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George W. Luckey, A. B. F. Duncan, and W. Albert Noyes

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The Fluorescence of Acetone Vapor¹

GEORGE W. LUCKEY, A. B. F. DUNCAN, AND W. ALBERT NOYES, JR.

Department of Chemistry, University of Rochester, Rochester, New York

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The "blue" fluorescence of acetone vapor has been photographed with a large Littrow-type spectrograph giving a dispersion of about 16Å/mm in the range used. Numerous bands having a roughly uniform spacing of about 122 ± 10 – 15 cm^{-1} have been observed and their frequencies determined. Certain suggestions are made concerning the vibration analysis, but neither a detailed analysis nor a discussion of the relationship of these bands to the absorption spectrum is justified at present. The existence of structure in this fluorescence shows that it is unnecessary to assume that dissociation of the molecule accompanies the emission of fluorescent radiation. On the other hand, the existence of structure cannot be taken to prove the absence of dissociation following the emission process.

THE existence of fluorescence in acetone vapor when excited by wave-lengths of the mercury arc from 3130 to 2537Å seems to have been reported first by Damon and Daniels.² Many other articles have appeared which present studies of the effects of various variables on the fluorescence efficiency and on the spectrum.³

Damon and Daniels² showed that the fluorescence may be divided roughly into "green" and "blue" parts. The former has been shown quite conclusively to be associated with some photo-chemical reaction product, presumably biacetyl,⁴ whereas the latter is emitted from carefully purified acetone and seems to be due mainly to acetone itself.

A simple Stern-Volmer mechanism is not obeyed for the "blue" fluorescence.³ It appears necessary to assume at least two upper states with quite different half-lives to explain the data, but many more may be involved. At temperatures of 100 to 200°C the quantum yield of acetone decomposition is high⁵ while the intensity of the blue retains from 20 to 50 percent of its room temperature value.³ Thus the fraction of the molecules which fluoresce instead of dissoci-

ating following absorption of radiation must be very small unless by some mechanism fluorescence is accompanied by dissociation. An estimate made by Damon and Daniels² indicates that the fluorescence efficiency must be exceedingly low.

Under certain experimental conditions some structure can be observed in the absorption spectrum of acetone vapor.⁶ This gives rise to the hope that structure might also be found in the spectrum of the fluorescence under suitable conditions. Experimental conditions were such in most previous studies that the presence of structure could not have been detected even if it were present.

It is recognized that for polyatomic molecules such as acetone the structure might be so complex as to give the appearance of a continuum even under the best experimental conditions. On the other hand, the existence of structure in the fluorescence spectrum will show both that the acetone molecule is capable of existence in an excited electronic level without immediate decomposition and that the lower level to which the molecule goes with emission of radiation is capable of existence for a sufficient time to give the discrete spectrum. The sharpness of the structure will be related qualitatively to the life of the molecule in either the initial or the final state or both. A diffuse spectrum would indicate that the life is relatively short in one state or the other.

¹ This work was supported in part under Contract N6onr-241, Task I with the Office of Naval Research, United States Navy.

² G. H. Damon and F. Daniels, *J. Am. Chem. Soc.* **56**, 2370 (1933).

³ For a fairly complete bibliography see R. E. Hunt and W. A. Noyes, Jr., *J. Am. Chem. Soc.* **70**, 467 (1948).

⁴ M. S. Matheson and W. A. Noyes, Jr., *J. Am. Chem. Soc.* **60**, 1857 (1938); M. S. Matheson and J. W. Zabor, *J. Chem. Phys.* **7**, 536 (1939); G. M. Almy and S. Anderson, *ibid.* **8**, 805 (1940).

⁵ D. S. Herr and W. A. Noyes, Jr., *J. Am. Chem. Soc.* **62**, 2052 (1940).

⁶ H. G. Crone and R. G. W. Norrish, *Nature* **132**, 241 (1933); W. A. Noyes, Jr., A. B. F. Duncan, and W. M. Manning, *J. Chem. Phys.* **2**, 717 (1934); W. A. Noyes, Jr., *Trans. Faraday Soc.* **33**, 1495 (1937).

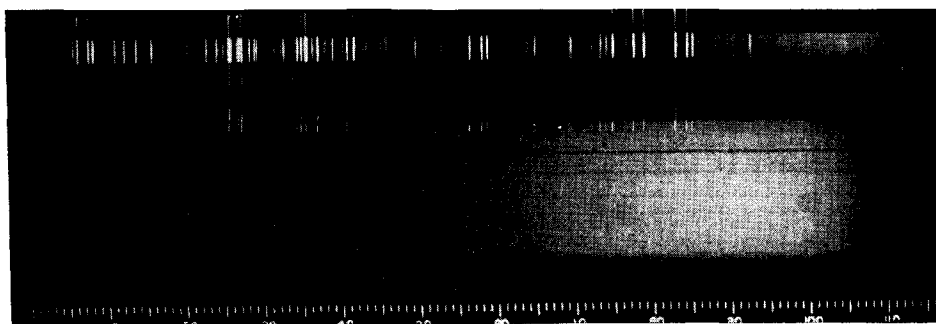


FIG. 1. The "blue" fluorescence of acetone vapor.

Structure has been found experimentally in the "blue" fluorescence spectrum of acetone (Fig. 1).

EXPERIMENTAL

Since biacetyl is produced photo-chemically when acetone is exposed to radiation of wavelength 3130A and since biacetyl gives a strong green fluorescence (as well as possibly some in the blue³), it was necessary to use a flow system in studying the "blue." The acetone vapor was flowed through the cell by distilling liquid acetone from a large bulb through the cell, through capillary tubing to regulate the flow, and condensing the vapor in a bulb maintained at 0°C. The pressure of vapor in the cell was in the range 80–110 mm. The acetone was dried by distillation from over anhydrous calcium sulfate.

Two quartz cells made of fused quartz with plane ends were used. The diameters of both were 25 mm and the lengths 100 and 200 mm, respectively.

A General Electric Company Type AH-6 mercury arc was used. The light passed through a slit, was collimated by a quartz lens of focal length about 12 cm, passed through a filter solution, and condensed by a second lens into a narrow beam about 1 mm wide and 20 mm long. Highly monochromatic light did not prove feasible because of the low intensity of the fluorescence, but 10 mm of 0.89 m NiCl₂ and 10 mm of Red Purple Correx Glass removed radiation longer than 3660A, although a small amount of this line was transmitted. Some radiation below 3130A was transmitted but such wave-lengths seem not to excite the blue fluorescence to any appreciable extent.⁷

⁷ Cf. Noyes, W. A., Jr., and Henriques, F. C., Jr., *J. Chem. Phys.* **7**, 773 (1939) for a discussion. Data on this point are not conclusive.

A Sinclair Smith Recording Microphotometer was used to make density tracings of the plates. Wave-lengths were established by using the iron arc as a standard.

Eastman Type I-0 plates were used and developed with D-19 developer.

Biacetyl fluorescence was photographed as a check of the apparatus. In this instance a static system was used and Eastman Kodak biacetyl was used without further purification.

Most of the photographs were taken with a large Bausch and Lomb Littrow mounting spectrograph, although one or two were taken with a small Bausch and Lomb glass prism spectrograph. The former had a dispersion of about 16A/mm and the latter of about 32A/mm in the range used.

RESULTS

Four plates in all were taken with the small glass prism spectrograph. The first three plates showed only continuous emission, but for two of these the slit widths were 0.9 and 0.3 mm, respectively. The third plate showed so little blackening that no conclusions could be drawn. The fourth plate did show evidence of structure.

Ten plates in all were taken with the large Littrow spectrograph, most of them with a slit width of 0.1 mm. During exposure of one plate an accident caused the color filter to be displaced and the 4070 and 4358A-lines of mercury were incident on the acetone. Eight plates showed evidence of structure. One plate was taken of the fluorescence of the cell without any acetone and proved that the weak fluorescence of the quartz could not be responsible for the results.

The wave-lengths were determined by reference to a dispersion curve based on the iron arc.

The frequencies of the maxima and the differences between adjacent bands are shown in Table I.

TABLE I. Maxima in the "blue" fluorescence of acetone.

Band number	Frequency	Difference	Band number	Frequency	Difference
1	20988	116	14	22570	110
2	21104	110	15	22680	132
3	21214	122	16	22812	108
4	21336	132	17	22920	128
5	21468	112	18	23048	115
6	21580	119	19	23163	108
7	21699	136	20	23271	131
8	21835	117	21	23402	136
9	21952	123	22	23538	129
10	22075	117	23	23667	108
11	22192	120	24	23775	100
12	22312	134	25	23875	
13	22446	124			

The accuracy of the frequencies given in Table I is probably not greater than ± 10 – 15 cm^{-1} because of the difficulty in determining the exact position of the maxima.

The frequency difference between adjacent bands is fairly constant and for that reason a diffraction or interference phenomenon was suspected. To obtain evidence on this matter the following experiments were performed:

(1) One photograph was taken with the 100-mm cell rotated so that the face made an angle of approximately 30° with the slit.

(2) One photograph was taken with the 100-mm cell rotated through 180° so that the fluorescence was photographed through a different face.

(3) For two photographs a quartz plate was cemented to the face of the 200-mm cell with Apiezon grease and the space between the two plates filled with cyclohexanol which has the same index of refraction as fused quartz.

(4) Two different lengths of cell were used.

(5) Two different spectrographs were used.

(6) Biacetyl fluorescence (in the same region of the spectrum) excited by 3660Å was photographed in a static system, showing a series of weak maxima separated by about 85 instead of by about 120 cm^{-1} .

The first four lines of evidence indicate quite definitely that any diffraction or interference phenomenon does not arise from the cells themselves. Point (5) indicates that probably the phenomenon does not arise in the spectrograph.

The best evidence that the bands are definite is found in point (6). This experiment shows, moreover, that the bands are not due to biacetyl. This was further indicated by taking one plate of acetone in a static system, thus showing the bands due to acetone with superposition of some of the biacetyl bands.

It seems safe to conclude, therefore, that the fluorescence of acetone in the blue and near ultraviolet parts of the spectrum has some structure which cannot be ascribed to biacetyl.

DISCUSSION OF RESULTS

There seems to be little point in attempting a detailed analysis of these fluorescence bands of acetone. The nearly constant frequency difference of about 120 cm^{-1} may be explained in several ways. It is quite a bit lower than any known Raman or infra-red frequency of the acetone molecule.⁸ Possibly it is a "difference" frequency. There is a Raman frequency of 488 cm^{-1} in acetone and there is evidence, obtained from the effect of temperature on the absorption spectrum, that there is an upper state vibration frequency of 366 cm^{-1} .⁶ The difference between these is 122 which coincides with the average frequency difference between adjacent bands. Thus a long sequence involving these two frequencies would give the spacing shown in Table I. Such a long sequence would be somewhat surprising and probably affords only a partial explanation of the data. An additional periodicity in the bands is evident in the intensities as observed by the naked eye, but microphotometer tracings fail to afford definite proof on this point. There may be involved an additional upper state frequency of about 600 cm^{-1} , but positive statements in this connection are not warranted.

The short wave end of the blue fluorescence lies at about 26000 cm^{-1} , while the lowest frequency band in absorption lies near 30800 cm^{-1} . This large difference of nearly 5000 cm^{-1} indicates but does not prove that radiation occurs from a different electronic level from that produced directly by the absorption of radiation. Better evidence on this point can be obtained from other sources.

The mechanism of photo-chemical decomposi-

⁸ Cf. M. Lawson and A. B. F. Duncan, J. Chem. Phys. 12, 330 (1944).

tion of acetone is quite complex and need not be discussed in detail here.⁹ Some evidence exists for the assumption that an excited acetone molecule may dissociate directly into ethane and carbon monoxide.¹⁰ Since ΔH for the reaction $\text{CH}_3\text{COCH}_3 = \text{C}_2\text{H}_6 + \text{CO}$ is nearly zero, an excited or metastable molecule might dissociate by falling to a repulsive state giving these products. The transfer could be accompanied by the

⁹ For a review see W. Davis, Jr., *Chem. Rev.* **40**, 201 (1947).

¹⁰ R. Spence and W. Wild, *J. Chem. Soc.* 352 (1937); 590 (1941); M. H. Feldman, M. Burton, J. E. Ricci, and T. W. Davis, *J. Chem. Phys.* **13**, 440 (1945).

emission of continuous radiation. This possibility has been suggested.³ The existence of bands in the fluorescence spectrum makes the postulation of immediate dissociation following emission of fluorescent radiation unnecessary and indeed improbable. On the other hand, this evidence cannot be taken to prove that a single step dissociation into ethane and carbon monoxide by some other mechanism does not occur. The best evidence on the latter point can be obtained from a detailed study of the photo-chemical reaction kinetics. Such a study will be published in the near future.

Thermodynamic Properties of the Internal Rotator. Double Minimum with Repulsive Forces

J. O. HALFORD

Department of Chemistry, University of Michigan, Ann Arbor, Michigan

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The basis for calculating the thermodynamic properties of the unsymmetrical internal rotator from energy levels derived from the old quantum theory is described, and a method is outlined for calculations with a potential energy function consisting of linked sections of cosine curve with the width of each section proportional to the barrier height. A table of values of a general quantum number index for the cosine function is presented and its application to the unsymmetrical internal rotator is illustrated. Thermodynamic properties are calculated for a double minimum system of optical isomers for which the forces restricting rotation must be repulsive. It is found that the entropy of such a system may be greater by nearly 0.5 unit than that of the limiting system with equal potential maxima, that is, with the symmetrical cosine potential function.

THE contributions of internal rotation to the thermodynamic properties of a molecule consisting of a rigid framework with one symmetrical top attached have been calculated in detail by Pitzer and Gwinn.¹ Their results are published in the form of extensive tables of free energy, heat content, entropy, and heat capacity for various combinations of the variables $1/Q_f$ and V/RT , with Q_f denoting the partition function for free rotation and V representing the height of the potential energy barrier. The energy states used by these workers to obtain the thermodynamic properties were calculated by means of the wave mechanics and are based

upon a potential energy function of the form $V = V_0(1 - \cos n\theta)/2$ in which n is the symmetry number of the rotation, or the number of potential energy maxima in the cycle.

Pitzer and Gwinn have demonstrated that their tables may be used for a molecule having several internal rotations if the potential energy can be expressed as a simple sum of terms $V = V_0(1 - \cos n\theta)/2$, that is, if there are no significant cross products in the potential energy expression. Further, they have developed an approximation valid for lower temperatures and higher moments of inertia which can be applied when such cross products are significant. They go on to consider changes in the shape of the potential energy curve to forms with broader

¹ K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.* **10**, 428 (1942).