

THE BENZENE-SO₂ AND PYRIDINE-SO₂ COMPLEXES

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The benzene-SO₂ and pyridine-SO₂ complexes have been observed for the first time using Fourier transform microwave spectroscopy. The complexes have different geometries. In benzene-SO₂, the two planar species are stacked one above the other. In pyridine-SO₂, the pyridine plane rotates by 70°, so that it is more nearly perpendicular to the SO₂ plane.

High resolution spectroscopic studies of the dimeric complexes of SO₂ with acids [1-4], trimethylamine (TMA) [5], argon [6] and another SO₂ [7]

have been reported. Their structures are diverse and might be described as arising from interaction of the oxygen with the acidic hydrogen in SO₂·HX, the sul-

Table 1
Transition frequencies (MHz) for C₆H₆-SO₂

J'	K'_p	K'_o	J''	K''_p	K''_o	$\nu(\text{obs})$	$\nu(\text{obs}) - \nu(\text{calc})$
1	1	0	0	0	0	9995.844	-0.0028
1	1	1	1	0	1	8067.952	-0.0062
2	1	1	1	0	1	11923.633	0.0002
2	1	2	2	0	2	7996.963	-0.0081
3	1	2	2	0	2	13887.213	0.0111
3	1	3	3	0	3	7891.368	-0.0104
4	1	4	4	0	4	7752.239	-0.0082
5	1	5	5	0	5	7581.003	0.0007
6	1	6	6	0	6	7379.449	0.0238
4	0	4	3	0	3	7421.159	-0.0008
4	1	4	3	1	3	7282.031	0.0024
4	1	3	3	1	2	7567.507	0.0098
4	2	3	3	2	2	7424.820	-0.0144
5	0	5	4	0	4	9272.781	-0.0052
5	1	5	4	1	4	9101.545	0.0036
5	1	4	4	1	3	9458.347	0.0142
5	2	4	4	2	3	9280.306	-0.0130
6	0	6	5	0	5	11121.964	-0.0152
6	1	6	5	1	5	10920.408	0.0060
6	1	5	5	1	4	11348.482	0.0169
6	2	5	5	2	4	11135.314	-0.0071
6	2	4	5	2	3	11151.807	-0.0104
7	0	7	6	0	6	12968.239	-0.0277
7	1	7	6	1	6	12738.503	0.0122
7	1	6	6	1	5	13237.764	0.0213
7	2	6	6	2	5	12989.747	0.0026
7	2	5	6	2	4	13016.103	-0.0024

Table 2

Rotational constants (MHz) and centrifugal distortion constants (kHz) for benzene-SO₂ and pyridine-SO₂ (Watson S reduction, representation I')

	C ₆ H ₆ -SO ₂	C ₆ D ₆ -SO ₂	C ₅ H ₅ N-SO ₂ ^{a)}	C ₅ H ₅ ¹⁵ N-SO ₂	C ₅ H ₅ N-S ¹⁸ O ₂
<i>A</i>	9031.946(55)	8949.728(70)	3534.94(11)	3533.18(6)	3377.70(5)
<i>B</i>	963.946(12)	907.907(11)	759.923(1)	759.831(1)	736.754(5)
<i>C</i>	892.569(16)	845.023(17)	647.635(1)	647.612(1)	627.099(4)
<i>D_J</i>	0.737(12)	0.617(12)	0.281(19)	0.320(10)	0.317(28)
<i>D_{JK}</i>	20.92(17)	18.77(13)	41.2(11)	41.4(1)	38.3(3)
<i>D_K</i>	-	-	-37.0(130)	-153.0(70)	-29.0(100)
<i>d₁</i>	-0.050(10)	-0.039(8)	-0.105(4)	-0.106(2)	-0.119(23)
<i>d₂</i>	0.012(6)	0.0005(60)	-0.012(3)	-0.009(1)	0.007(10)
<i>n</i> ^{b)}	27	20	29	22	12
$\Delta\nu$ ^{c)}	0.012	0.009	0.003	0.001	0.007

^{a)} ¹⁴N coupling constants (MHz): $\chi_{aa} = -4.086(2)$; $\chi_{bb} = 1.347(2)$; $\chi_{cc} = 2.740(2)$.

^{b)} Number of transitions in fit. ^{c)} rms deviation of the fit in MHz.

fur with the basic nitrogen in SO₂·TMA or the π orbitals with the rare gas in SO₂·Ar.

We have investigated the complexes of SO₂ with two aromatic compounds, benzene and pyridine, by Fourier transform microwave (FTMW) spectroscopy; the two adducts have contrasting spectra and structures. In benzene-SO₂, the two planar moieties are stacked one above the other suggestive of a π - π interaction. The spectral features indicate an internal rotation or tunneling motion between the benzene and SO₂. In pyridine-SO₂, the pyridine plane rotates by approximately 70° and is more nearly perpendicular to the SO₂ plane. The nitrogen end is directed towards the SO₂ suggestive of a σ - π interaction. No evidence for facile internal rotation has been found.

The spectra were observed in a pulsed molecular beam FTMW spectrometer [8]. Mixtures of approximately 98% Ne, 1% SO₂ and 1% C₆H₆ or C₅H₅N were employed. In the case of benzene-SO₂, 27 *a* and *c* dipole transitions were assigned and are shown in table 1. The second-order Stark effects and frequency fit (12 kHz rms) confirmed the assignment. The rotational constants for this species and for C₆D₆-SO₂ which was fit similarly are given in table 2. There are additional transitions with first-order Stark effects which form series at roughly $(B+C)(J+1)$, somewhat similar but not identical to compounds with a low barrier to internal rotation such as CH₃NO₂ [9]; they have not yet been assigned. These transitions and the large *A* constant of

the complex indicate that we have assigned the transitions in the $m=0$ state (no quantum of internal rotational angular momentum) while the unassigned lines either have $m \neq 0$ (one or more internal quanta) in a low barrier limit or originate from states tunneling through a more appreciable barrier. Because

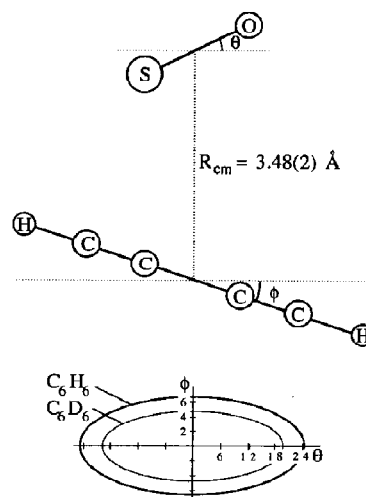


Fig. 1. Projection of benzene-SO₂ onto its symmetry plane showing the definitions of R_{cm} , θ , and ϕ . The bottom curves indicate the correlated values of θ and ϕ consistent with the rotational constants for C₆H₆-SO₂ and C₆D₆-SO₂. Note: R_{cm} is not drawn to scale for fig. 1 or 2. In both figures, the *a* inertial axis is nearly parallel to R_{cm} , and the *c* axis lies in the symmetry plane perpendicular to *a*.

Table 3
Transition frequencies (MHz, unsplit centers) for $C_6H_5N-SO_2$

J'	K'_p	K'_o	J''	K''_p	K''_o	$\nu(\text{obs})$	$\nu(\text{obs}) - \nu(\text{calc})$
2	2	0	1	1	0	11255.436	0.0004
2	2	1	1	1	1	11364.386	0.0024
2	2	0	2	1	2	8665.066	-0.0002
2	2	1	2	1	1	8324.868	-0.0056
3	2	2	3	1	2	8157.780	0.0016
3	2	1	2	1	1	12563.145	0.0007
3	2	2	2	1	2	12883.324	-0.0010
3	1	2	2	0	2	7391.416	0.0022
3	2	1	3	1	3	8848.084	0.0008
4	2	3	3	1	3	14457.573	0.0009
4	1	3	3	0	3	9029.609	0.0005
5	1	4	4	0	4	10735.278	-0.0027
5	0	5	4	0	4	6971.721	-0.0013
5	1	5	4	1	4	6742.579	-0.0024
5	1	4	4	1	3	7302.607	-0.0047
5	2	4	4	2	3	7028.468	-0.0018
5	2	3	4	2	2	7094.370	-0.0013
5	3	3	4	3	2	7044.274	-0.0001
5	3	2	4	3	1	7045.576	0.0006
6	0	6	5	0	5	8331.317	0.0049
6	1	6	5	1	5	8082.780	0.0007
6	1	5	5	1	4	8752.864	0.0057
6	2	5	5	2	4	8427.958	0.0010
6	2	4	5	2	3	8541.680	0.0007
6	3	4	5	3	3	8456.685	-0.0020
6	3	3	5	3	2	8460.152	0.0014
7	0	7	6	0	6	9674.379	-0.0044
7	1	7	6	1	6	9418.957	0.0016
7	1	6	6	1	5	10196.910	-0.0005

benzene- SO_2 has both a and c selection rules the axis of internal rotation is not necessarily a principal inertial axis, although it appears to be approximately aligned with the a axis since the A rotational constant is close to the constant for free SO_2 perpendicular to its C_2 axis (8799.65 MHz) [10]. If the B and C constants are assumed to be unperturbed by the internal rotation (and if C_6 symmetry is preserved and the benzene and SO_2 structures do not change upon complexation), some structural information can be determined. A model which describes the complex involves three parameters: $R_{c.m.}$ which joins the centers-of-mass of both partners and two angles, $\theta+90^\circ$ and $\phi+90^\circ$, which describe the angle that the SO_2 or benzene planes respectively make with $R_{c.m.}$ (fig. 1). While $R_{c.m.}$ can be determined from the B constant (parallel axis theorem), only pairs of

θ and ϕ can be obtained by fitting C . The values consistent with the data are given in fig. 1. The different curves for θ and ϕ for the C_6H_6 and C_6D_6 complexes are indicative of large amplitude vibrational motions for the van der Waals modes in these weak complexes. While the signs and magnitudes of the angles are ambiguous, the gross configuration of the complex is undoubtedly correct.

The spectrum of pyridine- SO_2 is also characterized by a and c selection rules. Twenty-nine transitions have been assigned for the normal isotopic species (6 kHz rms) which are given in table 3. Transitions are split by the nuclear quadrupole interaction of ^{14}N which confirms the assignment. The rotational and quadrupole coupling constants are given in table 2 for the normal species and two other isotopes which were fit similarly. The A constant is

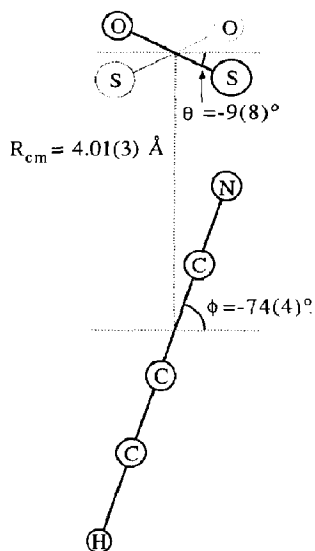


Fig. 2. Projection of pyridine-SO₂ onto its symmetry plane showing the values of $R_{c.m.}$, θ , and ϕ consistent with the rotational constants. Either orientation of the SO₂ fits the data. See also the note in fig. 1.

normal and no series indicative of a low internal rotation barrier or tunneling have been observed. Values of $R_{c.m.}$, θ and ϕ are given in fig. 2. The values are the result from fitting the three isotopic species. While two orientations of the SO₂ are consistent with the data, the L-shaped conformer with $d(N-S) = 2.61(3)$ Å is similar to (CH₃)₃N-SO₂ where $d(N-S)$ is 2.28(3) Å [5]. However, the second conformation cannot be excluded at the present time. Additional study of these systems will be necessary to provide more detail on the precise structures, vibrational averaging effects, etc.

In the introduction, these dimers were described as π - π and σ - π complexes. While these descriptions using HOMO-LUMO language have some pictorial and perhaps predictive effectiveness, a growing body of evidence indicates that electrostatic interactions play a major role in determining the structures of weak complexes [11-15]. For example, studies of

TMA-SO₂ and H₃N-SO₂ [5,11], where the amine nitrogen is oriented towards the SO₂ plane in a fashion similar to pyridine-SO₂, indicate that electrostatic interactions can account for its geometry. Thus, it seems likely that an electrostatic model involving the interaction of the electric fields and polarizabilities of benzene, pyridine and SO₂ can rationalize the different structures. We are exploring this question for the complexes as well as obtaining more precise structures, vibrational averaging effects, barrier information, etc. from the spectroscopic data.

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