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Laser Induced Fluorescence of 1,3 Benzodioxole in a Supersonic Jet

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Abstract: Fluorescence excitation by Nd:YAG pumped dye laser and single vibrational level fluorescence spectra of 1,3 benzodioxole in a supersonic jet have been obtained and interpreted. The previous assignment of the $0\,^{0}_{0}$ band was incorrect. In addition, many other bands involving ν_{20} and ν_{19} vibrations of a_2 symmetry were confirmed. As far as a_1 totally symmetric vibration is concerned. The ν_{14} was assigned to be located in the five-membered ring whereas ν_{13} seem to be located in the benzene ring as a result of the electronic transition in the benzene ring which affects ν_{13} and not ν_{14} wavenumber.

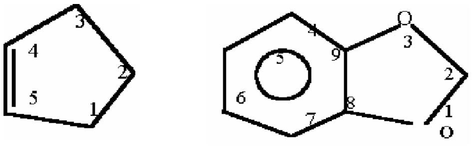
Introduction

Pseudo four- membered ring compounds are those of five atoms with one double band in the ring. Because the double band is much more resistance to twisting than the other four single bands, the vibrational twist or puckering motion is more like that of a five- membered ring with four single bands, than that of five– membered ring, for example the puckering vibration of cyclopenten, shown in Fig. (1a). The CH_2 group in the 2-position moves through the plane of the carbon atoms, resembles that of cyclopentene, puckering vibration transitions were observed in the far-infrared spectrum [1] and fitted to a vibrational potential function of the form:

$$\nu\,(x) = Ax^2 + Bx^4 \qquad (1)$$

where ν (x) is the potential energy in cm^{-1}, x is the displacement coordinate in ^{0}A, while A and B are constants with units of $cm^{-1}\ {}^{0}A^{-2}$ and $cm^{-1}\ {}^{0}A^{-4}$ respectively with a negative value of A. The resulting W-shaped potential has a barrier, whose height is given by $A^2/4B$ between equivalent minima. Fitting ten observed puckering vibrational transition of cyclopentene to such a potential showed that the molecule has non-planer C_5 carbon skeleton with a barrier to planarity of 232 cm^{-1} [1].

The 1,3 benzodioxole (BDO) has the structural formula shown in Fig. (1b).



(a) **(b)**

Fig. 1: Structure of **(a)** cyclopentene and **(b)** 1,3 benzodioxole

Assuming that BOD has a planer skeleton in the ground electronic state and belongs to the C_{2v} point group, the total number of vibrations (3N-6) is 39 distributed as $14a_1 + 6a_2 + 7b_1 + 12b_2$.

The gas phase far infrared spectrum in the 50-500 cm^{-1} region, of BDO, indane, phthalan and indoline have been obtained and interpreted by Duckett [2] and Sulskus [3]. From the assignment of the $\Delta\nu = 1$ sequences involving the puckering vibration of the CH_2 group, and fitting them to the potential as shown in Fig. (1), it was deduced that BDO has a planer skeleton in S_0. They assigned the lowest wavenumber a_1 vibration ν_{14} (five-membered ring skeleton, 298 cm^{-1}) and the three lowest wavenumber b_1 vibration, ν_{25} (Benzene ring skeleton, 412.5 cm^{-1}), ν_{26} (butterfly, 236.4 cm^{-1}) and ν_{27} (Pucker, 157.6 cm^{-1}) from the far-infrared spectrum [2]. Table (1) gives the Mulliken numbers for the non-totally symmetric vibrations, which are important in the electronic spectrum of BDO.

Table 1: Numbering of low wavenumber vibrations in BDO.

Symmetry	Description	No.	Wave No.	No. in Ref. (4)
b_1	Puckering	ν_{27}	157.6^a	ν_8
b_1	Butterfly	ν_{26}	236.4^a	ν_7
b_1	6-memb. ring deformation	ν_{25}	412.5^a	ν_6
a_2	Twist in 5-memb. ring	ν_{20}	4^c	ν_5
a_2	Twist in 6-memb. ring	ν_{19}	552^b	-
a_1	5-memb. ring expansion	ν_{14}	298^a	ν_2

a: from Ref. 2
b: from Ref. 3
c: calculated from W-shaped potential

The electronic spectrum of BDO showed two strong overlapping bands, the first one was assigned by Alves et al [5], while the second one was assigned by Sulskus et al. [3] as the O_0^0 band.

Experimental Method

Single Vibrational Level Fluorescence

The CW supersonic free jet apparatus employed is shown in Fig. (2). In our experiments the fluorescence was observed by exciting the BDO molecules with a Quantel Datachrom 500 Nd:YAG Pumped dye laser system. Rhodamine 590 dye solution was used to obtain a green region i.e. at about 576 nm which was frequency doubled using a KDP (potassium dihydrogen phosphate) crystal to produce a wavelength of a bout 288nm to match the O_o^o band region of BOD.

For the single vibronic level fluorescence (SVLF) spectrum [6, 7] the fluorescence is dispersed using a 1 m scanning spectrometer, the second order of 18400 grooves per grating and slit width of 200μm.

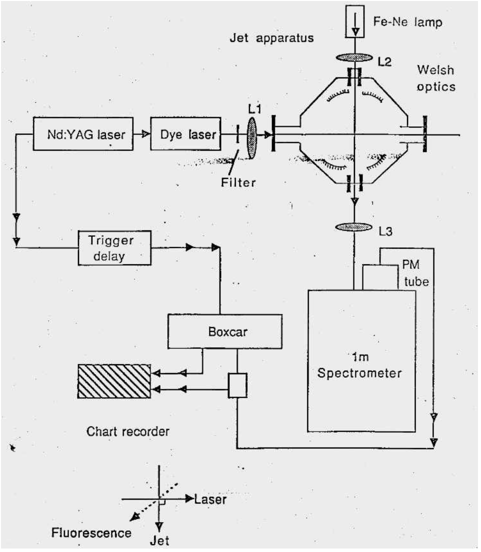


Fig. 2. The experimental set up of supersonic jet apparatus

The signal is detected by an EMI 9789 QB photomultiplier and fed to a Stanford Research Systems boxcar averager. Calibration of the spectra is achieved by simultaneous recording of the spectrum of an iron/neon hollow cathode lamp. The fluorescence excitation (FE) spectrum is obtained by passing the total fluorescence through a Schott WG 335 filter and into the spectrometer with the grating angle set to zero for all the spectra of BDO. The sample was seeded into the jet by flowing Helium gas at a pressure of 1.2 atm, over the surface of liquid BDO at a temperature of 333 K.

IR Spectra

The infrared spectra of BDO were recorded on a Perkin Elmer 983 spectrometer. From this spectrum many of the fundamental vibration wavenumbers in the ground electronic state were obtained.

Results and Discussion

The FE spectrum of BDO obtained in the supersonic jet is shown in Fig. (3). The spectrum shows that the previous assignments of the O_o^o band [3, 5] are incorrect. The intense 34882.6 cm^{-1} band is greatly reduced in intensity in the jet spectrum and is therefore not a cold band at all while the 34892 cm^{-1} band, although its cold, forms part of a progression. This progression starts with the band at 34789.2 cm^{-1}, which must, therefore, be the O_0^o band, an assignment that could not have been made from the absorption spectrum alone.

The FE spectrum displays a strong progression with a constant interval of 102 cm^{-1}. This together with interpretation of the SVLF spectra in Figs. 4, 5 and 6, the progression must be in even quanta of an approximately harmonic a_2 vibration with an unusually low wavenumber of 51cm^{-1} [8]. Since it is the lowest wavenumber a_2 vibration in S_1 we label it ν_{20}^1 although it probably involves mainly twisting of the benzene ring, such vibration was observed in substituted Benzene [9-12].

Also many other bands are shown in Fig. (3) with assignments based on the observed of SVLF(as discussed later) of these bands the cross-sequence band $19_0^1\,20_1^0$ was assigned on the base of its SVLF spectrum in the jet (see Fig. 4). The assignment of the $19_0^1\,20_1^0$ band, together with the $19_0^1 20_0^2$band form the basis of our interpretation of many other bands such as $19_0^1\,20_0^1$and 19_0^2, where ν_{19} is the second lowest $a_2$vibration. Of the bands involving totally symmetric vibration 14_0^1 and 13_0^1 seem to fit quiet reasonably with the corresponding SVLF spectra. In addition, many combination bands with 20_0^2 such as $14_0^1 20_0^2, 13_0^1 20_0^2$ were also assigned on the basis of their SVLF.

The observation of the 26_0^2 band, but not the 27_0^2 band, may be attributed to a very low fluorescence quantum yield from $\nu_{27}= 2$ but not from $\nu_{26}^1 = 2$where ν_{27}, ν_{26} are b_1 vibration.

Table (2) shows a wavenumber separations and assignments of bands in the FE spectrum of BDO in a supersonic jet. The combined activity of ν_{19}^{11} and ν_{20}^{11} is a result of the Duschinsky effect [13,14] in which the normal coordinates $Q_{19}^1$and Q_{20}^1 in the excited state are heavy mixtures of $Q_{1`9}^{11}$ and Q_{20}^{11} in the ground state, ν_{19} is the second lowest a_2 vibration. The assignment of the band at 35077 *cm*$^{-1}$ is based on the observation of a very strong 14_0^1 band in SVLF spectrum of Fig. (5). Since the vibrational wavenumber changes very little from 298 cm^{-1} in S_0 [2] to 288 cm^{-1} in S_1 [O_0^0 (34789cm^{-1})- 14_0^1 (35077cm^{-1})], this suggest a very small geometry changes from S_0 to S_1 and agree with the fact that ν_{14} is located in the five-membered ring [2] and hence by electronic excitation which occurs primarily in the benzene ring.

Table (2): Wave number separations and assignments of bands in the FE spectrum of BDO in a supersonic jet.

$\Delta\nu$ `	Assignment
0	0_0^0
93	$19_0^1 20_1^0$
102	20_0^2
139	$19_0^1 20_0^1$
180	19_0^2
204	20_0^4
273	$19_0^2 20_0^2$
288	14_0^1
353	13_0^1
381	$26_0^1 27_0^1$
393	$14_0^1 20_0^2$
443	$13_0^1 19_0^1 20_1^0$
456	$13_0^1 20_0^2$
462	26_0^2
471	$20_0^2 26_0^1 27_0^1$

The wavenumbers and assignments of the SVLF spectrum are given in Table (3). Figure (6) shows the SVLF spectrum obtained by the excitation of the band at 35142 cm^{-1} assigned in the FE spectrum as 13_0^1 where ν_{13} is the second lowest wavenumber totally symmetric vibrations. In addition to the progression in ν_{20} and the other totally symmetric vibrations, the SVLF spectrum is dominated by a very intense 13_1^1 transition, which confirms the 13_0^1 assignment. This vibration shows a relatively large decrease in wavenumber from 537 cm^{-1} in S_0 to 353 cm^{-1} in S_1(O_0^0 34789 cm^{-1}, 13_0^1 35142 cm^{-1}). This indicates a very large geometry changes from S_0 to S_1 15, 16]. Table (4) shows our experimental values for some of the a_1 fundamentals obtained from SVLF spectra and those of Ref. [2]. These are compared with values we have obtained from IR spectrum of a thin liquid film of BDO recorded with a Perkin Elmer 983 spectrometer.

Table (3): Assignments of the SVLF spectra of BDO following excitation of the 14^1_0 bands at 35077 *cm*$^{-1}$ and the 13^1_0 band at 35142 *cm*$^{-1}$.

14^1_0 band

No.	Δν	Assignment	No.	Δν	Assignment	No.	Δν	Assignment
1	0	14^1_0	11	691	$14^1_1\ 26^0_1\ 27^0_1$	21	1131	-
2	101	$14^1_0 20^0_2$	12	714	$12^0_1\ 14^1_0$	22	1233	$10^0_1\ 14^1_1$
3	234	$14^1_0 20^0_4$	13	764	$13^0_1\ 14^1_0\ 20^0_4$	23	1295	$9^0_1\ 14^1_1$
4	295	14^1_1	14	785	$14^1_0 26^0_2\ 27^0_2$	24	1386	$13^0_2\ 14^1_1\ (7^0_1\ 14^1_0)$
5	393	$14^1_0 26^0_1\ 27^0_1$	15	834	$13^0_1\ 14^1_1$	25	1404	$14^1_1\ 19^0_2$
6	425	$14^1_0 20^0_6$	16	935	$10^0_1\ 14^1_0$	26	1504	$14^1_1\ 19^0_2\ 20^0_2$
7	497	$14^1_0 20^0_2\ 26^0_1\ 27^0_1$	17	1000	$9^0_1\ 14^1_0$	27	1533	$8^0_1\ 14^1_1$
8	527	$14^1_1\ 20^0_4$	18	1022	$12^0_1\ 14^1_1$	28	1658	$7^0_1\ 14^1_1$
9	540	$13^0_1 14^1_0$	19	1077	$14^1_1\ 26^0_2\ 27^0_2$	29	1733	$10^0_1\ 11^0_1\ 14^1_0$
10	555	$14^1_0 19^0_1\ 20^0_1$	20	1104	$14^1_0\ 19^0_2$	30	1899	$7^0_1\ 13^0_1\ 14^1_0$

13^1_0 band

No.	Δν	Assignment	No.	Δν	Assignment	No.	Δν	Assignment
1	0	13^1_0	8	714	$13^1_1\ 20^0_2$	15	996	$9^0_1\ 13^1_0$
2	101	$13^1_0 20^0_2$	9	764	--	16	1076	13^1_2
3	234	$13^1_0 20^0_4$	10	785	$12^0_1 13^1_0$	17	1107	$13^1_0\ 19^0_2$
4	296	$13^1_0 14^0_1$	11	834	$13^1_1\ 20^0_4$	18	1174	$13^1_2\ 20^0_2$
5	472	$13^1_0 26^0_2$	12	935	$13^1_0\ 25^0_2$	19	1250	$12^0_1\ 13^1_1$
6	573	13^1_1	13	1000	$11^0_1\ 13^1_0\ 20^0_2$	20	1360	
7	575	$13^1_0 20^0_2\ 26^0_2$	14	1022	$13^1_1\ 20^0_6$			

$\Delta\nu = \nu_L - \nu_1$ where ν_L is the wavenumber of the laser radiation.

Table (4): Wavenumbers of a_1 fundamentals of BDO in S_0 state obtained from the IR and SVLF spectra.

Vibration	0^0_0 band	20^2_0 band	20^4_0 band	IR value
ν_7	1359	1361	1358	1360
ν_8	1240	1238	1229	1235
ν_9	1011	1004	997	1003
ν_{10}	935	934	935	936
ν_{11}	803	802	798	798
ν_{12}	719	716	714	715
ν_{13}	536	534	538	537
ν_{14}	300	302	300	298.0[a]

a: from Ref. 2

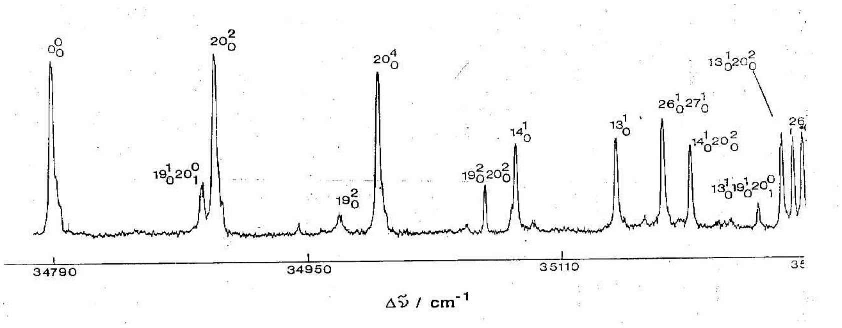


Fig. 3: Fluorescence excitation spectrum of 1,3 Benzodioxole in a supersonic jet.

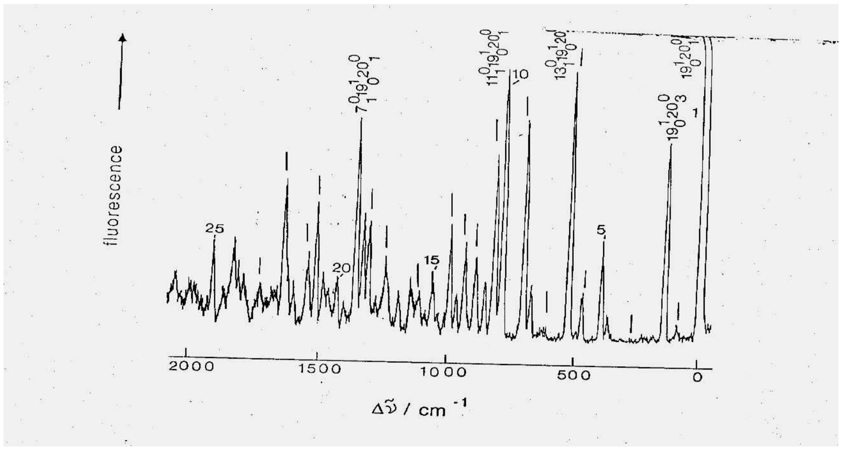


Fig. 4: SVLF spectrum of BDO in a supersonic jet with excitation in the $19^1_0\ 20^0_1$.

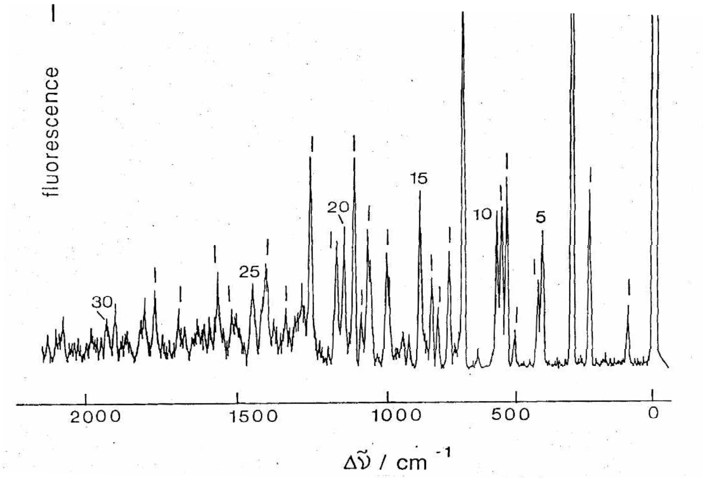


Fig. 5: SVLF spectrum of BDO in a supersonic jet excitation in the 14^1_0 band.

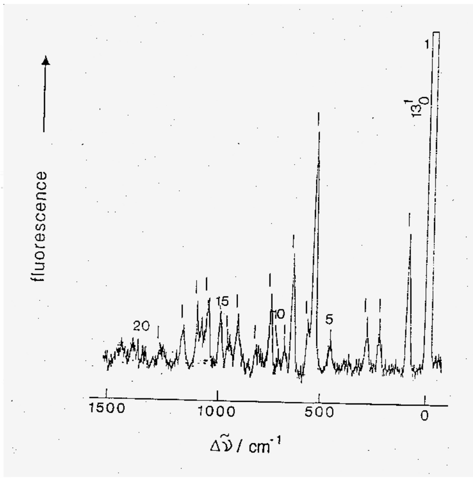


Fig. 6: SVLF spectrum of BDO in with a supersonic jet with excitation in the 13^1_0 band.

Conclusions

From the extracted results, it is concluded that the intense 34882.6 cm^{-1} band is greatly reduced in intensity in the jet spectrum while the 34892 cm^{-1} band although, it is cold, forms part of a progression. This progression starts with the band 34789.2 cm^{-1}, which must therefore be the O_0^0 band. The assignments of a_1 vibrations ν_{14} and ν_{13} indicated that ν_{13} is located in the benzene ring while ν_{14} seems to be located in the five- membered ring.

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التفلور المحتث بالليزر لجزيئة 1، 3 بنزودايوكسول في النفث فوق الصوتي

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الخلاصة

تم الحصول على التفلور الكلي للمستويات التهيجة والتفلور من مستويات اهتزازية أحادية لجزيئة 3،1 بنزودايو كسول في النفث فوق الصوتي وتم دراستها وتحليلها. لقد تم تحديد العدد الموجي للانتقال الالكتروني . بالاضافة الى ذلك تم العمل على تعيين الاهتزازات من نوع التناظر a_2 والعائدة الى الالتواء في الحلقة الخماسية $\boldsymbol{\nu}_{20}$ وحلقة البنزين $\boldsymbol{\nu}_{19}$. اما بالنسبة الى الاهتزازات من نوع a_1 فقد تم تحديد نوعين من الاهتزازات العائدة الى الحلقة الخماسية $\boldsymbol{\nu}_{14}$ وحلقة البنزين $\boldsymbol{\nu}_{13}$.