deposition commenced. Then the KBr window was rotated into place and metal and Ar codeposition were begun. After deposition for a desired period of time the window was rotated 90°, protective shutter in place, and Ar flow stopped. A spectrum was recorded. This cycle was carried out as many times as necessary to determine the growth rate of M, M_2, M_3, and M_x species.

When changing the matrix gas from Ar to Ar/CH_3X or vice versa, the following adjustments were made. First the valve on the Ar gas bulb was closed. Then both gas valves were closed and any gaseous Ar in the apparatus was pumped away. Both gate valves were again opened and background pressure was allowed to stabilize. The valve on the Ar/CH_3X gas bulb was then opened and the flow rate into the matrix chamber controlled by the needle valve. The deposition procedure was then identical with that stated above. (Note that the furnace remained at constant vaporization temperature throughout all manipulations; metal vapor was collected on the shutter while spectra were being recorded or other manipulations made.)

When the deposition cycles were complete, an annealing experiment was carried out by first closing the needle valve and any opened gas bulb valves. The window was then rotated into the spectroscopic observation path and the annealing temperature was adjusted using the Digital temperaure controller. When the annealing time was complete, the KBr window was cooled back down to 9 K and a spectrum recorded.

When the experiment was completed, the shut-down procedure began by turning off the diffusion pump and isolating it from the rest of the system by closing the appropriate gate valve. Then the furnace as well as cryocooler were were shut off. The circulating water for the diffusion pump, electrodes, and cryocooler was left on until the system was adequately equilibrated. It took approximately 6 h for the KBr window to warm to room temperature. At this time the window could be changed and another experiment carried out.

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Registry No. Ca, 7440-70-2; Ca_2, 12595-85-6; Mg, 7439-95-4; Mg_2, 29904-79-8; Mg_3, 72673-77-9; Mg_4, 73767-50-7; CH_3Cl, 74-87-3; CH_3Br, 74-83-9; CH_3F, 593-53-3; CH_3I, 74-88-4; CH_4, 74-82-8.

Is Butatrienone ($H_2C{=}C{=}C{=}C{=}O$) Kinked?

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Abstract: We have studied by microwave spectroscopy the vibrational satellite series of H_2C_4O and D_2C_4O that is associated with the lowest out-of-plane bending mode ν_{15}. From a semirigid bender analysis, including data of up to $\nu_{15} = 5$, it is concluded that a shallow single-minimum potential is responsible for the observed pattern. Parallel to this study we carried out 6-31G** MO calculations, which yielded a barrier to planarity of only 5.6 cm^{-1}, in contrast to a value of 433 cm^{-1} obtained in a previous study by Farnell and Radom. We conclude that butatrienone is *not* kinked in its equilibrium configuration.

The cumulenones, H_2C_nO, are compounds of particular interest in structural chemistry because at least two members of the series display structural features that are in conflict with the predictions of ab initio molecular orbital calculations. For one of these there is also conflict with classical structural theory which implies that all members of the series have a symmetrical planar C_{2v} structure, and this is known to be the case for formaldehyde and ketene. When the microwave spectrum of propadienone was first studied[1] there were indications that it might not have C_{2v} symmetry, and this has subsequentally been demonstrated conclusively in a series of spectral studies.[2-5] Parallel theoretical studies of its structure based on ab initio molecular orbital calculations taken to the Hartree-Fock level with substantial basis sets (such as 6-31G**) erroneously predicted a symmetrical geometry.[6] It was only when electron correlation was included that the kinked in-plane geometry (Figure 1) was correctly predicted.[7,8]

When butatrienone was first characterized,[9] the spectra of the main species and of two isotopic variants were consistent with that of a symmetrical C_{2v} structure. Some recent molecular orbital calculations[10] that included electron correlation however have predicted that butatrienone is strongly kinked, as shown in Figure 2. The predicted barrier to the symmetrical shape (433 cm^{-1} at the MP3/6-31G level calculation) was higher than that for propadienone (167 cm^{-1} at the MP3/6-31G level). We believe, however, that the way in which these MO calculations were carried out does not lead to reliable results and have consequently performed additional calculations reported below.

The previous experimental demonstration that butatrienone is not kinked but is planar, in clear disagreement with MO theory published until now, was mainly dependent on the value of the inertial defect and thus subject to the appreciable uncertainty in I_a which cannot be determined with high precision by microwave spectroscopy alone for this molecule. It therefore seemed desirable to establish the geometry of butatrienone more precisely by studying the out-of-plane vibrations directly via the vibrational satellites in the microwave spectrum. Thus further study, and finally the use of the semirigid bender model analogous to that recently reported for propadienone,[4,5] is reported here.

Experimental Section

The microwave spectrometer involved a microprocessor-controlled synthesized microwave source designed and constructed at Monash University. The synthesizer was referenced to our laboratory frequency standard and the Australian frequency standard at C.S.I.R.O. Division of Applied Physics. The microwave oscillator was a Hewlett Packard 8690 series plug-in BWO. The cell was a 3-m length of G-band waveguide, Stark modulation being at 6.525 kHz. The spectral data were collected and reduced in a Sperry-Univac V75 computer system.

Double resonance (microwave–radio frequency) studies were performed by locking the microwave source to the center frequency of an absorption line and feeding a radio frequency signal into the Stark septum of the cell. The radio frequency signal was swept through the double-

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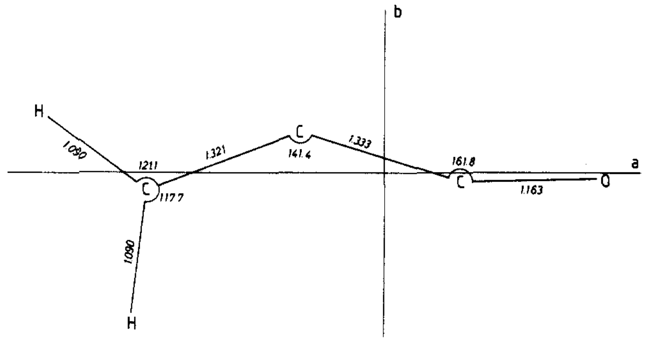

Figure 1. In-plane kinked geometry of propadienone derived by microwave spectroscopy.[4]

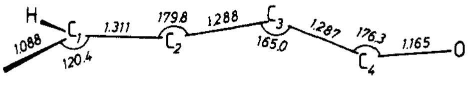

Figure 2. Theoretically predicted geometry[7] of butatrienone.

resonance value (normally in the range 1–300 MHz) to observe the double-resonance signals.

Because of the transient nature of butatrienone, the pyrolysate was continuously pumped through the cell. Pressures at the inlet were usually ca. 0.25 Pa. The butatrienone was generated, as previously reported,[9] by pyrolysis of butadienoic trifluoroacetic anhydride, the furnace being a silica tube 400 × 25 mm i.d. heated to 540–600 °C. The pyrolysis conditions effectively left no precursor unchanged, the major products flowing through the spectrometer cell being butatrienone and trifluoroacetic acid. Lines of the acid were separately observed and subtracted from the spectrum of the pyrolysate.

Results of Spectroscopic Study

The previously reported[9] ground-state lines of butatrienone were readily observed and the assignments and intensity alternations between different K states were confirmed. Accompanying them, a very rich vibrational satellite spectrum was apparent, all satellites being on the high-frequency side of the main line. This behavior is the opposite to that observed in propadienone, where the majority of the vibrational satellites appear to the low-frequency side of the main line. Thus the overall satellite pattern on a simple basis is itself indicative of a linear equilibrium structure becoming bent in excited vibrational states, the opposite case to that of propadienone. Figure 3 shows a "stick" diagram showing only the assigned lines of the spectrum of H_2C_4O in the region 25.8–26.6 GHz. Only transitions with $K_{-1} = 0$ or 1 are included to simplify the figure but many lines of higher K_{-1} values also were present in this frequency range. Only μ_a-type R-branch transitions have been detected. The K_{-1}-assignment was achieved by carefully studying the Stark effect. The $K_{-1} = 0$, 1, and 2 transitions could be discriminated unequivocally. Distinction between $K_{-1} = 3$, 4, and 5 proved to be difficult for weaker lines because all these lines are already fully modulated at 5 V cm^{-1}. In these cases a low voltage Stark generator was used to assure stable electric fields in the Stark cell. The use of radio frequency microwave double resonance turned out to be vital in order to decide which $K_{-1} = 1$ lines belong together because $B - C$ varied from 15 to 1 MHz for different vibrational states. The next step was to find out which lines with different K_{-1} values belong to the same vibrational state. The dideuterated butatrienone was more favorable in this respect because the rotational constant A is smaller than for H_2C_4O and therefore higher order centrifugal distortion constants could be neglected for lines with $K_{-1} \leq 3$. The quality of the least-squares fit and the relative intensities were the criteria used to resolve the issue. For higher excited states of H_2C_4O we sometimes failed because either the lines were too weak or they were shifted due to perturbations.

The vibrational assignments of these groups of lines proved to be very demanding. Transitions belonging to at least 17 different vibrational states were found, and no regular patterns were recognizable. Infrared frequencies obtained from ab initio molecular orbital calculations[10] indicate that there exist only two low-frequency vibrations (<200 cm^{-1}) and that all other vibrations are above 450 cm^{-1}. The lowest vibration is predicted to be an out-of-plane bending motion while the second low-frequency mode should be an in-plane bending motion. If this was correct one would expect that most of the 17 states found correspond to different levels of excitation of these two vibrations. A very similar situation was found for cyclopropylidenemethanone[11] for which 10 different vibrational states were eventually assigned to different excitations of the two lowest modes. The method which was used in that study to assign the vibrational satellites was also applied to butatrienone. It is based on an expansion of the rotational constants in a series of expectation values of even powers of the vibrational coordinate τ, e.g.

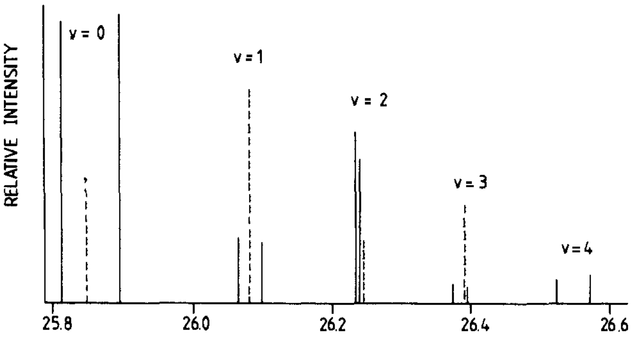

Figure 3. The assigned vibrational satellite spectrum of the $J = 6$–5 region of butatrienone. K_{-1} transitions are shown as solid lines and $K_{-1} = 0$ transitions are dashed lines.

$$B_v = B_e + \alpha_B\langle\tau^2\rangle_v + \beta_B\langle\tau^4\rangle_v$$

If the series converges rapidly the ratios

$$\frac{B_i - B_j}{C_i - C_j} \qquad i, j = 1, 2, ..., 17$$

should be approximately constant for all rotational constants belonging to a series of vibrational excitations and equal to α_B/α_C. When this method was applied to H_2C_4O it revealed a set of five vibrational states with very similar ratios. The vibrational ground state was part of this series. Comparison of the relative intensities and taking into account the spin statistics allowed the establishment of the order within the series. These states could represent either different levels of excitation of the out-of-plane mode with the in-plane mode not being excited or vice versa. This question could be decided by studying the rotational constants of the members of the series. Geometrical calculations were carried out to estimate the variation of B and C as a function of different in-plane and out-of-plane bending angles. The most distinctive trend was that $B - C$ slightly increased as the molecule was bent in-plane, whereas bending out-of-plane led to a rather sharp initial decrease in $B - C$. At a certain bending angle the molecule represents a symmetric top ($B = C$). Further increase of the bending angle led to an increase in $B - C$ again, but with the b and c axes interchanged. This second type of behavior was indeed observed in the series. For H_2C_4O, the experimental $B - C$ values for consecutive members of the series ($\nu_{15} = 0$, 1, 2, 3, 4) were 13.9, 5.6, 1.0, 3.5, and 8.4 MHz. The corresponding analysis was carried out for D_2C_4O and revealed a series of 6 vibrational satellites belonging to $\nu_{15} = 0, 1, ..., 5$. As Table I shows, the variation of rotational constants with ν_{15} in D_2C_4O is very similar to the trend in H_2C_4O. The spectroscopic constants of the vibrational states in H_2C_4O and D_2C_4O belonging to the series are given in Table I. The centrifugal distortion constants are defined according to Watson's symmetric reduction in the I^r representation.[12] For D_2C_4O the sextic centrifugal distortion constant H_{KJ}

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Table I. Experimentally Determined Rotational Constants (MHz) and Centrifugal Distortion Constants (MHz) of H_2C_4O and D_2C_4O for Different Excitations of the Lowest Out-of-Plane Bending Vibration (ν_{15})

	ν_{15}	B	C	D_{JK}	H_{KJ}
$H_2C_4O^a$	0	2160.77 (2)	2146.88 (2)	−0.291 (6)	0.0480 (6)
	1	2176.27 (5)	2170.71 (5)	+0.119 (9)	
	2	2187.54 (3)	2186.52 (3)	+0.429 (5)	
	3	2201.18^b	2197.64^b		
	4	2216.48^b	2208.13^b		
$D_2C_4O^c$	0	1996.13 (1)	1970.76 (1)	−0.124 (2)	0.0065 (1)
	1	2010.92 (8)	1992.01 (8)	−0.063 (2)	0.0044 (1)
	2	2020.33 (5)	2005.43 (5)	+0.100 (1)	0.0016 (1)
	3	2029.37 (3)	2018.56 (3)	+0.379 (7)	
	4	2038.17 (2)	2030.67 (2)	+0.319 (4)	
	5	2046.34 (2)	2042.16 (2)	+0.265 (4)	0.0033 (2)

[a] An A rotational constant of 220 000 MHz was assumed. [b] Only the $K_{-1} = 1$ doublets could be assigned. [c] An A rotational constant of 135 000 MHz was assumed.

was only included in the fit if transitions with K_{-1} larger than three were fitted. Otherwise only D_{JK} was adjusted. For H_2C_4O, H_{KJ} had to be added to obtain a good fit as soon as $K_{-1} = 3$ was included.

Ab Initio Molecular Orbital Calculations

Only one theoretical study can be found in the literature which investigated the structure of butatrienone in some detail.[10] The authors fully optimized the geometry at the Hartree–Fock level (HF) using the 4-31G basis set. The resulting structure showed C_{2v} symmetry. In addition, optimizations were also performed in which some CCC angles were kept fixed at different values. The same basis set was used. The potential of out-of-plane bending of the molecule was calculated to be much more shallow than for in-plane bending. At some of the optimized structures, single-point calculations were performed at the MP2/6-31G level. This method includes the effect of electron correlation in a perturbation approach.[13] The energy minimum was now calculated to correspond to an orthogonal bent structure with the C_{2v} structure being 504 cm^{-1} higher in energy.

We believe that two points are questionable in this study. First, it is nowadays widely recognized that the basis set should include polarization functions if bond angles are wanted to agree quantitatively and sometimes even qualitatively with experiment.[14] Bond angles are of primary importance in the present problem. Second, single-point calculations (that is no complete geometry optimization) have to be interpreted with caution if they are carried out at different theoretical level than that used to optimize the geometry. Experimental results and calculations at substantially higher levels of computation have already shown for propadienone that this method of estimating equilibrium configuration is unreliable.

Thus we considered it worthwhile to carry out full optimizations with a basis set which includes polarization functions on all atoms. They also supplied information to estimate a sensible coordinate for the large amplitude motion. The 6-31G** basis set was used as it is implemented in the GAUSSIAN 82 system of programs.[15] First only one plane of symmetry was retained and allowed the search for an orthogonal bent minimum. Indeed a nonplanar equilibrium structure was obtained. In order to calculate the barrier to planarity a full geometry optimization was performed assuming C_{2v} symmetry. The barrier was found to be only 5.6 cm^{-1}. The structures and energies of these optimized structures are given in Table II. It is interesting to note that Farnell and Radom[10] did calculations using a very similar basis set (6-31G*) and found the C_2v structure to be of minimal energy. This discrepancy is most probably due to the fact that the geometry employed for their calculation was not optimized with the same basis set.

Table II. Fully Optimized Structures[a] and Energies of Butatrienone with the Symmetry Constrained to C_s and C_{2v} with the 6-31G** Basis Set

parameter[b]	C_s (minimum)	C_{2v} (saddle point)
bond lengths		
C_1C_2	1.2979	1.2981
C_2C_3	1.2701	1.2689
C_3C_4	1.2746	1.2715
C_4O	1.1472	1.1478
C_1H	1.0744	1.0744
bond angles		
HC_1C_2	120.4	120.4
$C_1C_2C_3$	180.79	180
$C_2C_3C_4$	168.48	180
C_3C_4O	183.02	180
$HC_1C_2C_3$	89.88	90
E^c	−227.385609	−227.385583
ΔE^d	0.0	5.6

[a] The atomic numbering scheme is the following: $H_1H_2C_1{=}C_2{=}C_3{=}C_4{=}O$. [b] Bond lengths in Å, bond angles in deg. [c] in hartrees. [d] Energy difference in cm^{-1} (83.6 cm^{-1} = 1 kJ/mol).

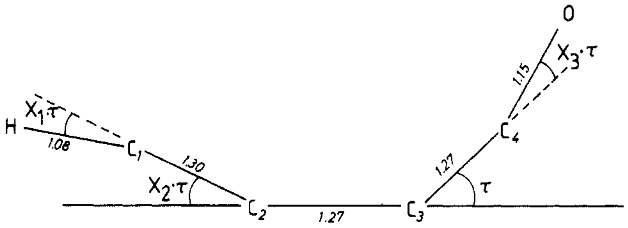

Figure 4. The structure of butatrienone during the out-of-plane bending motion. The HCH angle is fixed at 120°.

Semirigid Bender Analysis of the Out-of-Plane Vibrational Satellites

The position of vibrational satellite spectra relative to the ground-state lines in microwave spectrum contains direct information about the potential function and the nature of the associated vibrational motion. Already the most simple graph of variation of rotational constants vs. vibrational quantum number can reveal whether the potential has a single or multiple minimum yielding the answer to the question raised in the title of this paper. On a much more advanced theoretical level one can apply the semirigid bender model which was originally developed by Bunker and co-workers[16] and later extended by Szalay[17] and us.[18] It provides an elegant treatment of the effects of large amplitude motions on spectra as is the case for the out-of-plane bending in butatrienone. Starting with a geometrical description of the molecule during the vibration and specifying the potential function, ground and excited vibrational satellite spectra are calculated as well as various other properties. In the semirigid bender model the vibrational motion of interest is separated from the other vibrational modes and is treated on the same footing as rotation. By using a coordinate system that follows the large amplitude motion, interaction terms between vibration and rotation are minimized and the contributions from the vibration to the rotational constants and frequencies are accurately accounted for. We have in the past applied the semirigid bender model to the analysis of experimental data of microwave and infrared spectra of cyanamide,[19] cyclopropylidenemethanone,[18] and propadienone[4,5] and were able to obtain simultaneous agreement for all available data.

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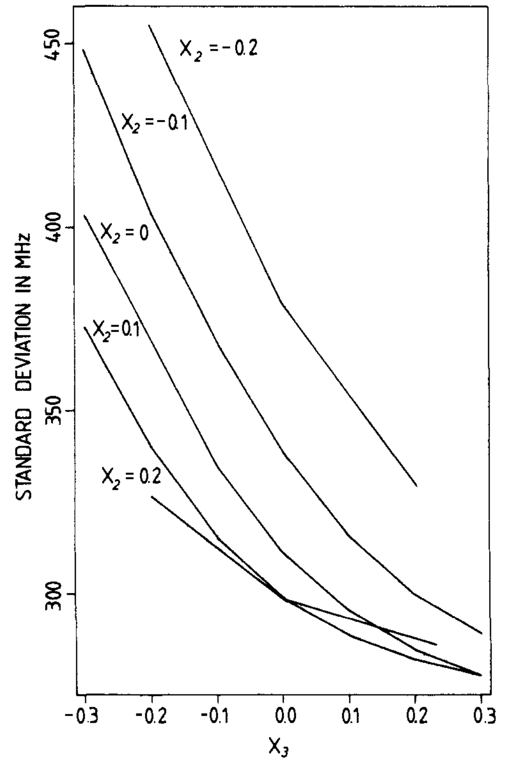

Figure 5. Standard deviations of semirigid bender fits vs. X_2 and X_3 for $X_1 = 0$.

The value of 5.6 cm^{-1} predicted from our MO calculations is much smaller than an estimate of at least 200 cm^{-1} for the uncertainity of barrier heights at this level of calculation. Hence on the basis of the theoretical study we are not able to determine the number of potential minima, but we expect to find a very shallow potential, probably with very large quartic character like in cyclopropylidenemethanone. On the other hand the MO calculations could provide a description of the pathway of butatrienone during the large amplitude motion. As shown in Table II, the motion is predicted to be mainly an out-of-plane bend at C_3 with smaller bends at the other carbons leading to a zigzag shape.

In the semirigid bender calculations we kept all bond lengths and the HCH angle fixed and varied the other angles (as defined in Figure 4) by the specifications

$$\angle HC_1C_2 = 180 + X_1\tau$$

$$\angle C_1C_2C_3 = 180 + X_2\tau$$

$$\angle C_2C_3C_4 = 180 + \tau$$

$$\angle C_3C_4O = 180 + X_3\tau$$

According to our definitions the combination $X_1 < 0, X_2 > 0$, and $X_3 > 0$ refers to a boat-shaped motion. A potential $V = a\tau^2 + b\tau^4$ was assumed with a in cm^{-1} rad^{-2} and b in cm^{-1} rad^{-4}. From the observed frequencies of H_2C_4O and D_2C_4O we calculated pseudoobservations of the 2_{12}–1_{11}, 2_{02}–1_{01}, and 2_{11}–1_{10} transitions and used the shifts of these lines from the corresponding ground-state lines as input for the least-squares procedure. All transitions were given the same weight because the inherent errors in our model, i.e., lack of knowledge of the exact structure of butatrienone and neglect of the remaining vibrations, are larger than experimental uncertainties of individual lines.

Keeping in mind the very small predicted barrier to planarity we had to consider the possibility that a slightly wrong description of the nature of the out-of-plane bending motion could lead to a qualitatively erroneous potential function. Since butatrienone is a fairly large molecule in terms of MO calculations, it was not clear whether the geometrical changes predicted on going from the planar C_{2v} to the equilibrium C_s structure were reliable enough to prevent such a misinterpretation of the satellite spectra. We therefore decided to carry out semirigid bender calculations assuming a wide range of parameters X_1, X_2, and X_3. This would then also help us to assess on the basis of the standard deviations of the fits whether the experimental data allowed the determination of any of those parameters.

Table III. Semirigid Bender Results for Butatrienone with $X_1 = 0$, $X_2 = 0$, and $X_3 = 0.3$.

ν_{15}'	ν_{15}	$J(K_p,K_o)$–$J(K_p,K_o)$	obsd	calcd	obsd - calcd
		Vibrational Satellite Shifts of H_2C_4O			
1	0	2(1,2)–1(1,1)	85.215	83.945	1.270
1	0	2(1,1)–1(1,0)	68.564	71.819	–3.255
1	0	2(0,2)–1(0,1)	78.643	77.342	1.301
2	0	2(1,2)–1(1,1)	142.656	140.514	2.142
2	0	2(1,1)–1(1,0)	116.938	119.997	–3.059
2	0	2(0,2)–1(0,1)	132.818	131.340	1.478
3	0	2(1,2)–1(1,1)	188.109	189.337	–1.228
3	0	2(1,1)–1(1,0)	167.416	170.916	–3.500
3	0	2(0,2)–1(0,1)	182.504	181.264	1.240
4	0	2(1,2)–1(1,1)	238.031	230.979	7.052
4	0	2(1,1)–1(1,0)	226.968	220.052	6.916
		Vibrational Satellite Shifts of D_2C_4O			
1	0	2(1,2)–1(1,1)	78.293	74.904	3.389
1	0	2(1,1)–1(1,0)	65.370	64.743	0.627
1	0	2(0,2)–1(0,1)	72.160	69.499	2.661
2	0	2(1,2)–1(1,1)	127.270	127.553	–0.283
2	0	2(1,1)–1(1,0)	106.337	110.068	–3.731
2	0	2(0,2)–1(0,1)	117.823	118.882	–1.059
3	0	2(1,2)–1(1,1)	174.493	175.490	–0.997
3	0	2(1,1)–1(1,0)	145.377	151.237	–5.860
3	0	2(0,2)–1(0,1)	162.504	163.514	–1.010
4	0	2(0,2)–1(0,1)	203.840	204.507	–0.667
4	0	2(1,2)–1(1,1)	220.083	219.563	0.520
4	0	2(1,1)–1(1,0)	184.323	188.996	–4.673
5	0	2(1,2)–1(1,1)	262.787	260.989	1.798
5	0	2(1,1)–1(1,0)	220.453	224.412	–3.959
5	0	2(0,2)–1(0,1)	243.303	242.977	0.326

In Figure 5 we present the results of fitting a and b to satellite shifts of up to $\nu_{15} = 4$ in H_2C_4O and $\nu_{15} = 5$ in D_2C_4O while keeping $X_1 = 0$. The standard deviations show no pronounced minimum, but there is clear indication that a boat-shape motion gives the best fit whereas the prediction from the MO calculations indicates a zigzag motion. Table III shows the results of the fitting for $X_1 = 0$, $X_2 = 0$, and $X_3 = 0.3$. We have performed similar calculations fixing X_1 at 0.1 and –0.1. In each case the standard deviations varied only by ca. 1% as compared to $X_1 = 0$. Hence we have to conclude that our experimental data do not allow us to determine the direction of the movement of the hydrogens relative to the rest of the molecule although we have isotopically substituted these atoms. This is understandable because the hydrogens make only a small contribution to the reduced mass of the bending motion, which mainly occurs at C_3. As a consequence, vibrational satellite shifts in H_2C_4O and D_2C_4O are very similar (Table I).

As a general result of 31 fits it emerged that in all cases a and b were positive with $93 < a < 185$ and $1450 < b < 3400$ in the units quoted above. Typically the standard deviations of a were 50, but since each of the values of a is larger than twice its standard deviation we conclude that a is positive. We conclude that butatrienone in the vibrational ground state of all other vibrations has a single-minimum out-of-plane bending potential; it is *not* kinked. The large value of b indicates that it is a largely quartic potential. However, until we can obtain data which are more reliable than microwave intensity measurements, i.e., far-infrared bands or direct bending transitions in the microwave region, we are not able to determine the parameter b or the finer details of the out-of-plane bending motion. When comparing the semirigid bender results with ab initio predictions one has to keep in mind that the former apply to the vibrational ground state of the remaining vibrations, while the latter represent the equilibrium geometry. It would thus be necessary to obtain bending potentials at least in all first excited states of the remaining vibrations and then to extrapolate back to the hypothetically vibrationless state.

In the case of HCNO such a study was carried out thoroughly,[20] and a slight dependence of the barrier height on vibrational state was observed. The equilibrium structure of HCNO is linear, but even in the ground state the zero-point vibrational contributions from the stretching vibrations ν_1 and ν_2 to the effective HCN bending potential give a barrier of 11.5 cm^{-1} to linearity. Because of the large number of vibrations and difficulties arising from additional pyrolysis products such a project is not feasible for butatrienone. However, we have shown that in cyclopropylidenemethanone which also has a low-lying in-plane and out-of-plane bending motion the barrier height does not change significantly on excitation of the in-plane mode.[18]

Unfortunately we have not been able to carry out a similar analysis including the in-plane mode for butatrienone although a sufficient number of vibrational statellites are still available. However, in analogy to cyclopropylidenemethanone we do not expect a large dependence of the potential on excitation of other modes and hence no reduction of symmetry when going to the vibrationless state. We therefore conclude that butatrienone is *not* kinked.

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Registry No. H_2C_4O, 63766-91-6; D_2C_4O, 71546-36-6.

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Hydration Dynamics of Protons from Photon Initiated Acids

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Abstract: Proton transfer from the excited states of 1-naphthol and 2-naphthol to the water solvent is studied in water/alcohol mixtures. In pure water, the deprotonation rate of 1-naphthol is insensitive to temperature ($\Delta H^{\ddagger} \approx 0$), while that of 2-naphthol exhibits an activation energy of about 2600 cal mol^{-1}. The deprotonation rates in both molecules decrease nonlinearly as the alcohol concentration increases, becoming effectively zero in pure alcohol. Variation of solvent concentrations in the mixed solvent thus serves as a probe for studying the local reaction environment. Using a Markov random walk theory, a water cluster, $(H_2O)_{4\pm1}$, is identified as the effective acceptor for both molecules, indicating that the structure $H_9O_4^+$ plays a direct role in the proton hydration dynamics. At high water concentrations the proton hydration rate is "reaction controlled", while at high alcohol concentrations it can become "diffusion controlled". Proton transfer dynamics in the naphthol systems are similar to the dynamics measured for electron photoionization into water, with the rates having low or zero activation barrier but being entropically inhibited to various degrees. The ~1:3 deuterium effect on the rates is in fact derived almost entirely from entropic considerations. A correspondence between the thermodynamic quantities ΔH°_i and ΔS°_i and the rate parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for acid dissociation processes is suggested.

1. Introduction

Reactions of acids and bases constitute some of the most fundamental processes in chemistry.[1,2] Though the concept of spontaneous ionic dissociation in aqueous solutions is about 100 years old,[3] the exact nature of the process and the role played by the surrounding solvent remain subjects of considerable speculation. Central questions concern the state of H^+ and OH^- ions in water and the rates of hydration of these ions. Applications of picosecond spectroscopy to the study of fast chemical reactions[4] has made it possible to observe such ion hydration processes directly. For example, measurement of the rates of electron[5-7] and proton[8-12] charge transfer to the water solvent has already revealed the importance of solvent structure on very short timescales.

Early seminal studies[13,14] have shown that moderately strong acids ($pK_a^* < 3$) can be prepared "instantaneously" by light-pulse excitation of certain molecules to their excited electronic states. Thus the sudden introduction of an acid into an otherwise unchanged solution[11] is possible. The molecules 2-naphthol and 1-naphthol in their excited states are good examples of such "photon initiated acids", and they constitute relatively simple systems on which to base modern investigations of proton transfer and hydration dynamics on ultrafast timescales.

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(12) Lee, J.; Griffin, R. D.; Robinson, G. W. *J. Chem. Phys.* **1985**, *82*, 4920–4925. Because of error compensation, evaluation of good prefactors and activation energies requires very accurate rate determinations. The 2-naphthol data in this reference were obtained without a cavity dumper. Values originally reported for the rate parameters (H_2O) were $k_{dis}^{\circ} = 3.99 \times 10^{10}$ s^{-1} and $\Delta H_{dis}^{\ddagger} = 3.45$ kcal mol^{-1} with χ^2 for the data fit about 3.5. The new determinations, using data obtained with a cavity dumper, are $k_{dis}^{\circ} = 8.5 \times 10^9$ s^{-1} (H_2O), 2.2×10^9 s^{-1} (D_2O); and $\Delta H_{dis}^{\ddagger} = 2.6$ kcal mol^{-1} (H_2O), 2.4 kcal mol^{-1} (D_2O), with $\chi^2 \simeq 1.5$.

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