A New Method of Measuring the Electric Dipole Moment and Moment of Inertia of Diatomic Polar Molecules[*]

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September 18, 1946

THIS paper will report on experiments in which the molecules of a molecular beam are caused to undergo a transition in a steady homogeneous electric field by an oscillating electric field at right angles to the d.c. component. This experiment is, therefore, closely analogous to the magnetic resonance method[1] which has been applied previously to atoms and molecules. The method to be described can be considered as an advance over previous methods in that a single rotational state of the molecule is studied even though it is present to only one part in ten thousand as a component of the beam.

The transition with which we are concerned is that in which the molecule, in this case CsF, goes from $R=1$, $p=0$ to $R=1$, $p=\pm 1$, where R is the rotational quantum number and p is the electric quantum number. This $\Delta R=0$ transition is ordinarily forbidden but the selection rule breaks down in the presence of the constant electric field, E.

Several persons[2] have calculated by perturbation methods the splitting of rotational energy levels in an electric field. As applied to the $1, 0\rightarrow 1, \pm 1$ transition the frequency f, in cycles per second, is given by the expression

$$f=\frac{6\mu^2 IE^2}{20(9)10^4 h\hbar^2}=4.529\times 10^{75}\mu IE^2, \tag{1}$$

where μ is the permanent dipole moment in e.s.u., I is the moment of inertia in g cm^2, and E is the electric field strength in volts per cm. This method has been applied to cesium fluoride and a value of $9.89\times 10^{-73}\pm 1.2$ percent obtained for $\mu^2 I$.

For values of the parameter $\lambda=\mu E/cBh=2\mu EI/\hbar^2$ which are $\ll 1$, it is seen that the energy difference between the states is proportional to $\mu^2 I$. At larger values, there is an important deviation from this functional relation which allows for an independent determination of both μ and I. Brouwer's second-order perturbation formula[3]

$$f=\frac{3\mu^2 E^2}{20h(\hbar^2/2I)}-\frac{(0.00959)\mu^4 E^4}{h(\hbar^2/2I)^3} \tag{2}$$

is good to 0.1 percent up to $\lambda=1$, and was used in these experiments.

If we define two experimentally determined constants, α and β, by the equation

$$f/E^2=\alpha-\beta E^2, \tag{3}$$

then it may be shown that

$$I=\beta\alpha^2(1.97\times 10^{-28}),\ \text{g cm}^2. \tag{4}$$

Final values for the $R=1$ state of CsF are: $\alpha=448\pm 5.4$, $\beta=(1.91\pm 0.23)\times 10^{-5}$, $\mu=7.3\pm 0.5$ debye,[4] $I=(187\pm 22)\times 10^{-40}$ g cm^2 and $r=2.60\pm 0.16$ angstroms. It is to be noted that while $\mu^2 I$ is quite accurate, the values of μ and I separately are only approximate. This stems from the fact that μ and I can be determined separately only by a knowledge of β which is of the form of a correction term to α at high values of E. The present limitations on the accuracy of β are entirely instrumental and can be largely eliminated. The method is, therefore, inherently very accurate.

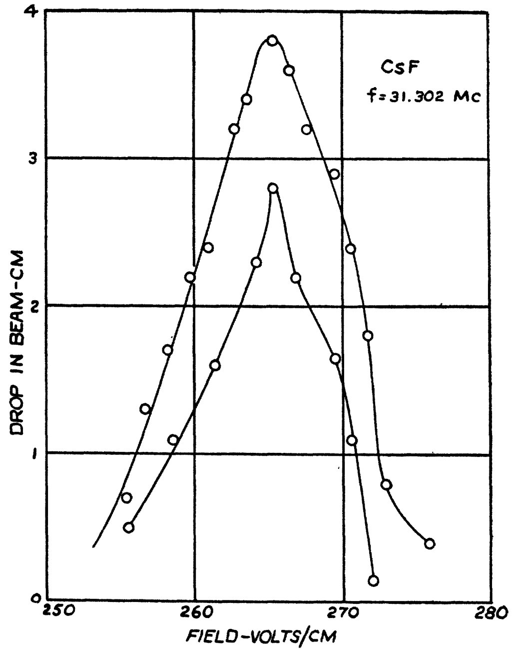

FIG. 1. Decrease in beam intensity as a function of the homogeneous electric field. The upper and lower curves are for relatively large and small amplitudes of the oscillating electric field.

A feature of the method, in common with the magnetic resonance method, is its extraordinary resolution of close energy levels which so far exceeds that of infra-red spectroscopy that moments of inertia may be obtained for heavy molecules which have previously been beyond reach. These experiments differ very markedly from earlier molecular beam deflection experiments which measured μ only, and with very limited accuracy.[5] In contrast to solution methods wherein the variation of permittivity is measured as a function of temperature, this procedure yields the electric moment entirely independent of mass interference effects.

The selection of the state for observation is accomplished as follows. The beam of molecules is produced and collimated in an evacuated apparatus in the usual way but instead of allowing it to fall upon the detector, a wire stop is interposed in the direct path. Only those molecules strike the detector which have been refocused around the stop in a sigmoid path by two inhomogeneous electric fields (named the A- and B-fields) which are transverse to the beam and pointed in the same direction.

The ability of the present method to isolate rotational states depends essentially on the fact that the effective electric moment of the molecule is a function of the electric field. The functional dependence of the moment on field is itself dependent on the state so that, by a suitable choice of the A- and B-electric fields, it is possible to refocus a single electric state (quantized orientation of the angular momentum vector for a single rotational state). The effective induced moment of the 1, 0 state is positive at high fields (in the A-field) and negative at low fields (in the B-field). The states 0, 0 and 1, ±1 do not have this property. Furthermore, the effective induced moment in a given electric field is inversely proportional to R^2 and the higher rotational states, therefore, have small effective moments relative to that for $R=1$. The function of the wire is to stop all molecules of small effective moment, the overwhelming fraction, which are not susceptible to refocusing operations. The relative population of the low rotational states is small and only 0.01 percent of the total beam is refocused at any one time. Relative electric moments for all orientations of the three lowest rotational states were obtained from a relationship derived by Lamb[6] which is good for all values of λ.

Between the refocusing A- and B-fields the beam passes through a homogeneous C-field wherein a superimposed radiofrequency electric field, normal to the d.c. component, induces transitions between electric levels. After this transition the molecules are in a new electric level with a different, indeed reversed effective electric moment in the B-field, and they are no longer refocused. This is observed by a decrease in the beam when the oscillator frequency equals the energy separation of the levels divided by Planck's constant. (Fig. 1.)

Further details will be discussed in a forthcoming article in *The Physical Review*.

This research was proposed to me by Professor I. I. Rabi and executed under his direction. I am also under obligation to several other members of the physics department. In particular, Professor P. Kusch gave me guidance during the last stage of the work and, with Dr. J. Trischka, assisted in the collection and evaluation of the data.

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* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

[1] I. I. Rabi, S. Millman, P. Kusch, and J. R. Zacharias, Phys. Rev. 55, 526 (1939).

[2] See, for example, R. de L. Kronig, Proc. Nat. Acad. Wash. 12, 608 (1926).

[3] Brouwer, Dissertation, Amsterdam, 1930.

[4] 1 debye $=10^{-18}$ e.s.u.

[5] For literature references, consult Fraser, *Molecular Beams* (Chemical Publishing Corporation, New York, 1938), Chap. IV.

[6] Professor W. E. Lamb, private communication.

Secondary Emission from Germanium, Boron, and Silicon

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September 9, 1946

MEASUREMENTS of secondary emission were made on the semi-conductors germanium, boron, and silicon. No previous measurements on germanium or boron are given in the literature.

The silicon and germanium were cut from very pure vacuum melts which had been prepared in the laboratory for crystal rectifier studies. The boron was deposited on an iron disk by thermal decomposition of boron hydride.

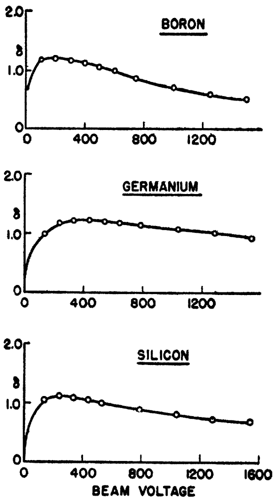

FIG. 1. Secondary emission from boron, germanium, and silicon.

The measurements were made in an electron gun type of tube. The electron beam was focused on the target through a hole in a cylindrical collector surrounding the target. The primary velocity was varied from 100 volts to 1500 volts. The beam current was 10^{-5} amp. and the spot diameter approximately 1 mm. The collector was held at +40 volts with respect to the target.

The measurements were made in tubes while on the pump at a pressure of 10^{-6} to 10^{-7} mm. The germanium and silicon were heated by high frequency to dull red before making measurements. The boron only received a 425°C bake out as at higher temperatures there was a possibility of interdiffusion of the iron and boron.

The maximum values of δ (the secondary to primary ratio) and the primary voltage at which they occur are as follows:

	S	V
Boron	1.2	150
Germanium	1.2	400
Silicon	1.1	250

The relation between δ and primary voltage for the three surfaces is given in Fig. 1.

Conductivity of Metal-Amine Solutions

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September 20, 1946

IT has been reported recently by Ogg[1] that when a solution of sodium in liquid ammonia, in the concentration range which yields two liquid phases, is rapidly frozen, a large decrease in resistance occurs. The writer has observed this decrease in resistance by a current-potential method, and has found in agreement with the work of Daunt, Désirant, Mendelssohn, and Birch[2] that the small resistance of the frozen solution resided in the solid itself and not in the solid-electrode contact. It is still possible that this resistance is a property of the contacts between