Measurement of Atomic and Molecular Excitation by a Trapped-Electron Method

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A trapped-electron method is used to study inelastic processes in helium, mercury, and hydrogen. In this method, an electron beam traverses an electric and magnetic field configuration in which the low-energy electrons resulting from inelastic collisions are prevented from reaching the electron beam collector by a potential well. The low-energy electrons can reach a cylindrical collector surrounding the electron beam. The collection efficiency appears to be close to unity for electrons in the range 0 to 0.1 electron volt and zero at higher energies. The design of the tube and applied potentials determine the range of collection. A complete spectrum of energy levels is obtained in He, Hg, H_2, within the resolution of the instrument (better than 0.2 ev). The experiment yields approximate slopes of the resolved excitation functions near threshold. The method is well suited for a study of excitation events in molecules.

ELECTRON beam experiments have been used extensively for the measurement of excitation functions of atomic states. The excited atoms produced by an electron beam can be detected in the following ways: (a) by their radiation, (b) by their absorption of a particular wavelength, (c) by the emission of secondary electrons when excited atoms reach a metal electrode, and (d) by measuring the slow electrons resulting from an inelastic collision. Method (a) suffers from a low sensitivity of detection because the detector intercepts only a small fraction of the quanta produced in the tube and because the quanta are transformed into electrons at a photosensitive surface having a low efficiency. Method (b) has inherently low sensitivity because the absorption cross section is low. Method (c) is not limited by these considerations; however it can be used only for metastable states of atoms and molecules. Up to 25% of all metastables produced in the tube can register as electron current.[1] Method (d) is the subject of this paper; it can be applied to any atomic or molecular level within the resolution of the instrument. Every excitation event near the threshold of excitation results in a low-energy electron; the low-energy electrons may be then collected with high efficiency. The method thus has inherently high sensitivity which is especially important in studying the threshold behavior of excitation functions. The method to be described can also be used for studying electronic excitation in molecules. This aspect is discussed in Sec. V.

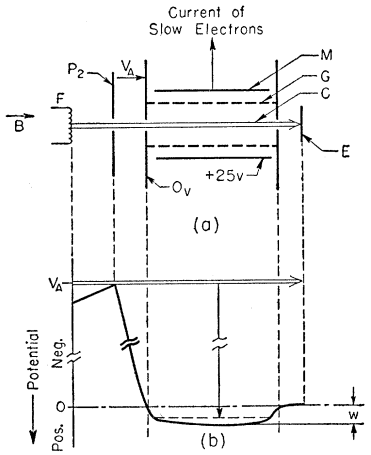

FIG. 1. Schematic diagram of tube (a) and potential distribution at the axis of the tube (b). F is the filament, P_2 is the retarding electrode, G is the cylindrical grid surrounding the collision chamber C, M is the cylinder for collection of trapped electrons, E is the electron beam collector. V_A is the accelerating voltage and w is the depth of the well. The double line in (b) indicates the energy of the electron beam and the arrow indicates the energy lost by an electron in an inelastic collision near the threshold of excitation. The electron energy in the collision chamber is V_A+w.

I. TRAPPED-ELECTRON METHOD

The method discussed in this paper consists of trapping low-energy ("slow") electrons in an electrostatic well and collecting them with high efficiency. The construction of the tube used for this experiment is identical to that described previously.[1] Different potentials, however, are applied to the electrodes around the collision chamber resulting in a different mode of operation. A simplified diagram of the tube is shown in Fig. 1(a). The "retarding potential difference method"[1,2] is utilized in this experiment in order to study effects caused by nearly monoenergetic incident electrons. The details of the electron gun for use with the retarding potential difference method are not shown since they have been described in reference 1. The filament F emits electrons which pass through the electron gun (only the "retarding electrode" P_2 is shown) into the collision chamber C and are collected at the electron collector E. The "collision chamber electrodes" consist of the grid[3] G and the entrance and exit plates, all at the same potential. A well-insulated cylindrical collector, M, surrounds the grid. All electrodes are gold-

[1] G. J. Schulz and R. E. Fox, Phys. Rev. **106**, 1179 (1957).
[2] Fox, Hickam, Grove, and Kjeldaas, Rev. Sci. Instr. **26**, 1101 (1955).
[3] Actually, two concentric cylindrical grids were mounted in the tube but they were placed at the same potential so that their combined action can be replaced by a single grid. The grid mesh is made of 0.002-in. diameter wire with a spacing of 0.038 in. between wires.

plated. A magnetic field of about 100 gauss aligns the electron beam.

When a positive potential is applied to the collector M with respect to the grid G, a small part of the applied potential penetrates into the collision chamber C. Electrolytic mapping shows that the potential at the axis of the present tube is of the order of $\frac{1}{2}\%$ of the potential between M and G. This penetration can be changed by altering the grid spacing. Figure 1(b) shows, schematically, the potential distribution along the axis of the tube for the case that the electron collector, E, is at the potential of the collision chamber electrodes. The potential of the collision chamber electrodes is taken as zero. The electrode P_2 is at a high negative potential with respect to the grid since electrons are accelerated from zero to their final velocity between P_2 and G. This potential difference is denoted by V_A in Fig. 1. The filament is slightly positive with respect to P_2 so that a portion of the electrons emitted

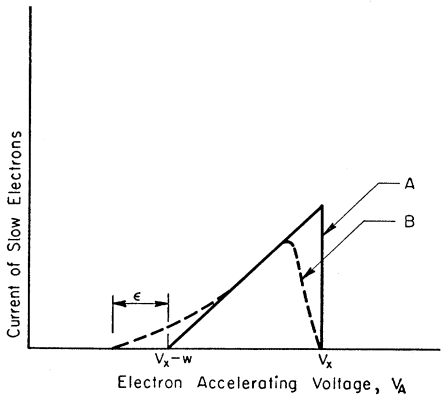

FIG. 2. Theoretical peak shape for collection of slow electrons in atomic excitation. A rectangular well and a linear excitation function are assumed. V_x is the excitation energy of the atomic level, and w is the well depth. Curve A is for monoenergetic electrons, curve B for electrons with energy spread ϵ. The true electron energy in the collision chamber is V_A+w (see Fig. 1).

by the filament is retarded at P_2. This is necessary for the operation of the retarding potential difference method. The energy of the electrons is indicated by the double horizontal line in Fig. 1(b). When electrons in the beam lose nearly all of their energy in an inelastic collision, as they do just above the threshold of excitation, they will end up in the potential well and be trapped in the axial direction. Since they can reach neither of the collision chamber electrodes, they will oscillate in the tube until they find their way to the positive electrode M. The collection mechanism is discussed later. Electrons which have lost an amount of energy smaller than V_A can reach the electron beam collector E or the end plates.

II. PEAK SHAPE AND COLLECTION MECHANISMS

It can be seen readily from Fig. 1(b) that the electron energy in the collision chamber is the electron accelerating voltage V_A plus the well depth w. Since we collect electrons at M only after they have been trapped by the potential well, we would expect to receive only those electrons at M which have lost an amount of energy between V_A and V_A+w.

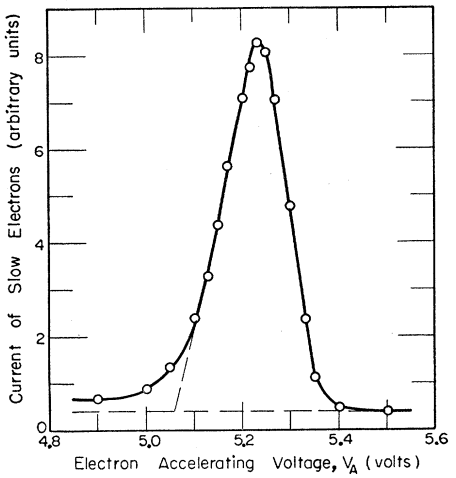

FIG. 3. Experimental peak shape for collection of slow electrons resulting from the excitation of the $6\,^3P_2$ level in mercury.

Consider an excitation function which is a linear function of electron energy above the excitation potential, V_x, for a range of energy greater than w (where w is the well depth). The electron current collected at M should have an onset at $V_A=V_x-w$ (the electron energy in the collision chamber is then V_x) and peak at $V_A=V_x$. This is shown in Fig. 2 for an idealized case where w is constant along the length of the chamber. Curve A indicates the theoretical peak shape for monoenergetic electrons and curve B for a spread in electron energy of ϵ. The width of curve B thus is $w+\epsilon$. Further changes in shape are caused by the nonconstancy of w. Figure 3 shows a typical experimental peak shape for the $6\,^3P_2$ level in mercury. The tail of the curve at the high-energy side should extrapolate to the axis at the excitation potential (5.43 volts); it actually extrapolates to 5.35 ± 0.15 volts.

The well depth w can be determined in an independent experiment. By extrapolating to the onset potential of positive ions with various potentials applied between G and M, one finds a shift in onset potential of 0.1 volt at $V_{GM}=25.0$ volts. Since the spread in energy of the electron beam is of the order of 0.1 volt, $\epsilon+w$ is equal to 0.2 volt. However, the width of the curve in Fig. 3 is approximately 0.35 volt. The mechanism by which the peak shape is broadened to nearly twice its expected value is not understood at present.

The peak height is linear with pressure (in the pressure range 2×10^{-5} to 2×10^{-4} mm Hg in mercury and 1×10^{-3} to 1×10^{-2} in helium) and is also proportional to the beam current up to about 1×10^{-7} ampere (using a magnetic field of 125 gauss and a well depth of 0.1 volt). All experiments are performed in the range in

which linearity of peak height *vs.* beam current is strictly preserved. The departure from linearity at beam currents in excess of 1×10^{-7} ampere is attributed to space charge effects.

The departure from linearity of the peak height with beam current depends on the magnetic field and the well depth. The departure from linearity occurs at higher beam currents when the well depth is larger or the magnetic field smaller. Whereas the effect of well depth on the departure from linearity can be understood in terms of the influence of the space charge on the depth of the well, the effect of magnetic field is not clearly understood at present.[4] The collection mechanism described in the following paragraph may be responsible for this effect.

The mechanism by which the slow electrons trapped in the axial direction in the center of the collision chamber reach the cylinder M may be understood in terms of a diffusion mechanism.[5] The guiding center of the electron motion can be displaced in the radial direction only by collisions. The time, τ, for a slow electron to diffuse out of the center of the tube is given by[5]

$$\tau=\Lambda_b^2/D, \qquad (1)$$

where Λ_b is the effective diffusion length in the presence of the magnetic field, and D is the field-free diffusion coefficient given by $D=v^2/3\nu_c$. For our case where the cyclotron frequency ω is much larger than the frequency

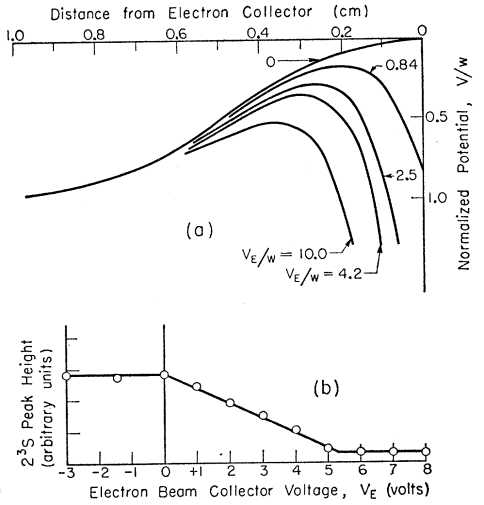

FIG. 4. Effect of reduction of well barrier. Part (a) shows the potential distribution along the axis of the tube, as a function of the electron collector voltage, V_E, normalized with respect to the well depth, w. The curves are results of potential mapping. Curve (b) shows the peak height of the current of slow electrons resulting from excitations to the $2\,^3S$ level in helium as a function of V_E. The points are experimental.

[4] A change of magnetic field which causes the change in the behavior of the current of slow electrons causes no change in the primary beam current. Magnetic fields between 120 and 200 gauss are used.

[5] W. P. Allis, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. 21, p. 396.

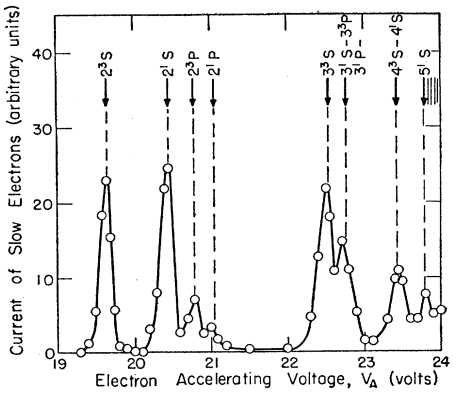

FIG. 5. Excitation spectrum of helium. The curve represents the collection of axially trapped ("slow") electrons. The peak height of any resolved level is the cross section for that level about 0.1 volts above the threshold of excitation and it is proportional, approximately, to the slope of the corresponding excitation function near threshold. The ratios of the peak heights to that of $2\,^3S$ level are: $2\,^1S-1.06$; $2\,^3P-0.31$; $2\,^1P-0.13$; $3\,^3S-0.95$. The effective cross section, defined in the text, at the peak of the $2\,^3S$ curve is 1.0×10^{-18} cm^2.

of collision ν_c, the effective diffusion length is given by $\Lambda_b^2=(R/2.4)^2(\omega^2/\nu_c^2)$. R is the radius of the grid structure,[6] and v is the electron velocity. Substituting the above equations into Eq. (1), we obtain

$$\tau=(R/2.4)^2(3\omega^2/\nu_c v^2). \qquad (2)$$

Equation (2) can be simplified by substituting $\omega=eB/m$ and $\frac{1}{2}mv^2/e=V$, where V is the electron energy in volts. We obtain

$$\tau=0.26eB^2R^2/(mV\nu_c). \qquad (3)$$

In the present experiment, τ should be of the order of a millisecond.[7] It should be noted that τ, and therefore the space charge created by the slow electrons, is a function of B^2.

III. CONFIRMATION OF WELL MODEL

The trapping mechanism can be further explored by varying the voltage between the collision chamber and the electron collector, V_E. Figure 4(a) shows the effect of V_E on the shape of the potential well at the axis of the tube. The plot is obtained by electrolytic potential mapping. As V_E increases, the well barrier decreases. This causes a decrease in the number of electrons trapped in the well and therefore a decrease in the number of slow electrons collected. Figure 4(b) is a plot of the peak height of the first maximum in helium ($2\,^3S$) as a function of V_E. The current does not reach zero at high positive values of V_E because the well barrier cannot be reduced to zero and also because there exists a small background electron current to the collector due

[6] Once the slow electrons reach the neighborhood of the grid structure they can travel to the collector M without further collisions because of the high potential applied between G and M.

[7] For helium, $p=10^{-3}$ mm Hg, $B=1.2\times10^{-2}$ weber/m^2, $R=3\times10^{-3}$ meters, $\nu_c=4\times10^8 p$, $V=0.1$ volt. Measurements of the diffusion time τ are being planned.

to helium metastables releasing secondary electrons at the grid wires.

IV. EXCITATION SPECTRUM IN He AND Hg

Figures 5 and 6 show the results obtained in helium and mercury, respectively. The current of slow electrons is plotted against the accelerating voltage V_A. Each observed peak can be associated with a particular energy level of the atom involved. The agreement in energy difference between the first level and any higher resolved level is within 0.05 electron volt. The resolution of the present experiment is better than 0.2 volt, as can be seen in Fig. 6 where the $6\,^3P_0$ and $6\,^3P_1$ levels of mercury, of unequal height and 0.3 volt apart, are resolved.

The excitation function of the $2\,^3S$ level in helium has been shown previously to be linear near threshold.[1] Since the shapes of the subsequent resolved peaks in helium are similar to the peak for the $2\,^3S$ level, it may be reasonable to assume that the other excitation functions are also linear near threshold.[8] With this assumption the peak height of the slow electron current is an indication of the slope of the corresponding excitation function near threshold. The ratio of the peak height of any resolved peak to the height of the first peak is listed in the captions to Fig. 5 and Fig. 6. The slope of the $2\,^3S$ level in helium is 1.1×10^{-17} cm^2/volt near threshold,[1] so that the slope of any excitation function near threshold can be found from the ratio given in Fig. 4 by multiplying with the above number.

We can assign a value for the effective cross section, Q, to the peaks of Figs. 5 and 6 by the equation

$$i_-=i_0NQl,$$

where i_- is the peak current of slow electrons, i_0 is the electron beam current, Q is the effective cross section, l is the length of the collision chamber, and N is the gas density. The value of Q found for the first peak of Fig. 5 ($2\,^3S$ level) is 1.0×10^{-18} cm^2. From reference 1, one can deduce the slope of the first excitation function in helium to be 1.1×10^{-17} cm^2/volt near threshold. If one assumes that the collection efficiency of slow electrons is 100%, it follows that the effective well depth is 0.1 volt, in agreement with the determination discussed previously. However, an exact determination of the well depth is rendered difficult in the present tube by the variation of well depth along the axis of the tube. In a new design of the tube, a more nearly constant well depth and a simpler geometry (using only longitudinal wires instead of the mesh grid) are used.

The large peak for the $2\,^1S$ level in helium (Fig. 5) indicates that the slope of the $2\,^1S$ excitation function is about equal to that of the $2\,^3S$ level. This is consistent with the original results of Maier-Leibnitz[9] and other experimental results[10] but has not been predicted by theory.[11] Phelps suggested that the slopes given in Fig. 5 be used for an analysis of the threshold behavior of the lowest excitation functions in helium, using values for the total metastable production given in the literature. It is found that the slopes given in Fig. 5 fit into a consistent picture.[12]

V. APPLICATION OF TRAPPED-ELECTRON METHOD TO MOLECULAR GASES—HYDROGEN

The method described in the preceding paragraphs has applications in studying the excitation functions for electron impact in molecules. A curve taken under identical experimental conditions as Fig. 5 and Fig. 6 for H_2 is shown in Fig. 7. It is, as in the atomic case, the appearance of electrons in the range 0–0.1 volt as a function of energy of the electron beam. The first part of the curve, peaking at 9.5 volts, is due to the repulsive state $1\,^3\Sigma_u$ and the second part of the curve, peaking at 11.7 volts is due to the $2\,^1\Sigma_u$ and higher excited states.[13] Figure 8 shows schematically how data obtained by the trapped-electron method can be interpreted in the case of a molecular gas. Figure 8 shows a plot of the potential energy *vs.* internuclear separation for the ground and repulsive states of a molecule. The Franck-Condon region is indicated by the outer vertical dashed lines. An incoming electron finds the molecule at a particular internuclear separation X and the transition to the repulsive state takes place without any change of internuclear separation. The electron energy in

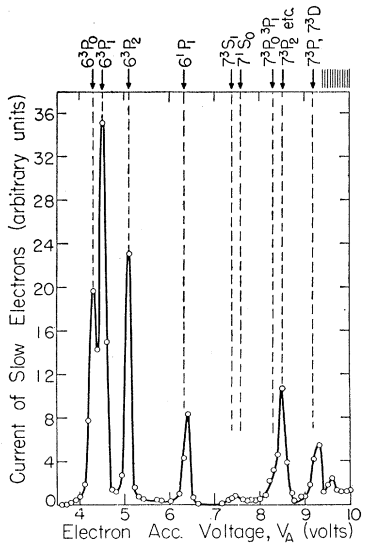

FIG. 6. Excitation spectrum of mercury. The curve represents the collection of axially trapped electrons (see Fig. 5). The ratios of peak heights to that of the $6\,^3P_0$ are: $6\,^3P_1$ -1.8; $6\,^3P_2-1.2$; $6\,^1P_1-0.43$.

[8] An experiment is planned to examine this hypothesis. A tube with a coarser grid has been constructed. By increasing the well depth one could follow the shape of the excitation functions of the various resolved levels to higher energies.

[9] H. Maier-Leibnitz, Z. Physik **95**, 499 (1956).

[10] R. Dorrestein, Physica **9**, 477 (1942). See also reference 1.

[11] H. S. W. Massey and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **A66**, 406 (1953).

[12] L. S. Frost and A. V. Phelps, Westinghouse Research Report 6-94439-6-R3 (unpublished).

[13] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952), p. 232.

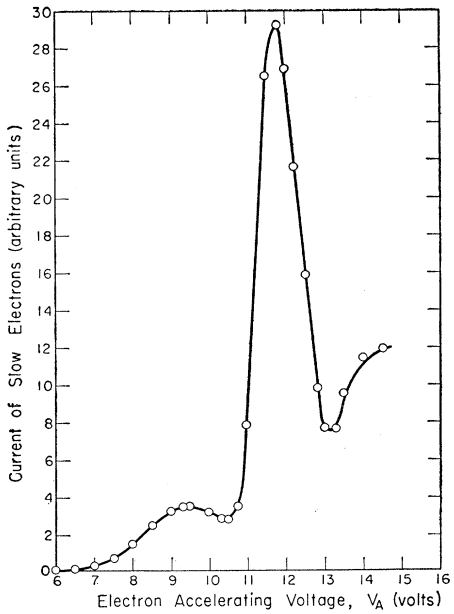

FIG. 7. Collection of slow electrons in H_2. The curve represents the appearance of electrons in the range 0–0.1 volt as a function of electron energy. It is taken under similar conditions as Figs. 5 and 6. The low-energy part of the curve, peaking at 9.5 volts, represents transitions to the repulsive $1\,^3\Sigma_u$ state. Above 11 volts transitions to the $2\,^1\Sigma_u$ and higher states appear. The value for the effective cross section at 9.5 volts is 1.7×10^{-19} cm².

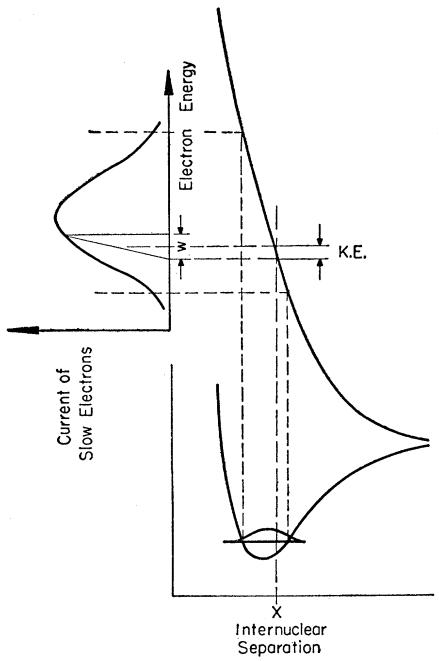

FIG. 8. Schematic diagram of the application of the trapped-electron method to molecules.

excess of that needed to make a transition at an internuclear separation X is denoted by K.E. in Fig. 8. If we could imagine the internuclear separation X to be fixed, and could vary the electron energy, then we would collect a current of slow electrons as indicated by the triangle on the left side of Fig. 8. This is identical to the peak shape discussed for the atomic case in connection with Fig. 2 and is subject to the same limitations as discussed previously. The contributions of all internuclear separations within the Franck-Condon region have to be integrated in order to obtain the total current of slow electrons *vs.* electron energy. The full curve on the left upper part of Fig. 8 shows the shape schematically.

The trapped-electron method thus can be used for finding the relative cross sections for various electronic excitations in molecules.

Vibrational Excitation

It would seem that the present method should lend itself to the observation of vibrational excitation of H_2 at 0.5 electron volt above the ground state. In the present experiment a peak due to this transition should be observable provided that the cross section is larger than 10^{-21} cm² at 0.1 volt above threshold. Repeated search did not reveal any indication of this transition. Extrapolating Ramien's results[14] linearly to 0.1 volt above threshold gives a cross section of the order of 10^{-18} cm². If this value were correct within three orders of magnitude, it should have been observed in the present experiment. It may be, however, that the linear extrapolation used here is not at all applicable to the vibrational cross section. If the cross section increases with a high power of the energy excess above the threshold, the failure to observe the cross section in the present experiment may not be in contradiction with Ramien's value at 3.5 volts.

VI. CONCLUSIONS

The trapped-electron method has been shown to be applicable for studying excitation events in atoms and molecules. It lends itself readily to a study of electronic levels in complicated molecules. Such data are difficult to obtain by any other method.

By increasing the potential penetration and therefore the well depth, it should be possible to follow various resolved excitation functions over an energy range of the order of 1 electron volt or larger and thus establish the threshold behavior of excitation functions over this energy range. A tube for this purpose has been built.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to A. V. Phelps and T. Kjeldaas for many helpful suggestions during the course of the work.

[14] H. Ramien, Z. Physik **70**, 353 (1931). Ramien attributes an energy loss in his swarm experiment at 3.5 ev to the excitation of the lowest vibrational level in H_2 with a cross section of 4×10^{-17} cm².