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E. Arunan and H. S. Gutowsky

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The rotational spectrum, structure and dynamics of a benzene dimer

E. Arunan and H. S. Gutowsky

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801

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The low J (2 to 7) rotational spectrum of a symmetric-top benzene dimer has been obtained with a Balle/Flygare Fourier transform microwave spectrometer. Each transition is a symmetrical quartet with two J - and K -dependent tunneling splittings of 30 to 400 kHz. Rotational constants \bar{B} , D_J , and D_{JK} were determined to be 427.76(2) MHz, 7.2(3) kHz, and 0.869(5) MHz. The dimer is T -shaped with a benzene c.m. to c.m. distance of 4.96 Å.

The benzene-benzene interaction is typical of aromatic systems. As such it has been an attractive target for both theoretical and experimental study. Theoretical analysis of the dimer^{1,2} has converged on a T -shaped structure, in which the planes of the two benzenes are perpendicular, with C_{2v} symmetry or nearly so. Early molecular beam observations^{3,4} showed the dimer to be polar, and "coarsely identified" the structure as a T -shaped asymmetric top, the configuration found for nearest neighbor pairs in x -ray studies⁵ of the solid. Qualitative support for this view and also for the dimer's floppiness has been provided by more recent studies of mass coincidence in time-of-flight multiphoton mass spectrometry⁶ and of Raman-vibronic double resonance spectroscopy.⁷ However, quantitative structural information about this important dimer has been elusive.

Our Communication addresses that gap. We report initial observations of low J (2 to 7) rotational transition for benzene dimers $(\text{Bzn})_2$ produced in pulsed supersonic nozzle experiments. The spectrum is "complicated and dense" as reported for the $(\text{H}_2\text{O})_2$ dimer.⁸ However, in the latter most of the complexity stems from tunneling while in $(\text{Bzn})_2$ there appear to be several dynamic states as well as low frequency (≈ 400 kHz) tunneling to challenge the analyst. We have assigned and fitted transitions of a *symmetric* top with a large centrifugal distortion constant D_{JK} of 0.869(5) MHz. The \bar{B} of 427.76(2) MHz found for the state corresponds to a center of mass (c.m.) to c.m. separation R of the two benzenes by 4.96 Å in a T -shaped structure.

The rotational transitions were observed with a modified⁹ Balle/Flygare Fourier transform microwave spectrometer¹⁰ fitted with a pulsed nozzle as the sample source. Neon first run (70% Ne and 30% He) gave the best results as the carrier gas. It was seeded with benzene vapor by passing 3% of the carrier gas through a bubbler containing liquid benzene at ambient temperature. The backing pressure was an atmosphere and the nozzle diameter was 1 mm. We have searched for low J transitions ($J=2 \rightarrow 3$ to $6 \rightarrow 7$) of $(\text{Bzn})_2$ in the 2.5 to 6 GHz region. About 1 GHz has been covered and more than a hundred transitions listed. Benzene has been verified as the sole origin of each

signal by cutting off the bubbler and, separately, by changing the carrier gas to pure He or Ar.

So far 22 transitions have been found with a distinctive quartet structure, each with components of comparable intensity extending over 200 to 400 kHz and with splittings in a 1 to 3 ratio. A typical transition, that for $J=5 \rightarrow 6$, $K=1$, is reproduced in Fig. 1. The results are summarized in Table I for which the frequencies of the four components were averaged to give a "line center." The splittings are listed by size in the table as ν_1 and ν_2 . The line centers occur in the K^2 progressions characteristic of a symmetric top. The $K=0$ transitions are noticeably weaker than the $K>0$ components of the same $J \rightarrow J+1$. They were fitted by the usual expression¹¹

$$\nu = 2\bar{B}(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2 + \text{higher terms.} \quad (1)$$

The fit with the three basic terms gave an unusually large rms deviation of 1.7 MHz, so higher order terms were tested. Inclusion of H_{JK} and, to a lesser extent, of H_{KJ} improved the fit significantly, giving an rms deviation of 0.27 MHz. The best-fit values of the five parameters are $\bar{B}=427.76(2)$ MHz; $D_J=7.2(3)$ kHz; $D_{JK}=0.869(5)$ MHz; $H_{JK}=1.32(5)$ kHz; and $H_{KJ}=0.67(12)$ kHz. The residues of the fit are included in Table I. They exhibit some regularities.

Determination of the benzene separation R requires consideration of the symmetric top behavior of the dimer. Figure 2 shows a T -shaped dimer with the benzene planes perpendicular to each other. For the configuration drawn, the moments of inertia of the rigid dimer (I_G) are given in terms of R and the moments of inertia for the monomer ($I_a=I_b=I_c/2$) by the following expressions which neglect any vibrational or equilibrium tilt of the monomers:

$$I_A = I_c(1) + I_a(2) = 3I_b, \quad (2a)$$

$$I_B = I_b(1) + I_b(2) + \mu_d R^2 = 2I_b + \mu_d R^2, \quad (2b)$$

$$I_C = I_a(1) + I_c(2) + \mu_d R^2 = 3I_b + \mu_d R^2, \quad (2c)$$

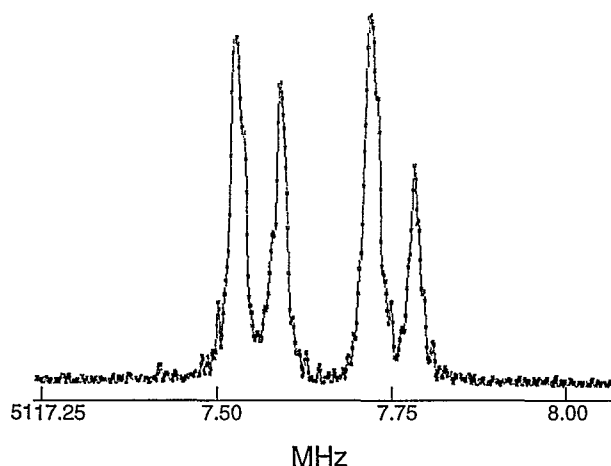


FIG. 1. The quartet fine structure observed in the $J=5 \rightarrow 6$, $K=1$ transition of the $(\text{Bzn})_2$ dimer at 5117.65 MHz. The Doppler doubling has been suppressed by the use of slits.

where (n) identifies the benzene monomers as given in Fig. 2 and μ_d is the reduced mass of the dimer, treated as pseudodiatom. The inertial asymmetry of this configuration is appreciable, with $(B-C)=32.5$ MHz if one assumes an R of 4.9 Å.

Just how the dimer becomes a symmetric top is spec-

TABLE I. Rotational transitions and tunneling splittings observed for a symmetric top dimer of benzene.

Transition ($J, K \rightarrow J', K'$)	Line center (MHz)	Residue (MHz)	Splittings	
			ν_1 (kHz)	ν_2 (kHz)
2,2 \rightarrow 3,2	2 545.8450	0.2515	32.0	115.0
1 1	2 460.7610	0.0174	30.0	115.0
0 0	2 565.6712 ^a	-0.1386	27.6	90.0
3,3 \rightarrow 4,3	3 360.8641	-0.3388	67.0	196.1
2 2	3 394.2252	0.3126	48.5	150.1
1 1	3 413.6892	0.0215	39.1	128.6
0 0	3 420.1125	-0.1619	37.2	124.1
4,4 \rightarrow 5,4	b			
3 3	4 202.2641	-0.0906	77.0	229.1
2 2	4 242.3811	0.3313	62.6	185.5
1 1	4 266.0375	0.0088	53.3	158.0
0 0	4 273.8795	-0.1690	51.5	155.5
5,5 \rightarrow 6,5	4 900.2968 ^a	0.3416	61.0	182.4
4 4	4 979.8225	-0.6900	74.0	223.0
3 3	5 044.3020	0.2282	89.2	261.2
2 2	5 090.2390	0.2791	74.5	221.3
1 1	5 117.6502	-0.0353	62.3	193.3
0 0	5 126.7939	-0.1659	59.7	187.2
6,6 \rightarrow 7,6	b			
5 5	b			
4 4	5 815.3870	-0.3064	116.0	347.3
3 3	5 886.9433 ^a	0.4695	98.4	291.9
2 2	5 937.7084	0.1112	85.5	253.1
1 1	5 968.3905	-0.1071	75.4	228.7
0 0	5 978.6863	-0.1492	71.6	221.4

^aOverlapped or perturbed by other transitions; assigned on the basis of the J and K dependence of the splittings.

^bSearches for these lines were unsuccessful.

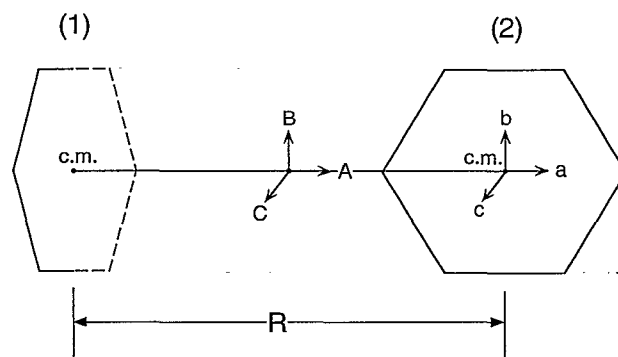


FIG. 2. Inertial axis systems of free benzene (right) and of a T-shaped benzene dimer with C_{2v} symmetry (center) drawn to scale.

ulative at this point. The problem could lie in Eq. (2) which is based on a rigid structure while the interactions of the two benzenes are weak and relatively isotropic. In particular, MMC (molecular mechanics for clusters) calculations give a barrier of only 1 or 2 cm^{-1} to internal rotation of the benzenes about the A axis.² Accordingly, benzene (2) is close to being a free molecule in its own rotational state (designated by little j) with $j=0$ or perhaps $j=1$. If the wave function of this state has axial symmetry about its a -axis, the dimer in effect spends half its time in the configuration given and half its time with benzene (2) rotated by 90° about its a axis. The dimer then becomes a symmetric top with

$$I_B = I_C = (5/2)I_b + \mu_d R^2. \quad (3)$$

In this event the experimental value of 427.76 MHz for \bar{B} of the dimer and the B_0 of 5688.9156 for the monomer¹² lead to an R of 4.96 Å. For comparison, the neutron diffraction cell dimensions¹³ at -135°C correspond to a nearest-neighbor c.m. distance of 5.025 Å in solid benzene.⁵

There is considerably more information about the tunneling than about the symmetric top behavior. As noted above, the components of each quartet are of comparable intensity. Also, although the ν_1 and ν_2 splittings are strongly affected by centrifugal distortion (J and K dependences), they extrapolate to substantial values (15 and 50 kHz) for zero J and K . Both observations indicate that the splittings are indeed tunneling frequencies.¹¹

The two splittings are indicative of two pathways which are likely to be similar because of the small ratio (3/1) of the splittings. C_6 rotation of the benzene monomers is an improbable cause because it produces at most very small fluctuations in the induced dipole moment and is unlikely to give detectable splittings. Instead, there could be interconversion tunneling like that in the water dimer,⁸ in which the two benzenes exchange roles by concerted rotation about equivalent axes, which are not necessarily inertial axes. This possibility is supported by the MMC calculations that give an equilibrium structure which is a somewhat skewed T , with benzene (1) rotated by 22° one way about its b -axis and benzene (2) rotated by 5° the opposite way.² The barrier to inversion of the skew is only

8 cm^{-1} . The two pathways might be interconversion in and counter to the direction of skew.

Finally, we consider the nature of the benzene dimer state reported and of those not yet identified. There is some evidence that the present symmetric top is not the ground state of the dimer. Addition of a few percent of argon to the neon first run carrier gas reduces the signals of the symmetric top from strong to weak. This might be due in part to competitive formation of Ar-Bzn dimer. However, Ar-Bzn is a somewhat weaker dimer^{14,15} than (Bzn)₂ ($429\text{ vs }550\text{ cm}^{-1}$) so the latter should predominate. At present, relaxation of an excited state seems to be a more probable interpretation of the effect of Ar on the (Bzn)₂ signal. Earlier work has shown that Ar is much more efficient than Ne or He at relaxing excited states of conformers and isomers to more stable forms.¹⁶

Some of the unassigned transitions of the benzene system are similar to those of a symmetric top with a free internal rotor. This case was analyzed by Kirchhoff and Lide¹⁷ and later described by Fraser *et al.*¹⁸ in the following notation:

$$\nu = 2(J+1) \{ B - D_{JK}K^2 - D_{Jm}m^2 - D_{JKm}Km - H_{JKm}m^2K^2 \} - 4(J+1)^3 D_J. \quad (4)$$

Here m specifies the internal rotation state of the dimer and D_{JK} , D_{Jm} , D_{JKm} , H_{JKm} , and D_J are centrifugal distortion constants. In this formalism the benzene symmetric top could correspond to an $m=0$ internal rotor state while the $|m| \geq 1$ states have not yet been recognized because of an appreciable internal barrier. Support for this view is provided by the benzene-water dimer which is fitted with Eq. (4). The symmetric top state was assigned first at higher J ,¹⁹ followed by low- J identification of the $|m|=1$ state and application of Eq. (4).²⁰ Further work on these interesting systems is in progress, including analysis of a benzene-water trimer, Bzn-(H₂O)₂ and Bzn-(D₂O)₂, and of several dimers incorporating C₆H₅D.

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