed fluorescence spectra have also been previously described[1,4] on the basis of a Continuum Nd:YAG Powerlite Model 9020 laser and a Sunlite EXOPO system with the FX-1 ultraviolet frequency extension.

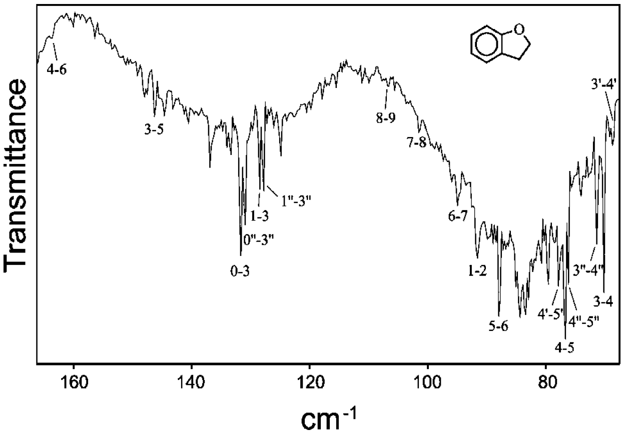

Figure 1. Far-infrared spectrum and assignments for the ring-puckering transitions of coumaran. Primes indicate puckering transitions in the flapping excited state ($v_F = 1$) and double primes indicate those in the twisting excited state ($v_T = 1$).

Results and Discussion

Figure 1 shows the far-infrared spectrum of coumaran which we reported previously.[2] This new figure reflects the revised assignments for the puckering transitions, which are also listed in Table 1. Figure 2 shows the energy level diagram for the ring-puckering levels when none of the other vibrations are excited and in the first excited states of the ring-flapping ($v_F = 1$) and ring-twisting ($v_T = 1$). These energy levels were derived from the far-infrared spectra,[2] Raman spectra,[2] ultraviolet absorption spectra, and dispersed fluorescence spectra. Table 2 lists some of the transition frequencies from which the energy levels were derived. As before, the ring-puckering level data were fitted using the one-dimensional ring-puckering Hamiltonian

$$\mathbf{H} = -\frac{\hbar^2}{2}\frac{d}{dx}g_{44}(x)\frac{d}{dx} + V(x) \tag{1}$$

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TABLE 1: Ring-Puckering Transitions of Coumaran

	observed		calculated		previous
transition	cm^{-1}	relative int.	cm^{-1}	relative int.	assign
0−1	3.1[a]		2.4	0.01	2−3
1−2	91.7	0.4	92.1	0.8	2−4
2−3	36.7		36.9		4−5
3−4	70.1	(1.0)	71.8	(1.0)	5−6
4−5	76.7	0.8	77.0	1.0	6−7
5−6	87.9	0.5	87.1	0.9	3−4
6−7	95.0	0.3	94.8	0.8	3′-4′
7−8	101.4	0.2	101.7	0.6	
8−9	106.7	0.1	107.8	0.5	
0−3	131.7	0.8	131.4	0.7	0−3
1−4	obscured		200.9	0.2	
2−5	183.9	w	185.8	0.2	
3−6	235.3	0.1	235.9	0.2	
0−2	(95.0)[b]	0.3	94.5	0.2	3′-4′
1−3	128.4	0.4	129.0	0.4	
2−4	(106.7)[b]	0.1	108.8	0.2	4−6
3−5	146.3	0.2	148.8	0.4	5−7
4−6	163.7	0.1	164.1	0.4	6−8
5−7	183.2	w	181.9	0.4	

[a] Reference 2. [b] Frequency used twice.

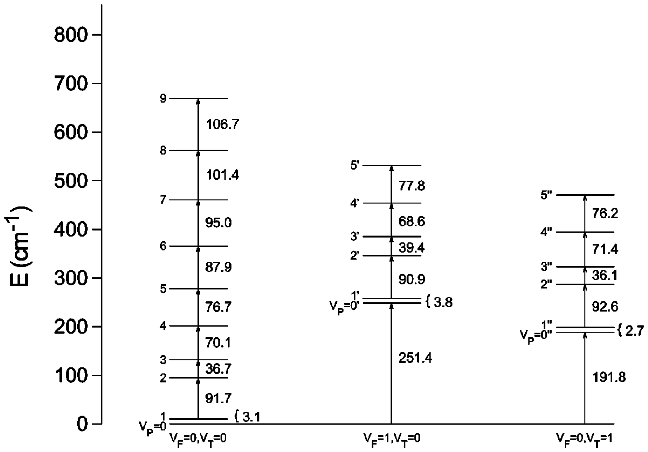

Figure 2. Energy level diagram for the ring-puckering quantum states for the ground state and the flapping ($v_F = 1$) and twisting ($v_T = 1$) vibrational excited states.

where the potential function has the form

$$V(x) = ax^4 + bx^2 \tag{2}$$

and where x is the ring-puckering coordinate as previously defined.[2] The coordinate dependent kinetic energy function (the reciprocal reduced mass), $g_{44}(x)$, was calculated in the previous work. Utilizing the revised assignments, the potential energy function was determined to be

$$V(\mathrm{cm}^{-1}) = (8.91 \times 10^5)x^4 - (2.35 \times 10^4)x^2 \tag{3}$$

where x is in units of Å. This function, along with the observed transitions, is shown in Figure 3. The barrier to planarity is 155 ± 4 cm^{-1} and the minima are at $x = \pm 0.11$ Å, which correspond to puckering angles of ±25°. The ring-puckering frequencies calculated with this potential function are compared to the observed ones in Table 1, and the average difference is 0.7 cm^{-1} or less than 1%. Using the previous assignments, we had calculated a barrier to planarity of 279 cm^{-1}, and this had agreed fortuitously well with our ab initio (MP2/6-31G*) result of 258 cm^{-1}. Ottoviani and Caminati[3] also reported ab initio calculations which produced barriers in the 52−270 cm^{-1} range. They calculated a potential function of the form

TABLE 2: Selected Spectroscopic Transitions Involving ν_{45}, ν_{44}, and ν_{43} of Coumaran[a]

		frequency (cm^{-1})	
transition[b]	method	experimental	inferred[c]
0−0″	IR, Raman	191.8	191.8
0−0′	IR	251.4	251.4
45^0_2	SVLF	−96	−94.5
$43^0_1 45^0_1/45^2_6$	UV	−255.2	−255.2
45^1_5	UV	−242.8	−243.1
45^0_4	UV	−201.8	−201.8
$44^1_1 45^0_2/44^1_1 45^1_3$	UV	−164.8	−164.8
$44^0_1 45^1_0$	UV	−157.0	−156.8
45^1_3	UV	−96.3	−96.5
45^0_2	UV	−94.5	−94.5
$44^0_1 45^2_1$	UV	−83.7	−83.7
$43^1_1/44^1_1$	UV	−70.0	−70.5/−69.5
$43^1_1 45^1_1$	UV	−38.7	−38.7
$44^1_1 45^1_1$	UV	−36.3	−36.1
45^1_1	UV, FES	31.9	31.9
45^2_0	UV, FES	110.8	110.8
$44^1_0 45^0_1$	UV, FES	119.2	119.2
$44^1_0 45^1_0$	UV, FES	158.4	158.4
$43^1_0 45^0_1$	UV, FES	177.8	177.8

[a] ν_{45}: ring-puckering; ν_{44}: ring-twisting; ν_{43}: ring-flapping. [b] Quantum numbers indicate puckering states; double primes indicate transitions in the ν_{44} ($v_T = 1$) excited state; single primes indicate transitions in the ν_{43} ($v_F = 1$) state. Ultraviolet absorption and SVLF cm^{-1} are relative to the 0^0_0 excitation frequency of 34 965.9 cm^{-1}. [c] Calculated from levels in Figure 2.

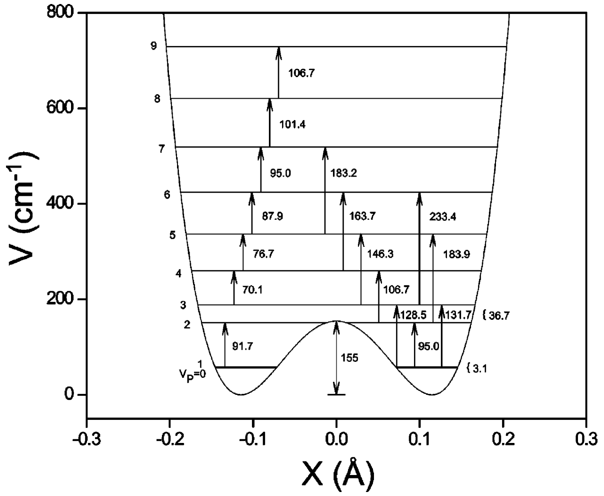

Figure 3. Vibrational potential energy function for the ring-puckering for $v_F = 0$ and $v_T = 0$.

$$V(\tau) = B_2[1 - (\tau/\tau_e)^2]^2 \tag{4}$$

where B_2 is the barrier and τ_e is the equilibrium puckering angle. On the basis of the ground-state splitting and inertial defect, and not utilizing our far-infrared data, they calculated a barrier of 152 cm^{-1} and a puckering angle of 23°, totally consistent with our results reported here. It is interesting to note that these barriers and puckering angles, which agree almost perfectly, derive from totally different data. Although it is true that the value of the ground-state splitting was invaluable for us in revising the far-infrared spectra, its exact value was not that critical for our calculation. In fact, as can be seen in Table 1, our calculated value of 2.37 cm^{-1} for the $v = 0$, 1 splitting

TABLE 3: Observed and Calculated Ring-Puckering Transition Frequencies (cm^{-1}) of Coumaran in Its Flapping and Twisting Excited States

	flapping ($\upsilon_F = 1$)		twisting ($\upsilon_T = 1$)	
transition	observed	calculated[a]	observed	calculated[b]
0−1	3.8	2.6	2.7	2.3
1−2	90.0	90.0	92.6	92.6
2−3	39.4	37.8	36.1	36.1
3−4	68.6	71.1	71.4	71.5
4−5	77.8	76.7	76.2	76.4

[a] From eq 5. [b] From eq 6.

differs from the observed value of 3.12 cm^{-1}. This splitting is extremely sensitive to not only the barrier height but also to the shape of the potential energy function near the energy minima. The far-infrared spectra, unlike the microwave data, are very sensitive near the top of the barrier, and thus are very reliable for determining the magnitude of the barrier, assuming the assignments are correct. To test how important the exact value of the ground-state splitting is for determining the barrier height in our case here, we forced the 0−1 splitting of 3.12 cm^{-1} and the 0−3 far-infrared transition at 131.7 cm^{-1} to be fit exactly. This resulted in a calculated barrier of 143 cm^{-1}. Because the use of this approach relies on data near the bottom of the potential energy well rather than near the top of the barrier, we feel confident that the 155 cm^{-1} value is the more accurate one.

We have also used a higher level basis set (MP2/cc-pvtz) to calculate the barrier to planarity. This results in a barrier of 238 cm^{-1} and a dihedral angle of 26.5°. If the benzene ring is forced to stay planar during the puckering, a barrier of 204 cm^{-1} is predicted, which is closer to the real value.

The ring-puckering levels shown in Figure 2 for the excited vibrational states of the ring-flapping ($\upsilon_F = 1$) and ring-twisting ($\upsilon_T = 1$) can also be used to determine the one-dimensional ring-puckering functions for these states. The functions determined are for the ring-flapping

$$V_F(\mathrm{cm}^{-1}) = (8.63 \times 10^5)x^4 - (2.27 \times 10^4)x^2 \qquad (5)$$

and for the ring-twisting

$$V_F(\mathrm{cm}^{-1}) = (8.80 \times 10^5)x^4 - (2.34 \times 10^4)x^2 \qquad (6)$$

The observed and calculated energy spacings for these excited states are shown in Table 3. In the flapping excited state ($\upsilon_F = 1$) the barrier to planarity is 149 cm^{-1} and in the twisting excited state ($\upsilon_T = 1$) it is 156 cm^{-1}. The change in the observed 0−1 splitting reflects the fact that a higher barrier produces a smaller splitting and vice versa.

We are continuing to investigate the ultraviolet absorption, laser induced fluorescence (LIF), and single vibronic level fluorescence (SVLF) spectra of coumaran and will report on the potential energy function for the $S_1(\pi,\pi^*)$ state. It is worth noting at this time, however, that the ultraviolet absorption spectra shows bands at −96.3 and −94.5 cm^{-1} (see Table 2) relative to the electronic origin at 34966 cm^{-1}, and these correspond to the 45^1_3 and 45^0_2 transitions (ν_{45} is the ring-puckering vibration). The SVLF spectrum shows the 45^0_2 band at 96 ± 2 cm^{-1}. Thus it would appear that between the millimeter-wave and far-infrared spectrum, the coumaran puzzle is now clearly resolved.

A valid question is why our previous assignment[2] could be fit so well with a potential energy calculation. This can be understood to some extent by examining Table 1 where the earlier assignment is also shown. From our spectra we identified the 3.1 cm^{-1} spacing but we assigned this as the 2−3 splitting rather than the 0−1. From its intensity the 131.7 cm^{-1} band was correctly assigned as the 0−3. Because the ab initio calculations predicted a barrier near 260 cm^{-1}, the 3.1 cm^{-1} assignment to the 0−1 splitting seemed less plausible because it yielded a considerably smaller barrier. It should also be noted that the sequence of transitions near the top of the barrier of 36.7, 70.1, and 76.7 cm^{-1} is the same for both the new and previous assignments, reflecting the effect of the barrier as well as the quartic nature of the potential function above it.

Conclusions

It is reassuring that analysis of the millimeter wave spectra[3] and the far-infrared spectra lead to essentially the same results for the barrier to planarity and puckering angle despite using different data. It is somewhat disappointing that the ab initio calculations are not as accurate as we had thought, but the barrier is calculated as the difference between two very large numbers. In our previous work, for example on 1,3-cyclohexadiene,[4,5] we have found that calculated barriers tend to be somewhat higher than the experimentally determined ones. One way to explain this is that molecules are smart in finding a somewhat less energetic path to inversion than going through the assumed planar structure.

The data in Figure 2 provide additional data for studying the interactions between the three lowest frequency out-of-plane modes, and we are pursuing that analysis using two-dimensional potential energy surfaces. The frequency changes in the $\upsilon_F = 1$ and $\upsilon_T = 1$ states reflect the degree of interaction between the ring-puckering and the ring-flapping or ring-twisting modes. These frequency changes are modest but do indicate that the accuracy of the one-dimensional potential function used here is limited somewhat by the interactions.

We are also in the process of further analyzing the laser induced fluorescence (LIF) spectra and ultraviolet absorption spectra of coumaran to determine the potential energy surface for the $S_1(\pi,\pi^*)$ state. Watkins and co-workers[6] have studied the REMPI and ZEKE spectra of this molecule and proposed assignments for the $S_1(\pi,\pi^*)$ excited states. Even at this stage it is evident that their assignments need revision, and we will be publishing our data for this state soon. It can be noted that the 31.9 and 110.8 cm^{-1} bands in the ultraviolet and the LIF spectra correspond to 45^1_1 and 45^2_0. Watkins et al. assigned the latter correctly but thought their 32 cm^{-1} band was either 45^1_1 or $44^1_0 45^2_0$.

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