



FIG. 5. Comparison of experimental and theoretical curves showing the relationship between average electron velocity and applied electric field. The experimental values are derived from a series of curves similar to those shown in Fig. 3, and the theoretical curve is determined from Eq. (5).

mental data and Eq. (4). A series of curves, similar to those shown in Fig. 3 provides the necessary experimental values. The average velocity as calculated from the electron temperature is plotted against the square root of the corresponding electric field for each case.

In comparing the two curves of Fig. 5, it is evident that the experimental data is in fairly good agreement

with what one might expect on a theoretical basis. Not only does the experimental curve follow a straight line, again indicating that the gas discharge laws may be suitably applied in describing the phenomenon of field dependent secondary emission, but the slope and magnitude of the experimental curve agree well with those of the theoretical plot. This may be regarded as a check on the form of the equations used and on the value utilized for the mean free path.

IV. CONCLUSIONS

Through the use of retarding potentials it has been experimentally determined that the emitted electrons closely follow a Maxwellian energy distribution with a rather wide energy range. Then, on the basis of such a distribution, equations normally associated with gaseous discharges have been used to explain the experimental results. Furthermore, values have been obtained for the average electron energy and for the mean free path of electrons in the oxide film.

In addition, the present method provides a means of measuring the surface potentials of magnesium oxide films.

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Microwave Spectra of Tritium Iodide and Tritium Bromide*

B. ROSENBLUM AND A. H. NETHERCOT, JR.
Columbia University, New York, New York
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The $J=1\leftarrow 0$ rotational transitions in TI and TBr have been observed. A tritium-deuterium mass ratio has been determined, and electronic effects which cause errors in this ratio considered.

THE microwave spectra of tritium iodide and tritium bromide have been observed by the use of a klystron-driven harmonic generator and techniques previously described.¹ The observed transitions and frequencies as well as ν_0 and eqQ are given in Table I.

Nuclear mass ratios can be determined by microwave

TABLE I. Observed frequencies for the $J=1\leftarrow 0$ transition and molecular constants of TI and TBr (Mc/sec).

	TI ¹²⁷	TBr ⁷⁹	TBr ⁸¹
$\Delta F=+1$	131 592.95 \pm 0.25	172 472.72 \pm 0.40	172 320.96 \pm 0.40
$\Delta F=0$	131 210.20 \pm 0.40	172 604.60 \pm 0.40	172 431.49 \pm 0.40
ν_0	131 501.75 \pm 0.40	172 499.10 \pm 0.40	172 343.07 \pm 0.40
eqQ	-1 822.6 \pm 3.0	527.6 \pm 2.0	442.1 \pm 2.0

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¹ Nethercot, Klein, and Townes, Phys. Rev. **86**, 798 (1952).

spectroscopy from the ratio of the rotational constants, B_0 , for two isotopic molecules. However, small electronic effects whose size is difficult to predict theoretically can cause small errors. In principle, these errors appear in all mass ratios determined by microwave spectroscopy, but they are particularly large for the isotopic hydrogen halides because of the large speed of rotation. This case is therefore an ideal one in which to measure the size of these errors and compare them with theoretical predictions.

All these small electronic effects can be represented as a single term in a perturbation calculation, but in order to estimate the size of this term it may be broken up into its components. For the hydrogen halides, the largest of these components is L -uncoupling (the excitation of higher electronic states by the rotation of the molecule).² Unless corrections are made for L -uncou-

² C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (to be published), Chap. 8.

pling the apparent tritium-deuterium mass ratio will be smaller than the actual value. From the pure precession hypothesis (which is probably not an accurate representation in this case) an approximate expression for the fractional error in the mass ratio (δ) can be derived:

$$\delta = \frac{L(L+1)h(\nu_0' - \nu_0'')}{2J(W_{\Pi} - W_{\Sigma})},$$

where L and J are both one in this case, $(\nu_0' - \nu_0'')$ is the frequency difference between the two isotopic molecules, and $(W_{\Pi} - W_{\Sigma})$ is the energy separation of the Π and Σ states. δ can also be approximately determined from a measurement of the $\mathbf{I} \cdot \mathbf{J}$ interaction. A smaller error in the opposite direction is caused by the ionic character of the bond since part of an electron is removed from the hydrogen isotope. Other electronic effects should be considerably smaller. The difference between the Dunham coefficient Y_{01} and B_e leads to an error somewhat smaller than those considered here.

Equilibrium rotational constants B_e were calculated from the ν_0 's given for TI and TBr in Table I, the B_0 's for DI^{3,4} and DBr,⁵ and the published infrared values of α and D .^{6,7} The apparent mass ratios were then computed to be $1.497467 \pm 12 \times 10^{-6}$ for the iodide and $1.497469 \pm 10 \times 10^{-6}$ for the bromide. The mass ratio from nuclear reaction data⁸ is $1.497466 \pm 7 \times 10^{-6}$. This good agreement is probably spurious in view of the appreciable electronic effects expected in this case.

For the iodide the L -uncoupling calculated from the above equation should decrease the apparent mass ratio by 60×10^{-6} . The ionic character of the bond of about 5 percent should increase the apparent mass ratio by

7×10^{-6} for a net decrease of 53×10^{-6} . A calculation based on the measured value⁴ of the $\mathbf{I} \cdot \mathbf{J}$ interaction in DI gives a value for the L -uncoupling about thirty percent lower than the pure precession hypothesis. In the bromide the calculated L -uncoupling should give a decrease of 80×10^{-6} and the ionic character of about 11 percent should give an increase of 14×10^{-6} . This leaves an expected net decrease in the apparent mass ratio of 66×10^{-6} .

New infrared measurements⁹ on the 2-0 and 3-0 bands of HI with somewhat higher accuracy indicate the existence of a quadratic term (γ) in the expansion for B_v , which slightly modifies the value of B_e calculated from infrared data. From these measurements an apparent mass ratio of $1.497448 \pm 20 \times 10^{-6}$ is derived, which is 18×10^{-6} lower than the nuclear reaction value. Within the large error this is almost the shift expected. The apparent absence of electronic effects in the bromide will probably be explained by a more accurate measurement of α and γ .

The present uncertainty in the magnitude of the electronic effects in HI is due largely to an uncertainty of $\pm 0.0013 \text{ cm}^{-1}$ in α . Further infrared measurements to determine α and γ more accurately in both molecules seem feasible and would be of considerable interest in fixing the magnitude of the electronic effects. In spite of the uncertainty in the value of α , it can be said that the error in the mass ratio is not greater than that predicted from the pure precession hypothesis. This indicates that mass ratios previously determined by microwave spectroscopy are not affected by the excitation of higher electronic states within their stated error.

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³ J. A. Klein and A. H. Nethercot, Phys. Rev. **91**, 1018 (1953).

⁴ C. A. Burrus and W. Gordy, Phys. Rev. **92**, 1437 (1953).

⁵ W. Gordy and C. A. Burrus, Phys. Rev. **93**, 419 (1954).

⁶ D. R. J. Boyd and H. W. Thompson, Spectrochim. Acta **5**, 308 (1952).

⁷ Thompson, Williams, and Callomon, Spectrochim. Acta **5**, 311 (1952).

⁸ Li, Whaling, Fowler, and Lauritsen, Phys. Rev. **83**, 512 (1951).

⁹ D. R. J. Boyd (private communication).