

RAMAN EFFECT IN MIXTURES OF ANISALDEHYDE WITH PHENOL AND METHANOL

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I. INTRODUCTION

THE inductive and the mesomeric effects of a methoxy substituent on the phenyl ring are well known. Raman frequencies of methoxy aromatics provide sufficient indications regarding the abnormal effects of such substitutions. The effects of hydrogen bond formation in addition to the methoxy substitution on the vibrational frequencies of the *p*-methoxy benzaldehyde are presented here.

2. EXPERIMENTAL TECHNIQUE

The Raman spectrum of anisaldehyde using Hg 4358 A.U. excitation was recorded with a Fuess Spectrograph and Hilger source unit. The spectrograph has a dispersion of 19 cm.⁻¹ per mm. in λ 4358 region. The exposure time of 20 minutes for recording an intense Raman spectrum of anisaldehyde was increased proportionally for mixtures, so that the lines of the aldehyde could be recorded with comparable intensity.

Two new lines, one at 140 cm.⁻¹ and another at 1699 cm.⁻¹ have been recorded for the first time. The other frequencies closely agree with those recorded by Kahovec and Kohlrausch.¹


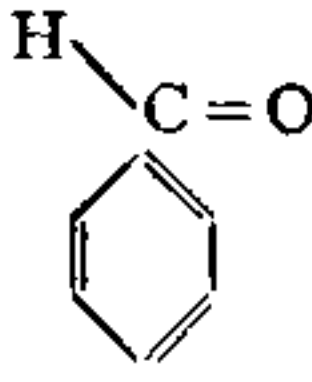
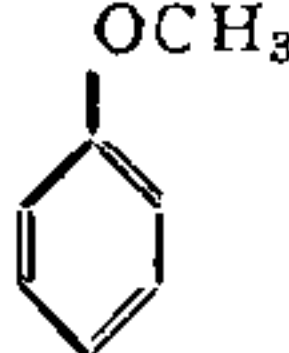
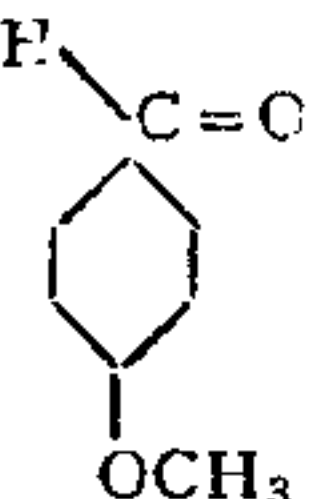
The frequencies associated with the vibrations of the phenyl group of the aldehyde are 640, 988, 1008, 1161 and 1600 cm.⁻¹. The line at 1161 cm.⁻¹ is due to the vibrations of C-H bond in the plane of the ring.

Some of the relevant frequencies of a few ring compounds are given in Table I.

By a comparative study of Table I, the frequencies associated with different bonds of anisaldehyde can be identified easily. Benzene has no lines at about 1200 cm.⁻¹. By the methoxy substitution, a line at 1244 cm.⁻¹ makes its appearance. Therefore, this appears to be the line arising due to the vibrations of C-O connecting the phenyl ring to the methoxy group.

The line at 1197 cm.⁻¹ in benzaldehyde has been assigned by the author² to the vibrations

TABLE I

1		Benzene	..	1178	1478	1584 1600	..
2		Benzaldehyde	..	1159	1197	..	1448 1493	1591	1694
3		Methoxy Benzene	..	1177	..	1244	1452	1587 1603	..
4		Anisaldehyde	..	1161	1216	1263	1427 1461	1577 1600	1699

3. RESULTS AND TENTATIVE ASSIGNMENTS

The Raman frequencies of anisaldehyde are tabulated below with the conventional notations.

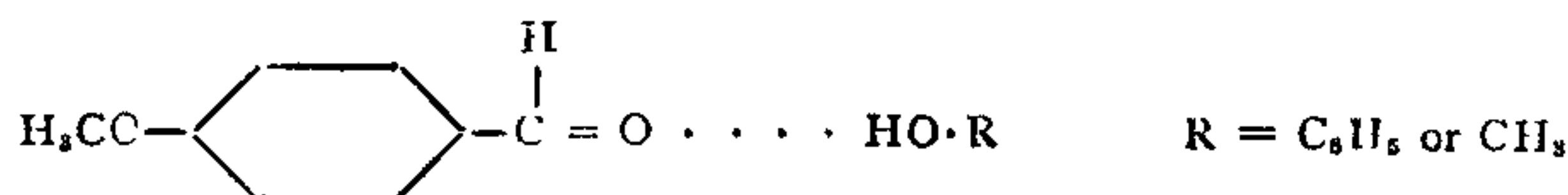
140(1), 190(1 b), 276(2), 332(1), 370(1), 602(2 b), 640(3), 720(1), 746(2), 835(3), 857(3), 988(2 s), 1008(0), 1161(6), 1216(4), 1263(4), 1317(3), 1393(0), 1427(5), 1461(2), 1577(4), 1600(8), 1681(8), 1699(5), 2957(4), 2989(4), 3024(3).

of C-C bond linking the aldehydic group to the phenyl ring. The frequencies of anisaldehyde are in general higher than the corresponding ones in benzaldehyde. As such the line at 1216 cm.⁻¹ in anisaldehyde can correspond to a line at 1197 cm.⁻¹ in benzaldehyde. Therefore, the line at 1216 cm.⁻¹ in anisaldehyde can be assigned to C-C bond connecting the aldehydic group and the phenyl ring of the aldehyde.

4. HYDROGEN BOND FORMATION

In order to create opportunities for the hydrogen bond formation, anisaldehyde was mixed with acceptor solvents like phenol and methanol


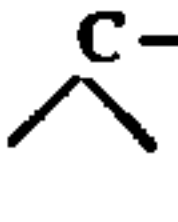
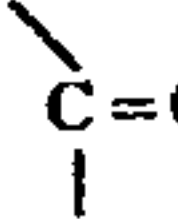
to the change in the polarizability of the environment of each anisaldehyde molecule. In the case of frequency 1600 cm^{-1} there is an initial reduction by 3 cm^{-1} and then at concentration ratio 1 : 4 a further reduction of 4 cm^{-1} is observed.



The frequency shifts observed for anisaldehyde hydrogen bonded to phenol or methanol are given in Table II.

This probably means the frequency shifts in this case are entirely due to polarizability changes in the environment and hydro-

TABLE II
Mixtures of anisaldehyde with phenol and methanol

Link	Frequencies of Anisaldehyde	Frequencies in Phenol, Ratio by volume			Frequencies in Methanol, Ratio by volume		
		Aldehyde : Phenol			Aldehyde : Methanol		
		1 : 1	1 : 2	1 : 4	1 : 1	1 : 2	1 : 4
	1161	1165	1165	1164	1169	1169	1167
C-C ald. ring	1216	1222	1222	1222	1223	1223	1222
C-OCH ₃	1263	1270	1270	1270
	1427	1432	1432	1433
C-C (ring)	1577 1600	1572 1597	1572 1593	1562 1593
	1681	1662	1662	1657	1678	1678	1678

Due to hydrogen bond formation, C=O which is the direct participant in the bond formation, gets weakened, as shown by the decrease in frequency of the vibration of C=O. With the aldehyde-phenol ratio going up to 1 : 2, the frequency is lowered by 19 cm^{-1} on further increasing the ratio up to 1 : 4, there is a further reduction of 5 cm^{-1} only. With the exception of the frequency at 1600 cm^{-1} , all other frequencies exhibit a similar behaviour, the magnitude of the variations being different in each case. It can be postulated that the first steep variation in the frequency is due to hydrogen bond formation, and the further small reduction or increase in the frequency, is due

gen bonding apparently does not affect this frequency. On the other hand, polarizability changes do not seem to have affected the frequency at 1263 cm^{-1} .

When the proportion of the solvent was increased more than four times, critical opalescence appears to set in, and the entire spectrum gets blackened.

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1. Kahovec and Kohlrausch, *Z. Physik. Chem.*, 1937, **83 B**, 119.
2. Paranik, P. G., *Proc. Ind. Acad. Sci.*, 1953, **38**, 239.