Preliminary Analysis of the Microwave Spectrum of Ketene

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MICROWAVE spectra of $CH_2=CO$, $CHD=CO$ and $CD_2=CO$ 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 $CH_2=CO$ 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 H_2O-D_2O 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 $-70°C$.

$CH_2=CO$ absorbed at 20,200 Mc/sec. (middle intensity) and at 20,257 (weak), near[1,2] $N^{15}H_3$ at[3] 20,272.3 and[1,4] $N^{14}H_3$ at[4] 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 spectrum[2] and infrared measurements[5] 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 affect (at $\sim$500 volts $\Delta\nu \sim 6$ Mc/sec.) which is in agreement with the molecular dipole moment[1] (1.45 D.U.). Ketene prepared from acetone contains CH_4, $CH_2=CH_2$, CO and acetone as impurities. It was shown by experiment that acetone does not absorb at the frequencies assigned to ketene.

Correspondingly $CHD=CO$ showed weak absorption at 18,892, stronger at 18,825 (close to[4,6] $N^{14}H_3$ at 18,884.9 and[1,7] $N^{14}H_3$ at[3] 18,808.7. $CD_2=CO$ absorbed with middle strength at 17,690 (close to[6,8] $N^{15}H_3$ at 17,548.4 and[1,7] $N^{15}H_3$ at[3] 17,855.3). No weak line was observed in the case of $CD_2=CO$.

From the interatomic distances determined by election diffraction[6] ($d_{CC}=1.35\pm0.02A$, $d_{CO}=1.17\pm0.02A$) and the selection rules[9] it follows that the absorption frequencies found must correspond to a $0_0 \rightarrow 1_{-1}$ transition. $CH_2=CO$ 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 $d_{CH}=1.05A$, $\angle HCH=110°$ resp. $d_{CH}=1.09A$, $\angle HCH=130°$. 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 $CH_2=CO$ and $CD_2=CO$ 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 $\angle HCH(=2\varphi)$. If reasonable values of d_{CH}(1.05–1.09A) and 2φ(110°–130°) are assumed a number of corresponding d_{CC} and d_{CO} values can be calculated. For $d_{CC}=1.07A$ fine agreement with the election diffraction data is obtained at $2\varphi=123°.7\pm1°.0$. For $d_{CH}=1.05A$ $2\varphi=120°.3\pm1°$. For $d_{CH}=1.09A$ $2\varphi=127°.1 \pm1.0$. We thus know that $119°<2\varphi<128°$. The electron diffraction pattern was analyzed by assuming $2\varphi=110°$, 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 $d_{CC}=1.330$–$1.340A$ and $d_{CO}=1.140$–$1.170A$.

The results for $CHD=CO$ can be utilized preliminarily by assuming that the moments of inertia of $CHD=CO$ are close to those for an imaginary molecule $CX_2=CO$, where the mass of X is the average of H and D. If this is done the values $d_{CH}=1.06$, $d_{CC}=1.333$, $d_{CO}=1.150$ and $2\varphi=122°.5$ must be favored. This means that d_{CO} comes close to the CO distance in CO_2 and in[7] OCS (1.162A) and d_{CC} close to 1.353A from ethylene.[8] Likewise $\angle HCH=122°.5$ is near the ethylene value[8] 120° and the formaldehyde value[10] (123°.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.[2] 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_VT 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:

$$p(K)=[(Z_VT)^K/K!]\exp(-Z_VT). \tag{1}$$

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

$$q(\theta)=Z_V\exp(-Z_V\theta)d\theta. \tag{2}$$

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:

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

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:

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

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

where $\bar{I}=\langle I(t)\rangle_{Av}$ = average electron current, $\omega=2\pi f$ = angular frequency of observation, $G(\omega)$ = a.c. conduction of gas discharge plasma, N = total number of electrons in the plasma.

The available noise power P_ω from a gas discharge plasma placed in the transverse plane of a rectangular wave guide propagating only in its lowest mode is

$$P_\omega=|I_E|^2/4G(\omega). \quad (6)$$

Here I_E = a.c. electron current in the direction of the E vector of the wave guide. Hence in this case,

$$P_\omega=\left\{kT_e+\frac{P_0}{NZ}\cos^2\theta\left[2+\frac{Z^2-\omega^2}{Z^2+\omega^2}\right]\right\}df, \quad (7)$$

where θ = angle between E vector and axis of gas tube, and P_0 = d.c. power dissipated in tube. For ordinary gas tubes that are used as microwave noise standards, the contribution of the frequency sensitive term is of the order of a few percent of the total noise power output. This calculation does not account for noise power due to other fluctuations.

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Nuclear Magnetic Resonance of Sb^{121} and Sb^{123}*

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We have made attempts to find the nuclear resonance of Sb in Sb_2O_3 and $SbCl_3$ without success. On the supposition that this failure was due to a large interaction between the electric quadrupole moment of the Sb nucleus and the non-uniform electric field of the above molecules a search was made in an ion in which the electric field would be symmetrical. This requirement is fulfilled in the $SbCl_6^-$ ion in which the Cl atoms are believed to be arranged in a regular octahedral configuration about the Sb.

A search was made in a solution of $HSbCl_6$ in HCl guided roughly by the spectroscopic values of the magnetic moments as given by Crawford and Bateson[1] using a radiofrequency magnetic resonance spectrometer.[2] Distinct resonances were observed in the vicinity of 9800 kc and 5300 kc which from the spectroscopic information would presumably be associated with Sb^{121} and Sb^{123} respectively. Repeated series of readings were taken comparing the Sb^{121} resonance to that of Na in solid NaCl, and the Sb^{123} resonance to that of D in D_2O. The frequencies of resonance were measured by means of a U. S. Signal Corps frequency meter type EC 221−Q, calibrated at 100 kc intervals against harmonics generated by a General Radio crystal controlled oscillator operating at 100 kc and in turn standardized against Station WWV. The magnetic field was electronically controlled to a constancy of about one part in 50,000.

The average values of the ratios of the observed frequencies are:

$$[\nu(Sb^{121})/\nu(Na^{23})]=0.90469\pm0.00004$$

and

$$[\nu(Sb^{123})/\nu(D^2)]=0.8442\pm0.0001.$$

If we take Bitter's[3] value of the observed ratio of $\nu Na/\nu H = 0.26450\pm0.01$ percent, and used a first-order atomic diamagnetic correction for Sb of 1.00517 as calculated from the Hartree-Fock functions[4] and the value[5] for H^2 of 1.000027, we get for the ratio $g(Sb^{121})/g(H^1)=0.24052\pm0.00003$. Taking the spectroscopic value of 5/2 for the spin of Sb^{121} and the value for μ_H as measured by Taub and Kusch,[6] we get

$$\mu(Sb^{121})=3.3595\pm0.0004.$$

One must note that this value of the magnetic moment may possibly be in error as a result of second-order molecular effects which we are unable to evaluate at this time.

Similarly, taking Bloch's[7] value of

$$\mu(P)/\mu(D)=3.257195\pm0.00002,$$

we get $[g(Sb^{123})/g(H)]=0.13025\pm0.00002$, and taking the value 7/2 for the spin, we get for the magnetic moment

$$\mu=2.5470\pm0.0003 \text{ nuclear magnetons.}$$

It is of interest to compare the ratio of the g-values of the two Sb isotopes as obtained spectroscopically by Crawford and Bateson,

$$[g(Sb^{121})/g(Sb^{123})]=1.82\pm0.02 \text{ to our } 1.8466.$$

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Effect of Magnetic Fields on Conduction—"Tube Integrals"

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The effect of a magnetic field **H** on electrical conduction can be reduced to integrals by using "tubes." Choose parallel to **H** an axis $\mathbf{P}_H$ in the $\mathbf{P}=\hbar\mathbf{k}$ space of the Brillouin zone. Then the region lying between planes $\mathbf{P}_H$ and $\mathbf{P}_H+d\mathbf{P}_H$ and energy surfaces $E(\mathbf{P})=E$ and $E+dE$ is a "tube." For spherical energy surfaces the tube is a torus with a parallelogram cross section. For more complex surfaces and for energies for which the surfaces reach the boundary of the Brillouin zone the tube may possibly take a helical path and eventually fill most of the space between E and $E+dE$. We shall discuss only simple closed tubes of interest for semiconductors.

For any tube α an angle variable θ and a tube mass m_α are defined by equations

$$m_\alpha\theta=\int_0^{P_l} dP_l/v_l, \quad 2\pi m_\alpha=\oint dP_l/v_\alpha, \quad (1)$$

where P_l is the distance in the **P**-space along the tube from an arbitrarily selected fixed point and v_α is the scalar magnitude of the component perpendicular to **H** of the group velocity $\mathbf{v}=\nabla E(\mathbf{P})$. **H** produces incompressible flow along the tube α with

$$\begin{gathered} d\mathbf{P}/dt=(-e/c)\mathbf{v}\times\mathbf{H}, \quad \dot{P}_l=(-e/c)v_\alpha H \\ \dot{\theta}=\dot{P}_l/v_\alpha m_\alpha=-eH/m_\alpha c=\omega_\alpha, \end{gathered} \quad (2)$$

so that $\dot{\theta}$ is constant and the period is given by the classical formula with a mass m_l.

If we assume that after one transition, due to thermal vibration for example, an electron will have average velocity zero, then the current produced by a given tube can be reduced to closed form as follows. When an electric field **E** is applied each element dV_P of volume in **P**-space becomes a source of electrons of strength

$$(-eV/kTh^3)f(1-f)\mathbf{E}\cdot\mathbf{v}dV_P, \quad (3)$$

where V is the volume of the crystal, f the Fermi-Dirac distribution function and e, k, T, h are as usual. If $\nu(\varphi)=1/\tau(\varphi)$ is the probability of being scattered per unit time at tube position φ, the total current density $d\mathbf{I}_\alpha(=(-e/V)\epsilon\mathbf{v}(\varphi))$ due to electrons brought into tube α by **E** is

$$\begin{gathered} d\mathbf{I}_\alpha=(e^2/kTh^3)f(1-f)dEdP_H(m_\alpha/\omega_\alpha). \\ \int_\theta^{2\pi} d\theta\int_0^\infty d\varphi\mathbf{E}\cdot\mathbf{v}(\theta)\mathbf{v}(\varphi)\exp\left[-\int_\theta^\varphi \nu(\varphi')d\varphi'/\omega_\alpha\right]. \end{gathered} \quad (4)$$