The Near Ultraviolet Absorption Spectra of Acetophenone and Benzophenone Vapors and the Long Wave-lengths Absorption System of Benzaldehyde Vapor

By Sunao IMANISHI, Kimio SEMBA, Mitsuo ITO and Toshinobu ANNO

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Introduction

Recently, one of the authors⁽¹⁾ analyzed the near ultraviolet absorption band system lying in the 2480-2970 A. region and arising from the electronic transition of the type $^1A_1-^1B_1$, which is allowed in C_{2v} symmetry, of the benzaldehyde molecule. The present paper is concerned with similar attempts for the acetophenone and benzophenone spectra, together with some accounts on another, wave absorption region in the benzaldehyde spectrum which has longer wave-lengths than that mentioned above.

Absorption measurements for acetophenone and benzophenone in alcohol or hexane solutions have been reported, but their vapor spectra have not been studied in detail.⁽²⁾ There are two absorption regions in each of these spectra, just as in the case of benzaldehyde. The long wave-lengths absorption region fo acetophenone, and both the short and long wave-lengths regions of benzophenone are continuous. Only the short wave-lengths absorption region of acetophenone has a discrete band structure, which, however, is much more diffuse than that of the benzaldehyde referred to above. The general diffuseness of these spectra are attributable to the introduction of heavier and more complicated substituents into the molecule.

Experimental

The spectra of acetophenone and benzophenone were photographed with a Hilger $E-2$ medium quartz spectrograph having a linear dispersion of about 10 A. per mm. at 2700 A. The absorption cell was a quartz tube 40 cm. in length and 3 cm. in diameter, to which a side recess was attached for placing the substance to be investigated in liquid form and sealed in a small thin-walled glass ampoule. The cell was evacuated and the liquid was vaporized by raising the temperature of the cell in an electrically heated mantle, after

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(1) S. Imanishi, *J. Chem. Phys.*, **19**, 389 (1951).

(2) Y. Hukumoto, *Sci. Rep. Tohoku Univ.*, **25**, 1162 (1936). S. Kato and F. Someno, *Sci. Pap. Inst. Phys. Chem. Res.*, **12**, 329 (1944)

breaking the ampoule containing the liquid. The continuous background was supplied by a water-cooled hydrogen discharge lamp consuming about 2.5 kW. at 5,000 volts terminal voltage. To cover the great change in absorbance of the vapors with wave-length it was necessary to make many exposures, each of 40 min. duration on Fuji panchromatic plates, at different temperatures of the vapor and liquid, ranging from 20 to 100°C for acetophenone, and from 70 to 170°C for benzophenone. Iron arc was used to supply the comparison spectrum for the calibration of wave-lengths. Wave-lengths were determined from dispersion curves for each set of measurements of a spectrogram negative.

Acetophenone used was supplied by Takeda-Seiyaku Co. Ltd., and was redistilled before use, and benzophenone was synthesized from benzene and benzoyl chloride which had been prepared by the chlorination of benzoic acid in the presence of phosphorus pentachloride in carbon disulfide solution. The sample thus obtained was purified and distilled several times in vacuum.

Table 1

Wave-lengths Regions of Absorption (A.)

Substance	Long wave-lengths region		Short wave-lengths region	
	Vapor	Liquid	Vapor	Liquid
Acetophenone	3060 ~3500	3204 (alc. sol.)(3)	2480 ~2610	2785 (alc. sol.)(3)
Benzophenone	3270 ~3510	3389 (hexane sol.)(4)	2500 ~2910	2550 (hexane sol.)(4)

Analysis and Interpretation of Spectra

Short Wave-lengths Absorption Regions of Acetophenone and Benzophenone

The symmetry of the carbon-oxygen skeleton of the acetophenone molecule belongs to the point group C_s, in which the electronic transition derivable from the forbidden transition ${}^1A_{1g}-{}^1B_{2u}$ of the benzene molecule (D_{6h} symmetry) is of the type $A'-A'$, and is allowed in this symmetry having the transition moment in the plane of symmetry, *i. e.* the molecular plane. The electronic terms of representations A_{1g} and B_{2u} in D_{6h} symmetry go over into the A_1 and B_1 terms in molecules of C_{2v} symmetry, and the transition between these two terms is allowed having the transition moment in the molecular plane and perpendicular to the C_2 axis. The vibrational structures in the strong absorption systems lying in the 2500~2800 A. region of mono-substituted benzenes, *e. g.* mono-chlorobenzene(5) and benzaldehyde,(1) have been analyzed from this viewpoint. In these substituted benzene spectra the "forbidden" character of the benzene 2650 A. system still remains in that non-totally symmetric vibrations of proper symmetries, excited to an odd quantum state, can interact with the electronic transition to make bands bearing their frequencies to be observed.

Now, the B_1 term in C_{2v} is symmetric with respect to the molecular plane and anti-symmetric with respect to the plane perpendicular to it, so that by dropping the latter symmetry element both A_1 and B_1 terms go over into A' type terms in C_s.(6)

Wave-numbers of the observed band heads in the acetophenone short wave absorption are given in Table 2.

The strong and sharp head at 35375 cm^{-1} is taken to be the 0,0 vibrational transition.

Table 2

The Short Wave-lengths Absorption Bands of Acetophenone Vapor

Wave-length A.	Wave-number cm.$^{-1}$	Intensity	Distance from the 0,0 band cm.$^{-1}$	Combination
2826	35375	s.	0	0,0
2797	35742	v. w.	367	0,367
2783	35922	v. w.	547	0,547
2752	36326	s.	951	0,954
2724	36700	w.	1325	0,367+954
2711	36876	w.	1501	0,547+954
2681	37288	m. w.	1913	0,2×954
2645	37796	v. w.	2421	0,547+2×954
2615	38230	v. w.	2855	0,3×954

In the intensity column: s. strong; w. weak; m. medium.

Table 3

Fundamental Vibration Frequencies of the Acetophenone Molecule found in U. V. Absorption

Raman effect (ground state)(7)			U. V. Absorption (excited state)	Symmetry	
$\Delta\nu$ cm.$^{-1}$	Intensity	Depolarization Factor ρ		C_{2v}	C_s
368	3b	p?	367	α_1	α'
406	1/2	—			
617	6s	0.78	547	β_1	α'
999	15s	0.10	954	α_1	α'

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(3) J. Bielecki and V. Henri, *Ber.*, **47**, 1690 (1914).

(4) International Critical Tables, Vol. V.

(5) H. Sponer and S. H. Wollman, *J. Chem. Phys.*, **9**, 816 (1941).

(6) H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 75 (1941).

This band and the three bands at 36326, 37288, and 38230 cm.$^{-1}$ form the main progression, giving a frequency interval of 954 cm.$^{-1}$, which is the mean value obtained from these four bands and other bands containing multiples of this frequency in combination with other fundamentals. This 954 cm.$^{-1}$ must be the excited state value of the 999 cm.$^{-1}$ frequency found in the Raman effect for this substance. The intensity decreases regularly along this progression in accordance with the Boltzmann law. Two weak bands with wave-numbers 35742 and 35922 cm.$^{-1}$ are separated from the 0,0 band by 367 and 547 cm.$^{-1}$, respectively, on its violet side. These distances probably represent the upper state values of the 368 and 617cm.$^{-1}$ ground state frequencies observed in Raman effect, and are analogues of the 404 and 549 cm.$^{-1}$ excited state frequencies of the benzaldehyde molecule observed in ultraviolet absorption,(1) whose ground state values are 439 and 623 cm.$^{-1}$, respectively. We may apply to these bands the same interpretation as done for benzaldehyde, and say that they arise from the splitting of the degenerate 606 cm.$^{-1}$ (ground state value) $\mathcal{E}_g^+$ vibration of the benzene molecule into one of the β_1 type non-totally symmetric vibration of a frequency nearly of the unchanged magnitude, and another of the α_1 type totally symmetric vibration of a much lower frequency in going over into mono-substituted benzenes having C_{2v} symmetry. In such cases usually the α_1 type vibration appears with a much higher intensity than the β_1 type. In acetophenone, however, these bands are observed with almost the same intensity. This may be understood if we assume that the symmetry of the molecule is still lowered to C_s, and, by the same reason as stated above for the electronic states (which applies as well to the symmetry properties of molecular vibrations), the two types of vibration have become indistinguishable. On the other hand, polarization measurements of Raman lines clearly indicate the C_{2v} characters of these vibrations as seen in Table 3, so that we may consider there still remains a pronounced two-fold axis in the acetophenone molecule.

Other bands on the shorter wave-length side are all very diffuse, but several peaks can be measured and assigned to combinations of the fundamental frequencies found above as given in Table 2.

The short wave-lengths absorption of benzophenone vapor (2910-2500 A.) is continuous as stated earlier. This is to be expected because chances of the occurrence of predissociation increase as the molecule becomes more complex, and although this absorption region arises from electronic transition of the same type as the acetophenone short wave region, it has lost the discrete vibrational structure possessed by the latter.

Long Wave-lengths Absorption Regions of Acetophenone, Benzophenone and Benzaldehyde

The absorption region between 3060 and 3500 A. of acetophenone and that between 3270 and 3510 A. of benzophenone are both very weak and continuous. In connection with these weak absorptions, we may consider the corresponding long wave absorption bands of benzaldehyde vapor previously reported by Almasy.(8) This system (Almasy's première région) extends from 3160 to 3747 A., and contains a large number (159 measured by Almasy) of narrow weak bands, showing a pronounced group appearance. We have reexamined this region using the 1st. order of a 3 meter focus concave grating spectrograph,

Table 4

Long-wave Absorption System in Benzaldehyde Vapor

Wave-number cm.$^{-1}$	Relative intensity	Wave-number distance from band 26915 cm.$^{-1}$	Vibrational assignment
26892	s.	−23	
26915 } 28	v. s.	0	0
26943	v. s.		
26973	s.		
27636	s.	721	721
28005	s.	1090	1090
28098	s.		
28156	s.		
28229 } 24	v. s.	1314	1310
28253	s.		
28280	s.		
28357	m.	1442	2×721
28386	s.		
28949	m.	2031	721+1310
29319	s.	2404	1090+1310
29340	s.		
29404	s.		
29440	s.		
29528 } 31	v. s.	2613	2×1310
29559	v. s.		
30259	s.	3344	721+2×1310
30627	s.	3713	1090+2×1310
30842	m.	3927	3×1310

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(7) K. W. F. Kohlrausch, "Ramanspektren", Akademische Verlagsges. Leipzig, 1943.

(8) F. Almasy, *J. Chim. Phys.*, **30**, 528, 634, 713 (1933).

and an absorption path of 1 meter at saturation pressures of benzaldehyde corresponding to 180°C at the highest (over 1 atmosphere). The total absorption intensity of this system appears to be of the order of 10^{-3} or smaller compared with that of the short wave system. Stronger bands in this system, according to our measurements, are listed in Table 4, together with probable vibrational assignments.

The three excited state frequencies 721, 1090 and 1310 cm.$^{-1}$ found in the above analysis may be identified in mode with the ground state frequencies of the benzaldehyde molecule 799, 1208 and 1434 cm.$^{-1}$, respectively, found in the analysis of the short wave absorption system.(1) All of these are of the α_1 type, and the ratio of the excited state value to the ground state value is 0.90 in all cases. The completely different appearances of the vibrational structures of the short and the long wave systems are due to the fact that no common vibrational modes are excited in the respective upper electronic states. This may be understood by considering the difference in nature of the two upper electronic states as stated below, but the fact that the carrier molecule is the same for the two systems is established unambiguously by the relations found above.

McMurry(9) has discussed, using mainly liquid phase data, the elctronic transition of the long wave-lengths absorption near 3500 A. invariably appearing in spectra of aliphatic and aromatic aldehydes and ketones, and has concluded that the upper state of this transition is the one which arises from the excitation of one of the non-bonding electrons localyzed on the oxygen atom of the C=0 group, while the short wave system corresponds to the excitation of the ring π electron. The weakness of the long wave absorption is attributed to the fact that its upper state is one of the ^1E states theoretically predicted by Mulliken, to which the electronic transition from the ground state ^1N is forbidden.

Assuming this interpretation to be true, and if the forbiddenness is due to the symmetries of the electronic eigenfunctions, the band 26915 cm.$^{-1}$, the strongest first member of the progression with the 1310 cm.$^{-1}$ interval which is arbitrarily chosen as the origin in the above analysis (Table 4), may not be the 0,0 band of the system, and the 0,0 frequency may lie, just as in th case of the benzene 2650 A. forbidden transition, at a still longer wave-length shifted by the frequency of a certain non-totally symmetrical vibration which makes this system to be observed on the spectrum.

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Chmical Laboratory, Faculty of Science,
Kyushu University, Fukuoka.

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(9) H. L. McMurry, *J. Chem. Phys.*, **9**, 231, 241 (1941).