

2. Both water and organic liquids (of high surface tension) form contact angles on these solids, thus indicating that the surface tension of these solids is low.

3. Soft solids of low surface tension are wetted less readily by liquids than are hard solids which possess a higher surface tension.

4. On talc, accurate measurements could

be made of interfacial contact angles as well as of contact angles in air both with water and with organic liquids. This made possible the experimental testing of the Bartell-Osterhof equation relating adhesion tension and interfacial contact angles. This equation was found to hold.

ANN ARBOR, MICHIGAN

RECEIVED MAY 11, 1936

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

## The Absorption Spectrum of Ethyl Methyl Ketone

BY A. B. F. DUNCAN, VICTOR R. ELLS AND W. ALBERT NOYES, JR.

The spectroscopy and photochemistry of acetone have been the subjects of numerous investigations. The spectrum consists of a broad absorption region extending from about 2200 to about 3200 Å. with a definite fine structure on the long wave end, a series of discrete bands extending from 1995 to about 1820 Å., and at shorter wave lengths other bands, some of which fitted a Rydberg formula predicting an ionization potential of 10.2 volts.<sup>1</sup> At still shorter wave lengths there is continuous absorption extending down to the limit of the observations made, about 800 Å. In the near ultraviolet fluorescence is observed, although attempts to find this phenomenon in the neighborhood of 1900 Å. failed.<sup>2</sup>

The next higher ketone is ethyl methyl ketone. The electronic structure of the carbonyl group must be very similar to that in acetone. However, the symmetry operations which may be performed on the two molecules differ considerably. If the methyl group forming part of the ethyl group is considered to execute a perfectly symmetrical rotation around the adjacent carbon-carbon bond, there will be only one symmetry operation aside from the identity, namely, reflection in the plane containing the carbonyl group and the two adjacent carbon atoms. However, due to various types of interaction between the different parts of the molecule, this particular rotation might not be expected to be completely symmetrical so that ethyl methyl ketone must be

considered to possess a very low order of symmetry.

### Experimental Procedure and Discussion of Results

The methyl ethyl ketone used in these experiments was prepared by the acetoacetic ester synthesis, using acetoacetic ethyl ester and methyl iodide. It was purified by formation of the sodium bisulfite compound, dried with potassium carbonate and fractionally distilled.<sup>3</sup>

For investigation of the near ultraviolet absorption a Hilger E<sub>3</sub> spectrograph was used together with Eastman III-O and 33 plates.

The absorption spectrum of the liquid in this region has been investigated, but that of the vapor has not been reported. Two absorbing columns of 1 and 10 meters with pressures of 3 to 86 mm. (the vapor pressure at 25°) were used. At the highest pressure the absorption extended from approximately 3200 to 2400 Å. No trace of vibrational fine structure was observed under any conditions.

Ethyl methyl ketone shows strong fluorescence when illuminated with approximately monochromatic 3130 Å. radiation. The fluorescence viewed with a hand spectrograph appeared to consist of a continuous band in the green. We were unable to obtain photographs of the fluorescence with the E<sub>3</sub> spectrograph, but the matter is being pursued further.

In view of this fluorescence, particular care was used in making the absorption measurements to vary the pressures over a wide range, and at each

(1) (a) Damon and Daniels, *THIS JOURNAL*, **55**, 2363 (1933); (b) Scheibe, Povenz and Linstrom, *Z. physik. Chem.*, **B20**, 297 (1933); (c) Crone and Norrish, *Nature*, **132**, 241 (1933); (d) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, **1934**, 1456; (e) Noyes, Duncan and Manning, *J. Chem. Phys.*, **2**, 717 (1934); (f) Duncan, *ibid.*, **3**, 131 (1935).

(2) Howe and Noyes, *THIS JOURNAL*, **58**, 1404 (1936).

(3) The authors wish to express their appreciation to Professor C. B. Wooster for suggesting the method of synthesis and supervising its execution.

pressure to make a number of exposures for different lengths of time, in order to provide suitable contrast. It is possible that the lowest pressure was still too high to permit the observation of structure and a still longer column may be necessary.

The near ultraviolet spectrum is followed by a region of almost complete transmission extending down to 1975 Å. At this point a spectrum consisting of discrete bands begins, which continues, broken by short regions of high transmission, down to about 1550 Å. At still shorter wave lengths there is strong continuous absorption extending down to about 780 Å., the limit of the observations. No structure could be found in this continuum even at low pressures where the continuous absorption was weak. Any discrete bands must be weaker than the continuous absorption below 1567 Å.

A one-meter, normal incidence vacuum spectrograph with a 120,000 line glass grating was used to photograph this region. The modified Lyman continuum served as the source.<sup>1e,1f</sup> Eastman III-O plates sensitized with Nujol were used. The plates were measured and reduced in the usual way and emission lines in the source, chiefly due to carbon, were used as standards. The dispersion was approximately 8.5 Å./mm.

The frequencies of the bands are given in Table I with visually estimated intensities. The intensity of the weakest band is arbitrarily placed as 1, which means that some rather high values must be given without implying, however, any greater accuracy in estimating intensities than was obtained with acetone. The red edges of the bands are given.

TABLE I  
FAR ULTRAVIOLET BANDS OF ETHYL METHYL KETONE

Frequency, cm. <sup>-1</sup>	Intensity	Frequency, cm. <sup>-1</sup>	Intensity
50634	8	53119	2
50675	8	58110	12
50728	8	58662	20
50857	6	59102	1
50891	6	59360	1
50948	6	62283	16
51209	4	63523	200
51915	3	63817	250
52426	3		

The edges of the first six bands are quite sharp and the accuracy should be five to ten wave numbers. For most of the other bands the edges were quite diffuse, but it is felt that in no case does the error exceed fifty wave numbers.

The first ten bands, 50,634 to 53,119 cm.<sup>-1</sup>, evidently involve one upper electronic state. The spectrum here is similar to that in acetone in the region 51,000 to 55,000 cm.<sup>-1</sup>. There are three main bands forming an upper state progression involving a frequency of 1281 cm.<sup>-1</sup>. Two other upper state frequencies appear, one about 220 and the other 575. The origin of the system is the triple band (50,634, 50,675, 50,728), which corresponds to the (51,171, 51,226, 51,285) band in acetone which is also triple headed. Table II shows the arrangement of the bands.

TABLE II  
ARRANGEMENT OF ETHYL METHYL KETONE BANDS  
(50,634 to 53,119)

(All transitions are considered to occur from the lowest level of the ground state)

$\nu_1, \nu_2$ , etc. = 0	50634	50675	50728
	223	216	220
$\nu_1 = 1$	50857	50891	50948
	1281		
$\nu_2 = 1$	51915		
	1204		
$\nu_2 = 2$	53119		
	575		
$\nu_3 = 1$	51209		
	514		
$\nu_2 = 1, \nu_3 = 1$	52426		

The second electronic state involving a transition below 1975 is evidenced by four bands, the two of shortest wave length being of extremely low intensity. Acetone has an analogous state giving transitions between 60,086 and 62,529 cm.<sup>-1</sup>. The two strongest bands are separated by 552 cm.<sup>-1</sup>. It appears probable that this is an upper state difference and that the origin of this state lies at 58,110 cm.<sup>-1</sup>. One of the weak bands, 59,360, is separated from this by 1250 cm.<sup>-1</sup>.

The differences between the remaining three bands are as follows: 63,523 to 62,283 = 1240; 63,817 to 63,523 = 294. The two bands of highest frequency evidently belong to the same electronic transition; the first of the three may also belong to the same transition. If the three bands belong together, the intensity relationships are such that 62,283 cannot be the origin of the system, in which case 1240 would have to be a ground state difference. This is unlikely due to the small Boltzmann factor (0.0015) for such a large frequency. It seems better, then, to put 62,283 in a separate electronic transition. Whether the 294 difference for the remaining two

bands is an upper or ground state difference cannot be determined.

The significance of the various frequency differences may be discussed briefly.  $\nu_2$  is most probably a carbon-oxygen frequency which is  $1734 \text{ cm.}^{-1}$  in the normal state. The corresponding frequency in acetone for this state is about  $1200 \text{ cm.}^{-1}$  ( $1712$  in the normal state).  $\nu_1$  is probably analogous to  $321$  found in acetone in this region. It is probably associated with a simultaneous bending of the methyl and ethyl groups with respect to the carbon-oxygen axis.  $\nu_3$  may possibly represent a motion in which the ethyl and methyl groups are stretched as units in reference to the carbonyl group.

### The Electronic States of Ethyl Methyl Ketone

It is apparent from the above discussion that four, or more probably five, well separated excited electronic states of ethyl methyl ketone have been found here. The first excited state probably has unresolved fine structure, since fluorescence is caused by absorption in this region. The other states possess discrete vibrational levels as indicated. In addition there are other states, perhaps repulsive, which are necessary to account for the continuum overlying the discrete structure, particularly at short wave lengths.

Obviously no two of the origins of these states fit a Rydberg formula which would converge to a reasonable limit.<sup>4</sup> The band in ethyl methyl ketone most similar to a member of the acetone Rydberg series<sup>1f</sup> is either  $63,525$  or  $63,817$  (depending on which is considered to be the origin of this particular electron transition). One of these bands is believed to be the first member of a Rydberg series whose other members are masked by continuous absorption. Accordingly the ionization potential of the molecule could not be determined by spectroscopic means.

The ionization potential was then determined

(4) Mulliken, *J. Chem. Phys.*, **3**, 564 (1935).

by the method of electron bombardment.<sup>5</sup> The value obtained was  $10.5 \pm 0.5$  volts, as compared to  $10.1$  volts (by electron impact) for acetone.

According to Mulliken<sup>4</sup> a ( $2 p_y b_2$ ) electron in formaldehyde should have a lower ionization potential than any other and the agreement between the theoretically predicted value and that obtained by convergence of a Rydberg series lends support to this statement.<sup>6</sup> In acetone a similar electron must be involved in the Rydberg series and this must be true for the hypothetical Rydberg series in ethyl methyl ketone. This electron is described as one occupying a non-bonding oxygen orbital and transitions involving it should change the fundamental frequency of the carbonyl group only slightly.

Since most of the discrete bands and the near ultraviolet continuum do not fit a Rydberg series, it is probable that other electrons of the bonding or anti-bonding types are involved in these transitions. Little of a definite nature can be said concerning these electron states, although others have attempted to correlate frequencies of the various states of carbon monoxide with the frequencies of the carbonyl group.

### Summary

1. The absorption spectrum of ethyl methyl ketone has been investigated at room temperature from the visible down to about  $780 \text{ \AA}$ .
  2. Four (possibly five) different excited electron states in addition to any which may be involved in the short wave continuum must be used to explain the different absorption regions.
  3. The bands in the region from  $1975$  to  $1883 \text{ \AA}$ . may be classified as belonging to a single electron transition, using three vibration frequencies in the upper state.
  4. A brief discussion, including a general comparison with the acetone bands, has been given.
- PROVIDENCE, RHODE ISLAND RECEIVED JUNE 10, 1936

(5) Noyes, *ibid.*, **3**, 430 (1935).

(6) Price, *Phys. Rev.*, **46**, 529 (1934).