

## Photochemical Studies. XIX The Ultraviolet Absorption Spectrum of Acetone Vapor

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Citation: *The Journal of Chemical Physics* **2**, 717 (1934); doi: 10.1063/1.1749385

View online: <http://dx.doi.org/10.1063/1.1749385>

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# THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 2

NOVEMBER, 1934

NUMBER 11

## Photochemical Studies. XIX

### The Ultraviolet Absorption Spectrum of Acetone Vapor<sup>1</sup>

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(Received August 15, 1934)

The ultraviolet absorption spectrum of acetone vapor has been photographed. The well-known absorption region in the neighborhood of 3000Å, common to all ketones, is found to have on its long wave end a series of discrete absorption bands. The wave-lengths of many of these bands have been measured and a vibrational analysis is given. A second absorption region beginning about 1960Å and extending toward shorter wave-lengths is found to consist of several groups of bands, the bands within each

group being separated by relatively small frequency differences. The analysis of this band system may be accomplished by assuming several energy levels close together in the upper state together with four fundamental frequencies in the upper state and two in the lower. Evidence for further absorption regions extending to below 1200Å has been found and the approximate positions of these regions are given. These bands evidently belong to different electron transitions from the others.

THE absorption spectrum of acetone vapor in the infrared and near ultraviolet regions has been investigated.<sup>2</sup> The photochemical decomposition and polymerization have also been studied.<sup>3</sup>

The ultraviolet absorption spectrum of acetone vapor, formerly thought to consist of a broad band of continuous absorption with a maximum about 2700Å, has been shown recently by Crone and Norrish<sup>2(e)</sup> to have a region of

discrete absorption overlying the continuum on the long wave end. In this respect, therefore, acetone shows an important resemblance to acetaldehyde.<sup>4</sup> A consideration of the photochemical behavior of acetone vapor led to an unsuccessful search for such a discrete absorption.<sup>5</sup> The fluorescence of acetone vapor would require a discrete absorption for its explanation.<sup>6</sup>

By use of longer absorption tubes and varying pressures the results of Crone and Norrish have been confirmed. Recently Bowen and Thompson<sup>2(f)</sup> have stated that the entire continuum in reality consists of fine bands and that the general overlapping of the rotational fine structure is responsible for the appearance of the spectrum. Norrish<sup>2(g)</sup> has objected to this viewpoint. In the present work no bands shorter than

<sup>1</sup> The authors wish to express their appreciation for a grant-in-aid obtained from the National Research Council.

<sup>2</sup> (a) V. Henri and R. Wurmser, *Compt. rend.* **156**, 1013 (1913); (b) V. Henri, *Etudes de Photochimie*, Gauthier Villars et Cie., Paris, 1919, pp. 74, 76; (c) C. W. Porter and C. Iddings, *J. Am. Chem. Soc.* **48**, 40 (1926); (d) R. Titeica, *Bul. bilunar soc. fiz. romania*, No. 57, 31 (1933); (e) H. G. Crone and R. G. W. Norrish, *Nature* **132**, 241 (1933); (f) E. J. Bowen and H. W. Thompson, *ibid.*, **133**, 571 (1934); (g) R. G. W. Norrish, *ibid.* **133**, 837 (1934).

<sup>3</sup> Cf. reference 2(c); (a) D. Berthelot and Gaudechon, *Compt. rend.* **155**, 207 (1912); (b) F. W. Kirkbride and R. G. W. Norrish, *Trans. Faraday Soc.* **27**, 407 (1931); (c) G. H. Damon and F. Daniels, *J. Am. Chem. Soc.* **55**, 2363 (1933); (d) R. G. W. Norrish and Margaret E. S. Appleyard, *J. Chem. Soc.* **1934**, 874.

<sup>4</sup> See P. A. Leighton and F. E. Blacet, *J. Am. Chem. Soc.* **55**, 1766 (1933).

<sup>5</sup> For mention see W. A. Noyes, Jr., *Rev. Mod. Phys.* **5**, 280 (1933).

<sup>6</sup> Cf. reference 3(c), 2(e), C. F. Fisk and W. A. Noyes, Jr., *J. Chem. Phys.* **2**, 644 (1934).

3027Å have been observed although some search was made under conditions similar to those used by Bowen and Thompson. It is possible that higher pressures and longer exposures should be used.

Scheibe and Linström,<sup>7</sup> in investigating the absorption spectrum of acetone vapor in the Schumann region, have reported the existence of three bands located at approximately 51,300, 52,300 and 53,400  $\text{cm}^{-1}$ , respectively.

The present work was undertaken with the object of obtaining a satisfactory explanation of the spectroscopic and photochemical behavior of acetone vapor.

## I. THE SPECTRUM NEAR 3000Å

### (a) Experimental procedure

The acetone used in these experiments had been purified for solubility work in the laboratory of Professor Kraus. It was fractionally distilled at reduced pressure and allowed to react with carefully dried sodium iodide. The resulting complex,  $\text{NaI} \cdot 2(\text{CH}_3)_2\text{CO}$ , is a convenient source of acetone.

For most of the present work a tube 30 mm in diameter and 10 meters in length was employed. Plain fused quartz windows were attached to the end by means of picein wax. A 1000 watt tungsten filament lamp was used as a source of continuous radiation, a quartz water cell being interposed to prevent undue heating. Although approximately parallel radiation was used, internal reflection prevented the intensity from falling off as rapidly as would be expected. In exposures of one-half hour a good continuum extending to about 3050Å was obtained.

A few exposures were made with a one meter absorption tube and a discharge through hydrogen as a source of radiation in an effort to extend the spectrum to shorter wave-lengths.

A Hilger  $E_3$  spectrograph was used for this region of the spectrum. The iron arc burning in air was used to furnish wave-length standards. In a few instances a mercury arc, together with a Hartmann dispersion formula for interpolation, was employed.

Great difficulty was experienced in measuring the band positions. Under the microscope it was possible to see only a very few of the strongest bands, the rest being lost in the continuum due to the magnification. Somewhat better results were obtained with a small hand microscope, although more bands could always be identified with the naked eye. The best results were obtained by use of a projection lantern and measurement on the screen. In this way most of the bands were measured.

After consideration of the appearance of the bands it was decided to measure the long wave edges rather than the centers of gravity. A few of the bands seemed to have sharp edges, but many presented a real diffuse character. In view of the faintness and the diffuse appearance of the bands, the accuracy for some of the weaker bands may not exceed 2Å, although for some of the stronger bands it may be better than 1Å. Each recorded measurement is the average of a large number of measurements, except for a few bands at the long wave and short wave ends of the region investigated. The accuracy may be taken as  $\pm 10\text{--}15 \text{ cm}^{-1}$ .

The system of discrete bands fades off into complete transmission at one end and into complete absorption at the other, so that probably all bands have not been measured. The analysis to be given predicts bands at both extremes. Some indication of bands at wave-lengths longer than those recorded was obtained, but it proved impossible to measure them with any certainty. Undoubtedly some of the faint bands in the region covered have also been missed.

It is impossible to state definitely that a real continuum is present, but we are inclined strongly to the belief that such is the case. In the one meter tube photographs were taken at pressures so low as to give nearly complete transmission down to the limit of the spectrograph without definite indication of bands at wave-lengths shorter than those recorded. The spectrum seems to be very similar to that of acetaldehyde.<sup>4</sup>

### (b) Results

The majority of the bands observed in this region of the spectrum may be shown to fit the following three equations:

<sup>7</sup> G. Scheibe and C. F. Linström, *Zeits. f. physik. Chemie* **B12**, 387 (1931); see also G. Scheibe, F. Povenz and C. F. Linström, *ibid.* **B20**, 292 (1933).

$$\nu = 30923.7 + 208.6 (v_1' + \frac{1}{2}) - 368 (v_1'' + \frac{1}{2}), \quad (1)$$

$$\nu = 31000.9 + 216.2 (v_1' + \frac{1}{2}) - 368 (v_1'' + \frac{1}{2}), \quad (2)$$

$$\nu = 32121.8 + 214.3 (v_1' + \frac{1}{2}) - 368 (v_1'' + \frac{1}{2}). \quad (3)$$

Anharmonic terms could be included, but they would be small in any case and these empirical equations accord with the facts within the limits of experimental error. Table I shows the comparison between calculated and observed wave numbers.

One band (in addition to weak bands at longer wave-lengths which could not be measured) has not been included: 30,431.

The intensities of the bands are difficult to estimate, partly because of their faintness and probably also due to the underlying continuous absorption. In general one can say that bands with  $v_1''=0$  are stronger than those with  $v_1''=1$  or 2, and that the intensity is greatest when  $v_1'$  is small but not zero.

The bands obeying Eq. (3) lie in a region where the continuous absorption is quite important and this probably accounts for the fact that more members of this system were not observed. It is possible that the three bands in this system for which  $v_1''=2$  belong in reality to another system.

TABLE I. *Near ultraviolet bands of acetone.*

$v_1'$	$v_1''$	0		1		2	
		obs.	calc.	obs.	calc.	obs.	calc.
0		30839	30844				
1		31052	31053	(370)	30682	30685	
2		31262	31261	(367)	30895	30893	
3		31471	31470	(360)	31111	31102	
4		31682	31678	(357)	31325	31310	
5		31898	31887	(369)	31529	31519	
6		32093	32096	(366)	31727	31728	
7		32304	32304	(370)	31934	31936	
8		32502	32513	(371)	32131	32145	
9		32722	32721		<i>32375</i>	<i>32353</i>	<i>31971</i>
10					32569	32562	32194
11					<i>32785</i>	32771	(384) <i>32401</i>
12							32820
13							<i>33036</i> 33029
0		30925	30925	(366)	30558	30557	
1		31151	31141	(371)	30780	30773	
2		31362	31357	(377)	30985	30989	
3		31568	31574	(363)	31205	31206	
4		31798	31790	(375)	31423	31422	
5		32007	32006				
6		32213	32222				
7		32434	32438				
8		32653	32655				
9		32882	32871				
0		32045	32045				
1		32261	32259	(363)	(31898)	31891	
2		32478	32474	(385)	( <i>32093</i> )	32106	
3		32688	32688	(384)	32304	32320	
4					32545	32534	(392) <i>32153</i>
5							32166
6							<i>32375</i> 32380
							<i>32605</i> 32595

Bands in parentheses have been included twice. The assignments of those printed in italics may be considered as doubtful.

It is impossible to state whether the diffuseness is really of the predissociation type or not, as the apparent lengths of the bands change during a progression. In general the diffuse character seems to increase as  $v_1'$  increases.

### (c) Discussion of results

The frequency difference of approximately 370  $\text{cm}^{-1}$  has been assigned to the ground state for two reasons: (1) A strong Raman line has been reported of frequency from 376 to 391  $\text{cm}^{-1}$ ;<sup>8</sup> (2) It seems necessary to use this same frequency in classifying the bands in the Schumann region.

This frequency is probably due to the motion of the acetone molecule represented schematically in Fig. 1.<sup>9</sup> One would expect this sort of deformation motion to have a low frequency compared to those due to ordinary bond bending and stretching.

The constants 216.2, 208.6 and 214.3 seem logically to be ascribed to the upper state. The first two differ by more than experimental error (not enough bands are observed in the third matrix to make it possible to state whether the 214.3 differs from either of the others by more than the experimental error). Tentatively these frequencies may be assigned to the same type of motion in the upper state as the 370 in the lower state. This would mean, therefore, a weaker restoring force for this type of motion in the

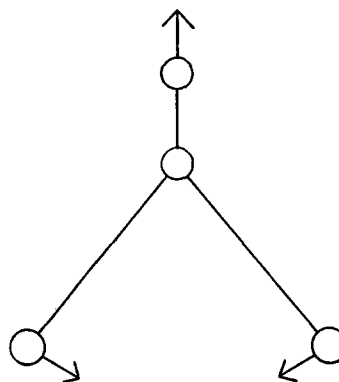


FIG. 1.

<sup>8</sup> Cf. K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt*, p. 314, Julius Springer, Berlin, 1931; K. W. F. Kohlrausch and F. Köppl, *Zeits. f. physik. Chemie* **B24**, 370 (1934).

<sup>9</sup> The authors wish to express their appreciation to Professor D. H. Andrews and Dr. J. W. Murray of Johns Hopkins University for communicating an interpretation of the Raman spectrum of acetone.

upper electronic state than in the lower, or in all probability a wider angle between the carbon-carbon bonds.

There remains the explanation of the difference between the 208.6 and 216.2. It has been pointed out that some of the weaker bands at longer wave-lengths may have been missed and that the correct assignment of the 0,0 band may not have been made in either matrix. The frequency difference of  $77\text{ cm}^{-1}$  is quite low for either a deformation or a bond frequency. It seems more probable that the true difference between the frequencies of the 0,0 bands should be  $77 + 216n$ , where  $n$  is probably small (1 or 2). Thus we would have an additional frequency (necessarily in the *upper* state) of 77, 293 or  $509\text{ cm}^{-1}$  corresponding to one of the other types of deformation vibration. To this frequency we will assign the quantum number  $v_2$ . The compounding of two deformation frequencies leads, as would be expected, to a small change in the frequency associated with  $v_1$ .

The two remaining differences between constant terms, 1198 and  $1121\text{ cm}^{-1}$ , respectively, are open to the same doubt as the frequency corresponding to  $v_2$ . Suffice to say that both of these frequency differences are too large to be ascribed to a stretching of the carbon-carbon single bond, unless the strength of this bond is greater in the upper than in the lower state. These frequencies do fall, however, in the general region in which one finds carbon-hydrogen bending frequencies. Indeed the normal acetone molecule shows four such Raman frequencies 1220, 1354, 1423 and  $1438\text{ cm}^{-1}$ . The exact nature of the upper electron state is unknown, but it seems improbable that the fundamental frequencies within the methyl groups would differ widely from those in the normal state. Tentatively we will accept 1198.1 as corresponding to a quantum number  $v_3$  in the upper state. There are two reasons for not assigning it to the ground state: (1) whereas the intensities are difficult to estimate, the general appearance of the bands is such that the Boltzmann factor could scarcely be decisive in determining the relative intensities; (2) although 1198.1 differs from an accepted Raman frequency by only  $22\text{ cm}^{-1}$ , it would be illogical to assign it to the ground state since none of the other fundamental frequencies of the

ground state other than 370 seem to be necessary.

The complete description of the observed bands may be made with three quantum numbers in the upper state and one in the lower state.

Since acetone is diamagnetic the electrons in the normal state are all paired. For the upper electron state all of the spins may be paired, or the spins of two of the electrons may become uncoupled leading to the formation of a single bond between the carbon and oxygen. In the latter case one should expect to find electronic sublevels whose spacing would be difficult to predict. This would lead to the formation of many sub-bands and might give a possible explanation of the relatively small separation (frequently as small as 30 or  $40\text{ cm}^{-1}$ ) of the band heads. In this event the vibrational analysis given above would be entirely meaningless and the separation of the vibration levels would have to be regarded as unknown. It is probable that sub-bands of the type observed by Dieke and Kistiakowsky<sup>10</sup> for formaldehyde should also appear in acetone, but they probably would not be observed as separate bands in the present experiments.

The absorption region in question is characteristic of ketones and aldehydes and is to be ascribed in some way to the presence of the  $>\text{C}=\text{O}$  group. If the electron system associated with this group is changed during absorption, the carbon-carbon valences will also be affected and the stable angle between these valences will differ from that in the normal state. An application of the Franck-Condon principle leads one to predict that the most intense bands should occur when the change in  $v_1$  is greater than zero. This is in accord with the facts presented above.

Since the absorption region in question corresponds to about four electron volts, more than enough energy is being provided to dissociate the carbon-carbon bond and nearly enough to dissociate a carbon-hydrogen bond. If either type of bond is to be broken as a result of predissociation two explanations are possible: (1) There exists another electron state of the acetone molecule whose polydimensional surface describing the various types of vibratory motion intersects

<sup>10</sup> G. H. Dieke and G. B. Kistiakowsky, Phys. Rev. **45**, 4 (1934).

that of the upper state of the present band system. The bands might or might not be diffuse depending upon the way in which the two surfaces intersect. The predissociation process would be described in terms similar to those used in discussing unimolecular reactions. (2) The process may be very similar to that described in (1), but the electron term for the present band system would be less than the energy of dissociation of one of the bonds. Rearrangement of the vibrational energy alone, without the presence of an additional electron state, might then lead to dissociation. Here again the absorption bands might or might not be diffuse depending upon the nature of the energy surface. Of course predissociation by collision may be important. Final decision with regard to the mechanism of dissociation must await information from other sources.

## II. THE SPECTRUM IN THE FAR ULTRAVIOLET

For the bands in this region a one meter focus glass grating was used. There were 30,000 lines to the inch and the dispersion was 8.52 Å/mm in the first order. For part of the work the continuum from an uncondensed discharge in hydrogen was used. The discharge took place in a 1.5 mm capillary tube and the continuum was entirely free from lines down to the beginning of the Lyman bands.

As wave-length standards the nitrogen doublet (1745.260; 1742.740) and the 1931.027 line due to C III were used. The former were superimposed by passing nitrogen through the discharge tube for a short time and the latter occurred merely due to impurities in the gas. The first strong line in the Lyman bands (1644.48 Å) could be used as an auxiliary standard.

Since the grating was used at nearly normal incidence the dispersion was nearly independent of wave-length and interpolation could be made directly. Table II shows values for the dispersion obtained on a characteristic plate.

For a continuum below 1650 Å, a condensed discharge in hydrogen was used. An 8 mfd. condenser, fully charged to 3000 volts by a d.c. generator, was discharged twice a second through a 1 mm capillary by means of a rotating contact. This gave a satisfactory continuum throughout the Schumann region with lines of silicon, car-

TABLE II. Dispersion of grating spectrograph.

Distance (mm)	Wave-length	Dispersion	
<i>a</i> —97.140	1931.027	<i>a</i> — <i>b</i>	8.5343
<i>b</i> —75.373	1745.260	<i>a</i> — <i>c</i>	8.5321
<i>c</i> —75.072	1742.74	<i>d</i> — <i>a</i>	8.5305
<i>d</i> —63.549	1644.48	<i>d</i> — <i>b</i>	8.5233
		<i>d</i> — <i>c</i>	8.5273
		Average	8.5295 ±0.0034 (0.03%)

bon and boron superimposed. Neither hydrogen lines nor lines from the aluminum electrodes appeared.

For those plates on which the nitrogen lines and the carbon line were not present, the wave-lengths of a few prominent lines were determined with reference to previously determined bands of acetone. Thus the wave-lengths of all of the bands are determined either directly or indirectly with respect to the standards mentioned above. While the absolute wave-lengths as given in the table may be subject to some inaccuracies, the relative values should probably be good to 0.1 Å for the strong sharp bands and be somewhat less accurate for the others.

It was possible even with the capillary sources to cover about 3/4 of the grating (ruled surface 4.25 in.); accordingly the resolving power was quite large.

In some experiments the spectrograph containing acetone vapor was separated from the discharge by a fluorite window. This served the double purpose of removing the second order hydrogen bands (which came out quite intensely) and preventing the acetone vapor from diffusing through the slit into the discharge. Exposure times were always less than a half hour (only a few minutes with the condensed discharge) so that it was not necessary to pump acetone through the spectrograph. In other experiments no window was used. A slight amount of acetone was probably pumped through the slit in this case, but caused no trouble in the condensed discharge.

The absorbing column was about two meters in length and hence the acetone pressures required were extremely low. The appearance of the bands depended greatly on pressure, so that it was necessary to take a long series of exposures

TABLE III. *Acetone bands 2000-1800A.*

1. Number of times measured; 2. wave-length (A); 3. average deviation from mean; 4. frequency ( $\text{cm}^{-1}$ ); 5. pressure (mm); 6. estimated intensity.

1	2	3	4	5	6	1	2	3	4	5	6
1	1995.50	—	50113	50	00	9	1917.12	0.13	52162	0.025	4
5	1962.67	0.10	50951	0.28	0	3	1916.27	0.06	52185	0.015	6
11	1960.78	0.08	51000	0.015	6	15	1914.99	0.11	52220	0.005	9
7	1960.05	0.08	51019	0.015	6	10	1914.21	0.09	52241	0.005	9
6	1958.82	0.09	51051	0.015	6	6	1912.69	0.17	52282	0.005	9
4	1957.98	0.14	51073	0.02	4	6	1909.66	0.09	52365	0.0075	8
14	1956.58	0.15	51110	0.015	6	4	1907.38	0.09	52428	0.0075	8
20	1954.22	0.14	51171	0.0025	10	3	1905.92	0.04	52468	0.0075	8
11	1953.30	0.12	51195	0.005	9	4	1884.36	0.11	53068	0.08	2
3	1952.15	0.07	51226	0.0075	8	3	1881.94	0.07	53137	0.08	2
4	1951.33	0.11	51247	0.005	9	7	1878.42	0.18	53236	0.035	3
7	1949.89	0.24	51285	0.005	9	11	1877.55	0.16	53261	0.035	3
3	1943.86	0.07	51444	0.015	6	12	1872.42	0.10	53407	0.015	6
5	1942.05	0.09	51492	0.015	6	3	1870.27	0.07	53468	0.035	3
3	1941.12	0.13	51517	0.015	6	5	1868.88	0.12	53508	0.015	6
2	1939.82	0.30	51551	0.015	6	2	1866.67	0.25	53571	0.035	3
3	1938.89	0.18	51576	0.015	6	1	1841.85		54293	0.13	0
6	1927.18	0.08	51889	0.025	4	9	1836.96	0.15	54438	0.122	1
3	1926.38	0.05	51911	0.035	3	5	1835.07	0.23	54494	0.13	1
8	1925.25	0.17	51941	0.035	3	2	1833.29	0.03	54547	0.218	0
5	1922.95	0.10	52003	0.035	3	5	1831.15	0.10	54611	0.122	1
6	1921.11	0.12	52053	0.02	4	5	1829.12	0.08	54671	0.114	1
3	1918.94	0.06	52112	0.02	4	5	1826.91	0.07	54737	0.130	1
						2	1819.71	0.01	54954	0.16	0

at pressures ranging from 0.0025 to 0.15 mm in pressure intervals of 0.005 mm.

Since a few of the bands seemed to have wave-lengths corresponding fairly closely to those reported for methyl iodide by Scheibe, Povenz and Linström,<sup>7</sup> the entire spectrum was rephotographed, using acetone which had not been subjected to the second purification by sodium iodide. The agreement between the bands observed with commercial C.P. acetone purified with sodium iodide and fractionally distilled in vacuum and the bands obtained with acetone from the laboratory of Professor Kraus was complete.

#### (a) Results

Beginning about 1960A and extending down to nearly 1800A a great many bands have been observed and the wave-lengths measured. The wave-lengths and wave numbers of these bands are given in Table III.

Because of the fact that the bands tend to become diffuse in appearance as the pressure is increased, the accuracy of the measurements is usually greatest at nearly the lowest pressure at which a given band can be observed. Also for this reason a slightly displaced wave-length may

be observed at higher pressures which, without care, may be taken as the wave-length of a new band. In general it proved unsafe to classify bands close together as separate bands unless they were observed on the same spectrum.

The bands were always shaded toward the violet so that the wave-lengths are those of the long wave edges. Fig. 2 shows a reproduction of two spectra.

The intensities (given on a scale of ten) are estimated from the appearance of the bands and the pressures at which they are first observed.

#### (b) Description of bands

An examination of the plates covering an extended pressure range shows that there are four well defined regions of absorption above 1800A which tend to merge as the pressure is increased. On the long wave end of the band system there is complete transmission persisting to the saturation pressure of acetone vapor at room temperature. Below 1800A there is also a transmission region up to this same high pressure, although some continuous absorption shows up here at high pressures. Below 1664A there are undoubtedly other band systems.

Three absorption regions separated by 1000-

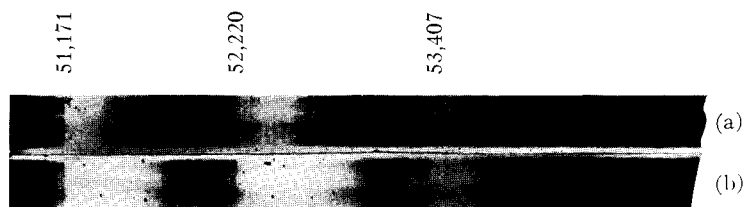


Fig. 2. Acetone absorption bands. (a)  $p=0.002$  mm. (b)  $p=0.045$  mm. Enlarged  $2\frac{1}{2}$  times.

$1200\text{ cm}^{-1}$  were noted by Scheibe and Linström<sup>7</sup> who considered them single bands due to the low resolving power employed. The fourth region appears only at relatively high pressures (above  $0.1$  mm). As the pressure is increased by steps new bands appear both to the red and to the violet in each of the three first regions. New bands to the red appear more slowly than do those on the violet side and the former remain closer to the low pressure bands than do the latter. The original low pressure bands become more diffuse as the pressure is increased. A pressure is then reached for each region beyond which no new bands appear, although a transmission region still exists between each pair of adjacent band groups. These intermediate transmission regions disappear at still higher pressures. This behavior of the bands with pressure indicates that a slight continuous absorption is present in the entire region rather than that new bands or new branches to the original bands are appearing so close together that the structure is obscured.

While the grating is not adequate to resolve possible rotational lines in the bands, it should be capable of showing rotational branches if such exist. Since the moments of inertia in acetone are approximately equal (one about double the other two), widely separated branches such as are observed in formaldehyde<sup>10</sup> would not be expected. Several bands were, however, observed which were separated by about  $20\text{ cm}^{-1}$  from strong bands. These would appear to be branches of the strong bands. Examples are  $51,019$  and  $51,000$ ,  $51,195$  and  $51,171$ ,  $52,241$  and  $52,220$ .

The question of predissociation is of interest, especially in respect to the photochemical decomposition of acetone in this region. None of the bands have the appearance of predissociation bands, excepting possibly those of frequency greater than  $54,293$ . These are diffuse even at the

lowest pressure observed. Continuous absorption, while it seems to exist, is very much weaker than that between  $2500$  and  $3200\text{Å}$ .

### (c) Analysis of the bands

A close examination of the regions separately shows no obvious grouping of the bands in progressions or sequences. However it is apparent that a band group in one region is very similar to a group in the next region and often this similarity is repeated in a third region. This shows that the vibration frequency differences must be large and of the order of  $1000$  to  $1200\text{ cm}^{-1}$ . After a search for constant differences it was found that these numbers were  $1052\pm 4$  and  $1194\pm 7\text{ cm}^{-1}$ . In addition a few bands showed differences of  $717\pm 2$ ,  $321\pm 1$ ,  $381$  (used once) and  $493\pm 2$ .  $1052$ ,  $1194$  and  $717$  seemed most surely to be upper state differences while  $381$  and  $493$  belong probably to the lower state since they are well-known Raman frequencies in acetone.<sup>8</sup>

The very large number of bands throughout the four regions separated by  $50$ – $60\text{ cm}^{-1}$  led finally to the discovery that all the bands could be classified in three systems whose lowest levels in the upper state differ by  $55$  and  $59\text{ cm}^{-1}$  respectively. The connection between these three levels is somewhat doubtful, but a triplet electronic upper state is not out of the question.

The arrangement of the bands is presented in Table IV. The transitions from the ground level to the three lowest levels in the upper state are  $51,171$ ,  $51,226$  and  $51,285\text{ cm}^{-1}$ . The higher levels in the upper state are obtained usually as differences from  $51,171$  and  $51,226$  with the above mentioned frequencies.  $51,285$  shows only one difference,  $1183$ , but we could not classify these two bands in any other way. The assignment of  $52,003$  is very doubtful on the basis of intensity.



TABLE IV. *Classification of acetone bands (2000-1800A).*

<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> 1194 52365 </div> <div style="text-align: center;"> 1049 52220 } 52241 } </div> <div style="text-align: center;"> 51171 } 51195 } 718 51889 } 51911 } </div> <div style="text-align: center;"> 321 51492 } 51517 } </div> <div style="text-align: center;"> (492) </div> <div style="text-align: center;"> 51000 } 51019 } </div> </div>			
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> 1143 53508 </div> <div style="text-align: center;"> 1016 53236 } 53261 } </div> <div style="text-align: center;"> 1053 52053 </div> </div>			
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> 1103 54611 </div> <div style="text-align: center;"> 52220 } 52241 } </div> <div style="text-align: center;"> 1015 53068 </div> </div>			
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> 1187 53407 </div> <div style="text-align: center;"> 51000 </div> </div>			
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> 1140 54547 </div> <div style="text-align: center;"> 51185 52185 </div> </div>			
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> 53236 } 53261 } </div> <div style="text-align: center;"> 51492 } 51517 } (382) </div> <div style="text-align: center;"> 51110 </div> </div>			
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> 1202 54438 </div> <div style="text-align: center;"> 1052 52162 </div> </div>			
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> 1202 52428 </div> <div style="text-align: center;"> 1056 52282 </div> <div style="text-align: center;"> 715 51941 </div> <div style="text-align: center;"> 51226 } 51247 } </div> <div style="text-align: center;"> 51444 (493) </div> <div style="text-align: center;"> 50951 (51551 ) 51576 } (500) </div> <div style="text-align: center;"> 325 51051 } 51073 } </div> </div>			
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> 1143 53571 </div> <div style="text-align: center;"> 1052 52003 </div> <div style="text-align: center;"> 1061 52112 </div> </div>			
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> 1100 54671 </div> <div style="text-align: center;"> 1025 53137 </div> </div>			
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> 52428 </div> <div style="text-align: center;"> 51285 ↓ 1183 52468 </div> </div>			
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> 1040 53468 </div> </div>			
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> 1026 54494 </div> </div>			

The bands at 54,737 and 54,954 could not be classified except by the use of very high and different frequencies. In the case of bands with two branches the differences were taken for the low frequency heads.

The band 50,113 seems to be a case by itself and very probably arises from a high level in the ground state. The difference 51,171-50,113 is 1058.

#### (d) Discussion

Several points in regard to the classification of the bands may be emphasized. The frequency differences in a progression decrease rather rapidly with increasing quantum number. Since the number in a progression is never over three, second differences must be compared in corresponding progressions as 51,051-52,112-53,137 and 51,000-52,053-53,065. The constancy of these differences supports the classification given.

The numbers in the upper state are most certainly modifications of Raman frequencies 391, 787, 1066 and 1220.<sup>8</sup> The first is used and discussed in the classification of the near ultra-violet bands; 787 is associated with symmetrical stretching of the molecule;<sup>9</sup> 1066 is an unsymmetrical stretching of the molecule, one methyl and the oxygen atom moving toward the center of gravity and the other methyl and the central carbon atom moving away; 1220 is due to change of the angle between the carbon-hydrogen bonds. The frequency 381 in the lower state is certainly the Raman frequency 391 and 492 is the Raman frequency 486. The latter does not appear in the upper state.

Decreases take place in the fundamental frequencies when they appear in the upper state, this being least in the case of 1066 and 1220 and greatest in the case of 391 and 787. The change in regard to the change of 391 to 322 is analogous to that present in the near ultraviolet bands, although for some reason the restoring force is nearer the normal value and the angle between the carbon-carbon bonds is not so wide. It would appear that this type of motion may be compounded with higher frequency motions since bands separated by 1052 and 1194 are also separated ultimately from the origin by the difference 321.

A decision as to which of these types of motion would lead most easily to disruption of the molecule is impossible, but certain generalizations may be stated. The 787 motion could scarcely lead to the breaking of a single bond. In any case progressions involving this frequency are all short. The 1220 motion alone might, if carried to convergence, lead to the rupture of the carbon-hydrogen bond, but series involving this frequency converge relatively slowly and do not extend beyond a quantum number of three (the approximate convergence limit would be 65,000  $\text{cm}^{-1}$ ). The progressions based on 1052 converge at about the same rate, but extend only a very short distance. This motion might eventually lead to the rupture of a carbon-carbon bond. Unless some repulsive perturbing state exists so that dissociation could result by predissociation, rupture of any of the bonds in the acetone molecule by the absorption of radiation in this region would seem improbable. Whether the

apparent slight continuous absorption mentioned above gives evidence for such a perturbing state is uncertain.

In conclusion, it seems that rupture of a carbon-carbon bond by absorption in this region would be most probable, and the rupture of a carbon-hydrogen bond the next most probable case. Experiments by one of us (W.M.M.) indicate that relatively more hydrogen is produced in this region of the spectrum than at longer wave-lengths. Hydrogen must come from the splitting of a carbon-hydrogen bond in the primary process. However it is impossible to decide whether the hydrogen comes from pre-dissociation or from the continuous absorption observed in this region. Perhaps a decision could be made by the use of strictly monochromatic light in the band region, although this seems doubtful. Results obtained at relatively low pressure indicate that collision phenomena are not solely responsible for the production of hydrogen.

### III. THE ABSORPTION BELOW 1800Å

The data in this region are still incomplete and will be made the subject of a future article. With the present setting of the grating the region from 2200 to 1250 is covered in the first order. Without a fluorite window the hydrogen bands from 1100 to about 900Å appear at one end of the plate in the second order, with the uncondensed discharge, while in the condensed

discharge strong lines in these bands appear in absorption. When acetone is present all of the second order is removed by continuous absorption of acetone from 1100 to 900Å, the probable actual limit being at even shorter wave-lengths.

The bands given in Table V have been found between 1250 and 1700Å. An analysis will not be attempted until this region is covered more thoroughly.

TABLE V. *Acetone bands between 1700 and 1250Å*

1. Number of times measured; 2. wave-length (Å); 3. average deviation from mean; 4. frequency ( $\text{cm}^{-1}$ ); 5. pressure (mm).

1	2	3	4	5
2	1710.4	0.12	58466	0.02
11	1664.9	0.40	60065	0.03
1	1636.6		61104	0.053
2	1630.5	0.11	61332	0.053
1	1620.5		61710	0.053
2	1608.4	0.32	62173	0.053
1	1600.6		62477	0.053
1	1380.1		72458	0.0025
1	1378.9		72519	0.0025

The bands in Table V show some differences similar to those found in Section II. The following may be mentioned in particular:

72519—72458	61	62477—61332	1145
62477—62173	304	62173—61104	1069
62477—61710	767	61104—60065	1039

In conclusion the authors express their appreciation to Dr. E. J. Hart who carried out some of the measurements reported in this paper.