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Microwave Spectrum of Chlorine Dioxide. I. Rotational Assignment*

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The microwave spectrum of chlorine dioxide has been investigated and several rotational transitions assigned. The resulting rotational constants (in Mc) are:

$Cl^{35}O_2$: $A=52\,072$, $B=9952$, $C=8332$;
$Cl^{37}O_2$: $A=50\,725$, $B=9952$, $C=8295$.

These constants are limited in precision by the presence of hyperfine structure which has been only approximately treated. The structural parameters of chlorine dioxide as obtained from the rotational constants are $r_{Cl-O}=1.473\pm0.01$ A; $<O-Cl-O=117°\,36'\pm1°$. Approximate hyperfine constants are given.

INTRODUCTION

A BRIEF history of the investigations of the microwave spectrum of chlorine dioxide seems appropriate in view of the large number of authors and institutions represented on the title page.

The first thorough investigation was made at the Oak Ridge Gaseous Diffusion Plant by D. F. Smith and D. W. Magnuson in 1953. Over two hundred lines were measured. The investigation was continued at Rice University by G. R. B. and J. C. B. and at Cambridge University by J. G. B., T. M. S., D. R. J., and C. N. K. Both of these investigations started about 1954. After G. R. B. left Rice University in 1958, the work there was continued by R. F. C., J. L. K., and R. F. H.

The assignment presented here was arrived at independently by the Cambridge and Rice groups. The Cambridge results were presented at the Bologna International Conference on Spectroscopy in September, 1959, the proceedings of which will be published in due course. The principles on which the assignment was made there are somewhat different from those of the present treatment, but led essentially to the same characterization of transitions. The Rice results were presented at The Ohio State Symposium, June, 1960. J. G. B. was on both papers.

Chlorine dioxide is a stable molecule with an odd number electrons and consequent resultant electronic spin. This electronic spin both complicates the microwave spectrum of ClO_2 and makes the analysis of the spectrum of interest. The only molecule similar to chlorine dioxide which has been investigated is nitrogen dioxide.[1]

The hyperfine interactions in molecules like ClO_2 have been discussed by Lin,[2] by Baker,[3] and by Curl and Kinsey.[4] In the case of chlorine dioxide each rotational energy level is split into eight by the interaction of the electron spin with molecular rotation and by the interaction of the electron spin with the nuclear spin. There may be as many as thirty-four hyperfine components for a single rotational transition corresponding to $\Delta J=\pm1, 0$, $\Delta F=\pm1, 0$. Usually, however, eight lines are observed for a rotational transition corresponding to $\Delta N=\Delta J=\Delta F$. These eight lines are grouped into two quartets corresponding to the two possible values of J for given N.

Of primary concern here is the rotational assignment and the determination of rotational constants. For these purposes a crude treatment of the hyperfine splitting has been made and is given in the Appendix. Some knowledge of the hyperfine interaction parameters is necessary in order to determine accurately the rotational constants. Indeed, as will be seen, the uncertainty in the rotational constants arises from the approximations made in the treatment of the hyperfine splitting.

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[1] George R. Bird, J. Chem. Phys. **25**, 1040 (1956).

[2] C. C. Lin, Phys. Rev. **116**, 903 (1959).

[3] J. G. Baker, thesis, Cambridge University, 1958 (unpublished).

[4] R. F. Curl and J. L. Kinsey (to be published).

EXPERIMENTAL

The spectra reported here were obtained by several spectrometers. The region from 7000–50 000 Mc was investigated to varying extents on three different spectrometers. The spectrometer at Rice University is a 100-kc Stark-modulated spectrometer of conventional design.[5] The frequency standard used with this spectrometer is stable 5 parts in 10^8 per day and was checked regularly with *WWV*. The spectrometer at Cambridge is a 85-kc Stark modulated spectrometer.[5] The frequency standard was controlled by the National Physical Laboratory 5-Mc transmission from Rugby.

A very useful atlas of about 225 lines of chlorine dioxide in the region between 7000 and 34 000 Mc was furnished us by D. F. Smith and D. W. Magnuson of the Oak Ridge Gaseous Diffusion Plant. Some of these lines are used in this paper with their kind permission.

Both normal and Cl^{35}-enriched (95 isotope % Cl^{35}) samples were used. The normal sample was prepared by the reaction between $KClO_3$ and oxalic acid.[6] The Cl^{35}-enriched samples were prepared by the electrolysis[7] of $NaCl^{35}$ to $NaCl^{35}O_3$. Proper conditions for a good yield from this electrolysis appear to be (1) vigorous stirring, (2) temperature about 50° to 60°C, and (3) anode current density less than about 0.4 amp/cm^2. The $NaCl^{35}O_3$ was then reacted with oxalic acid.

Over 300 lines were measured in the region from 7000 to 60 000 Mc and a list is available on request. The lines for which both isotopes have been assigned are listed in Table I. The estimated uncertainty is ±0.2 Mc.

ROTATIONAL ASSIGNMENT

Because ClO_2 has a two-fold axis of symmetry half of the rotational levels are missing. This is a consequence of the O^{16} zero spin.

The two O^{16} nuclei may be interchanged by rotating both nuclei and electrons about the symmetry axis by 180° and then rotating the electrons only by another 180°. The total wave function should be symmetric (or unchanged) by this over-all operation since the O^{16} nuclei obey Bose-Einstein statistics.

In the ground vibrational state, the total wave function has the symmetry of the rotational wave-function under the first operation, since the electronic coordinates are tied to the nuclei. For the second operation the total wave function has the symmetry of the electronic wave function. Therefore if the electronic wave function is symmetric, the rotational must also be symmetric. If the electronic wave function is antisymmetric the rotational wave-function must be antisymmetric.[8]

A cursory look at the molecular orbitals of ClO_2 indicates that the odd electron will probably go either into a $(2p\pi_1 B_1)$ antibonding orbital or into a $[2(sp^2)\sigma A_1]$ antibonding orbital. The first alternative is supported by the assignment of odd rotational levels (see below) and by the values of $(aa)_I$, $(bb)_I$, and $(cc)_I$ (see Appendix). Therefore, we conclude that

$$C_2\psi_{\mathrm{rot}} = -\psi_{\mathrm{rot}},$$

and the asymmetric rotor quantum number τ must be odd.

The hyperfine structure is useful in making the rotational assignment because the corresponding hyperfine splittings within a quartet for a given rotational transition should have the following relationship:

$$\Delta\nu_{\mathrm{Cl}^{35}}/\Delta\nu_{\mathrm{Cl}^{37}} \approx \mu_{\mathrm{Cl}^{35}}/\mu_{\mathrm{Cl}^{37}} = 1.2.$$

In addition, the splitting between quartets for a Cl^{35} transition should be about the same as the splitting between quartets for the corresponding Cl^{37} transition. Using these aids and the Stark and Zeeman effects, the assignment in Table I was made. The assignment of hyperfine structure quantum numbers should be regarded as tentative.

The average of the eight hyperfine component frequencies of a transition is not equal to the rigid-rotor frequency, but depends also on the hyperfine-interaction parameters. This average must be corrected to the rigid-rotor frequency by adding the following correction:

$$\Delta\nu_{\mathrm{corr}} = +(1/4)\left(\frac{\Sigma_S'}{2N'+1} - \frac{\Sigma_S}{2N+1}\right) - (15/4) \times\left[\frac{\Sigma_I'}{(4N'^2-1)(2N'+3)} - \frac{\Sigma_I}{(4N^2-1)(2N+3)}\right].$$

This formula does not hold when $N \leqq 1$. The primed state is the upper, and Σ_S and Σ_I are defined in the Appendix.

This correction was applied using the approximate parameters given in the Appendix. The $\Delta\nu_{\mathrm{corr}}$ and experimental rigid-rotor frequencies ν_0 obtained in this way are listed in Table I. The $1_{01}-1_{10}$ transitions are a special case and a special computation was required to obtain the ν_0.

The rotational constants were adjusted to reproduce as nearly as possible the ν_0's and are given in Table II. Comparison between observed and calculated ν_0's is made in Table I.

STRUCTURE OF CHLORINE DIOXIDE

The *a* and *b* coordinates of Cl^{35} in $Cl^{35}O_2$ may be found from the moments of inertia of $Cl^{35}O_7$ and $Cl^{37}O_2$ and Kraitchmann's equations. The *b* coordinate of the oxygens may then be found from the center-of-mass conditions assuming C_{2v} symmetry.

The *a* coordinate of the oxygen atoms can be found by fitting I_B for either species. This is not regarded as a

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[5] K. B. McAfee, R. H. Hughes, and E. B. Wilson, Jr., Rev. Sci. Instr. **20**, 821 (1949).

[6] R. W. Brown, Tappi **35**, 75 (1952).

[7] See E. Müller, *Electrochemisches Praktikum* (Theodor Steinkopff Verlag, Dresden, 1920), p. 130.

[8] For further discussion of this point, particularly with reference to the antisymmetric $^3\Sigma_g^-$ electronic ground state of O_2, see G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand, Company, Inc., Princeton, New Jersey, 1950), p. 238 ff.

TABLE I. Rotational assignment of chlorine dioxide.

		$Cl^{35}O_2$		
	Mc	Δν (corr) (Mc)	ν_0 (obs) (Mc)	ν_0 (calc) (Mc)
$1_{01} \rightarrow 1_{10}$			43 740	43 740
$J=\frac{3}{2} \rightarrow \frac{3}{2}$				
$F=1 \rightarrow 0$	43 416.10[a]			
$0 \rightarrow 1$				
$1 \rightarrow 1$	43 428.72[a]			
$2 \rightarrow 1$	43 398.08[a]			
$1 \rightarrow 2$	43 444.10[a]			
$2 \rightarrow 2$	43 413.60[a]			
$3 \rightarrow 2$	43 338.16[a]			
$2 \rightarrow 3$	43 423.60[a]			
$3 \rightarrow 3$	43 348.60[a]			
$J=\frac{3}{2} \rightarrow \frac{1}{2}$				
$F=0 \rightarrow 1$				
$1 \rightarrow 1$	44 545.80			
$2 \rightarrow 1$	44 515.28[a]			
$1 \rightarrow 2$				
$2 \rightarrow 2$	44 703.00[a]			
$3 \rightarrow 2$	44 627.20[a]			
$J=\frac{1}{2} \rightarrow \frac{3}{2}$				
$F=1 \rightarrow 0$	43 112.78			
$1 \rightarrow 1$	43 124.95[a]			
$2 \rightarrow 1$				
$1 \rightarrow 2$	43 140.30[a]			
$2 \rightarrow 2$	43 274.56[a]			
$2 \rightarrow 3$	43 285.5[a]			
$J=\frac{1}{2} \rightarrow \frac{1}{2}$				
$F=1 \rightarrow 1$	44 242.08[a]			
$2 \rightarrow 1$	44 376.00[a]			
$1 \rightarrow 2$	44 429.74[a]			
$2 \rightarrow 2$	44 564.10[a]			
$2_{12} \rightarrow 3_{03}$		55	14 125	14 122
$F=0 \rightarrow 1$	13 852.05[a]			
$1 \rightarrow 2$	13 858.45[a]			
$2 \rightarrow 3$	13 894.5[a]			
$3 \rightarrow 4$	13 953.6[a]			
$4 \rightarrow 5$	14 231.6[a]			
$3 \rightarrow 4$	14 246.7[a]			
$2 \rightarrow 3$	14 256.4[a]			
$1 \rightarrow 2$	14 262.5[a]			
$3_{03} \rightarrow 3_{12}$		−36	47 992	47 992
$F=5 \rightarrow 5$	47 697.2[a]			
$4 \rightarrow 4$	47 739.8[a]			
$3 \rightarrow 3$	47 764.6[a]			
$2 \rightarrow 2$	47 778.2[a]			
$1 \rightarrow 1$	48 232.10[a]			
$2 \rightarrow 2$	48 276.60[a]			
$3 \rightarrow 3$	48 336.0[a]			
$4 \rightarrow 4$	48 398.20[a]			
$5_{14} \rightarrow 4_{23}$		−45	25 515	25 515
$F=4 \rightarrow 3$	25 261.0[a]			
$5 \rightarrow 4$	25 274.6[a]			
$6 \rightarrow 5$	25 290.1[a]			
$7 \rightarrow 6$	25 306.7[a]			
$6 \rightarrow 5$	25 798.5[a]			
$5 \rightarrow 4$	25 828.1[a]			
$4 \rightarrow 3$	25 852.7[a]			
$3 \rightarrow 2$	25 870.1[a]			
$6_{25} \rightarrow 7_{16}$		15	20 823	20 845
	20 688.0[a]			
	20 713.3[a]			
	20 741.8[a]			
	20 770.6[a]			
	20 857.2[a]			
	20 881.2[a]			
	20 900.6[a]			
	20 915.9[a]			

		$Cl^{37}O_2$		
	Mc	Δν (corr) (Mc)	ν_0 (obs) (Mc)	ν_0 (calc) (Mc)
$1_{01} \rightarrow 1_{10}$			42 429	42 430
$J=\frac{3}{2} \rightarrow \frac{3}{2}$				
$F=1 \rightarrow 0$	42 112.40[a]			
$0 \rightarrow 1$				
$1 \rightarrow 1$				
$2 \rightarrow 1$	42 096.40			
$1 \rightarrow 2$	42 135.12[a]			
$2 \rightarrow 2$	42 109.20[a]			
$3 \rightarrow 2$	42 047.54[a]			
$2 \rightarrow 3$	42 117.52[a]			
$3 \rightarrow 3$	42 055.84[a]			
$J=\frac{3}{2} \rightarrow \frac{1}{2}$				
$F=0 \rightarrow 1$				
$1 \rightarrow 1$	43 227.26			
$2 \rightarrow 1$	43 201.54			
$1 \rightarrow 2$				
$2 \rightarrow 2$				
$3 \rightarrow 2$	43 294.8[a]			
$J=\frac{1}{2} \rightarrow \frac{3}{2}$				
$F=1 \rightarrow 2$	41 856.53			
$2 \rightarrow 2$	41 968.48			
$2 \rightarrow 3$	41 977.60[a]			
$J=\frac{1}{2} \rightarrow \frac{1}{2}$				
$F=1 \rightarrow 1$	42 948.50			
$2 \rightarrow 1$	43 060.24[a]			
$1 \rightarrow 2$	43 104.18[a]			
$2 \rightarrow 2$	43 215.84[a]			
$2_{12} \rightarrow 3_{03}$		50	15 382	15 377
$F=0 \rightarrow 1$	15 131.8[a]			
$1 \rightarrow 2$	15 136.9[a]			
$2 \rightarrow 3$	15 166.8[a]			
$3 \rightarrow 4$	15 215.3[a]			
$4 \rightarrow 5$	15 486.3[a]			
$3 \rightarrow 4$	15 499.2[a]			
$2 \rightarrow 3$	15 507.4[a]			
$1 \rightarrow 2$	15 512.4[a]			
$3_{03} \rightarrow 3_{12}$		−36	46 787	46 787
$F=5 \rightarrow 5$	46 503.6[a]			
$4 \rightarrow 4$	46 539.0[a]			
$3 \rightarrow 3$	46 560.0[a]			
$2 \rightarrow 2$	46 571.0[a]			
$1 \rightarrow 1$	47 037.0[a]			
$2 \rightarrow 2$	47 074.4[a]			
$3 \rightarrow 3$	47 122.6[a]			
$4 \rightarrow 4$	47 175.7[a]			
$5_{14} \rightarrow 4_{23}$		−43	21 465	21 465
$F=4 \rightarrow 3$	21 226.3[a]			
$5 \rightarrow 4$	21 237.5[a]			
$6 \rightarrow 5$	21 250.4[a]			
$7 \rightarrow 6$	21 264.3			
$6 \rightarrow 5$	21 739.2[a]			
$5 \rightarrow 4$	21 764.2[a]			
$4 \rightarrow 3$	21 784.1[a]			
$3 \rightarrow 2$	21 797.7[a]			
$6_{25} \rightarrow 7_{16}$		13	24 974	24 997
	24 856.0[a]			
	24 876.8[a]			
	24 898.5[a]			
	24 924.6[a]			
	25 006.3[a]			
	25 026.1[a]			
	25 041.0[a]			
	25 054.7[a]			

[a] The isotope has been verified by means of the Cl^{35} enriched sample.

TABLE II. Rotational constants of ClO_2, in Mc.

Cl^{35}	Cl^{37}
$A=52\,072\pm10$	$A=50\,725\pm10$
$B=9952\pm10$	$B=9952\pm10$
$C=8332\pm10$	$C=8295\pm10$

highly satisfactory procedure.[9] The structure obtained is $r_{\mathrm{Cl-O}}=1.473\pm0.01$ A, $<\mathrm{O-Cl-O}=117°\,36'\pm1°$. This may be compared to $r_{\mathrm{Cl-O}}=1.472\pm0.005$ A and $<\mathrm{O-Cl-O}=117°\,24'\pm12'$ obtained by Ward[10] from rotational analysis of infrared and ultraviolet. The latest electron diffraction result is $r_{\mathrm{Cl-O}}=1.491\pm0.014$ A, $<\mathrm{O-Cl-O}=116°\,30'\pm2.5°$.[11]

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Discussion of the problem with Chun C. Lin has been most helpful.

APPENDIX

The Hamiltonian to be considered is

$$H=H_R+H_S+H_F+H_D+H_Q,$$

where H_R is the rotational Hamiltonian, H_S is the electronic spin-molecular rotation interaction, H_F is the Fermi or contact interaction between electronic and nuclear spin, H_D is the magnetic dipole-dipole interaction between electronic and nuclear spins, and H_Q is the nuclear quadrupole coupling interaction.

$$H_R=AN_a^2+BN_b^2+CN_c^2,$$

$$H_S=(0)_S(\mathbf{N}\cdot\mathbf{S})+(aa)_SN_aS_a+(bb)_SN_bS_b+(cc)_SN_cS_c,$$

$$(aa)_S+(bb)_S+(cc)_S=0,$$

$$H_F=(0)_I(\mathbf{I}\cdot\mathbf{S}),$$

$$(0)_I=(16\pi/3)g_I\mu_B\mu_N|\psi(0)|^2,$$

$$\mu_B>0,$$

$$H_D=(aa)_II_aS_a+(bb)_II_bS_b+(cc)_II_cS_c,$$

$$(aa)_I+(bb)_I+(cc)_I=0,$$

$$(aa)_I=-g_Sg_I\mu_B\mu_N\left\langle\frac{1-3\hat{r}_a^2}{r^3}\right\rangle_{\mathrm{av}},$$

$$(bb)_I=-g_Sg_I\mu_B\mu_N\left\langle\frac{1-3\hat{r}_b^2}{r^3}\right\rangle_{\mathrm{av}},$$

$$(cc)_I=-g_Sg_I\mu_B\mu_N\left\langle\frac{1-3\hat{r}_c^2}{r^3}\right\rangle_{\mathrm{av}},$$

$$H_Q=(aa)_QI_a^2+(bb)_QI_b^2+(cc)_QI_c^2,$$

$$(aa)_Q+(bb)_Q+(cc)_Q=0,$$

$$(aa)_Q=\frac{-eQ}{2I(2I-1)}\frac{\partial^2V}{\partial a^2},$$

$$(bb)_Q=\frac{-eQ}{2I(2I-1)}\frac{\partial^2V}{\partial b^2},$$

$$(cc)_Q=\frac{-eQ}{2I(2I-1)}\frac{\partial^2V}{\partial c^2}.$$

All interactions consistent with the C_{2v} symmetry of ClO_2 have been listed.

The basis chosen is the asymmetric rotor basis and the J scheme. The basis quantum numbers are N, τ, J, F. The effects of matrix elements off-diagonal in N and τ were not considered. This approximation is not satisfactory and limits the validity of this treatment. The fit obtained is poor and indeed it is not worthwhile to consider the effects of $(aa)_Q$, $(bb)_Q$, and $(cc)_Q$ to this accuracy.

The levels of 1_{01} and 1_{10} were obtained by examining the hyperfine structure of the $1_{01}\rightarrow 1_{10}$ transition. Then $(0)_I$, $(aa)_I$, $(bb)_I$, $(cc)_I$, $(0)_S-\frac{1}{2}(aa)_S$, $(0)_S-(cc)_S$ were calculated by fitting these levels as nearly as possible. Different values of $(0)_I$ were necessary to fit the two sets of levels.

For most rotational levels there are two values of F which are unique and which do not interact, $F_U=N+2$ and $F_L=N-2$. For a rotational transition it can be shown that

$$\begin{aligned}\Delta\nu(F_U-F_L)&\\&=[\nu(F_U')-\nu(F_U)]-[\nu(F_L')-\nu(F_L)]\\&=\Delta N(0)_S+\tfrac{1}{2}\Sigma_S'-\tfrac{1}{2}\Sigma_S\\&\qquad-(9/2)\frac{\Sigma_I'}{(2N'-1)(2N'+3)}+(9/2)\frac{\Sigma_I}{(2N-1)(2N+3)},\end{aligned}$$

where the upper rotational level is primed and

$$\Sigma_S=\sum_{\tau''}(aa)_S{}^aS_{N\tau N\tau''}+(bb)_S{}^bS_{N\tau N\tau''}+(cc)_S{}^cS_{N\tau N\tau''},$$

$$\Sigma_I=\sum_{\tau''}(aa)_I{}^aS_{N\tau N\tau''}+(bb)_I{}^bS_{N\tau N\tau''}+(cc)_I{}^cS_{N\tau N\tau''}.$$

TABLE III. Interaction constants of ClO_2, in Mc.

Cl^{35}	Cl^{37}
$(0)_S=-538$	$(0)_S=-523$
$(aa)_S=-892$	$(aa)_S=-858$
$(bb)_S=342$	$(bb)_S=320$
$(cc)_S=550$	$(cc)_S=538$
$(0)_I=49\ (1_{10})$	$(0)_I=41\ (1_{10})$
$38\ (1_{01})$	$32\ (1_{01})$
$(aa)_I=-86$	$(aa)_I=-72$
$(bb)_I=-87.4$	$(bb)_I=-72$
$(cc)_I=173.4$	$(cc)_I=144$

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[9] C. C. Costain, J. Chem. Phys. **29**, 864 (1958).

[10] J. K. Ward, Phys. Rev. **96**, 845(A) (1954).

[11] J. D. Dunitz and K. H. Hedberg, J. Am. Chem. Soc. **72**, 3108 (1950).

The $S_{N\tau,N\tau''}$ are the asymmetric rotor line strengths and have been tabulated.[12]

The $\Delta\nu(F_U-F_L)$ of $3_{03}-3_{12}$ was used along with the 1_{01} and 1_{10} parameters to obtain $(0)_S$, $(aa)_S$, $(bb)_S$, $(cc)_S$. For Cl^{35}, $\Delta\nu(F_U-F_L)$ predicted for $2_{12}\rightarrow3_{03}=410$ Mc, $\Delta\nu_{obs}=380$ Mc; $\Delta\nu(F_U-F_L)$ predicted for $5_{14}\rightarrow4_{23}=-612$ Mc, $\Delta\nu_{obs}=-563$ Mc. For Cl^{37}, $\Delta\nu(F_U-F_L)$ predicted for $2_{12}-3_{03}=368$ Mc, $\Delta\nu_{obs}=355$ Mc; $\Delta\nu(F_U-F_L)$ predicted for $5_{14}-4_{23}=-556$ Mc, $\Delta\nu_{obs}=-533$ Mc. The spacings inside the quartet groups are predicted in error by ~10 Mc. All the parameters obtained are listed in Table III.

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[12] R. H. Schwendeman and V. W. Laurie, *Line Strengths of Rotational Transitions* (Pergamon Press, New York, 1958).

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Ionization Cross Sections for Protons on Hydrogen Gas in the Energy Range 0.15 to 1.10 Mev*

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Measurements have been made of the ionization cross section for protons incident on hydrogen gas in the energy range 0.15–1.10 Mev. The experimental cross section in this region can be represented by $\sigma_i=(3.45\pm0.20)E^{-(0.874\pm0.010)}\times10^{-17}$ cm^2/molecule, where E is the incident proton energy in Mev. The experimental results are in excellent agreement with a Born approximation calculation, which is discussed.

I. INTRODUCTION

THE gross ionization cross section for protons incident on hydrogen gas has been measured for incident particle energies over the range from 0.15 to 1.10 Mev. Previous measurements in this area have been confined to incident-particle energies below 0.18 Mev.[1,2] The work reported here represents an extension into a region that is largely unexplored.

The atomic and molecular reactions that can occur when fast atoms or atomic ions collide with the molecules of a target gas may be conveniently classed as either "ionization" or "charge-transfer" events. There is no general agreement on the exact definition of these terms—we choose to define them as follows: In an "ionization" event, the fast particle ionizes the struck molecule but emerges with no change in its own charge state, while in a "charge-transfer" event the fast particle either gains one or more electrons from, or loses one or more electrons to, the target particle. For a given projectile on a given target, each class of events in general includes several distinct kinds of reactions differing in the array of slow residual particles that are produced. The energies of the latter are usually low, although a small fraction of them may have energies as high as a few hundred electron volts. In either ionization or charge transfer, the incident particle almost always suffers only a small loss of energy and emerges with only a slight deviation from its original direction of motion.

In charge-transfer studies, the sum of the cross sections for all types of events that produce a given change in the charge state of the fast particle may be measured by observing the distribution of charge states in the emerging fast beam. Such measurements have been made previously for hydrogen atoms and ions incident on hydrogen gas with energies up to 1.0 Mev.[3] The observed cross sections indicate that in our energy range charge transfer events should not make a significant contribution to the gross ion production. (Our experimental results bear out this expectation.)

To study ionization events one must collect and observe the slow charged particles produced by the collision, since the emerging fast beam contains no information about the occurrence of these events. To avoid confusion due to multiple reactions by a single incident particle, the target must be "thin" in the sense that most of the incident particles will traverse the target with no collisions at all. One previous study of protons on hydrogen has been made for energies up to 0.18 Mev,[1] but the bulk of other previous work has been confined to energies of less than 0.04 Mev.[2]

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[1] V. V. Afrosimov, R. N. Il'in, and N. V. Fedorenko, Soviet Phys.—JETP **34**, 968 (1958).

[2] J. P. Keene, Phil. Mag. **40**, 369 (1949); Ia. M. Fogel, L. I. Krupnik, and B. G. Safronov, Soviet Phys.—JETP **1**, 415 (1955); H. B. Gilbody and J. B. Hasted, Proc. Roy. Soc. (London) **A240**, 382 (1957).

[3] C. F. Barnett and H. K. Reynolds, Phys. Rev. **109**, 355 (1958); P. M. Stier and C. F. Barnett, Phys. Rev. **103**, 896 (1956).