ROTATIONAL SPECTRUM OF 2,3-BENZOFURAN

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Dedicated to Professor Sergio Roffia on the occasion of his retirement.

The rotational spectra of the ground state and of one vibrational satellite of 2,3-benzofuran have been measured by millimetre-wave absorption free jet spectroscopy in the frequency range 60–78 GHz. The value of the inertial defect (-0.072 u$Å^2$) shows the molecule to be planar. The shifts of the rotational constants in going from the ground to the excited state indicate that the observed vibrational satellite does not belong to the two lowest energy motions, the butterfly and 1,3-ring-twisting, which undergo relaxation upon the supersonic expansion.

Keywords: Rotational spectroscopy; Free jets; Vibrational relaxation; Benzofurans; Oxygen heterocycles.

The rotational spectra of several aromatic molecules made by a combination of a six- and five-membered ring (indene can be considered the prototype) have been investigated[1–9]. These molecules are of interest in biochemistry because some biological bases (for example purine[8]) have such a shape. They often exist as tautomers; rotationally resolved spectroscopy is especially useful to find their relative energies[5,10,11], or, at least which is the most stable one[8]. Most of the cited investigations have been carried out with conventional microwave spectroscopy, so that the rotational spectra of the vibrational satellites of the two lowest energy vibrations, the ring puckering and the butterfly motions, have often been measured. They lie about 200 cm^{-1} above the ground state and can be easily identified by their characteristic changes, with respect to the ground state, of the values of the planar moments of inertia[8].

There is an important member of the family, 2,3-benzofuran (BF; Fig. 1), for which the rotational spectrum has never been reported. Since we would like to investigate some of its molecular complexes in order to determine, for example, the conformational preference of the complex with a noble

gas atom, we decided to assign, as a first step, the rotational spectrum of BF itself. We used for this purpose our millimetre-wave absorption free jet spectrometer. It is possible, with this technique, to obtain information on the vibrational relaxation upon supersonic expansion[12].

EXPERIMENTAL

The Stark and pulse modulated free jet absorption millimeter-wave spectrometer used in this study has already been described elsewhere[13,14]. A sample of BF was purchased from Aldrich and used without further purification. The rotational spectrum was observed by flowing Ar over BF, warmed to 40 °C in order to have a mixture with about 5% of BF, and expanding such a mixture from *ca* 3×10^4 Pa to about 0.5 Pa through a nozzle with a diameter of 0.35 mm, reaching an estimated "rotational" temperature of about 10–20 K.

ROTATIONAL SPECTRA

The first estimates of the rotational constants of BF were based on B3LYP/6-31G** theoretical calculations[15].

We could easily assign strong μ_b-R-type transitions, with K_a and J in the ranges 7–10 and 8–12, respectively. They are doubly overlapped due to the degeneracy of the involved rotational levels. Then we could measure lines with smaller K_a, split into the two asymmetry components, up to $J = 22$. We could also measure some transitions of the K_a 13–12 μ_b-Q-band. Finally it was possible to measure several transitions of the $J = 23$–22 μ_a-R-type band.

All the measured transition frequencies are collected in Table I. They have been fitted using Watson's quartic reduced hamiltonian (A-reduction and I^r-representation[16]). The spectroscopic constants obtained and some statistical parameters of the fits are shown in Table II. Weaker lines (with intensity *ca* 1/20 of that of the ground state) were observed in the spectrum. They have been assigned to a vibrational satellite. The corresponding
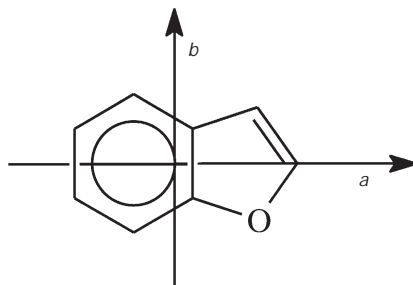

FIG. 1
Sketch of 2,3-benzofuran and of its principal axes

TABLE I
Experimental transition frequencies (in MHz) of BF

$J'(K'_a, K'_c) - J''(K''_a, K''_c)^a$	Frequency[b]		Frequency[c]	
	obs.	obs. – calc.	obs.	obs. – calc.
8(8) – 7(7)*	60 173.52	0.04	60 280.27	–0.01
9(8) – 8(7)*	63 023.98	0.03	63 131.10	0.02
9(9) – 8(8)*	68 006.42	0.04	68 127.27	–0.05
10(7,4) – 9(6,3)	60 875.21	0.01	60 968.87	0.04
10(7,3) – 9(6,4)	60 876.39	0.04	60 970.00	0.02
10(8) – 9(7)*	65 871.74	0.07	65 979.13	–0.01
10(9) – 9(8)*			70 978.40	0.00
10(10) – 9(9)	75 839.18	–0.04	75 974.27	0.02
11(7,5) – 10(6,4)	63 701.55	–0.01	63 795.53	–0.01
11(7,4) – 10(6,5)	63 706.11	–0.04	63 800.13	0.02
11(8) – 10(7)*	68 714.46	0.05	68 822.27	–0.06
11(9) – 10(8)*			73 827.47	0.04
12(6,7) – 11(5,6)	61 239.21	–0.08	61 320.00	0.03
12(6,6) – 11(5,7)	61 534.68	–0.05	61 614.80	–0.04
12(7,6) – 11(6,5)	66 508.22	–0.02	66 602.60	0.03
12(7,5) – 11(6,6)	66 523.65	–0.01	66 617.93	–0.03
12(8,5) – 11(7,4)	71 549.38	–0.02	71 657.60	0.04
12(8,4) – 11(7,5)	71 549.86	–0.03	71 658.00	–0.04
12(9) – 12(9)*			76 672.80	–0.01
13(5,8) – 12(4,9)	61 308.22	0.03		
13(6,8) – 12(5,7)			63 822.70	–0.02
13(6,7) – 12(5,8)			64 509.87	0.00
13(7,7) – 12(6,6)	69 283.04	–0.01	69 377.77	0.00
13(7,6) – 12(6,7)	69 328.52	–0.05	69 423.17	0.02
13(13) – 13(12)*	62 236.73	0.02		
14(5,9) – 13(4,10)	65 735.53	0.05		
14(7,8) – 13(6,7)	72 005.07	–0.01		
14(7,7) – 13(6,8)	72 125.61	–0.02		
14(8,7) – 13(7,6)	77 180.68	–0.02		

TABLE I
(*Continued*)

$J'(K'_a, K'_c) - J'(K''_a, K''_c)^a$	Frequency[b]		Frequency[c]	
	obs.	obs. – calc.	obs.	obs. – calc.
14(8,6) – 13(7,7)	77 186.68	–0.00		
14(13) – 14(12)*	62 201.67	0.01		
15(5,10) – 14(4,11)	70 954.47	0.03		
15(6,10) – 14(5,9)	67 864.19	–0.08		
15(6,9) – 14(5,10)	70 691.73	–0.08		
15(7,9) – 14(6,8)	74 638.47	0.03		
15(7,8) – 14(6,9)	74 929.63	0.05		
15(13) – 15(12)*	62 158.47	–0.03		
16(5,11) – 15(4,12)	77 053.50	0.03		
16(6,11) – 15(5,10)	69 272.13	–0.10		
16(6,10) – 15(5,11)	74 318.58	–0.06		
16(7,10) – 15(6,9)	77 124.30	0.05		
16(7,9) – 15(6,10)	77 772.13	0.04		
16(13) – 16(12)*	62 106.10	0.07		
17(6,12) – 16(5,11)	70 178.47	–0.01		
17(13) – 17(12)*	62 042.93	–0.02		
18(6,13) – 17(5,12)	70 632.93	0.09		
18(13) – 18(12)*	61 967.87	0.03		
19(6,14) – 18(5,13)	70 752.07	0.09		
19(13) – 19(12)*	61 879.17	–0.00		
20(5,16) – 19(4,15)	60 203.65	0.15		
20(6,15) – 19(5,14)	70 691.80	–0.12		
20(13) – 20(12)*	61 775.20	–0.07		
22(9,14) – 21(9,13)	64 154.23	–0.05		
22(9,13) – 21(9,12)	64 200.80	–0.07		
22(10) – 21(10)*	63 817.33	–0.06		
22(11) – 21(11)*	63 569.75	–0.06		
22(12) – 21(12)*	63 386.27	0.08		
22(13) – 21(13)*	63 246.27	0.09		

[a] Transitions marked with * are doubly overlapped transitions due to the near prolate degeneracy of the involved levels; only K_a is given. [b] Ground state. [c] $v_x = 1$.

frequencies are also reported in Table I, while the obtained molecular parameters are given in Table II. The agreements of the rotational constants with the values calculated with the B3LYP/6-31G** geometry mentioned above[15] are very good, the differences are at most 0.27%, for the *B* constant.

VIBRATIONAL SATELLITE

We already mentioned in the introduction that it is possible to assign the vibrational satellites on the basis of the shifts, with respect to the ground state, of the second moments of inertia. Second moments of inertia are defined as:

$$M_{aa}(v) = 1/2[-I_{aa}(v) + I_{bb}(v) + I_{cc}(v)], \quad etc. \tag{1}$$

Their changes in going from the ground to the excited state give the structural variation, for effect of the vibration, of the molecule along the consid-

TABLE II
Spectroscopic constants of 2,3-benzofuran[a]

State	A, MHz	B, MHz	C, MHz	D_J, kHz	D_{JK}, kHz	D_K, kHz
Ground[b]	3916.552(7)	1660.804(8)	1166.45(1)	0.053(9)	0.09(1)	0.15(5)
$v_x = 1$[c]	3923.681(4)	1661.400(6)	1166.146(6)	0.053[d]	0.017(3)	0.29(5)

[a] Errors in parentheses are expressed in units of the last digit. [b] Number of transitions in the fit was 53 and the standard deviation was 0.07 MHz. [c] Number of transitions in the fit was 23 and the standard deviation was 0.03 MHz. [d] Fixed at the ground state value.

TABLE III
Shifts of second moments of inertia upon vibrational excitation (in uÅ^2)

Vibration	ΔM_{aa}	ΔM_{bb}	ΔM_{cc}
		Indene[a]	
$v_b = 1$	–0.369	–0.011	0.239
$v_t = 1$	–0.168	–0.116	0.225
		2,3-Benzofuran[b]	
$v_x = 1$	0.119	–0.006	–0.228

[a] From ref.[1]. [b] For 2,3-benzofuran M_{aa} = 304.257, M_{bb} = 129.001 and M_{cc} = 0.036 uÅ^2.

ered axes, and can be used to understand which structural motion is associated with the considered vibration. It has been shown that shifts of second moments of inertia of the butterfly and 1,3-twisting motions for indene-like molecules are very similar throughout the family[1–7]. In Table III we compare the shifts of the vibrational satellite we have observed for BF to that, for instance, of indene. They are completely different and suggest that the vibrational satellite belongs to a higher-energy motion, not identifiable at the moment. We believe that the vibrational satellites of the butterfly and 1,3-twisting motions relax to the ground state during the supersonic expansion, while our "X" state does not find an efficient pathway for the relaxation process. This effect has been previously observed[12,17]. If the state "X" did not vibrationally relax upon supersonic expansion, its vibrational energy would be *ca* 670 cm^{-1} above the ground state. This value, however, is an upper limit, because we cannot exclude a partial relaxation during the expansion process. It could then be assigned, depending on the degree of relaxation, to the ν_{27} (401 cm^{-1}) or ν_{26} (539 cm^{-1}) or ν_{25} (611 cm^{-1}), the "in-plane" vibrations[18] below 670 cm^{-1}.

CONCLUSIONS

Free jet absorption millimetre wave spectroscopy was very useful for a rapid assignment of the rotational spectra of the ground and of one vibrational satellite of BF. We could easily show, from the value of the inertial defect, this indene-like molecule to be planar. The small negative value is in agreement, indeed, with the prevalence of the contributes from the out-of-plane motions, as shown in refs[1–9,19]. Shifts of second moments of inertia in going from the ground to the excited state indicate that the vibrational satellite does not belong to the lowest-energy vibrational modes, such as the butterfly and twisting modes. The negative value of ΔM_{cc} suggests such a state to belong to an "in-plane" mode. The vibrational relaxation upon supersonic expansion plays an important role on the observation of rotational spectra of vibrational excited states. Rotational transitions of excited vibrational states have also been observed in the molecular beam Fourier transform MW spectrum of benzo[*b*]thiophene[9]. Since no intensity evaluations are there given, it appears difficult to extract information on the vibrational relaxation. It seems, however, from the changes of rotational constants with respect to the ground state, that state labelled as ν_d, corresponds to the state ν_x of BF.

Further investigations will concern the study of complexes of benzofuran with noble gases in order to establish the position of the noble gas atom with respect to the two rings of the molecule.

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