similar to the origin in the mixed crystal spectrum. The origin appears to be absent from the weak component. Unlike the origin, which is completely polarized, the vibrational structure in the transition becomes increasingly depolarized toward higher energies, indicating a perturbation by a higher transition which is polarized oppositely to the ${}^1L_b \leftarrow {}^1A$, ${}^1B_1 \leftarrow {}^1A_1$ transition. The moderately intense transition at 26000 cm.$^{-1}$ (log ϵ 3.5) has been assigned as a ${}^1L_a \leftarrow {}^1A$, ${}^1A_1 \leftarrow {}^1A_1$ transition in section (A) of the Discussion. The crystal spectrum for this transition is too broad to enable the origin to be located, but the intensity dichroism is opposite to the ${}^1L_b \leftarrow {}^1A$ transition in the crystal, in agreement with the ${}^1L_a \leftarrow {}^1A$ assignment. Therefore, it seems likely that this transition, which is fairly close in energy to and much more intense than the ${}^1L_b \leftarrow {}^1A$ transition, may be perturbing the higher vibrational levels of the ${}^1L_b \leftarrow {}^1A$ transition, due to second-order crystal-induced mixing of molecular states belonging to different irreducible representations of the point group of the free molecule.[4a,38] This may occur only if the factor group of acepleiadiene crystal is lower than the assumed C_{2v} symmetry of the free molecule. Further interpretations must await additional knowledge about the structures of these unusual hydrocarbons.

Conclusions

The electronic spectra of acepleiadiene and acepleiadylene have been measured, analyzed and interpreted. The conclusions have been applied to several problems in molecular structure. The results appear to support the Platt FEMO theory and the Moffitt perturbation theory in several respects. It is hoped that additional experimental and theoretical work will lead to a more comprehensive understanding of the properties and structure of peri-condensed hydrocarbons.

Acknowledgments.—It is a great pleasure to acknowledge the generosity of Professor V. Boekelheide, who supplied the acepleiadylene and acepleiadiene used in these experiments. The sample of pure pyrene was obtained from Professor M. Szwarc, to whom I am also grateful. Finally, I wish to acknowledge the continued interest and encouragement of Professor A. B. F. Duncan, who greatly facilitated numerous matters connected with the low temperature research.

ROCHESTER, N. Y.

[CONTRIBUTION NO. 454 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Infrared Spectra of Aromatic Compounds. IV. The Nitro Valence Vibrations in *p*-Disubstituted Nitrobenzenes[1]

BY ROBERT D. KROSS AND VELMER A. FASSEL

RECEIVED MARCH 21, 1956

The characteristic nitro asymmetric and symmetric frequencies of *para*-substituted nitrobenzenes are correlated with structure related parameters which are sensitive to the electronic effect of the *para*-substituent on the nitrobenzene nucleus. It is shown that molecular dipole moments, as well as Hammett's σ constants for the *para* groups, yield straight line curves when plotted against the corresponding nitro asymmetric frequency. A plot of nitro asymmetric *vs.* symmetric frequency yields a discontinuous curve, the reasons for which are discussed. Evidence is also presented which places the C–NO_2 stretching frequency in aromatic nitro compounds in the 1300 cm.$^{-1}$ region.

In *para*-substituted nitrobenzenes, the nitro asymmetric stretching vibration usually appears in the frequency range 1500–1560 cm.$^{-1}$. When the *para* substituent is an electron donating group the frequencies fall in the lower end of this range.[2] On the other hand, the nitro symmetric stretching vibration, which usually appears in the 1300–1350 cm.$^{-1}$ region is generally less affected by *para* substituents, although strong electron donors usually give rise to the lowest frequencies. A recent study by Brown[3] related frequency changes in CNO_2 group vibrations to the electronic effects of neighboring constituents. The conclusions reached by Brown agree in principle with interpretations made by us in an independent unpublished study. The data presented in this paper provide a more complete examination of these interpretations as applied to *p*-disubstituted nitrobenzenes and suggest other correlations with structure related parameters. Evidence is also presented which places the C–N stretching frequency in aromatic nitro compounds in the 1300 cm.$^{-1}$ region.

Experimental

Solid spectra of all the compounds as nujol mulls were recorded on a Baird Associates model B double beam infrared spectrophotometer, with a calibration spectrum of polystyrene superimposed on each chart. Chloroform and bromoform, respectively, were used as solvents for obtaining the solution spectra in the 1300–1350 and 1500–1560 cm.$^{-1}$ region. The bands exhibited by chloroform in the 1500–1560 cm.$^{-1}$ region precluded its use as solvent for this frequency range. All solution spectra were obtained with 0.4 mm. cells on a Perkin–Elmer model #13 double beam infrared recording spectrophotometer. The data are presented in Table I.

Results and Discussion

I. The Nitro Asymmetric Stretching Vibration.—Brown[3] has shown that the asymmetric stretching frequency is primarily determined by the N–O bond order, and consequently the N–O stretching force constant. Since bond orders are determined by the relative contribution of reso-

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] (a) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 250. (b) R. R Randle and D. H. Whiffen, *J. Chem. Soc.*, 4153 (1952).

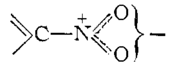
[3] J. F. Brown, Jr., THIS JOURNAL, **77**, 6341 (1955).

TABLE I

No.	Compound	Nitro asym. freq., cm.$^{-1}$ Soln.[a]	Nitro asym. freq., cm.$^{-1}$ Solid	Nitro sym. freq., cm.$^{-1}$ Soln.[b]	Nitro sym. freq., cm.$^{-1}$ Solid	σ Constant (group)	Dipole moment, Debye
1	Sodium *p*-nitrophenoxide		1501		1338		
2	*p*,*p*′-Dinitrodiphenyl disulfide		1504	1342	1336		
3	*p*-Nitrodiphenylamine	1505	1526	1329	1324		
4	*p*-Nitroaniline	1507	1504	1336	1333	−0.660[4]	6.3[5]
5	*p*,*p*′-Dinitrodiphenyl sulfide		1511		1337		
6	*p*-Nitro-*p*′-methyldiphenyl sulfide	1513	1507	1340	1335		
7	*p*-Nitrophenol	1513	1515	1342	1342	−0.357[8]	5 03[5]
8	Benzaldehyde *p*-nitroanil		1513	1341	1330		
9	*p*-Nitroanisole	1514	1517	1340	1342	−0.268[4]	4.753[11]
10	*p*,*p*′-Dinitrodiphenyl		1514		1340		
11	*p*-Nitrophenylacetic acid		1515	1352	1342		
12	*p*-Nitroacetanilide		1515		1335		
13	*p*-Nitrotoluene	1517	1517	1347	1344	−0.170[4]	4.4[5]
14	*p*-Nitrodiphenyl	1518	1510	1348	1342	−0.017[6]	4.28[7]
15	Sodium *p*-nitrobenzeneazo-salicylate		1518		1344		
16	Sodium *p*-nitrobenzoic acid		1521		1351		
17	*p*-Nitrodimethylaniline		1522	1320	1316	−0.600[8]	6.15[12]
18	*p*-Nitrophenylacetonitrile	1523	1512	1350	1341	−0.007[8]	3.84[9]
19	*p*-Nitrobenzyl bromide	1523	1534	1351	1345	0.22[13]	3.55[9]
20	Ethyl *p*-nitrocinnamate	1524	1517	1348	1341		
21	*p*-Nitrobenzonitrile		1524	1349	1348	0.628[8]	0.7[5]
22	*p*-Nitrochlorobenzene	1526	1526	1348	1343	0.227[4]	2.6[5]
23	*p*-Nitroiodobenzene	1526	1513	1349	1345	0.276[4]	3.045[10]
24	*p*-Nitrobromobenzene	1527	1532	1352	1345	0.232[4]	2.5[5]
25	*p*-Nitrocinnamic acid		1527	1340	1348		
26	*p*-Nitrobenzyl chloride	1527	1535	1351	1346	0.24[13]	3.55[9]
27	*p*-Nitrophenylglycine		1529	1335	1315		
28	*p*,*p*′-Dinitroazoxybenzene	1530	1528	1349	1343		
29	Methyl *p*-nitrobenzoate	1530	1535	1352	1348	0.636[d,8]	
30	*p*-Nitrobenzeneazoresorcinol		1530	1337	1340		
31	*p*-Nitromethylaniline		1532	1327	1315		
32	*p*-Nitrobenzaldehyde	1533	1533	1348	1343	1.126[d,4]	2.4[5]
33	*p*-Nitrobenzoic acid	1537	1541	1350	1351	0.728[d,4]	4.02[14]
34	*p*-Dinitrobenzene	1553	1560	1362	1344	1.27[d,4]	0.2[15]
				1343[c]			
	Av. values	1523	1525	1344	1339		
	Av. dev.	±8	±10	±7	±7		

[a] In bromoform. [b] In chloroform. [c] Average value of 1352 used in correlations. [d] σ^* values (see text).

nance forms I and II to the over-all structure, an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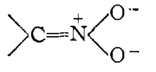
II

increase in the contribution of form II should result in lower asymmetric stretching frequencies. Strong electron donors substituted in the *para*-position of nitrobenzene have just this effect, hence the lowest frequencies are shown by these compounds, as is evident from the frequency data summarized in

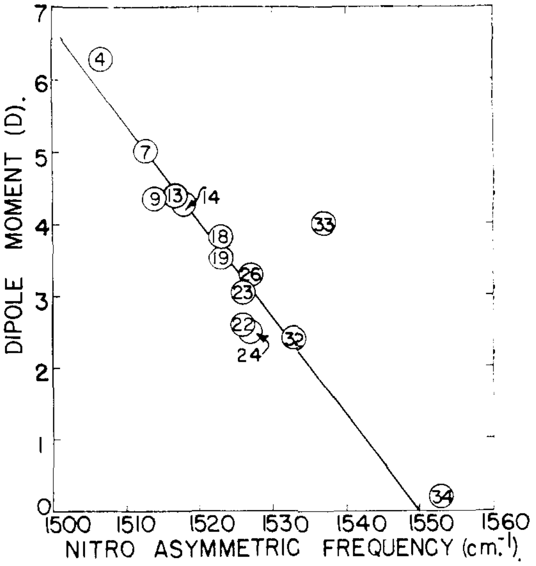

Fig. 1.—Plot of nitro asymmetric stretching frequency of *p*-substituted nitrobenzenes *vs.* dipole moment of the molecule.

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(4) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, pp. 186–194.

(5) R. J. W. LeFèvre, "Dipole Moments," Methuen Monograph, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 134.

(6) E. Berliner and L. H. Liu, THIS JOURNAL, **75**, 2417 (1953).

(7) E. Naeshagen, *Z. physik. Chem.*, **B25**, 157 (1934).

(8) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(9) C. P. Smyth and W. S. Walls, THIS JOURNAL, **54**, 1854 (1932).

(10) H. Poltz, *Z. physik. Chem.*, **B20**, 351 (1933).

(11) H. L. Donle and K. A. Gehrckens, *ibid.*, **B18**, 316 (1932).

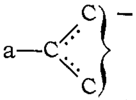
(12) E. Hertel and E. Dumont, *ibid.*, **B30**, 139 (1935).

(13) F. L. J. Sixma, *Rec. trav. chim.*, **72**, 673 (1953).

(14) C. J. Wilson and H. H. Wenzke, THIS JOURNAL, **57**, 1265 (1935).

(15) C. G. LeFèvre and R. J. W. LeFèvre, *J. Chem. Soc.*, 957 (1935).

Table I. A direct consequence of an increase in the contribution of the more ionic resonance form II to the over-all structure is an increase in the dipole moment of the compound. Thus, the dipole moment and nitro asymmetric stretching frequencies should be inversely related; this is confirmed by the data plotted in Fig. 1. The only point showing marked deviation from the curve is *p*-nitrobenzoic acid. However, because the *para*-carboxyl group sets up a large dipole in opposition to that of the nitro group, the reported dipole moment of *p*-nitrobenzoic acid is surprisingly high. The small scatter of the other points from the line suggests that the dipole moments for these molecules are primarily determined by the moment associated with the nitro group.

Jaffé[16a] has shown that Hammett's substituent constants[17] for *para* groups (σ_p) can be related to changes in the electron density at the carbon atom *para* to the substituent. For disubstituted benzenes (*e.g.*, *p*-substituted nitrobenzenes) the energies associated with localization of an electron pair in an atom of a  type side chain are found to be nearly proportional to σ_p^* constants.[16b] The latter have different, and distinctly higher values for those groups which lead to a larger-than-usual contribution of the *p*-quinoid structure to the ground state of the molecule. The nitro group falls in this category. For groups which are not of this type, it is presumed that σ_p^* and σ_p^* values merge, so that no distinct σ_p^* values exist (*i.e.*, in such cases, σ_p values would be proportional to electron density changes at the side chain atom as well as the *para* ring carbon).

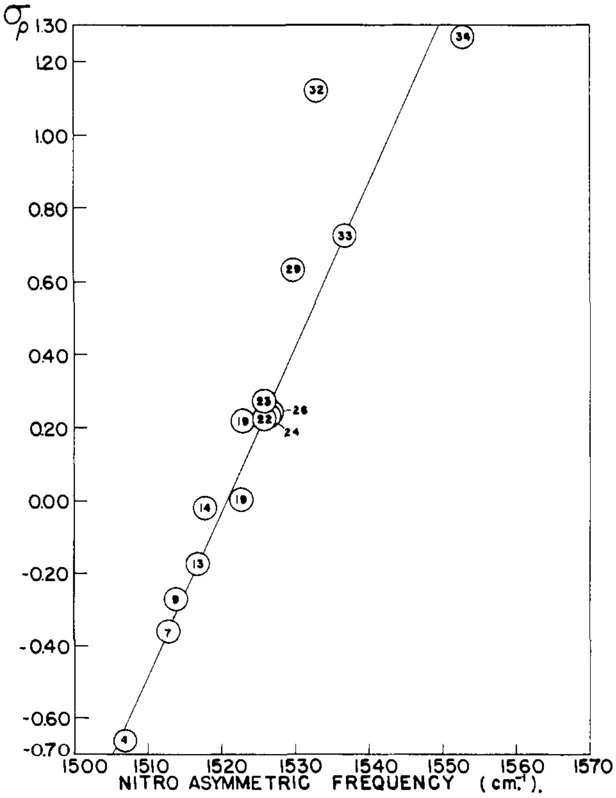


Fig. 2.—Plot of nitro asymmetric stretching frequency *vs.* Hammett's σ_p constants for correspondingly substituted *p*-substituted nitrobenzenes.

From the foregoing considerations, the value of Hammett's σ_p and σ_p^* constants, the frequency of the asymmetric stretching vibration, and the dipole moment should all show simple interrelations, as verified by Figs. 2 and 3. For reasons not yet apparent, σ_p values, exclusively, form a linear plot with dipole moments. The CHO point in Fig. 2 is apparently too high. From Jaffé's plot of localization energy *vs.* σ constant[16b] it appears that a value of ~0.6 would be more nearly correct, and would also be in much better agreement with the curve in Fig. 2.

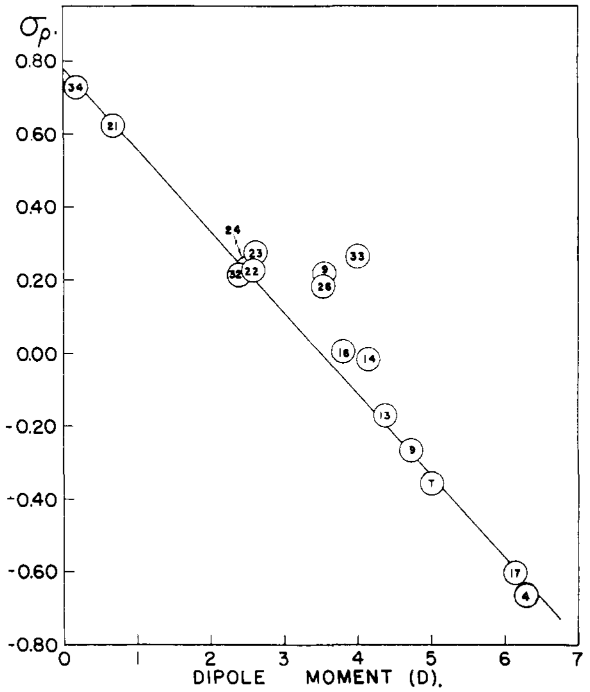


Fig. 3.—Plot of σ_p constants *vs.* dipole moments of *p*-substituted nitrobenzenes.

II. The Nitro Symmetric Stretching Vibration.—Brown[3] has noted that the nitro symmetric stretching vibration is in part influenced by the stretching of the C–N bond. Thus, *para* substituents will affect both asymmetric and symmetric stretching frequencies in a parallel manner only if the same C–N bond order is maintained.[3] Furthermore, a plot of these two frequencies should be linear if the C–N bond order changes at a constant rate. This condition is approximately obtained for electron donating groups, as shown in the lower portion of Fig. 4. The substitution of electron withdrawing groups in the para position causes an abrupt change in the C–N bond order, which is evidenced by the sharp break in the curve. (This break occurs almost precisely at a σ constant of

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[16] (a) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279, 778, 1554 (1952); (b) THIS JOURNAL, **76**, 5843 (1954).

[17] Although Brown has made a similar correlation, the more specific nature of this paper permits a more detailed and extensive treatment of σ_p constants and their relation to the nitro frequencies.

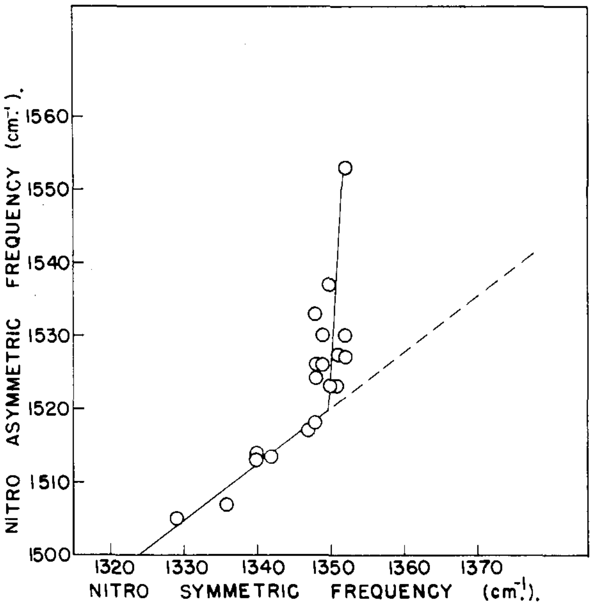


Fig. 4.—Relation between nitro symmetric and asymmetric stretching frequencies in *p*-substituted nitrobenzenes.

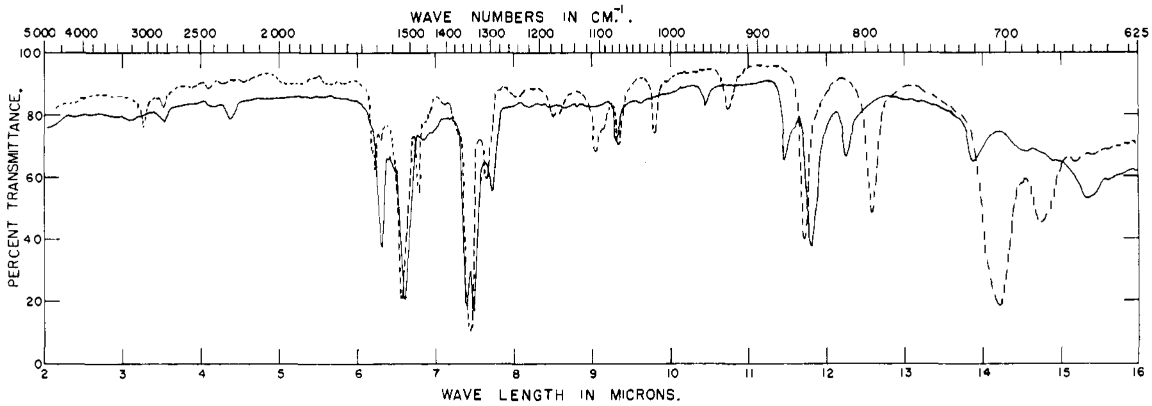
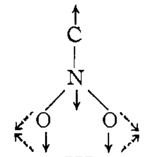


Fig. 5.—Spectra of nitrobenzene (- - - -) and pentadeuteronitrobenzene (———).

zero, since the lowest point on the top curve corresponds to a σ_p of 0.007, and the highest point on the lower curve corresponds to a σ_p of -0.017). Above the point of discontinuity, the changing C–N bond order results in the appearance of the nitro symmetric vibration at lower frequencies than would be expected from consideration of the increasing N–O force constants. The combined effect of the decreasing C–N bond order and the increasing N–O bond order is the maintenance of the nitro symmetric frequency at a nearly constant value.

III. The C–N Stretching Vibration.—Since most aromatic nitro compounds show a band in the 860 cm.$^{-1}$ region, and since the C–N stretching vibration of aliphatic nitro compounds also appears near this frequency,[18] the corresponding vibration in aromatic compounds has been arbitrarily assigned to this region. However, Brown[3] has pointed out that the varying bond order in diverse aromatic nitro compounds should lead to less constant C–N stretching frequencies. This led Brown to conclude that the frequency of the C–N stretching vibration is still uncertain.

The CNO$_2$ stretching mode illustrated in III[3] shows that the stretching of the C–N bond is accompanied by a simultaneous symmetric motion of the N–O bonds. This motion can be resolved into components along and perpendicular to the direction of a symmetric nitro stretching vibration. Just as the nitro symmetric frequency is influenced by the bond order of the C–N bond, so it is to be expected that the C–N stretching vibration will be influenced by the bond order of the N–O bonds, since the latter have vibrational components along the direction of the nitro symmetric vibration. When the double bond character of the C–N bond decreases from compound to compound, the order of the N–O bonds simultaneously increases. The net effect should be a tendency toward stabilization of the C–N stretching vibration to a narrower frequency range than would be expected for the large bond order changes in these compounds.



III

A comparison of the spectra of nitrobenzene and pentadeuteronitrobenzene (as provided by Fig. 5) should aid in the identification of the CNO$_2$ group fundamentals. Excluding the invariant ring stretching vibrations, there are two bands which are only slightly affected by the complete deuteration. These are the bands at about 850 and 1300 cm.$^{-1}$. All the *para*-substituted nitrobenzenes show bands very close to these frequencies. The 850 cm.$^{-1}$ frequency is often overlapped by the C–H out-of-plane bending frequency of *para*-substituted nitrobenzenes,[19] and the 1300 cm.$^{-1}$ frequency is generally surrounded by two or three other bands of equivalent intensity. It is therefore difficult to correlate the frequencies of these bands with the frequencies of the nitro stretching vibrations. In view of the partial double bond character of the C–N bond, the assignment of the C–NO$_2$ stretching

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[18] D. C. Smith, C. Y. Pan and J. R. Nielsen, *J. Chem. Phys.*, **18**, 706 (1950).

[19] M. Margoshes and V. A. Fassel, *Spectrochim. Acta*, **7**, 14 (1955).

vibration to the 1300 cm.$^{-1}$ region appears to hold more merit.

Acknowledgment.—The authors would like to express their gratitude to Professor Gwynn Williams of Royal Hollaway College, England, for the sample of pentadeuteronitrobenzene he provided for this study.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Infrared Study of the Acetone–Water System

BY PETER J. LUCCHESI[1]

RECEIVED APRIL 12, 1956

The infrared spectrum of liquid acetone gives a sharp absorption band at 3400 cm.$^{-1}$ and a broader band at 3600 cm.$^{-1}$. The latter increases in intensity upon addition of small quantities of water to the sample and is attributed to traces of water. Beer's law is not obeyed. The band does not disappear completely after repeated drying of acetone. The 3600 cm.$^{-1}$ band decreases in intensity when crystalline powders are mixed with the acetone–water solutions. This band can be considered a result of intermolecular hydrogen bonding, whereas the 3400 cm.$^{-1}$ band is probably the overtone of the carbonyl band which occurs at 1740 cm.$^{-1}$.

Introduction

It was the purpose of this investigation to study the changes in the infrared absorption spectrum of liquid acetone caused by the presence of small amounts of water, and to determine whether such effects could be useful in gaining insight into the interaction between water and carbonyl compounds at low water concentrations.

Bawn,[2] Lecomte,[3] and Marton[3] have reported an absorption band for liquid acetone which occurs in the infrared region of 2.90 μ. Water vapor also absorbs in this region, the absorption having been assigned to the overlapping of the ν_3 and ν_1 fundamentals. This band, as expected, is shifted to lower wave numbers in the condensed phase so that the net effect observed is that the spectrum of liquid acetone containing small amounts of water gives a sharp absorption band at 3400 cm.$^{-1}$ and a broader band in the 3600 cm.$^{-1}$ region. The band at 3400 cm.$^{-1}$ is not significantly altered by the addition of small amounts of water to the sample, whereas the absorption at 3600 cm.$^{-1}$ increases with increasing concentration of water in acetone. This increase is obvious from Fig. 1, which was reproduced from the spectra recorded by the spectrophotometer. The ν_2 fundamental of water, which occurs at 1595 cm.$^{-1}$,[4] is masked in acetone solutions by the strong absorption of the solvent in this region. The absorption in the 3400 cm.$^{-1}$ region has been observed at slightly higher wave numbers in the gas phase, and is known to occur in the liquid phase for some ketones, aldehydes and alcohols.[5] The effect of adding traces of water to acetone gives some insight regarding the nature of 3400 and 3600 cm.$^{-1}$ bands observed. Although intermolecular hydrogen bonds give absorption in the former region,[6] the low concentration of the enol form to be expected for acetone, and the fact that the 3400 cm.$^{-1}$ band is little changed by the addition of water, show that this band is not due to such bonds. A likely possibility is that the band represents the first overtone of the carbonyl band, which occurs near 1740 cm.$^{-1}$. The band at 3600 cm.$^{-1}$, however, is strongly affected by traces of water and the absorption in this region is most likely due to intermolecular hydrogen bonding between acetone and water. The strength of this interaction is evidenced by the extreme difficulty observed in attempts to eliminate the 3600 cm.$^{-1}$ absorption by repeated drying of the acetone.

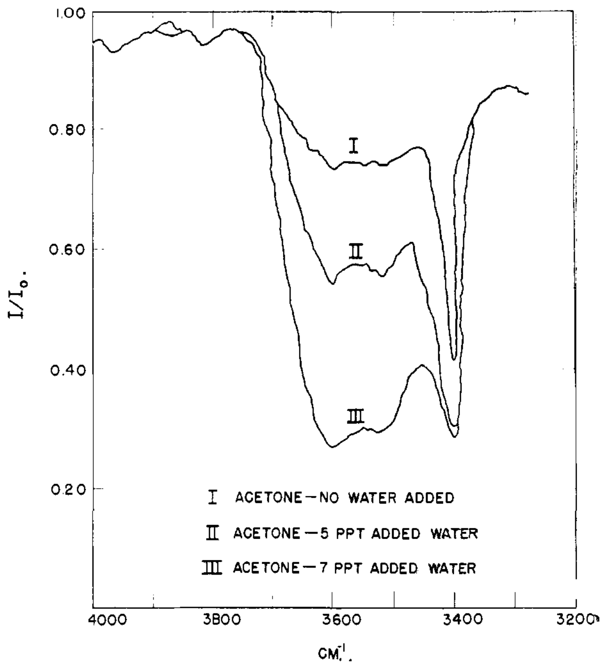

Fig. 1.—Spectrum of acetone-water mixtures in the 3600 cm.$^{-1}$ region. Curve I represents purified acetone; curves II and III show the effect of adding 5 and 7 p.p.t. by volume of water to the sample.

Experimental

The acetone used as starting material was obtained from the Eastman Kodak Company. The purification of this acetone was accomplished using the method of Shipsey and

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[1] Esso Research and Engineering Co., Linden, New Jersey.

[2] C. E. H. Bawn, *J. Chem. Soc.*, **135**, 1189 (1932).

[3] J. Lecomte, *Compt. rend.*, **180**, 1481 (1925); L. Marton, *Z. physik. Chem.*, **117**, 97 (1925).

[4] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 487.

[5] American Petroleum Institute Research Project 44, "Infrared Spectral Data," 1953.

[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1954.