Pure Quadrupole Spectra of CH₃I and CF₃I Vapors*

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This paper first gives the theory of $\Delta J=0$, $\Delta F=\pm1$ transitions of symmetric top molecules having a nucleus with a large quadrupole moment on the axis. The manner in which the gaseous state spectrum converges on the pure quadrupole sold state spectrum as J becomes infinite is discussed. Also is described an absorption experiment in which six quadrupole lines of CH₃I and one of CF₃I were observed in the region between 290 and 520 Mc/sec. The experiment yielded values of the quadrupole coupling constants of -1933.99 ± 0.25 Mc/sec and -2142.5 ± 1.8 Mc/sec respectively for CH₃I and CF₃I. These values are in agreement with previous values obtained elsewhere from rotational transitions.

INTRODUCTION

THIS paper[1] is concerned with the observation by an absorption method of the so-called "pure quadrupole" transitions in the vapors of symmetrical top molecules containing a nucleus with a large quadrupole interaction on the molecular symmetry axis. These are transitions arising from the reorientation of the nucleus with respect to the rotational angular momentum vector while the rotational quantum numbers J and K remain constant.

A more detailed description of these transitions may be given with reference to Fig. 1, which is an angular momentum vector diagram. **K** represents the quantized component of rotational angular momentum along the molecular axis. This precesses around the total rotational angular momentum vector **J**. The nuclear spin **I** is coupled to **J**, and these two vectors precess around their resultant **F**. In pure quadrupole transitions, the relative orientation of the nucleus and **J** changes such that the spin vector changes from **I** to **I'** with a new resultant angular momentum **F'**, as shown in Fig. 1, assuming a frame of reference fixed to **J**. At the same time the nuclear quadrupole moment changes in orientation with respect to the electric field of the molecule, involving a change in the energy, which is accompanied by the emission or absorption of radiation. These transitions, then may be seen to be those defined by the selection rules $\Delta J=0$, $\Delta K=0$, and $\Delta F=\pm1$.

Quadrupole coupling constants may be determined very accurately from these observations since these are the principal parameters determining the frequencies.

The conventional method of determining quadrupole coupling constants of vapors is from observations of the hyperfine splitting of rotational transitions. Those occur at much higher frequencies and are usually much easier to detect. However, sometimes quadrupole coupling constants cannot be determined very accurately since they are related to hyperfine splittings which represent only a small fraction of the frequency. This situation is particularly true for high-J transitions.

Mainly because pure quadrupole spectra exist at frequencies below 1000 Mc/sec, they have low intensities and are hard to observe. However, the recent development of a spectrometer for these frequencies in this laboratory[2,3] has made possible the observation of these spectra in a few favorable cases.

While pure quadrupole transitions in vapors have not been studied generally, the analogous transitions in the solid state have been observed very widely since their discovery by Dehmelt and Kruger.[4] Those are transitions arising from the reorientation of a quadrupolar nucleus with respect to the gradient of a crystalline electric field. The spectra of solids are very simple as the electric field is invariant, while with vapors the spectra are complex since the effective value of the gradient of the electric field is different with each rotational state. Although they are also at low frequencies, the solid state spectra are easy to observe, partly because the available intensity is concentrated in a very few lines and partly because it is practical to work with samples containing many more molecules. Since the quadrupole coupling constant has slightly different numerical values for the solid and vapor, the observations made in the two states are not equivalent. Although the spectra in the vapor state are complex, as will be shown later, they are very simply related theoretically to the spectra obtained in the corresponding solids if the change in the magnitude of the constant is neglected.

While the frequencies of the pure quadrupole lines are determined by nuclear quadrupolar interactions, the intensities are fortunately determined by changes in the effective electric dipole moments of the molecules. If the intensities were determined by the interaction of the nuclear quadrupoles with electromagnetic radiation, they would be much too weak to be observed.

The mechanism for the interaction of the dipole moment **P** with the radiation may be seen by reference

[1] A preliminary report of this work has been published: F. Sterzer and Y. Beers, Phys. Rev. **94**, 1410(A) (1954).

[2] Y. Beers and S. Weisbaum, Phys. Rev. **91**, 1014 (1953).

[3] Weisbaum, Beers, and Herrmann, J. Chem. Phys. **23**, 1601 (1955).

[4] H. G. Dehmelt and H. Kruger, Naturwiss, **37**, 111 (1950).

again to Fig. 1. **P** is parallel to **K** and has a component **P**$_J$ which persists with respect to the precession of **K** about **J**. **P**$_J$ in turn has a component **P**$_F$ which persists with respect to the precession of **J** about **F**. When the transition takes place, this persistent component changes to a new value **P**$_{F'}$ because of the change in the angle between **J** and the resultant angular momentum **F**. Thus there is a change in this persistant component, which is the effective value of the dipole moment.

This discussion indicates that the strongest lines occur with $K=J$ and that the intensities are zero when J and K are mutually perpendicular: that is, when $K=0$. Since a linear molecule in a ground vibrational state is equivalent to a symmetric top molecule with $K=0$, no transitions will be observable with such a molecule. The discussion also indicates that the strongest lines are obtained with I and J as nearly parallel as possible: that is, in the group of transitions $F=I+J-1$ to $F=I+J$. Another reason why this group of lines tends to have the greatest intensities is that for each given J and I the levels have the highest possible statistical weights. These qualitative conclusions are generally supported by quantum-mechanical calculations, but these indicate that there are a few transitions of other types which are relatively strong.

CALCULATION OF SPECTRA[5]

The interaction energy of a nuclear quadrupole moment Q located upon the axis of a symmetric top molecule as given by a first order quantum mechanical perturbation calculation is well known[6,7]

$$E_Q = \frac{eq_JQ}{2I(2I-1)J(2J-1)}[\tfrac{3}{4}C(C+1)$$

$$-I(I+1)J(J+1)], \quad (1)$$

where F, J, and I are respectively the quantum numbers associated with total angular momentum, total rotational angular momentum, and nuclear spin. e is the charge of the electron. By definition,

$$C=F(F+1)-I(I+1)-J(J+1).$$

q_J is the second derivative of the electrostatic potential at the nucleus with respect to a linear coordinate measured along a space-fixed axis, as averaged over the state with the quantum numbers J, K, and $m_J=J$. This potential is the result of the other charged particles in
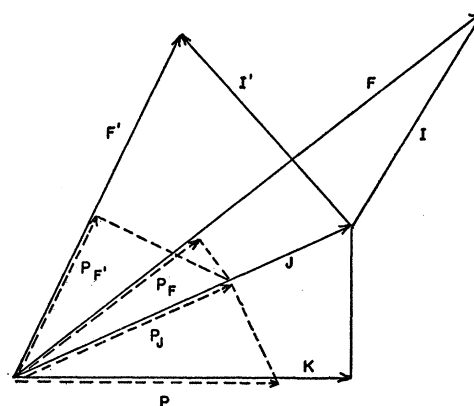

FIG. 1. Vector diagram of symmetric top molecule in frame of reference fixed to the total rotational angular momentum J.

the molecule. The value of q_J is given by

$$q_J = \frac{J}{2J+3}\left[\frac{3K^2}{J(J+1)}-1\right]q, \quad (2)$$

where q is the second derivative of the electrostatic potential at the nucleus with respect to a coordinate measured along the axis of symmetry of the molecule.

If the quadrupole coupling constant eQq is expressed in frequency units, the frequency of a spectral line is obtained by expressing the energies of the two levels by Eqs. (1) and (2) and taking the difference. In general, the selection rules for electric dipole transitions are $\Delta J=0,\pm 1$ (except $J=0\rightarrow 0$), $\Delta K=0$, and $\Delta F=0,\pm 1$, but in this paper by definition we are restricted to only those lines for which $\Delta J=0$ and $\Delta F=\pm 1$.

To discuss the spectra resulting from these latter selection rules, it is convenient to arrange the lines into groups. The allowed values of F may be written as $F=J+M$. Here M is to be considered as a mathematical parameter which takes on a sequence of values in integral steps ranging from $-I$ to I. According to our selection rules, a transition occurs between some level labeled by K, J, and M-1 and a level labeled by K, J, and M. We define a group of lines by giving M some fixed value and allowing J and K to vary.

First let us consider the $K=J$ groups, which, as we have said, tend to have the greatest intensities. For low values of J, the frequencies vary rapidly with J, but as J becomes very large, they converge upon definite limits. These limits may be determined by writing down the expression for the frequency in terms of J, K, and M and passing to the limit when $K=J$ becomes infinite. The resulting expression is

$$f_{\lim}=3eQq(2|M|-1)/4I(2I-1). \quad (3)$$

In considering groups for which $K\neq J$, we note that the only dependence of the frequency upon K is through the expression in the brackets in Eq. (2). If J and K approach infinity subject to the condition that $J-K$

[5] While preparing this manuscript we have learned that some calculations on these spectra have been made by T. Itoh of the University of Tokyo but most of the details of his calculations are unknown to us. See S. Kojima, Symposium on Molecular Physics at Nikko, 1953, p. 98.

[6] See for example, N. F. Ramsey, *Nuclear Moments* (John Wiley and Sons, Inc., New York, 1953).

[7] Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953).

$=L$, where L is any integer, this expression approaches a constant value 2, independent of L except that as L increases the convergence becomes slower. Therefore the limiting values of the frequencies depend only upon M and are given by Eq. (3). Also it is to be noted that in such limits, $q_J = q$. This latter fact may be explained by the facts that $\mathbf{J}$ and $\mathbf{K}$ become parallel in the limits, and, therefore, for the states $m_J = J$ the molecular-symmetry and space-fixed axes become parallel.

If we allow J to approach infinity subject to the condition that K maintain some constant value, we note that in Eq. (2) q_J approaches the value of $-\frac{1}{2}q$ and that the limiting frequencies are half the values given by Eq. (3). We can explain this behavior in the following way. In such limits $\mathbf{J}$ and $\mathbf{K}$ become perpendicular to one another while for the states $m_J = J$, $\mathbf{J}$ becomes parallel to the space-fixed axis. Therefore the molecular symmetry axis becomes perpendicular to the space-fixed axis. Hence the property of the electrostatic field which persists with respect to the precession of the various angular momentum vectors is the second spatial derivative of the potential with respect to a direction perpendicular to the symmetry axis. Since the potential must satisfy Laplace's equation and have axial symmetry, the second derivative with respect to a direction at right angles to the axis is equal to the second derivative along the axis multiplied by this factor $-\frac{1}{2}$.

Many of these remarks have been illustrated in Fig. 2 for the case when $I = 5/2$, which pertains to the experimental work to be described later. The frequencies of the five $K = J$ groups of lines are plotted against J in the solid curves. Two of these approach the limit 0.30 eQq from below; two others approach the limit 0.15 eQq, one from above and one from below; and the fifth group approaches zero in the limit. The frequencies of one of the $K = J - 1$ groups are plotted also with a
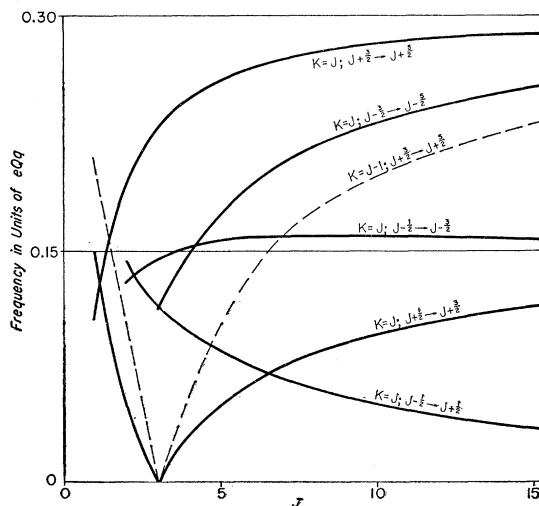

FIG. 2. Frequencies of principal groups of pure quadrupole lines of the vapor of a symmetric-top molecule with a nucleus having a spin $I = 5/2$ plotted as a function of J.

dashed line, and this curve is seen to converge upon the same limit as the corresponding $K = J$ curve but somewhat more slowly.

RELATION OF THE SPECTRA OF THE GASEOUS AND SOLID STATES

The physical significance of the limiting frequencies for large J as given by Eq. (3) may be seen by considering pure quadrupole transitions in the solid state which result from the change in orientation of a nucleus of spin I with respect to a crystalline electric field with axial symmetry. The theory of these transitions has been given by Pound,[8] and he has shown that the frequencies are given by a formula identical with Eq. (3). Here, however, M must be redefined as the quantum number giving the projection of I along the crystalline axis, and Q must be redefined as the second derivative of the electrostatic potential with respect to a linear coordinate measured along the crystalline axis.

The quantum mechanical theories for both the gaseous and solid states are, of course, based upon the same classical theory. It is not surprising that they should give results which coincide when we recall the discussion of the correspondence principle in many textbooks on quantum theory in which it is shown that when the angular momentum becomes large many of the quantities associated with the motion take on values which approach the classical ones. In fact Feld and Lamb[9] have used this approach to evaluate quadrupole splittings of diatomic molecules which have been observed to make magnetic dipole transitions in molecular beam experiments. Also in his paper, Pound[8] suggested that such an approach could be used for the crystalline state but he did not use it because in practical situations the theory must include provision for asymmetry of the field.

In the transitions which we are considering for the gaseous state the principal agent reacting with the radiation field is the electric dipole moment of the molecule while in the solid state the agent is the magnetic dipole moment of the nucleus. These facts may be reconciled by reference to Fig. 1 and by considering the case in which J becomes infinite while $J - K = L$. Then the vectors $\mathbf{J}$ and $\mathbf{K}$ become parallel, and their principal role is to define a direction which is the analog of the crystalline axis. At the same time the effective value of the dipole moment P_F approaches a constant value P, and, since it does not change in the transition, it becomes inactive. Then the role of principal agent must pass to the next higher available multipole which is the magnetic dipole moment of the nucleus.

HIGHER ORDER INTERACTIONS

The previous discussion is based upon a first-order perturbation theory which assumes that the quadrupole

[8] R. V. Pound, Phys. Rev. 79, 685 (1950).
[9] B. T. Feld and W. E. Lamb, Phys. Rev. 67, 15 (1945).

TABLE I. Measured pure quadrupole transitions of CH_3I and CF_3I.

$J = K$	Transition of F	Measured frequency Mc/sec	Calculated eqQ Mc/sec	Second order correction Mc/sec	Calculated intensity cm⁻¹
		(a) CH_3I			
1	$3/2 \to 5/2$	292.5 ± 0.4	-1934.6 ± 2.3	2.29	2.8×10^{-10}
2	$9/2 \to 7/2$	375.0 ± 0.3	-1934.0 ± 1.7	3.48	3.8×10^{-10}
3	$11/2 \to 9/2$	444.76 ± 0.10	-1934.0 ± 0.4	1.55	7.9×10^{-10}
4	$13/2 \to 11/2$	481.05 ± 0.10	-1933.8 ± 0.4	1.14	3.3×10^{-10}
5	$15/2 \to 13/2$	503.05 ± 0.15	-1934.4 ± 0.6	0.85	2.5×10^{-10}
6	$17/2 \to 15/2$	517.3 ± 0.4	-1933.95 ± 1.2	0.65	3.5×10^{-10}
		(b) CF_3I			
3	$11/2 \to 9/2$	500.4 ± 0.4	-2142.5 ± 1.8	9.39	1.7×10^{-11}

splittings are very small compared to the rotational splittings. However, pure quadrupole spectra are only observable with very large quadrupole interactions and this assumption is not completely valid. Corrections must be made by an application of the second order theory due to Bardeen and Townes.[10] The calculations of these corrections is straight-forward and will not be given in detail. As can be seen in Table I, these corrections amounted to several Mc/sec in the experiments which will be described.

The sign of the quadrupole coupling constant may be determined from a study of the second-order corrections. These corrections, depending upon the square of this constant, are independent of the sign. However, in the first-order theory a reversal of sign inverts the order of the two levels. Thus whether the second-order correction is to be added or subtracted to the frequency calculated from first-order theory depends on the sign. Therefore, both the magnitude and sign of the constant may be determined if two or more lines are measured accurately.

While the observation of quadrupole spectra affords a method of obtaining accurate values of quadrupole coupling constants, it does not seem to be a favorable method under present conditions for investigating the magnetic dipole ($I \cdot J$) interaction. The theory of this interaction has been developed by Henderson and Van Vleck.[11] With our present techniques we have been able to observe only $K = J$ and $F = I + J \to F = I + J - 1$ transitions. Except for $J = 1$ and $J = 2$, the change in frequency due to this interaction varies very slowly from line to line in this group. Furthermore, if we assume the interaction constants in CH_3I are not larger than those of NH_3, we cannot expect the total effect to be greater than about 50 kc/sec. Such an effect would be obscured by experimental errors.

CALCULATION OF INTENSITIES

The intensities can be calculated by methods given in standard texts.[7] However, a direct calculation required the evaluation of the matrix element of the

molecular dipole moment P between the state JKF and the state JKF^*, where $F^* = F \pm 1$, but we were unable to locate any explicit evaluation of these matrix elements. Therefore we devised a procedure employing standard reference material whereby these matrix elements were evaluated indirectly.

This procedure consisted of two principal steps. The first consisted of calculating the intensity of a fictitious transition connecting two states with the same J and K without any nuclear hyperfine splitting but occurring at the actual frequency of the spectral line. (An actual transition of this type, of course, would occur at zero frequency and therefore would have zero intensity.) This intensity could be calculated directly with matrix elements whose values are well known. The second step introduced the effect of hyperfine splitting. The intensity calculated in the first step was multiplied by the ratio of the relative intensity $I_{F \to F^*}$ of the transition from F to F^* to $\sum I$, the sum of all the intensities connecting all of the levels with the same J and K. These quantities have been calculated by several authors,[12-14] and numerical tables have been reprinted in several standard textbooks. By combining these two steps and evaluating all constants, the following final result was obtained:

$$\alpha = \frac{3.86 \times 10^{-14}(2J+1)K^2\nu^2BA^{\frac{1}{2}}\sigma g f_v P^2 I_{F \to F^*}}{T^{5/2}(\Delta\nu)_1 J(J+1)\sum I}$$

$$\times \exp\{-4.80 \times 10^{-5}[BJ(J+1)+(A-B)K^2]/T\}, \quad (4)$$

where α = absorption coefficient at center of line in cm⁻¹, ν = frequency in Mc/sec, B = rotational constant with respect to the principal axis of inertia parallel to the symmetry axis in Mc/sec, A = rotational constant with respect to a principal axis of inertia perpendicular to the symmetry axis in Mc/sec, f_v = fraction of the molecules in vibrational state in which the transitions take place, P = dipole moment in Debye units (1 Debye unit = 10^{-18} esu), T = temperature of the gas in degrees Kelvin, and $(\Delta\nu)_1$ = half-line width at half-maximum at 300°K and 1 mm Hg pressure expressed in Mc/sec.

[10] J. H. Bardeen and C. H. Townes, Phys. Rev. 73, 627 and 1204 (1948).
[11] R. S. Henderson and J. H. Van Vleck, Phys. Rev. 74, 106 (1948).

[12] R. De Kronig, Z. Physik. 31, 885 (1925); 33, 261 (1925).
[13] E. L. Hill, Proc. Natl. Acad. Sci. U. S. 15, 779 (1929).
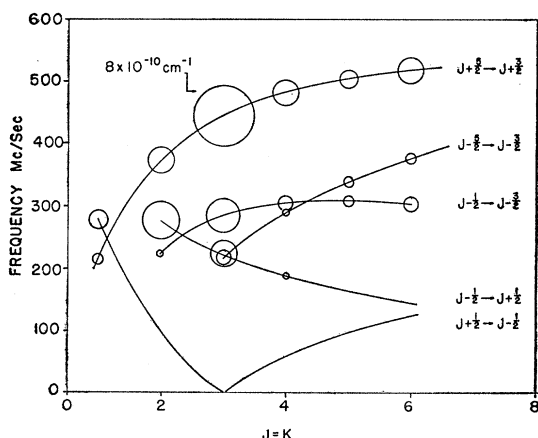[14] H. E. White and A. Y. Eliason, Phys. Rev. 44, 753 (1933).

FIG. 3. The frequencies of the principal pure quadrupole lines of CH_3I plotted against J. The intensities at room temperature are indicated by the diameters of the circles.

The values of g and σ in Eq. (4) can be evaluated as follows[7]:

$$g = g_I g_K, \qquad (5)$$

where

$$g_K = 1 \text{ for } K = 0, \quad g_K = 2 \text{ for } K \neq 0. \qquad (6)$$

For molecules with a threefold axis of symmetry with one set of three identical "off-axis" nuclei having spin I, $\sigma = 3$, and

$$g_I = \tfrac{1}{3}[1 + 2/(2I+1)^2] \quad \text{for } K \text{ divisible by 3,}$$
$$\text{including } K = 0, \qquad (7)$$
$$g_I = \tfrac{1}{3}[1 - 1/(2I+1)^2] \quad \text{for } K \text{ not divisible by 3.}$$

To determine which pure quadrupole transitions are likely to be the most intense ones, we note from Eq. (4) that the absorption coefficient is proportional to the square of the frequency. In general, the highest frequency lines are the $F = I + J - 1 \rightarrow F = I + J$ transitions, as indicated in Fig. 2. These are the transitions which we predicted from the vector model to be the strongest. Also in accord with the vector model, we note that for a given J, the intensity is proportional to K^2, and therefore, even aside from considerations of frequency, generally the strongest lines for a given J will occur for $K = J$.

For low values of $K = J$ the intensity increases with J because of the predominant effect is the increasing statistical weights. For large values of $K = J$, this effect is outweighed by the decrease in the ratio $I_{F \rightarrow F*}/(\sum I)$ in Eq. (4), and the net effect is to cause the intensity decrease rapidly with J. A further decrease is caused by the Boltzmann factor.

In Fig. 3 are shown the frequencies of the principal pure quadrupole lines of methyl iodide, CH_3I, plotted against J. Centered upon the appropriate points are circles whose diameters are proportional to the intensities at room temperature, the strongest line being the $K = J = 3$, $F = 11/2 \rightarrow 9/2$ with an intensity of 8×10^{-10} cm^{-1}. Mainly because the ratio $I_{F \rightarrow F*}/(\sum I)$ is

small compared to unity, these intensities are generally considerably smaller than those of rotational transitions in the same frequency region. (For example, the $5_2 \rightarrow 5_3$ line of HDO, which was observed in this laboratory[3] at 486.50 ± 0.15 Mc/sec, has a computed intensity of 1.5×10^{-8} cm^{-1}.) The smallness of this ratio is to be attributed to the fact that here we are dealing with "nondiagonal" $\Delta F = \pm 1$ transitions. On the other hand, it is to be noted in Fig. 1 that a few low-J lines not in the $F = J + I \rightarrow F = J + I - 1$ group have comparatively large intensities. This fact is explained by the existence of abnormally large values of this ratio.

EXPERIMENTAL TECHNIQUES

The experimental investigation employed a Stark-modulated spectroscope with a 3 in.$\times 1\frac{1}{2}$ in.$\times 20$ ft absorption cell. The details of the instrument itself are given elsewhere[2,3] and will not be given here. However, because of the very low intensities of the lines it was necessary to operate the equipment in an unorthodox fashion at the cost of resolution.

To obtain high sensitivity, it was necessary to operate at high-power levels, corresponding to rectified crystal detector currents of about 0.5 Ma. To avoid power saturation it was necessary to use high gas pressures such that the line width was comparable to the bandwidth of the rf system. Therefore it was not practical to operate at fixed pressure and sweep the frequency in the usual way. On the other hand, the high degree of absolute frequency stability obtainable at low frequencies made another procedure possible.

The system was tuned up near to the expected frequency of a line. The cell was filled with gas at such high pressure that the Stark modulation completely failed because of the absence of any resolution of the Stark components. The corresponding deflection of the output meter gave the zero. Then the pump was turned on, and the meter deflected as the pressure decreased. This deflection went through a maximum and ultimately decreased because of the onset power saturation. It was assumed this deflection decreased in the limit to the
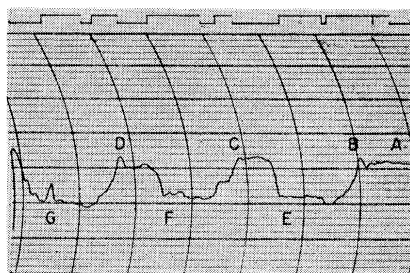

FIG. 4. Illustration of the pressure variation method. The zero is shown at A. With the gas at high pressure, the pump is turned on at B causing downward deflections followed by the beginning of a slow recovery. At E the pump is turned off and gas is admitted. The cycle is repeated at CF and again at DG. These data were obtained on the $K = J = 4$, $F = 13/2 \rightarrow 11/2$ line of CH_3I at 480.8 Mc/sec.

same value as that at high pressure, although it was impractical to verify this assumption since it would have required pumping such a long time that other factors could not be assumed to remain constant. This effect and its reproducibility is illustrated in Fig. 4. At A, the deflection is that pertaining to high pressure. Then at B, the pump was turned on, and the output deflected downward, and, after reaching a stationary value, tended to recover slowly to the value at A. After a few minutes at E, the pump was turned off and gas at high pressure was readmitted. The deflection returned to that at A. Then this cycle was repeated twice, C and D corresponded to B, and the F and G corresponded to E.

On a recording such as shown in Fig. 4 we observed either the maximum deflection, or, by the use of the pressure calibration which was introduced on to the record by the chronometer pen, we determined the deflection at some preassigned pressure. In either case some of the effects of noise were eliminated by smoothing. Having obtained either the maximum deflection or the deflection at some pressure at the original frequency, we repeated the process at other frequencies maintaining constant power. Then the line contour was obtained by plotting the deflections against frequency. Such a contour, obtained by the maximum deflection procedure, with the $K=J=3$, $F=11/2\rightarrow9/2$ line of CH₃I is shown in Fig. 5. The validity of these procedures for obtaining the line frequency may be illustrated by the fact that four values, two obtained by maximum deflection and two by the constant pressure method, lay within 70 kc/sec of their average value while we have assigned a probable error of 100 kc/sec to our final value of this frequency.

Confirmation of the identities of two of the CH₃I lines was obtained by observing some of their Stark components. A few of the measurements were made by this
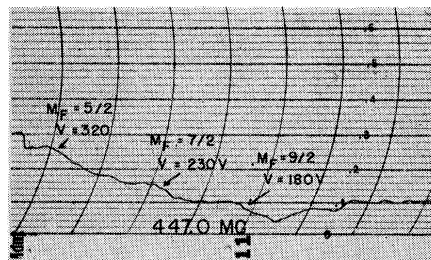
FIG. 6. Some Stark components of the $K=J=3$, $F=11/2\rightarrow9/2$ line of CH₂I by sweeping Stark voltage at a constant frequency of 447.0 Mc/sec.

same pressure variation technique, but a better method proved to be the one where at a constant frequency and pressure the Stark voltage was swept while the output was recorded as shown in Fig. 6. Because of a gradual change in stray pick-up, the base line has a large slope, but superimposed upon it are three small peaks corresponding to three of the components of the $K=J=3$, $F=11/2\rightarrow9/2$ line of CH₃I. Small as these peaks were, they were reproducible, and their positions changed with frequency in a manner consistent with their calculated Stark coefficient.

Whereas these techniques were developed for use in this low-frequency region, one of the present authors has also employed them to good advantage in observing the $J=0\rightarrow1$ rotational spectrum of trifluoriodomethane in the S-band.[15]

EXPERIMENTAL RESULTS

Observations were made upon two molecules, CH₃I and CF₃I. The CF₃I was obtained from the reaction of trifluroacetic acid with silver iodide. After partial distillation, the sample was observed to have the correct boiling point for CF₃I.

Listed in Table I are the measured frequencies and the corresponding values of eQq for the six lines which were observed for CH₃I. The weighted average is -1933.99 ± 0.25 Mc/sec, which is in good agreement with the value of -1934 Mc/sec obtained by Gordy, Simmons, and Smith[16] from the observation of microwave rotational transitions.

The spectrum of CF₃I is very much weaker than that of CH₃I mainly because of the less favorable population of the same energy levels, and it was possible to observe only one line, whose frequency is also listed in Table I. The corresponding value of eqQ is -2142.4 ± 2 Mc/sec in good agreement with the value of -2143.8 ± 2 Mc/sec obtained from the experiment on the $J=0\rightarrow1$ rotational transition mentioned above.[15] These values,
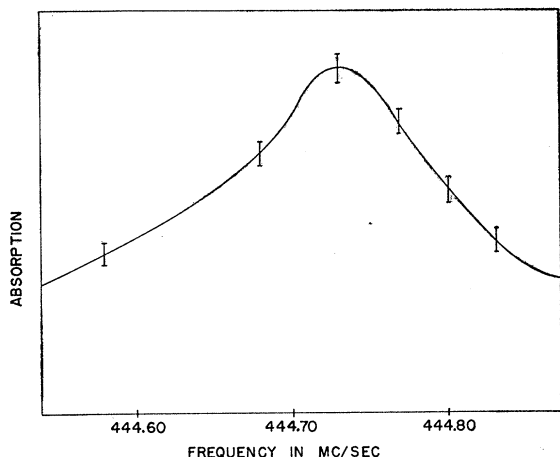

FIG. 5. Line contour computed from deflections obtained by pressure variation method as illustrated in Fig. 4. This is a plot of the $K=J=3$, $F=11/2\rightarrow9/2$ line of CH₃I.

[15] F. Sterzer, J. Chem. Phys. 22, 2094 (1954); 23, 762 (E) (1955).

[16] Gordy, Simmons, and Smith, Phys. Rev. 74, 243 (1948).

however, are not completely independent, since the rotational data were used to supply the second-order correction.[10] These values are also in good agreement with the earlier value of -2150 Mc/sec obtained by Sheridan and Gordy[17] from observations of higher rotational transitions in the K-band.

[17] J. Sheridan and W. Gordy, J. Chem. Phys. **20**, 591 (1952).

Threshold Law for Multiple Ionization

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On the basis of evidence from single ionization, an approximate threshold law for multiple ionization is derived.

TWO years ago, in a paper on the threshold law for single ionization[1] a serious effort was made to take into account the three-body character of the ionization process. It is a result of that calculation that the interaction of the two electrons is a relatively minor effect as far as the power law is concerned, the reason being that the two slow electrons, upon emerging from the ion, keep to opposite sides of it. A simplified type of reasoning which neglects the interaction of the emerging electrons outside the reaction zone has thus semiquantitative value. If it is applied to double ionization
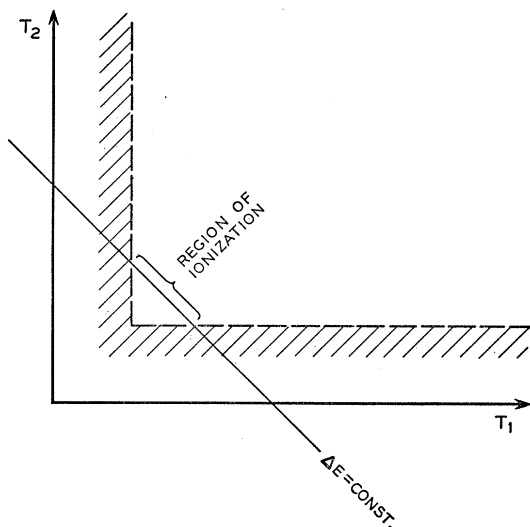

FIG. 1. Region in which ionization occurs in the case of single ionization. T_1 and T_2 are the kinetic energies of the two emerging electrons, and ΔE is the energy excess.

[1] G. H. Wannier, Phys. Rev. **90**, 817 (1953).

a quadratic dependence of the yield on the energy excess results. This was communicated to Fox, Hickam, and Kjeldaas and is mentioned in their paper.[2] It appears that these ideas are of some interest to the experimental workers in the field, and the derivation of this approximate threshold law will therefore be presented here.

Draw around the ion a spherical surface (whose radius b is, as is usual in this type of argument, unspecified) and let the electrons emerge from the sphere with "switched off" mutual interaction. Each electron must then have a kinetic energy T greater than e^2/b in order to escape. In Fig. 1, the case of single ionization is illustrated. The kinetic energies T_1 and T_2 of the two emerging electrons are plotted on abscissa and ordinate. The region in which ionization occurs is limited by two straight lines parallel to the axes. Now a line of constant energy excess ΔE in this diagram is straight and of slope -1; the segment of it leading to ionization is marked in the figure. Clearly, the length of this segment is proportional to the energy excess and so is the yield unless the probability distribution has a strong anomaly in the corner. This possibility is highly improbable. If more than two electrons emerge from the reaction zone, then one can plot their respective kinetic energies in a space of higher dimensions, and reason as above. For the case of double ionization, we work in three dimensions: the straight line $\Delta E =$ constant becomes a plane and the segment a triangle. Its area, and thus the yield, varies as the square of the energy excess. For n-fold ionization, the threshold law thus becomes the nth power. One can reason by analogy to single ionization that the true exponent is probably slightly larger than n.

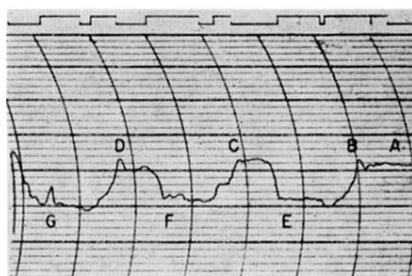[2] Hickam, Fox, and Kjeldaas, Phys. Rev. **96**, 65 (1954).

FIG. 4. Illustration of the pressure variation method. The zero is shown at A. With the gas at high pressure, the pump is turned on at B causing downward deflections followed by the beginning of a slow recovery. At E the pump is turned off and gas is admitted. The cycle is repeated at CF and again at DG. These data were obtained on the $K=J=4$, $F=13/2\rightarrow11/2$ line of CH_3I at 480.8 Mc/sec.
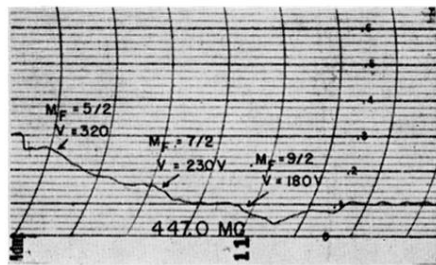
Fig. 6. Some Stark components of the $K=J=3$, $F=11/2 \rightarrow 9/2$ line of CH_2I by sweeping Stark voltage at a constant frequency of 447.0 Mc/sec.