

Preliminary Analysis of the Microwave Spectrum of Ketene

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MICROWAVE spectra of $\text{CH}_2=\text{CO}$, $\text{CHD}=\text{CO}$ and $\text{CD}_2=\text{CO}$ were taken at a pressure of 0.1 mm Hg in a 23-foot brass wave guide (X -band) with central steel electrode using Hughes-Wilson modulation technique. The oscillator was a 2K33 Klystron which, by proper adjustment of its largest screw (not the ordinary turning screw) and correct matching, oscillates between 16,000 to 21,200 and 22,000 to 25,800 Mc/sec. Wave-lengths were measured by a wave meter, carefully calibrated against well-determined N^{14}H_3 and N^{15}H_3 absorption frequencies. The frequencies obtained seem good to 2 to 3 Mc/sec.

A solution of $\text{CH}_2=\text{CO}$ in acetone was prepared by cracking of acetone. A solution of the deuterated species was prepared by cracking a mixture of deuterated acetones which were obtained by leaving a mixture of 18 g D_2O , 0.2 g NaOD and 16 g acetone for 36 hours and afterwards distilling off the acetones through an efficient column. In this way 15.2 g deuterated acetones were prepared. Density determination of the $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixture, subsequently distilled off, showed that exchange equilibrium had been reached. The various ketene species used for the absorption experiments were admitted to the gas cell from their acetone solution which was kept at -70°C .

$\text{CH}_2=\text{CO}$ absorbed at 20,200 Mc/sec. (middle intensity) and at 20,257 (weak), near^{1,2} N^{14}H_3 at³ 20,272.3 and^{4,4} N^{14}H_3 at⁴ 20,371.4.

By cooling of the gas cell to about -60°C it was seen that the intensity of the stronger line increased about 3 times while the weak line remained of constant intensity. The 20,200 Mc frequency thus must be assigned to the ground state of the molecule, 20,257 to an excited level. Both Raman spectrum² and infrared measurements⁵ show the existence of a vibrationally excited level at 510 (Raman) or 529 cm^{-1} (infra-red). The next level apparently lies at 600 cm^{-1} . The weak line, 20,257, may therefore be assigned to a molecule, excited by 510 cm^{-1} , but it remains unexplained why another, slightly weaker line, corresponding to 600 cm^{-1} excitation was not observed.

The strong line showed a Stark effect (at ~ 500 volts $\Delta\nu \sim 6$ Mc/sec.) which is in agreement with the molecular dipole moment¹ (1.45 D.U.). Ketene prepared from acetone contains CH_4 , $\text{CH}_2=\text{CH}_2$, CO and acetone as impurities. It was shown by experiment that acetone does not absorb at the frequencies assigned to ketene.

Correspondingly $\text{CHD}=\text{CO}$ showed weak absorption at 18,892, stronger at 18,825 (close to⁶ N^{14}H_3 at 18,884.9 and⁷ N^{14}H_3 at⁸ 18,808.7. $\text{CD}_2=\text{CO}$ absorbed with middle strength at 17,690 (close to⁸ N^{15}H_3 at 17,548.4 and⁷ N^{15}H_3 at⁹ 17,855.3). No weak line was observed in the case of $\text{CD}_2=\text{CO}$.

From the interatomic distances determined by electron diffraction⁶ ($d_{\text{CC}}=1.35\pm 0.02\text{A}$, $d_{\text{CO}}=1.17\pm 0.02\text{A}$) and the selection rules⁹ it follows that the absorption frequencies found must correspond to a $0_0 \rightarrow 1_{-1}$ transition. $\text{CH}_2=\text{CO}$ has 3 different moments of inertia $I_a \ll I_b < I_c$, where $I_c = I_a + I_b$. In units of chemical molecular weight times angstrom squared I_a may be assumed to vary between 1.49 and 1.97 corresponding to $d_{\text{CH}}=1.05\text{A}$, $\angle\text{HCH}=110^\circ$ resp. $d_{\text{CH}}=1.09\text{A}$, $\angle\text{HCH}=130^\circ$. This gives $I_b=49.28$, resp. 49.08, $I_c=50.77$ and 51.05.

The geometry of the molecule is somewhat better determined (although not completely) than has hitherto been the case. The results for $\text{CH}_2=\text{CO}$ and $\text{CD}_2=\text{CO}$ are easy to handle as here the dipole moment lies in the axis of least moment of inertia. The geometry of the molecule has 4 unknowns: d_{CH} , d_{CC} , d_{CO} and $\angle\text{HCH}(=2\varphi)$. If reasonable values of $d_{\text{CH}}(1.05-1.09\text{A})$ and $2\varphi(110^\circ-130^\circ)$ are assumed a number of corresponding d_{CC} and d_{CO} values can be calculated. For $d_{\text{CC}}=1.07\text{A}$ fine agreement with the electron diffraction data is obtained at $2\varphi=123^\circ.7\pm 1^\circ.0$. For $d_{\text{CH}}=1.05\text{A}$ $2\varphi=120^\circ.3\pm 1^\circ$. For $d_{\text{CH}}=1.09\text{A}$ $2\varphi=127^\circ.1$

± 1.0 . We thus know that $119^\circ < 2\varphi < 128^\circ$. The electron diffraction pattern was analyzed by assuming $2\varphi=110^\circ$, but the analysis is only slightly influenced by a change in the position of the hydrogen atoms. At the same time it is found that $d_{\text{CC}}=1.330-1.340\text{A}$ and $d_{\text{CO}}=1.140-1.170\text{A}$.

The results for $\text{CHD}=\text{CO}$ can be utilized preliminarily by assuming that the moments of inertia of $\text{CHD}=\text{CO}$ are close to those for an imaginary molecule $\text{CX}_2=\text{CO}$, where the mass of X is the average of H and D. If this is done the values $d_{\text{CH}}=1.06$, $d_{\text{CC}}=1.333$, $d_{\text{CO}}=1.150$ and $2\varphi=122^\circ.5$ must be favored. This means that d_{CO} comes close to the CO distance in CO_2 and in⁷ OCS (1.162A) and d_{CC} close to 1.353A from ethylene.⁸ Likewise $\angle\text{HCH}=122^\circ.5$ is near the ethylene value⁸ 120° and the formaldehyde value¹⁰ ($123^\circ.5$).

Further calculations are being postponed until better frequency determinations can be carried out.

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Current Fluctuations in D.C. Gas Discharge Plasma*

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RADIOFREQUENCY energy produced in a d.c. gas discharge plasma has been measured in the microwave region.^{1,2} The use of gas discharge tubes as microwave noise standards has recently been indicated.³ This noise power can be accounted for by a study of the electron current fluctuations in the plasma as follows.

An electron whose thermal speed lies between V and $V+dV$ will on the average suffer $Z_V T$ collisions in a time T . Actually there will be fluctuations in this number, and the probability $p(K)$ that it experiences K collisions in a time T is:

$$p(K) = [(Z_V T)^K / K!] \exp(-Z_V T). \quad (1)$$

The probability $q(\theta)$ that the time of consecutive collisions of an electron lies between θ and $\theta+d\theta$ is:

$$q(\theta) = Z_V \exp(-Z_V \theta) d\theta. \quad (2)$$

Now making the usual assumptions that the electron current exists only between collisions, the current i_x measured between the electrodes due to an electron which has collided at time t_k with a subsequent free time θ_k is:

$$i_x(t-t_k; \theta_k) = e/d [V_x + a(t-t_k)] \text{ for } t_k \leq t \leq t_k + \theta_k, \quad (3)$$

where d = length of tube parallel to direction of applied electric field E_x , $a = eE_x/m$, and V_x = thermal velocity of electron parallel to x axis.

There are similar expressions for the current in the Y and Z directions, except that a is set equal to zero. The total electron current $I(t)$ will be a function of the random variables t_k and θ_k and it is possible to find its fluctuations and spectrum by the usual methods.³ Under the assumptions that the electron distribution is Maxwellian with an electron temperature T_e and that the collision rate Z_V is independent of velocity, the spectrum $W(f)$ of the current fluctuations is given by:

$$\langle (I - \bar{I})^2 \rangle_{\text{av}} = \int_0^\infty W(f) df \quad (4)$$

$$W(f) = 4kT_e G(\omega) + 4 \frac{\bar{I}^2}{N} \frac{Z}{Z^2 + \omega^2} \left[2 + \frac{Z^2 - \omega^2}{Z^2 + \omega^2} \right], \quad (5)$$