

## The Ionization Potential of Acetone Vapor

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Citation: [The Journal of Chemical Physics](#) **3**, 430 (1935); doi: 10.1063/1.1749694

View online: <http://dx.doi.org/10.1063/1.1749694>

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These computations consider the dissociation  $\text{H}_2 = 2\text{H}$  and  $\text{H}_2\text{O} = \text{H}_2 + \frac{1}{2}\text{O}_2$ ; all thermal data being taken from Bulletin 139 of the University of Illinois Engineering Experiment Station.<sup>13</sup> It will be observed that when  $\rho$  is maximum, the corresponding velocity  $u_1$  is 2820.9 meters per

<sup>13</sup> The use of the recent spectroscopic thermal data will entail small modifications in Table I. The merits of the function  $\rho$ , of course, are independent of the correctness of the underlying data.

second which agrees with Dixon's experimental value. Referring to Eq. (11), it will be seen that the value of  $A_0$  will influence the magnitude of  $\rho$  without changing the position of its maximum on the Hugoniot curve. For the purposes of this example, this constant has been taken as zero. With appropriate values of  $A_0$ ,  $\rho$  would be smaller and its maximum, although less sharp, would identify the same detonation velocity.

JULY, 1935

JOURNAL OF CHEMICAL PHYSICS

VOLUME 3

## The Ionization Potential of Acetone Vapor

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(Received April 13, 1935)

The ionization potential of acetone vapor has been measured with a two-electrode tube. The value found agrees within experimental error with that predicted from spectroscopic data.

THE absorption spectrum of acetone vapor has been investigated recently both in the quartz region and with a vacuum grating to as far as 850A.<sup>1</sup> It consists of a continuous absorption in the neighborhood of 3000A with a faint discrete absorption on the long wave end, a rather complex system of bands extending from about 1960A to about 1800A and finally several other band systems obviously involving several different upper electron states at still shorter wavelengths. Among the latter bands Duncan<sup>1b</sup> found one series which could be represented by the Rydberg formula

$$\bar{\nu} = 82,767 - R/(n - 0.495)^2 (n = 3, 4, 5 \dots). \quad (1)$$

No other Rydberg series which were convincing from the standpoint of intensity relationships could be found, although it was thought at one time that two others existed. Eq. (1) predicts an ionization potential of 10.20 volts and the present work was undertaken with the object of verifying this value by the electron collision method.

### (A) EXPERIMENTAL PROCEDURE

The purification of the acetone has already been described.<sup>1a</sup> It was stored over calcium chloride.

<sup>1</sup> (a) W. A. Noyes, Jr., A. B. F. Duncan and W. M. Manning, *J. Chem. Phys.* **2**, 717 (1934); (b) A. B. F. Duncan, *ibid.* **3**, 131 (1935).

Fig. 1 shows a diagram of the apparatus. The acetone vapor was admitted through the capillary tube H from a supply bulb kept at one of the following temperatures:  $-77^\circ$  ( $\text{CO}_2$ -ether);  $-33^\circ$  (liquid ammonia);  $0^\circ$  (ice water). At these temperatures the vapor pressures of acetone are approximately 0.15, 7 and 67 mm, respectively. In general the best results were obtained at the lowest vapor pressure, although the rate of evacuation was sufficiently high to permit measurements to be made at the higher temperatures. At B are two diaphragms made of glass perforated by holes about 0.5 mm in diameter. The traps A and C were immersed in liquid air during a run and E was attached to a high speed diffusion pump. Since the vapor pressure of acetone is immeasurable on a McLeod gauge

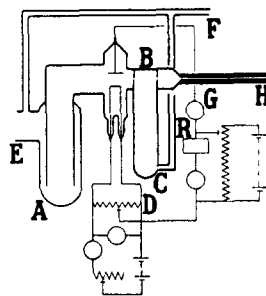


FIG. 1.

at the temperature of liquid air, the main removal of the acetone was accomplished by these traps rather than by the diffusion pump, the latter serving mainly to remove uncondensable gases either given out from various parts of the apparatus or by the decomposition of acetone by the hot filament. That such gases were effectively removed was indicated by the fact that during a run, even with the acetone at 0°C, the McLeod gauge attached to *F* always indicated a good "sticking" vacuum. With this experimental procedure a unidirectional stream of acetone vapor passed between the filament and the plate.

The electrical circuit needs little discussion. The resistance *D* permitted the potential between various portions of the filament and the plate to be utilized. It was found that the negative end of the filament gave the results requiring the smallest correction. The plate current was read by the galvanometer *G*. The resistance *R* served merely to reduce somewhat the personal equation, the plate voltage being calculated from the value of this resistance, the resistance of the voltmeter and the reading of the voltmeter. The filament was of the spiral type made of thoriated tungsten. The entire tube was surrounded by an electrostatic shield grounded to the filament.

As calibrating gases mercury vapor and hydrogen were used. For the former liquid air was merely removed from the traps and the source of acetone vapor cut off, the diffusion pumps being kept in operation. Electrolytic hydrogen was admitted to the apparatus to a pressure of a few hundredths of a millimeter, liquid air being kept on the traps.

### (B) RESULTS

Large scale graphs were made of the  $3/2$  power of the accelerating voltage against the galvanometer deflections. Since both from theoretical reasons and because of the nature of the experimental procedure, the exact position of the change in slope cannot be ascertained with high precision, readings were made at 0.5 (in some cases smaller) intervals and enough runs were made so that a statistical average would have some significance.

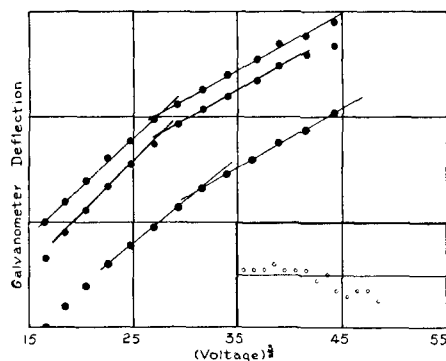


FIG. 2. Top curve,  $R=150\Omega$ ; middle curve,  $R=200\Omega$ ; bottom curve,  $R=0$ . In the lower right-hand corner a plot is given of successive differences in galvanometer deflection against the voltage for the data used in the middle curve.

Fig. 2 shows three typical curves. The fact that the current increased less rapidly with voltage after the "break" than before can be explained on the basis of the geometry of the tube and the electrostatic shield surrounding it.<sup>2</sup> At potentials just exceeding the ionization potential the positive ions would probably contribute little toward reducing the space charge in the neighborhood of the filament.

Table I presents a summary of the uncorrected results.

TABLE I. Average uncorrected values for ionization potentials

Gas	No. runs	Ave. P.D.	Ave. dev. from mean	Prob. error of arith. mean
Acetone	67	10.32 v	0.3 <sub>7</sub> v	0.03 <sub>9</sub> v
Mercury	15	10.4 <sub>1</sub> v	0.3 <sub>9</sub> v	0.07 <sub>7</sub> v
Hydrogen	25	16.2 <sub>6</sub> v	0.4 <sub>2</sub> v	0.07 <sub>6</sub> v

The ionization potential of mercury may be determined directly with high precision.<sup>3</sup> In the case of hydrogen the value obtained from Rydberg series is 15.36 volts and Bleakney has obtained experimentally a value in excellent agreement with this figure.<sup>4</sup> However, application of the Franck-Condon principle leads to the prediction that the most probable transition produced by electron bombardment would form

<sup>2</sup> Cf. A. R. Olson and T. F. Young, *Phys. Rev.* **25**, 58 (1925).

<sup>3</sup> Cf. E. O. Lawrence, *Phys. Rev.* **28**, 947 (1926).

<sup>4</sup> W. Bleakney, *Phys. Rev.* **40**, 496 (1932).

a hydrogen molecule ion possessing vibrational energy, and that usually the observed ionization potential should be several tenths of a volt in excess of the above figure, at 15.9 volts.<sup>5</sup> This value will be used. The two corrections obtained for calibration are, therefore, 0.03 and 0.36, average 0.20.

The ionization potential of acetone corrected by the above figure is, therefore, 10.1 with an uncertainty of several tenths of a volt.

### (C) DISCUSSION OF RESULTS

If the 0,0 bands have been chosen properly, the ionization potential predicted by the Rydberg series (Eq. (1)) would be that required to produce a positive acetone ion possessing only zero-point energy. While the value obtained in these experiments is not very precise, the agreement with the predicted value indicates that such an acetone ion is produced directly by electron bombardment.

The electrons in the carbonyl group may be described to a first approximation in the same manner as those for a diatomic molecule. Thus they would be given the designation  $\sigma_a^2\pi_a^2$  ( $\sigma^2\pi^2$ )<sub>c-o</sub>( $a^2b^2$ )<sub>c-c</sub>, where the subscripts indicate the atoms or the bonds with which the electrons are concerned.  $a$  and  $b$  are used for want of a better designation for the carbon-carbon electrons. Of the electrons associated with the oxygen atom two (probably  $\sigma_a$ ) would be classified as nonbonding and would have ionization potentials not differing much from that of the oxygen atom,<sup>6</sup> two (probably  $\pi_a$ ) would be classified as antibonding and would have ionization potentials lower than that of the oxygen atom. Of the four bonding electrons two should probably be weakly and two strongly bonding,

both sets probably having ionization potentials higher than either the oxygen or the carbon atom. One would predict, therefore, three and possibly four different ionization potentials for acetone, the lowest probably corresponding to the removal of a  $\pi_a$  electron which will, in reality, not be associated entirely with the oxygen atom but belong to the group as a whole. The predicted ionization potential would be lower than that of oxygen (13.55 volts) and probably lower than that of carbon (11.22 volts).<sup>7</sup> The values found both spectroscopically and in the present paper are in accord with this prediction. Other possible Rydberg series might be found.

The removal of a  $\pi_a$  antibonding electron probably would not lead to the production of an acetone ion in a highly excited vibration state. The two electronic band systems at 3000 and 1960A which do not obviously fit into Rydberg series are probably to be ascribed to transitions involving either the bonding electrons or the nonbonding electrons. Since, if the analysis of the band system at 3000A is correct, the lowest deformation frequency in the upper state differs considerably from that in the ground state, it is possible that transitions involving particularly the bonding electrons are involved. At 1960 since the fundamental frequencies do not seem to be so profoundly modified, it is possible that the nonbonding electrons are concerned. Higher states involving these two types of electrons do not seem to be stable and may be responsible for the weak continuous absorption observed throughout the Schumann region as well as between 2500 and 3000A. These suggested interpretations of the spectrum of acetone will be examined in the light of other evidence in the near future.

<sup>5</sup> See O. W. Richardson, *Molecular Hydrogen and Its Spectrum*, Yale University Press, 1934, pp. 1, 154ff.

<sup>6</sup> Cf. R. S. Mulliken, *Phys. Rev.* **46**, 549 (1934).

<sup>7</sup> Cf. R. F. Bacher and S. Goudsmit, *Atomic Energy States*, McGraw-Hill Book Co., New York, 1932, pp. 333, 101.