[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, ILLINOIS INSTITUTE OF TECHNOLOGY]

Raman Spectra of Some Aromatic Carbonyl and Nitro Compounds

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The Raman spectra of acetophenone, mesityl-aldehyde, acetylmesitylene, methyl 2,4,6-tri-methylbenzoate, 2,4,6-trimethylbenzoyl chloride, nitromesitylene and acetyldurene were obtained in connection with an investigation[1] of the effect of ortho substitution in hindering resonance between the benzene ring and carbonyl or nitro groups. In the previous paper, only the changes in the carbonyl frequency near 1700 and in the nitro frequency near 1350 cm.$^{-1}$ which resulted from the ortho substitution were discussed. The present paper gives a more complete discussion of the Raman data.

Details in regard to the apparatus, experimental technique, and the preparation and physical properties of the compounds were given in the previous paper and will not be repeated here. The Raman spectra were produced by use of Hg 4358 Å. The polaroid previously used in the polarization measurements has now been replaced by a Nicol prism.

Raman Spectrum of Acetophenone

The only one of the seven compounds for which previous data seem to have been reported is aceto-phenone. The previous results[2-5] are summarized in the columns at the left in Table I. The number following the ± sign is the mean deviation of the frequency. The depolarization factors are those of Simons[4] and the infrared frequencies are the ones listed in the paper of Ganesan and Venkateswaran[3] for comparison with their Raman data.

New Raman lines were observed at 404, 896 and 3006 cm.$^{-1}$, while the weak line at 1360, previously observed in one investigation, was not found. The depolarization factors agree well with those of Simons,[4] the mean deviation being 0.09. In addition, depolarization data were obtained for eleven lines for which no values were obtained in the previous investigation.

(1) Robert H. Saunders, M. J. Murray and Forrest F. Cleveland, THIS JOURNAL, **63**, 3121 (1941).

(2) A. Dadieu and K. W. F. Kohlrausch, *Sitzber. Akad. Wiss. Wien*, IIa, **138**, 335, 607 (1929).

(3) A. S. Ganesan and S. Venkateswaran, *Indian J. Phys.*, **4**, 196 (1929).

(4) L. Simons, *Soc. Scient. Fenn. Com. Phys. Math.*, **6**, No. 13 (1932).

(5) K. W. F. Kohlrausch and A. Pongratz, *Sitzber. Akad. Wiss. Wien*, IIb, **143**, 288 (1934).

TABLE I

RAMAN AND INFRARED SPECTRA OF ACETOPHENONE

N = number of times line has been observed in separate investigations, $\Delta\nu$ = Raman displacement in cm.$^{-1}$, I = estimated intensity, ρ = depolarization factor, ν = infrared frequency in cm.$^{-1}$, P means that the line is somewhat polarized but that a numerical value of ρ could not be obtained, brackets enclose data in regard to which there is some uncertainty.

| | Previous results | | | | Present results | | |
| | Raman | | | Infrared | | | |
N	$\Delta\nu$	I	ρ	ν	$\Delta\nu$	I	ρ
4	162 ± 2	5	0.87		165	5b	0.9
3	380 ± 10	2	0.36		371	3	0.4
					404	0	
1	468	1			461	0	
1	590	2			588	3	0.6
5	615 ± 2	3	0.82		617	5	0.6
5	729 ± 2	3	0.22		732	6	0.1
1	760	1		752	767	2	0.6
1	850	1/2		820	852	1	0.6
				917	896	0	
2	948 ± 2	2b			958	3	0.5
5	998 ± 2	7	0.04	1000	1002	10	0.3
5	1023 ± 3	3	0.24		1027	6	0.2
5	1074 ± 1	4	0.16		1076	6	0.2
5	1157 ± 2	2	[0.72]		1161	4	0.8
1	1182	2			1180	3	0.5
5	1263 ± 1	4	0.17	1250	1267	7	0.2
1	1309	0			1301	0	0.6
1	1360	00		1351			
1	1428	1		1429	1427	1	0.8
1	1450	1			1447	1	0.7
3	1483 ± 0	1/2	0.87		1493	3	0.8
5	1596 ± 1	8	0.86	1575	1597	10	0.8
5	1679 ± 0	7	0.32	1653	1684	10	0.4
4	2924 ± 2	4b	0.21	2857	2921	6	0.1
1	2970	00			2967	2	0.8
					3006	2	0.7
5	3063 ± 3	5	0.35		3065	10	0.3
1	3195	2			3187	1	P

The frequencies 617, 1002, 1027, 1161, 1180, 1597 and 3065 cm.$^{-1}$ are frequencies of the phenyl group which remain remarkably constant in a wide variety of monosubstituted benzenes.[6] The intensities and depolarization factors of these lines are likewise remarkably constant. Data previously obtained in this Laboratory[6] for these lines with five ethers containing one or more phenyl groups are compared with the present values for acetophenone in Table II. The values listed for the phenyl ethers represent the mean values of displacements, intensities and depolarization factors for the five compounds.

(6) *Cf.* M. J. Murray and Forrest F. Cleveland, *J. Chem. Phys.*, **9**, 129 (1941).

TABLE II

CONSTANT FREQUENCIES OF THE PHENYL GROUP

Acetophenone			Phenyl Ethers		
$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ
617	5	0.6	618	5	0.8
1002	10	0.3	1001	10	0.1
1027	6	0.2	1029	7	0.3
1161	4	0.8	1156	4	0.8
1180	3	0.5	1176	4	0.8
1597	10	0.8	1588 } 1604 }	6	0.7
3065	10	0.3	3058	9	0.3

A graphical overview of the data is given in Fig. 1. In the upper part of the figure the spectrum of acetophenone is compared with the spectra of benzene, benzene-d_1[7] and monochlorobenzene.[8] The spectra of the 1,2,4,6-benzenes appear in the lower central portion, followed finally by the spectrum of the 1,2,3,5,6-benzene. The height of the line is proportional to the estimated intensity, and Raman lines which were unusually broad are drawn with greater width in the figure.
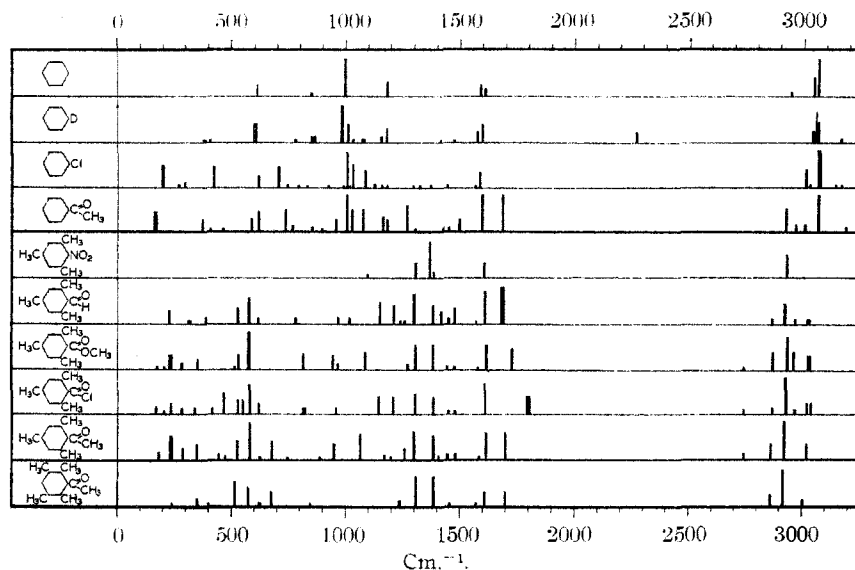

Fig. 1.—Raman spectra of some substituted benzenes.

The depolarized lines at 1427, 1447, 2967 and 3006 and the intense, polarized line at 2921 cm.$^{-1}$ are C–H frequencies characteristic of the methyl group. The weak line at 1360 is also probably due to this group. The corresponding frequencies for acetone,[9] whose only C–H bonds are those

(7) A. Langseth and R. C. Lord, Jr., *Kgl. Danske Vid. Sels. Math.-fys. Medd.*, **16**, No. 6 (1938).

(8) R. Ananthakrishnan, *Proc. Indian Acad. Sci.*, **3A**, 52 (1936). *Cf.* H. Sponer and J. S. Kirby-Smith, *J. Chem. Phys.*, **9**, 667 (1941).

(9) Forrest F. Cleveland, M. J. Murray, J. R. Coley and V. I. Komarewsky, *J. Chem. Phys.*, **10**, 18 (1942).

in methyl groups, are listed for comparison in Table III.

TABLE III

METHYL GROUP FREQUENCIES

Acetophenone			Acetone		
$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ
1360	00		1356	2	0.6
1427	1	0.8	1423	3 }	0.9
1447	1	0.7	1438	4 }	
2921	6	0.1	2922	10	0.22
2967	2	0.8	2965	4	0.9
3006	2	0.7	3005	4	0.8

The fact that the C=O line at 1684 is lower than the normal value (near 1715) indicates[1] that in acetophenone the ring and carbonyl group lie in the same plane.

Raman Spectra of the 1,2,4,6-Benzenes

The results for the 1,2,4,6-benzenes, nitromesitylene, mesitylaldehyde, methyl 2,4,6-trimethylbenzoate, 2,4,6-trimethylbenzoyl chloride and acetylmesitylene, are given in Table IV. The lines at 520 and 573 cm.$^{-1}$ appear with rather large intensities in all the spectra except that of nitromesitylene, which is incomplete. The strong lines near 1300 and 1380 cm.$^{-1}$ are likewise outstanding. The frequencies due to the methyl groups are presumably those near 1410, 1448, 2920 and 2960 cm.$^{-1}$. The line at 3032 appeared only for 2,4,6-trimethylbenzoyl chloride. The line near 1610 is a ring frequency while the lines near 1700 and 1363 are characteristic of the carbonyl and nitro groups, respectively. Their relatively high values in the last four spectra are, as pointed out in the previous paper,[1] due to the hindrance of resonance between the ring and the carbonyl (or nitro) group by the steric effect of the ortho methyl groups. The relatively low value observed in the spectrum of the aldehyde indicates that resonance exists and that therefore the carbonyl group and the ring are coplanar; this is possible because of the smaller size of the aldehyde group.

TABLE IV
RAMAN SPECTRA OF SOME 1,2,4,6-BENZENES AND ACETYLDURENE

Nitromesitylene (molten)		Mesitylaldehyde			Methyl 2,4-6-trimethylbenzoate			2,4,6-Trimethylbenzoyl chloride			Acetylmesitylene			Acetyldurene (in CCl₄ solution)	
Δν	I	Δν	I	ρ	Δν	I	ρ	Δν	I	ρ	Δν	I	ρ	Δν	I
					175	1		168	2	0.9	180	2	0.8		
					207	0		202	1						
		227	3	0.7	231	4b	0.7	232	3	0.9	231	6b	0.8	241	1
					281	2	0.6	280	2	0.7	282	3	0.8		
		312	1b	0.6											
					350	3	0.6	336	2	P	345	4	0.7	351	2
		385	2	0.5				411	2	P				397	1
								462	6	0.4	440	2	0.8		
											468	1			
					511	0									
		526	4	0.6	529	4	0.6	520	4	0.9	522	5	0.8	510	7
								546	4	0.7					
		573	7	0.3	571	10	0.1	576	8	0.3	577	10	0.3	572	5
		615	2	0.6				616	3	P	622	1		621	1
											675	5	0.3	676	4
											743	0			
		781	2	0.6											
					813	4	P	817	2b		888	0		846	1
					946	4	P	956	2	P	949	4	0.3		
		966	2	0.6	968	2	P								
		1015	2	0.7											
1091	1				1087	5	0.4				1062	7	0.3		
		1148	6	0.4				1141	5	0.3	1165	2	P		
											1194	0			
		1208	5	0.6				1204	5	0.4					
		1237	0											1236	2
		1254	1		1271	2	P				1253	3	0.4		
1302	4	1295	8	0.4	1302	7	0.4	1301	6	0.3	1299	8	0.3	1306	8
1363	10														
1385	2	1382	5	0.8	1381	7	0.4	1382	5	0.4	1382	7	0.4	1383	8
		1416	3	0.7							1405	1			
		1448	2	0.8	1446	2	0.7	1448	1		1448	2	0.7	1452	0
		1477	4	0.7	1478	1		1477	1		1480	2	0.7		
		1570	1		1580	0					1581	1	0.9	1571	1
1603	4	1608	9	0.6	1614	7	0.6	1609	8	0.4	1612	7	0.8	1606	4
		1687	10b	0.4	1728	6	0.3	1792	5b	0.1	1699	7	0.4	1699	4
					2739	0		2739	1		2740	2	P		
		2867	2	P	2863	5	P	2864	2	P	2862	4	0.6	2861	3
2926	6	2920	6	0.1	2927	9	0.1	2923	10	0.1	2919	10	0.2	2918	10
		2965	2	0.7	2954	5	P	2961	1	0.9					
		3022	2b	0.6	3022	4b	0.6	3017	3	0.6	3016	4	0.5	3003	2
								3032	3	0.6					

Raman Spectrum of Acetyldurene

The displacements and estimated intensities obtained for acetyldurene in carbon tetrachloride solution are given in the column at the right in Table IV; depolarization factors were not obtained for this compound. The spectrum of acetyldurene is obviously not so complete as that of acetylmesitylene. Lines which have approximately the same frequency and intensity in the two spectra are those near 621, 676, 1300, 1382, 1450, 2862 and 2918 cm.⁻¹. The doublet 510, 572 in acetyldurene appears at slightly lower frequencies than, and with a somewhat changed intensity distribution from, the corresponding doublet in acetylmesitylene. The strong frequency at 676 is present only for these two compounds and may therefore be supposed to require the acetyl group for its appearance. It doubtless corresponds to the 732 line in acetophenone and to the 787(7)0.20 line in acetone.[9] The frequencies 846, 1236, 1571, 1606 and 3003 have slightly lower values than the ones that seem to

correspond to them in the spectrum of acetyl-mesitylene. Again, the relatively high value of 1699 cm.$^{-1}$ for the C=O frequency indicates that the ring and carbonyl group are not coplanar.

Summary

Raman frequencies, estimated intensities and depolarization factors are reported for acetophenone, mesitylaldehyde, acetylmesitylene, methyl 2,4,6-trimethylbenzoate and 2,4,6-trimethylbenzoyl chloride; also, frequencies and intensities are reported for acetyldurene and nitromesitylene. For acetophenone, the only one for which previous data seem to have been reported, new lines were observed at 404, 896 and 3006 cm.$^{-1}$ and depolarization data were obtained for eleven additional lines.

The Structures of Nitrous Oxide and of Hydrogen Azide

BY VERNER SCHOMAKER AND ROBERT SPURR

Introduction.—Nitrous oxide and hydrogen azide present much the same structural problem. The two molecules contain the same number of valence electrons and have been shown by spectroscopic investigation[1,15] to be essentially linear. The expected resonating structures are similar; three which might be considered important are

(I)   :N = N = O: :N = N = N:
                                        \
                                         H

(II)   :N ≡ N – O: :N ≡ N – N:
                                        \
                                         H

(III)   :N – N ≡ O: :N – N ≡ N
                                        \
                                         H

The rule given by Pauling[2] that structures of the type III make little contribution, by reason of the instability associated with formal charges on adjacent atoms, is confirmed by the present investigation.

Let the interatomic distances in the molecules be labeled as follows

r_1 r_2 r_3 r_4
N—N—O   N—N—N
                                    \
                                     H

For resonance between structures I + II Pauling has predicted,[3] using known bond radii, that $r_1 = 1.12$ Å. and $r_2 = 1.19$ Å. When III is included, the values are $r_1 = 1.15$ Å. and $r_2 = 1.07$ Å. A similar calculation gives $r_3 = 1.12$ Å.

and $r_4 = 1.24$ Å. for I + II and $r_3 = r_4 = 1.15$ Å. for I + II + III.

Experimental.—The apparatus used has been described in a previous article.[4] The wave length of the electrons, 0.0616 Å., was determined from transmission pictures of gold foil, taking $a_0 = 4.070$ Å.

The nitrous oxide, which was taken from a commercial tank, was stated by the manufacturers to be 99.75% pure. Ten photographs were taken at a camera distance of 10.82 cm. from gas nozzle to film, and four at a camera distance of about five cm. These showed a series of heavy rings joined with shelf-like rings about half as intense on the side of greater scattering angle. Except for a more rapid damping of the intensity of the features with increasing scattering angle, the nitrous oxide photographs were very similar to those which have been taken of carbon dioxide in this Laboratory.[5] The features of the nitrous oxide pictures, which were examined out to the sixteenth maximum, corresponding to s values of over forty, did not reveal any definite departure from the regularity characteristic of the carbon dioxide photographs. Since measurements of the first ten maxima and minima yielded sufficient data for the evaluation of the long interatomic distance, it was not attempted to measure the faint features at higher s values.

Anhydrous hydrogen azide was prepared by the method of Dennis and Isham[6] and distilled. Photographs were taken of the vapor at the vapor

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(2) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 294 and 498 (1932); L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 13 (1937).

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(4) L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

(5) V. Schomaker and D. P. Stevenson, unpublished investigation.

(6) L. M. Dennis and Helen Isham, THIS JOURNAL, **29**, 216 (1907).