

INTENSITIES OF ELECTRONIC TRANSITIONS IN ALIPHATIC KETONES IN THE VACUUM ULTRAVIOLET¹

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The absolute intensities of the electronic transitions at 51,000 cm^{-1} and 60,000 cm^{-1} have been measured for the compounds methyl ethyl ketone, methyl isopropyl ketone, methyl *tert*-butyl ketone, diethyl ketone, diisopropyl ketone, and di-*tert*-butyl ketone. It was found that the intensity of the transition at 51,000 cm^{-1} is decreased when the α -hydrogens in acetone are replaced by methyl groups. The intensity of the transition at 60,000 cm^{-1} is increased when the hydrogens on one α -carbon are substituted by methyl groups and also increased to a lesser extent when the hydrogens on both α -carbons are symmetrically replaced by methyl groups.

To explain the decrease in the 51,000 cm^{-1} transition, the effects of polarity, bond angle, and bond length were studied. The combined effects of bond angle and polarity cannot account for the observed decreases. Bond length might explain the observed effects.

It is suggested that the electron excited in the 60,000 cm^{-1} transition does not come from the C=O group, but possibly is excited from an orbital of the $>\text{C}-$ group.

Many aliphatic ketones show absorption in the neighborhood of 51,000, 60,000, and 63,000 cm^{-1} , in addition to the well-known absorption near 35,000 cm^{-1} . There is also absorption beyond 65,000 cm^{-1} , where the electronic transitions overlap so that they cannot be resolved at present. We have studied the absolute intensities of the 51,000 and 60,000 transitions in the vapor state of seven ketones in which the hydrogens of acetone have been substituted by methyl in a systematic way. The complete experimental results are reported in the present paper, together with some tentative discussion.

The experimental absolute intensity of a transition can be measured by the *f*-number, or oscillator strength of the transition. To obtain reliable measurements of this quantity, it is necessary to include all rotational and vibrational levels connected with a given electronic transition (6). It is necessary also that the absorption coefficient be essentially constant over a frequency range larger than is covered by the width of the slit. At the pressures used the absorption spectra of the ketone vapors are truly continuous, except in the cases of acetone and methyl ethyl ketone. Rotational structure is absent in all cases, but in the two cases mentioned groups of unresolved vibrational levels give several broad maxima and minima (quasi-vibrational structure).

The *f*-number is found in the following way (9): A number of lines from a

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direct-current, constant-intensity source were photographed, on the same plate, through an absorption tube enclosed by lithium fluoride lenses, with the tube both empty and filled with vapor at an accurately measured pressure. Several exposures were made through the empty tube in which the time of exposure was varied at constant intensity, or in some cases the intensity at constant time was varied by calibrated diaphragms (1). Then one or more exposures were made with the vapor on the same plate. For each line of known frequency a density-log exposure curve was drawn, from which the absorption coefficient was found.

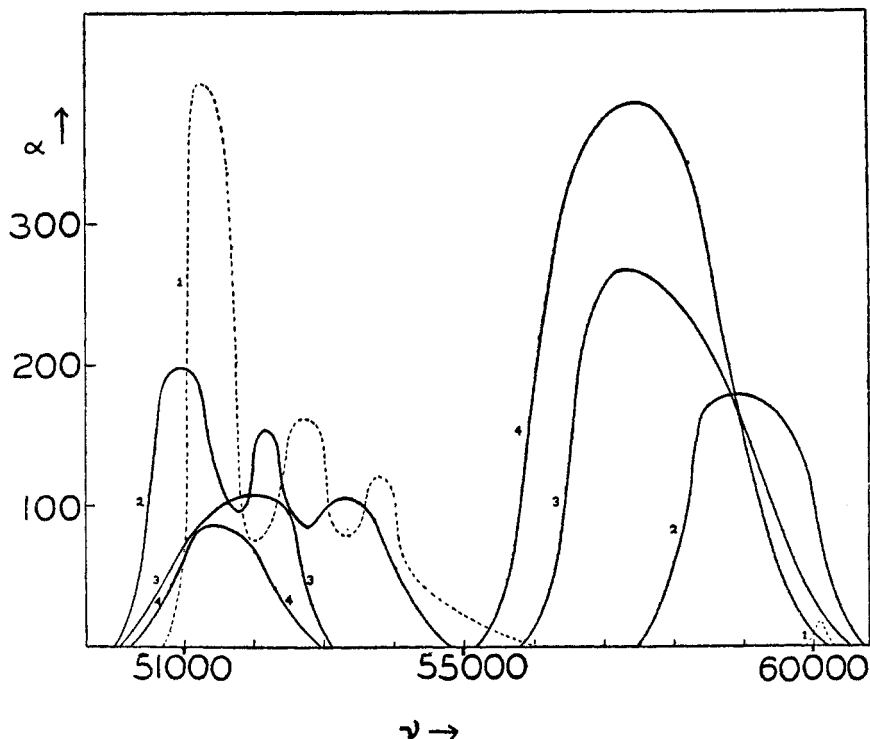


FIG. 1. Absorption curves for acetone (curve 1), methyl ethyl ketone (curve 2), methyl isopropyl ketone (curve 3), and methyl *tert*-butyl ketone (curve 4).

The f -number was found by integrating the absorption coefficient over the entire frequency width of the electronic transition. A number of plates were made for each compound in which the pressure was varied from 0.08 to 0.30 mm. The fact was established that the integrated absorption coefficient was independent of pressure. In the case of quasi-vibrational structure, the absorption coefficient was measured at so many frequencies that the contours were revealed in detail.

The absorption curves for the series acetone, methyl ethyl ketone, methyl isopropyl ketone, and methyl *tert*-butyl ketone (unsymmetrical series) are given in figure 1. Curves for acetone, diethyl ketone, diisopropyl ketone, and di-*tert*-butyl ketone (symmetrical series) are given in figure 2. The absorption coef-

ficient α equals $1/l_0 \log_e (I_0/I)$, where I_0 is the intensity of incident light and I is the intensity after passage through a column of absorbing gas of length l_0 , measured at 0°C. and 76 cm. pressure, and ν is the frequency in cm^{-1} . The values of f are given in table 1. The experimental values of the dipole moment integral Q are obtained (6) from the relation

$$Q^2 (\text{exptl.}) = 9.12 \times 10^4 f/\nu_M$$

where ν_M is the wave number of the intensity maximum of the transition.

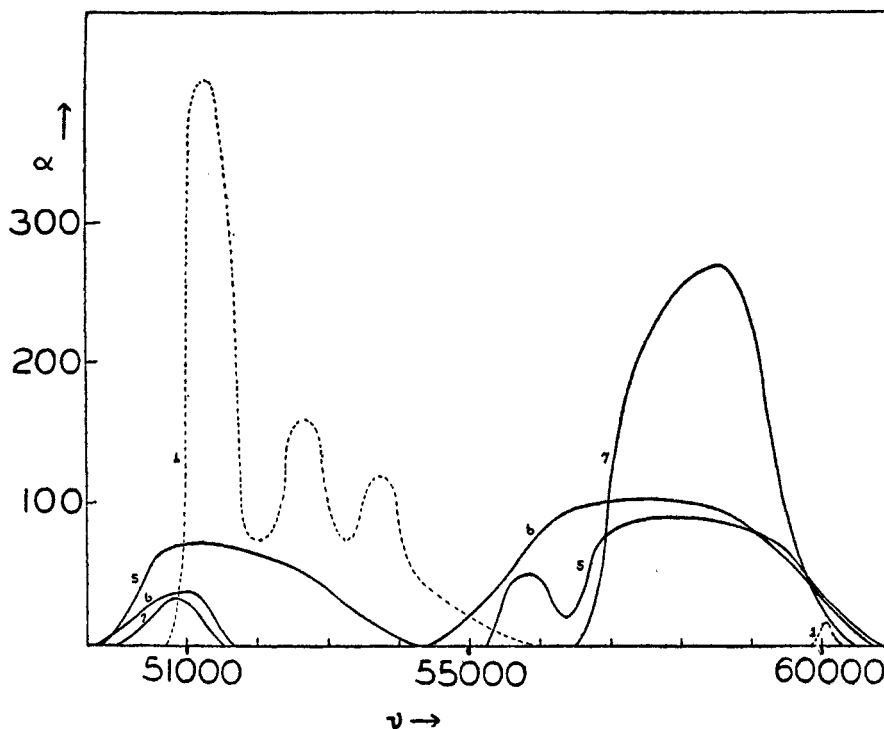


Fig. 2. Absorption curves for acetone (curve 1), diethyl ketone (curve 5), diisopropyl ketone (curve 6), and di-*tert*-butyl ketone (curve 7).

Unless some unexpectedly large error is present, the accuracy of the f -numbers is within 5–10 per cent. The 60,000 transition in acetone is a special case. It is narrow, but apparently weak at the highest pressures. The absorption coefficient can be measured at only one frequency, and so the curve given is schematic. The f -number in this case may be in error by a factor of ten, but it is definitely smaller than any other which we have measured.² Substantially the same values of f for the 51,000 transition in acetone, methyl ethyl ketone, and

² The measurements on the two transitions in acetone vapor were made by Miss Martha Lawson (Mrs. N. L. Morse), Dissertation, University of Rochester, 1944.

diethyl ketone in solution, which agree closely with these reported values, are given by Platt and Klevens (7).

Considerable attention was directed to the purity of the ketones used. Except for di-*tert*-butyl ketone, the starting materials were Eastman Kodak preparations. Acids, oxidizing agents, and biacetyl were removed by washing with dilute sodium bisulfite and sodium carbonate solutions. Samples were fractionated twice in a Purdue-type column, and the final products were taken with a boiling-point range of 0.5°C. or less. The resulting fractions were free of the above impurities.

The di-*tert*-butyl ketone³ was prepared by the method of Whitmore (10) and purified by fractional distillation. All ketones were freed from air in a vacuum


TABLE 1

COMPOUND	f	ν_M	Q
Transition at 51,000 cm. ⁻¹			
Acetone.....	0.020	52,000	0.19
Methyl ethyl ketone.....	0.018	51,600	0.18
Methyl isopropyl ketone.....	0.0095	51,600	0.13
Methyl <i>tert</i> -butyl ketone.....	0.0057	51,600	0.10
Diethyl ketone.....	0.0077	51,700	0.12
Diisopropyl ketone.....	0.0018	50,800	0.057
Di- <i>tert</i> -butyl ketone.....	0.0016	50,800	0.054
Transition at 60,000 cm. ⁻¹			
Acetone.....	0.0002	60,000	0.017
Methyl ethyl ketone.....	0.014	59,000	0.15
Methyl isopropyl ketone.....	0.033	58,000	0.23
Methyl <i>tert</i> -butyl ketone.....	0.052	57,400	0.29
Diethyl ketone.....	0.014	58,000	0.15
Diisopropyl ketone.....	0.018	57,500	0.17
Di- <i>tert</i> -butyl ketone.....	0.020	58,500	0.18

system attached to the absorption tube. In some cases they were fractionated further in the vacuum system.

DISCUSSION

We may suppose that the transition at 51,000 cm.⁻¹ arises from excitation of a $2p_{\nu(O)}$ non-bonding oxygen electron to an antibonding ($t_s - 2p_{\pi(O)}$) orbital (3). If it is assumed that the transition remains localized in the C—O group, and that the carbon-oxygen distance has the same value (1.215 Å.) as found in formaldehyde by electron diffraction (8), then a change in intensity caused by substi-

tution of hydrogen by methyl can be due to: (1) change of angle in the 

³ Obtained from Mr. C. E. Larrabee, University of Rochester.

configuration and (2) polarity in the C—O bond. The change of angle was investigated by variation of s - p hybridization in the t_3 function. It was found that the limiting values of the hybridization ratio could account for a change in intensity of about 30 per cent. Variation of the polarity coefficients of t_3 and $2p_{z(O)}$ produced smaller changes in intensity, about 10 per cent. If these effects were added, the observed differences in intensity cannot be accounted for.

Variation of the carbon-oxygen distance would produce much larger effects. There is no direct evidence, however, that this distance is appreciably changed in the substituted ketones. It does not appear worth while to attack the problem quantitatively by use of non-localized orbitals, in view of the complications pointed out by McMurry (4).

Examination of the data shows the following empirical facts, which are offered largely without comment, since their significance, if any, is not obvious at present. The sum of the f -numbers of the two transitions is substantially constant in the symmetrical series. In the unsymmetrical series (acetone, methyl ethyl ketone, methyl isopropyl ketone, and methyl *tert*-butyl ketone) the sum of f -numbers of the two transitions is not constant, but increases linearly with the number of hydrogens substituted. In the unsymmetrical series, the increase in f in the 60,000 transition and the decrease in f in the 51,000 transition are very nearly linear. In the symmetrical series the decrease and the increase are exponential for the two transitions.

The equivalent of the 60,000 transition is not found in formaldehyde and acetaldehyde. If the intensity in these molecules is no greater than in acetone, it might not have been observed. Starting with formaldehyde, it appears necessary to substitute three hydrogens by methyl (giving methyl ethyl ketone) to get an appreciable intensity for a 60,000 transition. The data show that the intensity increases much more rapidly in the unsymmetrical than in the symmetrical series.

In contrast with these transitions, the intensity of the transition at about 35,000 cm^{-1} is unchanged by methyl substitution. This transition is probably to an excited-state configuration $\dots (2p_{y(O)})(x_c - x_0)$ (3) and is confined strictly to the C—O group. We conclude from this that the 60,000 transition is not a second member of the type of transition $N \rightarrow E$.

It is possible that the 60,000 transition arises from a normal-state configuration $\dots (y)^2$ where (y) is an orbital (5) of the $\text{C} \begin{array}{l} \diagup \\ \diagdown \end{array}$ group. The form of this orbital will depend on the groups attached to carbon. We shall investigate this possibility, and hope to report later a more satisfactory explanation of these intensities.

Note added in proof: Calculations of the intensity of the 51,000 cm^{-1} transition have been made in which the C—O bond distance was varied from 1.22 to 2.0 Å., by which the intensity could be decreased by 75 per cent. This is sufficient to account for all observed decreases. Calculations were made on the 60,000 cm^{-1} transition, based on the assumption that the electron was excited

from an orbital located in the C—C bond adjacent to the C—O group, lying in the direction of the bond, to a semilocalized orbital perpendicular to this bond. The calculated values of Q are of the correct order of magnitude, and Q increases with methyl substitution roughly in accord with the experimental facts.

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