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# Vacuum-ultraviolet Absorption Spectra of Aliphatic Ketones

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The molar-absorptivity curves of various aliphatic ketones, mainly methyl alkyl ketones, in the gaseous state in the region from 1650 to 2000 Å have been obtained. In these ketones the absorption bands near 1950 Å and 1700 Å are denoted as A and B bands respectively. Di-*n*-propyl and diisopropyl ketones show, besides the A and B bands, an absorption band near 1650 Å (C band). The relations between the obtained spectra and the molecular structures of these ketones have been studied. On the basis of this study, the characteristics of the electronic transitions of A, B, and C bands have been discussed.

Up to now, there have been few data about absorption spectra in the vacuum-ultraviolet region. The number of molar absorptivity curves of organic compounds reported in this region have been especially few. Though the absorption spectra in this region are not so easily obtainable as those in the visible and near-ultraviolet regions, they may well provide much important information about structural and analytical chemistry.

Aliphatic ketones have, beside the $n \rightarrow \pi^*$ bands near 2800 Å and the $\pi \rightarrow \pi^*$ bands near 1550 Å, two or three moderately intense absorption bands in the range from 2000 to 1650 Å.[1-5] As for these absorption bands in the range from 2000 to 1650 Å, no accurate molar-absorptivity curves have been reported except for that of acetone.[2] In this work the molar-absorptivity curves of various aliphatic ketones, mainly methyl alkyl ketones, in the gaseous state, have been measured in the region from 2000 to 1650 Å; their relations to the molecular structures of the ketones will be discussed.

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[1] R. S. Holdsworth and A. B. F. Duncan, *Chem. Revs.*, **41**, 311 (1947).

[2] J. S. Lake and A. J. Harrison, *J. Chem. Phys.*, **30**, 361 (1959).

[3] E. E. Barnes and W. T. Simpson, *ibid.*, **39**, 670 (1963).

[4] J. F. Horwood and J. R. Williams, *Spectrochim. Acta*, **19**, 1351 (1963).

[5] A. Udvarhazi and M. A. El-Sayed, *J. Chem. Phys.*, **42**, 3335 (1965).

## Experimental

**Measurements.** The absorption spectra were measured with a VUV-3 vacuum-ultraviolet self-recording spectrophotometer (the radius of the curvature of the concave grating was one meter) of the Japan Spectroscopic Co., Ltd., at room temperature. This apparatus has a ratio-recording double-beam system using the rotating-cell method.[6] In this method, 30-mm gas-cell blocks, made of stainless steel and containing a sample cell on one side and a reference cell on the other, rotate at 8 Hz and function as "rotating sectors." Fluorite plates 1 mm thick were used as the windows of the cells. As the light source and light detector, a MH-225 Mitsubishi Deuterium Lamp and a photomultiplier (EMI 6256B) were used. The absorption peak of mercury vapor at 1849.6 Å was used for the wavelength calibration. The pressures of sample gases were measured with a mercury manometer with an inner diameter of 16 mm.[7] The mercury levels were read with a measuring microscope. The sensitivity of the pressure reading was *ca.* 0.01 mm. Each absorption spectrum was measured several times.

**Materials.** The ketones used were obtained from the Tokyo Kasei Kogyo Co., Ltd. Spectro-grade acetone and methyl ethyl ketone were used. Their purity was checked by gas chromatography. Methyl isopropyl, methyl *s*-butyl, methyl *t*-butyl, and diisopropyl ketones were purified by gas chromatography. Deuteroacetone (acetone-$d_6$) of Ciba Products, Ltd., the isotopic purity of which was greater than 99.5 per cent, was used without further purification.

## Results

The molar absorptivity curves obtained are shown in Figs. 1—6. The wavelengths and molar absorptivities of the absorption peaks in these absorptivity curves are given in Table 1. In Table 1 the accuracy of the wavelengths is ±1 Å, and the reproducibility of the molar absorptivities is within 10 per cent. The oscillator strengths (*f*-values) of the A and B bands are given in Table 2. Some photodecomposition of these ketones was found to occur during the measurements. This decomposition was the most remarkable in methyl *n*-amyl and methyl *n*-butyl ketones. In these cases several per cent of the original part was decomposed during the measurements. None of peaks obtained are believed to be characteristic of the photodecomposition products since they all decreased in intensity on continued irradiation. The obtained molar absorptivities of the longest-wavelength absorption peak of the band, near 1950 Å, of acetone and of the absorption maximum of the band, near 1950 Å, of diethyl ketone are in good agreement with those reported by Lake and Harrison[2] and by Barnes and Simpson[3] respectively. The shapes of the absorption bands near 1950 Å of these ketones are in good agreement with those of the transmittance curves of these ketones reported by Horwood and Williams.[4]

## Discussion

As may be seen in Figs. 1—6, methyl alkyl ketones and diethyl ketone show two absorption bands, near 1950 Å and 1700 Å. Di-*n*-propyl and diisopropyl ketones show an absorption band near 1650 Å besides these two absorption bands. In this paper these three kinds of absorption bands, near 1950 Å, 1700 Å, and 1650 Å, will be denoted as A, B, and C bands respectively. In these ketones

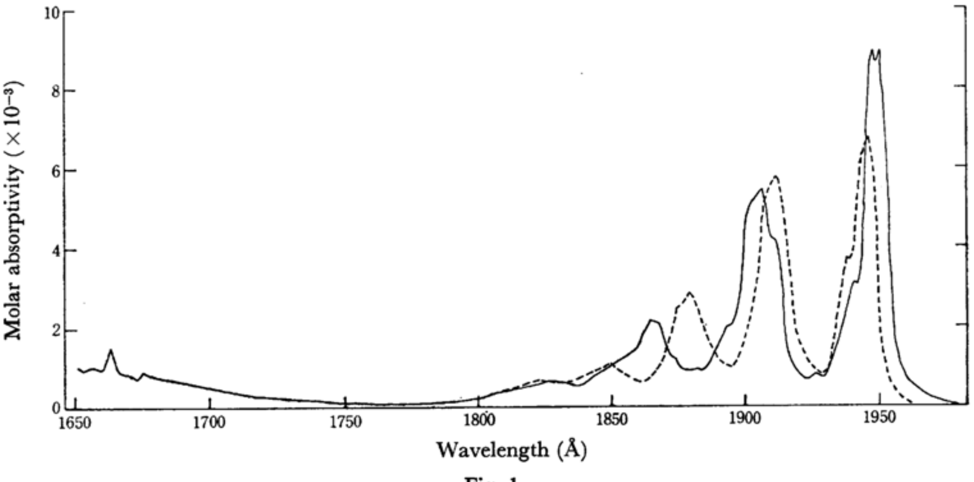

Fig. 1

—— Acetone ------ Acetone-$d_6$

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[6] Y. Nihei, S. Oda, E. Niki and H. Kamada, *Spectrochim. Acta*, **24A**, 457 (1968).

[7] The gas-sampling apparatus has been constructed according to the method of Tsubomura *et al.* (H. Tsubomura, K. Kimura, K. Kaya, J. Tanaka and S. Nagakura, This Bulletin, **37**, 417 (1964)).

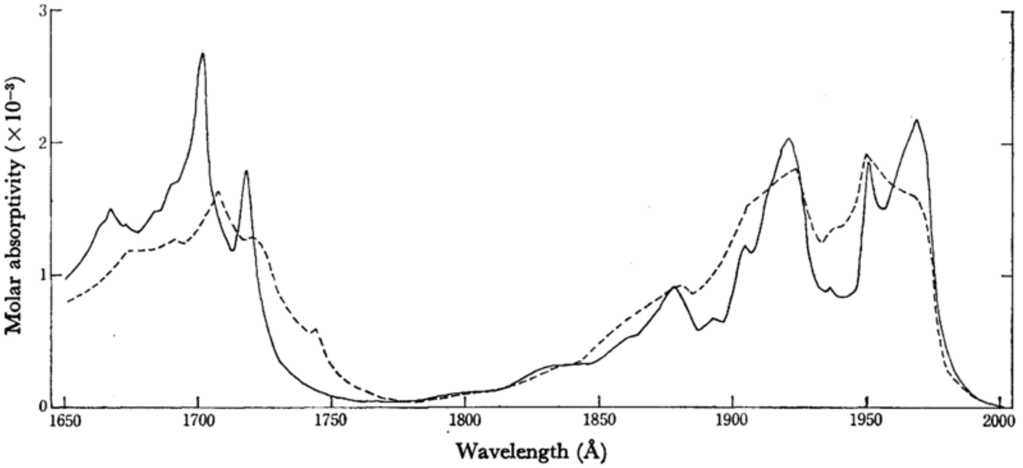

Fig. 2

—— Methyl ethyl ketone ----- Methyl *n*-propyl ketone

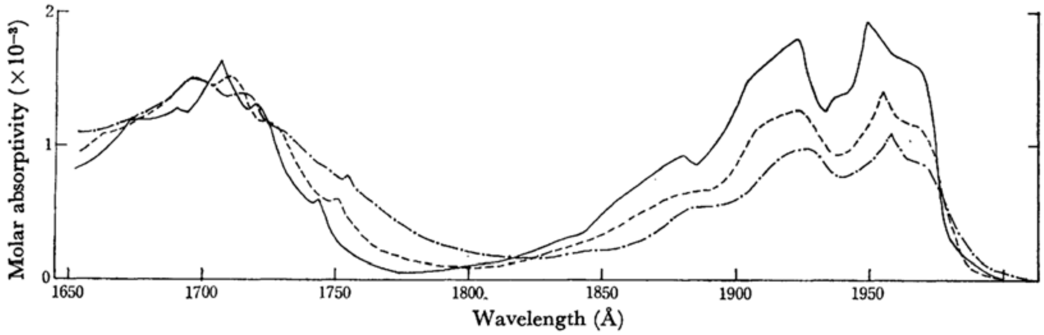

Fig. 3

—— Methyl *n*-propyl ketone ----- Methyl *n*-butyl ketone —·— Methyl *n*-amyl ketone

Fig. 4

—— Methyl isopropyl ketone ----- Methyl isobutyl ketone —·— Methyl *t*-butyl ketone

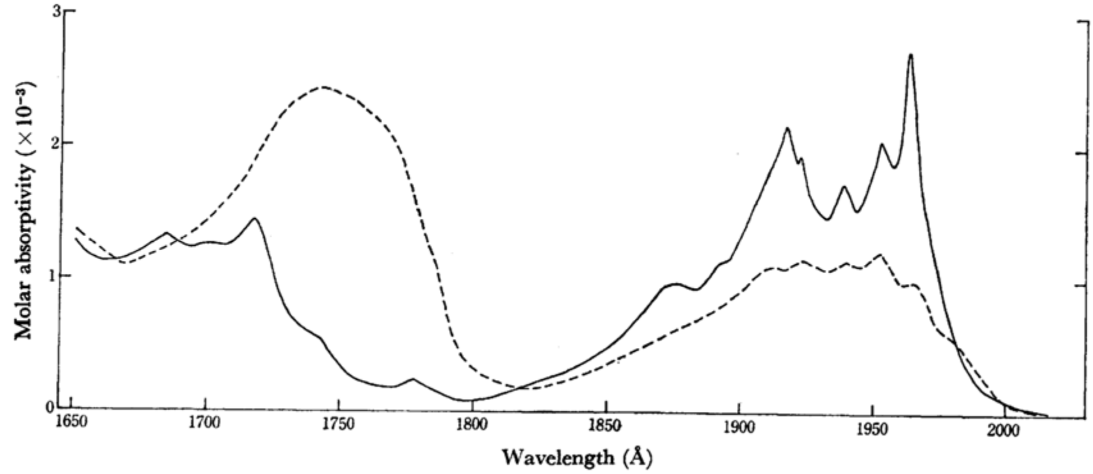

Fig. 5

—— Methyl *s*-butyl ketone ------ Methyl isobutyl ketone

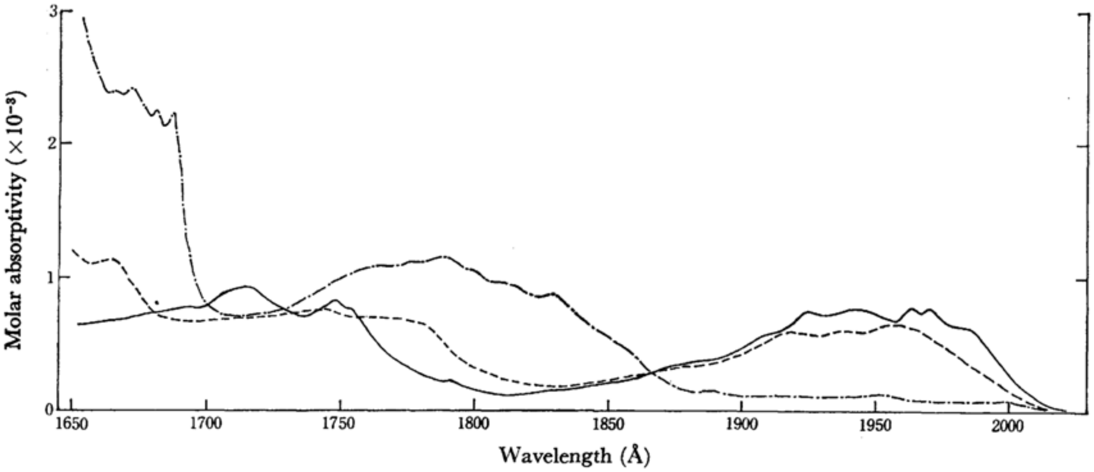

Fig. 6

—— Diethyl ketone ------ Di-*n*-propyl ketone –·– Di-isopropyl ketone

each of the three kinds of absorption bands is thought to have similar characteristics of the electronic transitions.

Methyl *n*-alkyl ketones, the methyl alkyl ketones in which the $\alpha$-carbons of the alkyl groups are the secondary or tertiary carbons, and di-(non-methyl)alkyl ketones are classified into Group I, II, and III respectively for convenience. Methyl *s*-butyl ketone is classified in Group I. The following distinct points about the positions and intensities of A and B bands may be found by comparing Fig. 1—6 and Table 2.

(1) As for the position of the A band, the A band of acetone is at wavelengths a little shorter than those of the other ketones.

(2) As for the intensity of the A band, that of acetone is considerably greater than those of other ketones. In methyl *n*-alkyl ketones the intensity generally decreases with the number of carbon atoms in the *n*-alkyl groups. Those of Group II and III are weak, that of diisopropyl ketone bing especially weak.

(3) As for the position of the B band, the B bands of Group II and III are at wavelengths considerably longer than those of Group I, that of diisopropyl ketone being at a wavelength especially much longer than those of Group I.

(4) As for the intensity of the B band, that of acetone is very weak and all those of Group I except for acetone are similar to each other. Those of Group II, especially that of methyl *t*-butyl ketone, are remarkably greater than those of Group I, while those of Group III are close to those of Group I (except for acetone).

Table 1. The wavelengths and molar absorptivities of the absorption peaks

| | $\lambda_{max}$ (Å) | $\varepsilon_{max}$ |
|---|---|---|
| Acetone | 1951 | 9000 |
| | 1948.5 | 9000 |
| | 1906 | 5600 |
| | 1865 | 2150 |
| | 1663 | 1500 |
| Acetone-$d_6$ | 1946 | 6900 |
| | 1911 | 5700 |
| | 1879 | 2850 |
| | 1849 | 1100 |
| | 1663 | 1500 |
| Methyl ethyl ketone | 1968.5 | 2200 |
| | 1951 | 1870 |
| | 1936 | 930 |
| | 1921 | 2100 |
| | 1905 | 1270 |
| | 1878 | 930 |
| | 1718 | 1800 |
| | 1701.5 | 2700 |
| | 1666 | 1500 |
| Methyl *n*-propyl ketone | 1950 | 1950 |
| | 1924 | 1800 |
| | 1881 | 930 |
| | 1744 | 600 |
| | 1707 | 1650 |
| Methyl *n*-butyl ketone | 1955 | 1400 |
| | 1924 | 1270 |
| | 1752 | 550 |
| | 1712 | 1450 |
| Methyl *n*-amyl ketone | 1958 | 1100 |
| | 1927 | 1000 |
| | 1756 | 700 |
| | 1697 | 1500 |
| Methyl isopropyl ketone | 1982 | 1070 |
| | 1967 | 1400 |
| | 1951 | 1130 |
| | 1935 | 1330 |
| | 1922 | 1300 |
| | 1746 | 3600 |
| | 1737 | 3800 |
| | 1727 | 3500 |
| Methyl isobutyl ketone | 1964 | 1000 |
| | 1952 | 1220 |
| | 1940 | 1150 |
| | 1924 | 1150 |
| | 1912 | 1100 |
| | 1742 | 2450 |
| Methyl *s*-butyl ketone | 1963 | 2730 |
| | 1952 | 2100 |
| | 1940 | 1770 |
| | 1923 | 2030 |
| | 1917 | 2170 |
| | 1878 | 1050 |
| | 1777 | 300 |
| | 1719 | 1450 |
| | 1685 | 1350 |
| Methyl *t*-butyl ketone | 1950 | 1100 |
| | 1750 | 5800 |
| Diethyl ketone | 1970 | 770 |
| | 1962 | 770 |
| | 1942 | 770 |
| | 1924 | 770 |
| | 1748 | 830 |
| | 1716 | 900 |
| Di-*n*-propyl ketone | 1958 | 650 |
| | 1920 | 600 |
| | 1745 | 800 |
| | 1667 | 1150 |
| Diisopropyl ketone | 1949 | 100 |
| | 1829 | 950 |
| | 1790 | 1150 |
| | 1687 | 2250 |
| | 1681 | 2300 |
| | 1672 | 2500 |
| | 1665 | 2400 |

As for the shapes of the A and B bands of each ketone, the A band shows a relatively sharp vibrational structure and its shape is very sensitive to the alkyl group. In the B band only that of methyl ethyl ketone shows a sharp vibrational structure. In acetone the frequency of the main vibrational progression is *ca.* 1140 cm$^{-1}$. On the other hand, that in deuteroacetone is *ca.* 940 cm$^{-1}$. On the basis of this fact, Lawson and Duncan[8] have safely assigned these frequencies to the C–H(D) bending vibration of the methyl groups. In the A bands of methyl ethyl and methyl *s*-butyl ketones the frequencies of the main vibrational progressions are *ca.* 1240 cm$^{-1}$ and 1220 cm$^{-1}$ respectively. These progressions may be similar to that in acetone. Besides these progressions, we found distinct progressions of two frequencies, 470 cm$^{-1}$ in the A band and 580 cm$^{-1}$ in the B band in methyl ethyl ketone, and two other frequencies, 290 cm$^{-1}$ and 660 cm$^{-1}$, in the A band of methyl *s*-butyl ketone. The 470 cm$^{-1}$ frequency in the A band of methyl

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[8] M. Lawson and A. B. F. Duncan, *J. Chem. Phys.*, **12**, 329 (1944).

TABLE 2. THE OSCILLATOR STRENGTHS OF A AND B BANDS

| | A Band<br>$f$ | B Band<br>$f$ |
|---|---|---|
| Acetone | 0.035 | |
| Acetone-$d_6$ | 0.033 | |
| Methyl ethyl ketone | 0.018 | 0.017 |
| Methyl *n*-propyl ketone | 0.020 | 0.016 |
| Methyl *n*-butyl ketone | 0.015 | 0.018 |
| Methyl *n*-amyl ketone | 0.011 | 0.022 |
| Methyl isopropyl ketone | 0.015 | 0.043 |
| Methyl isobutyl ketone | 0.015 | 0.031 |
| Methyl *s*-butyl ketone | 0.023 | 0.015 |
| Methyl *t*-butyl ketone | 0.013 | 0.072 |
| Diethyl *t*-butyl ketone | 0.010 | 0.014 |
| Di-*n*-propyl ketone | 0.008 | 0.012 |
| Diisopropyl ketone | 0.001 | 0.018 |

ethyl ketone is probably that of the C–O bending vibration.9) The sharp vibrational structure of that of methyl *s*-butyl ketone is remarkable in view of the complex structure of this ketone. This is thought to be due to the particular, rigid three-dimensional molecular structure of this ketone. Recently a study of the infrared spectra of these ketones has shown that the various rotational isomers exist in the liquid and gaseous states.9,10) The relation between the existence of the various rotational isomers and the band shapes is not clear at this stage. The co-existence of the various rotational isomers in the gas phase may contribute to the broadening of the absorption peaks.

The assignments of the A and B bands have been discussed by many authors. Heretofore, the A band has been identified as the $n\rightarrow\sigma^*$ band on the basis of its position and intensity by many people.5,11,12) As has been described before, the fact that the frequency of the main vibrational progression in the A band of acetone is that of the C–H bending vibration of the methyl groups is to show that the hyperconjugation of the methyl groups to the carbonyl $\pi$-bond plays an important role in the electronic transition of the A band. The large intensity of the A band of acetone, and the very small intensity of the A band of diisopropyl ketone, where the hypercojugation of the isopropyl groups to the CO $\pi$-bond is thought to be weak, offer strong support for this theory. Since these hyperconjugations seem not to play an important role in the $n\rightarrow\sigma^*$ transition, this theory does not support the assignment of the A band to the $n\rightarrow\sigma^*$ band. Therefore, further theoretical and experimental examination for this assignment are desireable.

As for the electronic transition of the B band, there are two possible explanations of the remarkable difference in the intensity of the B band between acetone and methyl ethyl ketone. One is that a C–C bond combining with the CO bond plays an important role in the electronic transition of the B band. The other one is that the nonequivalency of the two alkyl groups favors this transition. The fact that the intensity of the B band of methyl isopropyl ketone is far greater than that of diisopropyl ketone seems to support the latter possibility. On the other hand, it is also remarkable that the B band of diisopropyl ketone is at a wavelength considerably longer than that of methyl isopropyl ketone. As for the electronic transition of the C band, its intensity seems to be too weak to assign the C band to the $\pi\rightarrow\pi^*$ band. Further theoretical and experimental examinations for the assignments of B and C bands are also desirable.

In these ketones the Rydberg transitions are expected to appear in the region shorter than 1800 Å. For example, the peak at 1663 Å in acetone and the four peaks in the C band of diisopropyl ketone may be those of Rydberg transitions. However, the Rydberg-transition peaks can not be discussed at this stage.

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9) T. Shimanouchi, Y. Abe and M. Mikami, *Spectrochim. Acta*, **24A**, 1037 (1968).

10) M. Hirota, T. Hagiwara and H. Satonaka, This Bulletin, **40**, 2439 (1967).

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

12) W. C. Johnson, Jr., and W. T. Simpson, *ibid.*, **48**, 2168 (1963).