BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 622—625 (1970)

n-π^* Electronic Emission Spectrum of *o*-Methoxybenzaldehyde Vapour

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(Received March 27, 1969)

The n-π^* vapour emission spectrum of *o*-methoxybenzaldehyde has been excited in transformer discharge in flowing vapours of benzene and the substance. In the spectrum the C=O stretching frequency is the most prominent and its found to form progression of bands. The entire spectrum has been analyzed in terms of several ground state frequencies.

In recent years there has been a growing interest in the study of non-bonding electron transition specially in benzaldehyde derivatives. The n-π^* electronic emission and absorption spectra of benzaldehyde[1-3] and halobenzaldehydes[4-9] have been investigated in detail by many workers. The electronic absorption spectrum due to n-π^* system of *o*-methoxybenzaldehyde in vapour state was recorded by Dwivedi.[10] However, the emission spectrum of *o*-methoxybenzaldehyde was not studied by any earlier worker. The present paper deals with the detailed study of the emission spectrum of the compound in vapour state obtained for the first time in transformer discharge. To make the electronic study more comprehensive the infrared spectrum was also recorded.

Experimental

The emission spectrum has been obtained in transformer discharge through the flowing mixture of benzene and *o*-methoxybenzaldehyde vapour. The discharge tube was of π type 35 cm in length, narrower in the middle (14 mm diam.) and broader at the two ends.

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[1] S. N. Garg, *J. Sci. Res. Banaras Hindu Univ.*, **4**, 42 (1953—1954).

[2] G. W. Robinson, *J. Chem. Phys.*, **22**, 1384 (1954).

[3] S. N. Garg and I. S. Singh, *J. Sci. Res. Banaras Hindu Univ.*, **9**, 61 (1957—1958).

[4] M. R. Padhey and B. G. Viladkar, *Indian J. Pure Appl. Phys.*, **4**, 92 (1966).

[5] D. P. Juyal, *Curr. Sci.*, **6**, 175 (1965).

[6] M. P. Srivastava and I. S. Singh, *J. Sci. Res. Banaras Hindu Univ.*, **17** (1), 252 (1966—1967).

[7] M. P. Srivastava I. S. Singh, *Curr. Sci.*, **36**, 456 (1967).

[8] M. P. Stivatava and I. S. Singh, *ibid.*, **36**, 399 (1967).

[9] R. M. P. Jaiswal, *Indian J. Pure Appl. Phys.*, **3**, 405 (1965).

[10] C. P. D. Dwivedi, *ibid.*, **3**, 452 (1965).

TABLE 1. EMISSION BANDS OF *o*-METHOXYBENZALDEHYDE

Wave-length Å	Wave number cm^{-1}	Inten-sity	Separation from (0–0) band in cm^{-1}	Assignment
3750.4	26656	1	496	0+496
3788.8	26386	1	226	0+226
3791.5	26367	1	207	0+207
3800.5	26305	2	145	0+145
2821.5	26160	4	0	0−0
3834.5	26072	1	88	0−88
3840.6	26030	1	130	0−130
3849.8	25968	2	192	0−192
3861.2	25891	2	269	0−270
3879.6	25769	1	391	0−2×192
3892.1	25686	2	474	0−475; 0−270−192
3908.2	25580	2	580	0−580
3929.3	25443	3	717	0−717; 0−580−130
3945.8	25336	3	824	0−824
3971.1	25175	2	985	0−717−270
3974.0	25144	5	1016	0−1016; 0−824−192
3979.3	25123	4	1037	0−1037
3987.2	25073	2	1087	0−824−270
3998.1	25005	1	1155	0−1155
4012.2	24929	2	1231	0−1231
4019.8	24870	2	1290	0−1016−270
4031.7	24796	1	1364	0−1231−130
4039.6	24748	2	1412	0−1155−270
4045.4	24712	4	1448	0−1450
4051.8	24673	4	1487	0−1485
4061.4	24615	5	1545	0−824−717
4070.0	24563	6	1597	0−1597
4074.6	24535	6	1625	0−1155−475
4087.5	24458	9	1702	0−1702
4098.1	24395	5	1765	0−1485−270
4118.6	24273	5	1887	0−1702−192
4132.8	24190	4	1970	0−1702−270
4150.7	24086	2	2074	0−1597−475
4155.4	24058	5	2102	0−1702−2×192; 0−1016−824−270
4167.6	23988	4	2172	0−1702−475
4184.8	23889	2	2271	0−1702−580
4210.7	23742	5	2418	0−1702−717
4228.8	23641	6	2519	0−1702−824
4263.7	23447	5	2713	0−1702−1016
4266.3	23433	5	2727	0−1702−1037
4278.0	23369	4	2791	0−1702−824−270
4304.3	23226	6	2934	0−1702−1231
4313.4	23177	4	2983	0−1702−1016−270
4345.4	23006	4	3145	0−1702−1450
4371.7	22868	5	3292	0−1702−1597
4383.2	22808	5	3352	0−1702−2×824
4392.4	22670	10	3400	0−2×1702
4429.0	22572	7	3588	0−2×1702−192
4445.1	22490	5	3670	0−2×1702−270
4485.6	22287	6	3873	0−2×1702−475
4505.0	22191	4	3969	0−2×1702−580
4534.7	22046	2	4114	0−2×1702−717
4548.4	21980	3	4180	0−2×1702−580−192
4556.4	21914	5	4129	0−2×1702−824
4597.5	21745	4	4415	0−2×1702−1016
4644.7	21524	6	4636	0−2×1702−1231
4692.4	21305	5	4855	0−2×1702−1450
4723.0	21167	6	4993	0−2×1702−1597
4745.8	21065	8	5095	0−3×1702
4791.0	20867	5	5293	0−3×1702−192
4809.8	20785	5	5375	0−3×1702−270
4858.9	20575	3	5585	0−3×1702−2×192
4873.7	20513	3	5647	0−3×1702−2×270
4938.8	20242	4	5918	0−3×1702−824
4988.9	20039	2	6121	0−3×1702−1016
5021.3	19910	1	6250	0−3×1702−1155
5054.2	19780	3	6380	0−3×1702−1016−270
5098.8	19607	2	6553	0−3×1702−1450
5113.1	19552	2	6608	0−2×1702−2×1597
5136.3	19464	4	6696	0−3×1702−1597
5156.7	19387	5	6773	0−4×1702
5209.8	19189	3	6971	0−4×1702−192
5288.9	18902	2	7258	0−4×1702−270
5384.7	18566	2	7594	0−4×1702−824
5446.7	18361	1	7799	0−4×1702−1016; 0−4×1702−824−192

Two separate containers joined to each other in series to hold the substance and benzene, were attached to one end of the discharge tube facing the slit. The benzene container was provided with a fine capillary tube to control the flow of the benzene vapour whereas the substance container was externally heated to a desired temperature to give requisite vapour pressure in the discharge tube. The use of benzene in this experiment is to prevent dissociation of the molecules to a great extent. The stablized discharge condition was obtained at 4500—5000V and the discharge was bright blue in colour.

The spectrum was recorded on a Fuess glass spectrograph and a Q-24 Zeiss medium quartz spectrograph. Ilford HP-3 and ORWO blue rapid plates were used to photograph the spectra. With a slit-width of 40 μ, exposures of 6—10 hr were found sufficient on both the instruments. The wavelength and wave number of the bands, their relative intensities, separation from the 0–0 band and proposed assignments are given in Table 1.

Results

The emission spectrum lies in the region 3750—5447 Å and consists of about 75 bands. The spectrum consists of a long progression of bands. These bands form the head of the groups. The first group is observed with weak intensity but the intensity of the second group abruptly increases and is maximum for the third and then decreases gradually. Between each pair of successive bands in each group there is a recurring pattern of bands. A typical spectrogram of the emission spectrum is shown in Fig. 1.

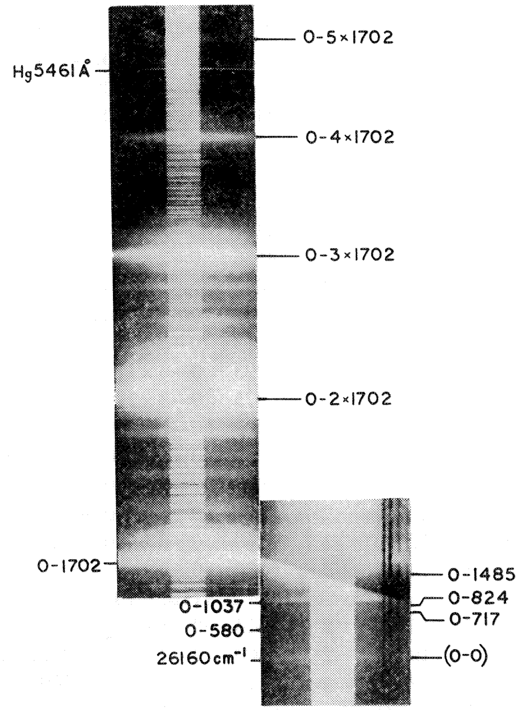

Fig. 1. Emission spectrum of *o*-methoxybenzaldehyde.

Analysis and Discussion

It is well established that the longest wavelength electronic transition of compounds containing carbonyl groups arises from the excitation of a non-bonding (*n*) electron localized on the oxygen atom to the anti-bonding π^* orbital. The eletronic transition is supposed to be confined to a large extent to the C=O part of the molecule and has been interpreted by McMurry[11] as corresponding to a transition in which a loosely bound electron occupying a non-bonding orbital lying in the molecular plane and across the C=O direction is excited to an anti-bonding π^* orbital with a mode in the plane. Padhye[12] and Sidman[13] have also reviewed the nature and characteristics of such non-bonding electron transition. The electronic transition responsible for the present system is similar to 3714 Å system in benzaldehyde and corresponds to the forbidden transition $^1A_2$–$^1A_1$ of formaldehyde. However, in *o*-methoxy benzaldehyde with lower symmetry C_s (considering the OCH_3 group to behave as a single mass point and CHO group to lie in the plane of the ring), the above forbidden transition becomes allowed and is ascribed to $^1A''$–$^1A'$.

The band 26160 cm^{-1} observed with medium weak intensity in the emission spectrum has been identified as the 0–0 band of the system. In the absorption spectrum of vapour, Dwivedi[10] has assigned the band at 26136 cm^{-1} as the 0–0 band of the system. The choice of the 0–0 band is supported by the smooth vibrational analysis as well as the good agreement of the ground state freqencies observed in the emission spectrum with those recorded in infrared spectrum.

The frequency 1702 cm^{-1} is the most prominent one which dominates the spectrum. Four quanta of it have been observed forming a progression of bands. This frequency with its overtones combines with most of the ground state frequencies giving thereby a recurring pattern of bands. It has been assigned as the C=O stretching frequency in the ground state. Its magnitude in both Raman and infrared spectrum in liquid phase is 1684 cm^{-1}. The difference in the C=O stretching frequency in liquid and vapour phase is probably due to hydrogen bonding resulting from the intermolecular interaction in the liquid phase. The molecules in the liquid phase are very close to each other and due to partial linking of the hydrogen atom of the CHO group of one molecule with the oxygen atom of the CHO group of another molecule, the C–O bond strength is slightly lowered and consequently the magnitude of the C=O stretching frequency is slightly lowered in liquid phase. Such shifts have also been observed in benzaldehyde,[3] fluoro and chlorobenzaldehydes.[5,8]

Another ground state frequency 1037 cm^{-1} is involved in the band at 25123 cm^{-1} occurring with weak intensity. The frequency is correlated with the totally symmetric 1039 cm^{-1} Raman and 1040 cm^{-1} infrared frequency and is assigned to the ring breathing mode corresponding to 992 cm^{-1} (a_{1g}) vibration of benzene.

Other ground state frequencies observed in the emission spectrum are: 130, 192, 270, 475, 580, 717, 824, 1016, 1155, 1231, 1450, 1485 and 1597 cm^{-1}. All these are observed to combine with the 1702 cm^{-1} C=O stretching frequency and its overtones. A correlation of ground state frequencies

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11) H. L. McMurry, *J. Chem. Phys.*, **9**, 231 (1941).

12) M. R. Padhye, *J. Univ. Bihar*, **5**, 41 (1958).

13) J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).

TABLE 2. CORRELATION AND ASSIGNMENT OF GROUND STATE FREQUENCIES OBSERVED IN RAMAN, INFRARED AND EMISSION SPECTRA OF *o*-METHOXYBENZALDEHYDE

Raman (liquid) Kahovec[14]		Infrared (liquid) Present work		Electronic emission (vapour) Present work		Mode of vibration
cm^{-1}	Int.*	cm^{-1}	Int.	cm^{-1}	Int.*	
124	1			130	1	a″ C–CHO twisting
195	1			192	2	a″ C–OCH$_3$ o.p. bending
270	½b	277	3	269	2	a″ C–C–C o.p. bending
478	2	472	9½	475	2	a′ C–C–C i.p. bending
580	3	575	6½	580	2	a′ C–OCH$_3$ i.p. bending
719	½	717	5	717	3½	a″ CH$_3$ wagging
830	1	830	10	824	3½	a′ C–CHO stretching
1018	½	1018	10	1016	3½	a′ C–C–C i.p. bending
1039	4½	1040	10	1037	1	a′ C–C stretching (breathing vibration)
1158	5½	1159	10	1155	1	a′ C–H i.p. bending
1238	9	1242	10	1231	2	a′ C–OCH$_3$ stretching
1458	1	1460	10	1450	2	a′ C–H asym. bending (in methyl group)
1483	4	1482	10	1485	2	a′ C=C stretching
1597	9	1588	10b	1597	6½	a′ C=C stretching
1684	10	1684	10	1702	10	a′ C=O stretching

* The intensities have been changed to the scale of 10 from the original table.
b=broad; i.p.=in plane; o.p.=out of plane; asym.=asymmetric

observed in Raman, infrared and emission spectra is given in Table 2. Besides these, there are some bands which are observed on the shorter wavelength side of the 0–0 band and involve excited state frequencies and their combination. These are also included in Table 1.

The authors are grateful to Professor N. L. Singh for his interest in the work. One of them (M.P.S.) is thankful to C.S.I.R. (India) for financial assistance.

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14) L. Kahovec and K. W. F. Kohlrausch, *Z. Phys. Chem.*, **38B**, 119 (1937).