humans from 0.19 mg K/g of blood serum to 4.20 mg K/g red blood cells. The average potassium content of sea water is 0.39 mg/g of water. Because this is only about 2.6 percent of the K which has been released by the decomposition of crustal rocks, it is assumed that the remainder has been adsorbed and is to be found in sedimentary deposits. Thus, the K content of the oceans may be assumed to have been at substantially its present concentration for at least the major portion of the earth's history. Suggestions have reappeared[23] recently concerning the possible early importance of the radiations from K^{40} on mutations and on the origin of species. Taking 4.9 Mev of γ-radiation plus 16.6 Mev of β-radiation per second per gram of potassium as the present rate of energy release, it can be shown from the ordinary principles of radiation dosage[24,25] that the K content of sea water now produces, on organisms whose dimensions are small compared with the range of the β-rays of K^{40}, a tissue dosage of only 1.4×10^{-5} rep./day. Taking the half-period of K^{40} as 0.45×10^{9}yr. and the K constant of ocean water as constant with respect to time, the corresponding tissue dosage 1.0×10^{9} yr. ago would have been 0.066×10^{-3} rep./day, while 2.0×10^{9} yr. ago the dosage would have been 0.31×10^{-3} rep./day. These are very small dosages, and can hardly be held accountable for any significant degree of mutation induced by radiation. By way of comparison, the cosmic radiation at sea level gives[24] a tissue dosage of 0.10×10^{-3} rep./day. On the other hand, a total dosage of about 50 rep. per generation is required to double the natural mutation rate in lower organisms.

[23] F. Ellis, Brit. J. Radiology **21**, 1 (1948).

[24] R. D. Evans, Am. J. Roent. **58**, 754 (1947).
[25] R. D. Evans, Nucleonics **1**, No. 2, 32 (October 1947).

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Effect of Large Quadrupole Interactions on Nuclear Radiofrequency Spectra at Twice Larmor Frequency

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The work of B. T. Feld and W. E. Lamb [Phys. Rev. **67**, 15 (1945)] on the effect of a nuclear electrical quadrupole moment on the radiofrequency absorption spectrum of a heteronuclear diatomic molecule in a magnetic field is extended to a special case not considered by them. This is a case in which the electrical quadrupole interaction energy is so large that even in magnetic fields of several thousand gauss the magnetic interaction energies are small compared to the electrical quadrupole interaction energy. In this case it is shown theoretically that for a spin of $\frac{3}{2}$ there are certain circumstances under which a maximum of absorption will occur at double the Larmor frequency instead of at the Larmor frequency and will have a field and molecule dependence similar in many ways to a resonance at the Larmor frequency. This result has the important implication that special care must be used in identifying the radiofrequency resonance absorption spectra or an error of a factor of two in the value of a nuclear magnetic moment can easily be made. The approximate shape and intensity of the radiofrequency absorption spectrum under these circumstances is calculated in order that a comparison of the theoretical shapes and intensities with the experimental ones can be used as a means of recognizing if an absorption is a double Larmor frequency one.

I. INTRODUCTION

DETAILED consideration has been given by Feld and Lamb[1] to the effect of a nuclear electrical quadrupole moment on the radiofrequency absorption spectra of heteronuclear diatomic molecules in magnetic fields as such spectra are observed in the molecular beam resonance method.[2-4] Although Feld and Lamb[1]

* Part of this work was done at Columbia University.
[1] B. T. Feld and W. E. Lamb, Phys. Rev. **67**, 15 (1945).

[2] Rabi, Millman, Kusch, and Zacharias, Phys. Rev. **55**, 526 (1939).
[3] Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **56**, 728 (1939).
[4] Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **57**, 677 (1940).

in the third section of their paper consider the case in which the electrical quadrupole interaction energy is large compared with the magnetic interaction energy, they do so from the point of view of considering the magnetic field to be very weak. Consequently, they omit consideration of transitions for which there is no difference of quadrupole energy since in a very weak magnetic field the resonance absorption would occur at frequencies below those at which measurements are usually made. However, in the case of a very large quadrupole interaction energy of the order of several hundred megacycles (as found by Townes, Holden, Bardeen, and Merritt[5] in such molecules as BrCN) the limit of quadrupole interaction being large compared to the magnetic interaction can be achieved in magnetic fields of several thousand gauss, for which the resonance absorption will be at several megacycles even for transitions for which there is no difference in quadrupole energy.

The purpose of this paper is to consider such transitions in detail for the case of nuclear spin $\frac{3}{2}$ and heteronuclear diatomic molecules. Since the same terminology and symbolism will be used here as in Feld and Lamb,[1] the definitions of the various quantities will not be repeated.

A preliminary indication as to the nature of the results to be expected can be obtained by differencing the middle two equations of the group designated as III (18) by Feld and Lamb,[1] in which case to the first order and for negligibly small g_J.

$$W(+, m; -, m-1) = 2\mu_0 g_I H(1-\tfrac{3}{4}z^2)^{\frac{1}{2}}. \quad (1)$$

Since z can vary between $+1$ and -1 this means that transitions will occur at frequencies between

$$\nu = W(+, m; -, m-1)/h = \mu_0 g_I H/h \quad (2)$$

when $z = \pm 1$, and

$$\nu = 2\mu_0 g_I H/h$$

when $z=0$. That is, transitions occur at all frequencies between the Larmor frequency and twice that frequency. A preliminary indication of the frequency at which the effect of the resonance absorption will be greatest can be obtained by calculating the density of transitions

$$D = 1/(dW/dz) = -2(1-\tfrac{3}{4}z^2)^{\frac{1}{2}}/3\mu_0 g_I H z, \quad (3)$$

which becomes infinite for $z=0$. Since, as will be shown later, the transition probability is only a slowly varying function of z, the effect of the resonance absorption will be greatest when $z=0$, i.e., at twice the Larmor frequency.

Although this preliminary discussion is adequate to indicate partially the nature of the result, it is not adequate to determine the shape of the resonance curve, since the assumption of a very large quadrupole interaction of the order of several hundred megacycles invalidates the assumption made by Feld and Lamb that J may be regarded essentially as infinite since the small added terms arising from the finiteness of J are multiplied by a large factor determined by the quadrupole interaction so that the product of the two is quite comparable to the energy change in the transition considered.

II. ENERGY VALUES

For quadrupole interactions much stronger than magnetic interactions with the external magnetic field, a representation in terms of a total angular momentum $\mathbf{F}=\mathbf{I}+\mathbf{J}$ may best be used as in Feld and Lamb (reference 1, page 24).

Calculation of the energy values for $I=\frac{3}{2}$ is complicated by the fact that the unperturbed (zero field) energy levels are degenerate to the extent to which J may be taken as infinite. Although the finite value of J removes this degeneracy in the case of a very large quadrupole interaction, it does so only by an amount comparable to or smaller than the magnitude of the magnetic interaction with the external field. Furthermore, there exist non-vanishing matrix elements of this magnetic interaction between the states $F=J+\frac{1}{2}$ and $F=J-\frac{1}{2}$. Consequently, these states are mixed by the application of the external magnetic field. The determination of the energy levels can be accomplished by solving the secular equation for a typical value of m or of $z=m/J$ since the matrix is diagonal in m.

As in Casimir[6] and in Feld and Lamb (reference 1, pages 19 and 25), the Hamiltonian for

[5] Townes, Holden, Bardeen, and Merritt, Phys. Rev. 71, 644 (1947).

[6] H. B. G. Casimir, "On the interaction between atomic nuclei and electrons," Archives du Musée Teyler (III) 8, 201 (1936).

the relevant interactions is

$$\mathcal{H}=\mathcal{H}_Q+\mathcal{H}_M, \tag{4}$$

where

$$\mathcal{H}_Q=-[e^2q'Q/(2J+3)(2J-1)I(2I-1)] \times[3(\mathbf{I}\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{I}\cdot\mathbf{J})-I(I+1)J(J+1)] \tag{5}$$

and

$$\mathcal{H}_M=\mu_0 g_I H I_z, \tag{6}$$

where g_J is taken as approximately equal to zero for simplification and the sign convention of Feld and Lamb is used in (6). Note that, in the above, q which is used by Feld and Lamb[1] and which is dependent[7] on J is replaced by q' used by Nordsieck where

$$q=-[2J/(2J+3)]q',$$

since q' is independent of J.[7] In two recent papers by Feld[8] and by Bardeen and Townes[9] alternative expressions for the interaction constant have been given. The relation of the q' of the present paper to the $\partial^2V/\partial z^2$ of Feld[8] and the q of Townes[9] is

$$q'=(1/2e)(\partial^2V/\partial z^2)=(1/2e)q.$$

The matrix elements $(F, m|\mathcal{H}|F', m)$ of $\mathcal{H}$ can be evaluated with the aid of Eqs. III (5) and III (11) of Feld and Lamb. The result after simplification is that for a single value of m or z all the non-zero matrix elements are one of the following:

$$\begin{aligned}
&(J+\tfrac{3}{2}, m|\mathcal{H}|J+\tfrac{3}{2}, m)=-a(1-\gamma)+\tfrac{3}{2}bz,\\
&(J+\tfrac{1}{2}, m|\mathcal{H}|J+\tfrac{1}{2}, m)=a(1+\gamma)+\tfrac{1}{2}bz,\\
&(J-\tfrac{1}{2}, m|\mathcal{H}|J-\tfrac{1}{2}, m)=a(1-\beta)-\tfrac{1}{2}bz,\\
&(J-\tfrac{3}{2}, m|\mathcal{H}|J-\tfrac{3}{2}, m)=-a(1+\beta)-\tfrac{3}{2}bz,\\
&(J+\tfrac{1}{2}, m|\mathcal{H}|J+\tfrac{3}{2}, m)=(J+\tfrac{3}{2}, m|\mathcal{H}|J+\tfrac{1}{2}, m)\\
&\qquad=(J-\tfrac{3}{2}, m|\mathcal{H}|J-\tfrac{1}{2}, m)\\
&\qquad=(J-\tfrac{1}{2}, m|\mathcal{H}|J-\tfrac{3}{2}, m)\\
&\qquad=\tfrac{1}{2}\sqrt{3}b(1-z^2)^{\frac{1}{2}},\\
&(J-\tfrac{1}{2}, m|\mathcal{H}|J+\tfrac{1}{2}, m)=(J+\tfrac{1}{2}, m|\mathcal{H}|J-\tfrac{1}{2}, m)\\
&\qquad=b(1-z^2)^{\frac{1}{2}},
\end{aligned} \tag{8}$$

where

$$a=e^2q'Q/4,\quad b=\mu_0 g_I H,$$
$$\gamma=3/(2J+3),\quad \beta=3/(2J-1).$$

Although in the above the effect of the finite size of J is included in the large quadrupole interaction, J is taken as essentially infinite in the much smaller magnetic interaction.

Since there are no matrix elements connecting the approximately degenerate states $J+\frac{3}{2}$ and $J-\frac{3}{2}$ and since $J\pm\frac{3}{2}$ is far from degenerate with $J\pm\frac{1}{2}$, the secular equation will approximately factor and the relevant factor for states involving $J\pm\frac{1}{2}$ is

$$(a+\gamma a+\tfrac{1}{2}bz-E)(a-\beta a-\tfrac{1}{2}bz-E) -b^2(1-z^2)=0, \tag{9}$$

whence

$$E=a[1+(\gamma-\beta)/2]\pm b[(1-\tfrac{3}{4}z^2) +\tfrac{1}{2}((\gamma+\beta)a/b)z+((\gamma+\beta)^2a^2/4b^2)]^{\frac{1}{2}}. \tag{10}$$

However, for large J we have two terms of order $1/J$:

$$\begin{aligned}
&\gamma-\beta=-10/(2J+3)(2J-1)\approx-5/2J^2\approx0,\\
&\gamma+\beta=6(2J+1)/(2J+3)(2J-1)\approx3/J.
\end{aligned} \tag{11}$$

Hence, to this order

$$E(\pm, m)=a\pm b[(1-\tfrac{3}{4}z^2) +\tfrac{3}{2}(a/Jb)z+\tfrac{9}{4}(a/Jb)^2]^{\frac{1}{2}}. \tag{12}$$

Since in (12) z is not multiplied by the large factor a but only by the much smaller factors of the order of b or (a/J), J may be considered to be sufficiently large that the change in $z=m/J$ for $\Delta m=\pm1$ may be neglected. In this case, with the notation of Feld and Lamb (reference 1, page 28)

$$W(+, m; -, m\pm1)=2b[(1-\tfrac{3}{4}z^2) +\tfrac{3}{2}(a/Jb)z+\tfrac{9}{4}(a/Jb)^2]^{\frac{1}{2}} \tag{13}$$

or, by rearrangement,

$$W(+, m; -, m\pm1)=2b \times[[1-\tfrac{3}{4}(z-(a/Jb)^2)]+3(a/Jb)^2]^{\frac{1}{2}}. \tag{14}$$

From (14), z can be expressed in terms of $W\equiv W(+, M; -, M\pm1)$ as

$$z-(a/Jb)=\pm(2/\sqrt{3}) \times[1-(W/2b)^2+3(a/Jb)^2]^{\frac{1}{2}}. \tag{15}$$

Since z must, by definition, be real and of absolute value less than one, J and W in this equation must be restricted to values such that this occurs. It may readily be seen from (15) that an absolute value of less than one is insured for z provided

$$|a/Jb|<0.2 \quad\text{and}\quad |W/2b|>0.9, \tag{16}$$

[7] A. Nordsieck, Phys. Rev. **58**, 310 (1940).
[8] B. T. Feld, Phys. Rev. **72**, 1116 (1947).
[9] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).

or provided

$$|a/Jb|<0.3 \quad \text{and} \quad |W/2b|>1.0. \tag{17}$$

These restrictions are not serious since the maximum of the resonance spectra, which is the part of interest, is at an energy consistent with these restrictions. The reality of z, which is a more pertinent restriction since the maximum occurs near $z=0$, is insured provided the J contributing to any energy W is restricted by

$$J\leqslant[3(a/b)^2/((W/2b)^2-1)]^{\frac{1}{2}}. \tag{18}$$

III. THE SPECTRUM

For a single J, the "density of transitions" as defined by Feld and Lamb is

$$D=\tfrac{1}{2}[|dz/dW|_+ + |dz/dW|_-] = W/2b^2\sqrt{3}[1-(W/2b)^2+3(a/Jb)^2]^{\frac{1}{2}}, \tag{19}$$

where the subscripts + and − correspond to the two different signs in (15) and where the normalization is such that DdW gives the probability that a molecule in rotational state J, with $F=+$, and with m randomly selected will have a transition energy between W and $W+dW$.

This density of transition must be multiplied by the transition probability, p. It may be readily confirmed that the transition $(+, m; -, m\pm1)$ is an allowed transition. This may be most easily done in the limit of infinite J in which case the quantity P of Feld and Lamb which is proportional to the transition probability for weak oscillating fields becomes

$$P(+, m; -, m-1) = \mu_0^2 g_I^2 H_x'^2 (+, m|I_x|-, m\pm1)^2. \tag{20}$$

The matrix element in (20) may readily be evaluated from Feld and Lamb's Eqs. III (16), III (17), and III (11). The resulting expression for (20) becomes

$$P(+, m; -, m\pm1) = \tfrac{1}{4}[1+(1/2(1-\tfrac{3}{4}z^2)^{\frac{1}{2}})]^2\mu_0^2 g_I^2 H_x'^2. \tag{21}$$

This is finite, varies by only a factor of two in the allowed range of z, and is comparable in magnitude to the values of P of Feld and Lamb. Consequently, the transition is completely an allowed one. If the procedure of Feld and Lamb were followed, Eq. (19) would be multiplied by Eq. (21). However, in most of the relevant experiments Feld and Lamb's assumption of a weak oscillating field does not apply whence (21) does not give the actual transition probability. Instead, such a strong oscillating field is used that the net transition probability is of the order of one-third for non-forbidden transitions. Consequently, the transition probability at present will merely be taken as an approximately constant quantity p which is less than one and of the order of one-third. Since the transitions from m to both $m+1$ and $m-1$ occur, the effective probability as concerns the line intensity is $2p$.

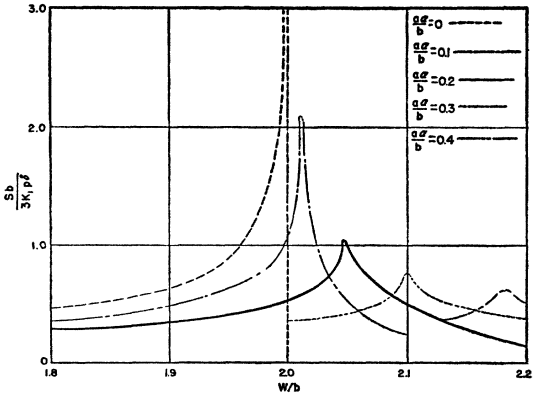

FIG. 1. $Sb/(3K_1p\delta)$ as a function of W/b for different values of $a\alpha/b$.

The resonance line intensity contributed by a single molecule in rotational state J with $F=+$ then would be $2pD$. For all the molecules, let S be the ratio of the intensity of the resonance at frequency W/h to the intensity of the entire beam. Then

$$S=\frac{\dfrac{2K_1\delta}{2I+1}\displaystyle\int_0^\infty 2pD2J\exp[-\alpha^2J^2]dJ}{\displaystyle\int_0^\infty 2J\exp[-\alpha^2J^2]dJ}, \tag{22}$$

where[10]

$$\alpha^2=h^2/8\pi^2I_0kT=(\pi/4)(1/(\tilde{J})^2), \tag{23}$$

and K_1 is a factor introduced[10] to compensate for lack of complete deflecting power of the apparatus; K_1 is necessarily of a magnitude less than unity. $2/(2I+1)$ is introduced because only 2 out

[10] W. A. Nierenberg and N. F. Ramsey, Phys. Rev. 72, 1075 (1947).

of $2I+1$ states of relative orientations between **I** and **J** can contribute to the transition. δ is $2h\Delta\bar{\nu}$ with the definition of $\Delta\bar{\nu}$ given by Nierenberg and Ramsey[10] so that δ may be interpreted as the energy spread over which the oscillating field is assumed to cause transitions with probability $2p$ (it is assumed that δ is small compared to the total energy spread of the observed resonance). δ may be evaluated approximately as equal to $2\Delta=H'/H$ where H' is the amplitude of the oscillating field and H the magnitude of the fixed field. Then with $I=\frac{3}{2}$,

$$S=K_1\delta\alpha^2p(W/b^2\sqrt{3})\times\int_0^\infty \frac{J\exp[-\alpha^2J^2]dJ}{[1-(W/2b)^2+3(a/Jb)^2]^{\frac{1}{2}}}, \quad (24)$$

where the integration must be carried out consistent with conditions (16), (17), and (18).

For purposes of convenient integration, the function $J\exp[-\alpha J^2]$ in (24) may be replaced by a rectangular step function which affords the closest fit to the original function and which has the same area, that is, the function is replaced by

$$F(J)=1/2.8\alpha \quad \text{for} \quad 0.2/\alpha<J<1.6/\alpha$$
$$=0 \text{ elsewhere.} \quad (25)$$

With this approximation the integration in (24) can readily be carried out with the result that

$$Sb/3K_1p\delta=(1/7.28)[(W/2b)/(1-(W/2b)^2)]\times[[[1-(W/2b)^2]2.6+3(a\alpha/b)^2]^{\frac{1}{2}}-[[1-(W/2b)^2]0.04+3(a\alpha/b)^2]^{\frac{1}{2}}] \quad (26)$$

where the condition (18) is automatically satisfied if any imaginary square root in (26) is replaced by zero.

From (26), $Sb/3K_1p\delta$ can be numerically evaluated as a function of $W/2b$ for different assumed values of $a\alpha/b$ with the result that a rather general family of curves can be plotted. With this family, the predicted line shape for a specific set of values of b, p, δ, α, etc., can be obtained by suitable multiplications of the ordinates and abscissae. This family of curves is given in Fig. 1.

IV. DISCUSSION

Since W/b is equal the ratio of the observed frequency to the Larmor frequency, it can be seen that the spectral maximum (beam intensity minimum) is at approximately double the Larmor frequency as anticipated in the introduction.

It can also be seen that there are allowable combinations of nuclear and molecular constants for which this double frequency resonance is observable. If $3K_1p$ is taken as 1, if δ is taken as 0.02 which is reasonable for H'/H and if $a\alpha/b<0.3$, then S, the line strength is greater than 1.4 percent which is easily observable. For $\alpha\approx0.2$, this implies

$$a<15b,$$

which is consistent with the requirement of $a\gg b$ in order for this coupling scheme to hold. As smaller intensity resonances are observable on a molecular beam apparatus than $S=1.4$ percent, a wider range of allowable ratios of a/b is possible to obtain this effect. However, it is noteworthy that with high fixed magnetic fields the allowable range of a/b consistent with both observable intensity and occurrence of the resonance near the double frequency is rather small. Consequently, although this phenomenon must be guarded against in magnetic moment measurements with diatomic molecules, its occurrence is rather unlikely at high fixed fields and weak oscillating fields. As H'/H is increased the likelihood of observing this phenomenon is markedly increased.

It should be noted that the intensities predicted by Eq. (26) and Fig. 1 depend upon the assumption that the molecule is strictly a diatomic one. The intensities could be markedly different if the molecule concerned were an associated molecule such as $(LiBr)_n$ with $n>1$.

To a first approximation the position of the resonance maximum will shift in proportion to H and will occur at approximately the same position in different molecules provided only that the quadrupole interaction is sufficiently similar for the assumed coupling to apply in both cases. These characteristics are particularly unfortunate since they provide the usual criteria for identifying the resonance as associated with the Larmor frequency of the common nucleus. However, a comparison of the experimental shape, intensity, and exact H dependence of the resonance with the theoretical ones here pre-

sented provides a means of identification of whether the observed resonance is a double frequency one.

In a separate paper by Brody, Nierenberg, and Ramsey[11] the theory here presented is applied to identify the Br and Cl resonances. Consideration is now being given to generalizing this study to other odd integral spins since similar results would be expected in these cases since the $J+\frac{1}{2}$ and $J-\frac{1}{2}$ states will be approximately degenerate in these cases also. Further study of the case of intermediate coupling is also contemplated.

The author wishes to thank Professor I. I. Rabi for several helpful discussions in the course of this work.

[11] S. B. Brody, W. A. Nierenberg, and N. F. Ramsey, Phys. Rev. **72**, 258 (1947), and a full paper in course of preparation.

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Breakdown of a Gas at Microwave Frequencies*

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An electric field of sufficiently high frequency applied to electrons in a gas may deliver energy to the electrons without imparting to them any continuous drift motion resulting from the field. The criterion for breakdown of a low pressure gas at microwave frequencies is therefore that ionization by collision of electrons with neutral gas molecules replace loss by diffusion to the walls of the discharge tube. The condition is mathematically expressed as a simple boundary value problem. This breakdown principle is applied to converting microwave breakdown measurements into measurements of ionization rates as a function of the electric field strength, pressure, and frequency. A new ionization coefficient is introduced appropriate to the high frequency discharge conditions, and its relation to the d.c. Townsend coefficient is explained. The energy transfer from the electric field to the electrons at a given E/p is shown to be most efficient when the pressure is high enough or the frequency low enough to result in many collisions of electrons with gas molecules per cycle. This maximum efficiency is equal to the d.c. energy transfer efficiency. When the pressure is lower or the frequency is higher, the electrons have an out-of-phase component of motion and do not receive energy so efficiently, resulting in lower ionization rates observed experimentally.

I. INTRODUCTION

THE Townsend theory for breakdown of a low pressure gas under the action of a d.c. electric field postulates two sources of electrons. Most of the electrons are generated in the volume of the gas through ionization by collision. The original source of electrons at the cathode results from secondary emission caused by positive ion or photon bombardment. Prediction of breakdown voltage requires numerical data on the efficiency of these processes. Thus attempts to determine ionization coefficients from breakdown data have been complicated by the operation of two electron generation processes.

Breakdown caused by a high frequency electric field is determined by the primary ionization process only; the electrons formed at the walls or in the gas by secondary emission have a negligible effect. It is therefore possible to predict the electric field for breakdown from a knowledge of the ionization coefficient only, or to measure the ionization coefficient from a breakdown experiment.

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II. MOTION OF ELECTRONS IN A HIGH FREQUENCY FIELD

Under the action of a d.c. electric field an electron is accelerated by the field until it collides with a gas molecule. The direction of motion is then reoriented almost randomly. Most of the kinetic energy gained during the acceleration period is kept during the scattering process, since the mass of the molecule is large compared to that of the electron. After collision, the electron is accelerated or decelerated by the field, depending on the direction of the electron velocity