

Letters to the Editor

PUBLICATION of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is five weeks prior to the date of issue. No proof will be sent to the authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not exceed 600 words in length.

Nuclear and Molecular Constants from Microwave Spectra: Methyl Chloride and Methyl Bromide*

WALTER GORDY, JAMES W. SIMMONS, AND A. G. SMITH
Department of Physics, Duke University, Durham, North Carolina
July 7, 1947

THE first rotational transition, $J=0$ to $J=1$, of $\text{CH}_3\text{Cl}^{35}$ and of $\text{CH}_3\text{Cl}^{37}$ and the second transition, $J=1$ to $J=2$, of $\text{CH}_3\text{Br}^{79}$ and of $\text{CH}_3\text{Br}^{81}$ have been measured and analyzed. The detecting system used and the method of analysis have been described in previous notes.¹

As in methyl iodide,¹ hyperfine structure caused by the nuclear quadrupole moments of the halogens was observed for both methyl chloride and methyl bromide. Figures 1 and 2 give comparisons of the calculated and observed hyperfine patterns. The quadrupole coupling factors, $eQ(\partial^2V/\partial z^2)$, determined from the line spacings are listed in Table I,

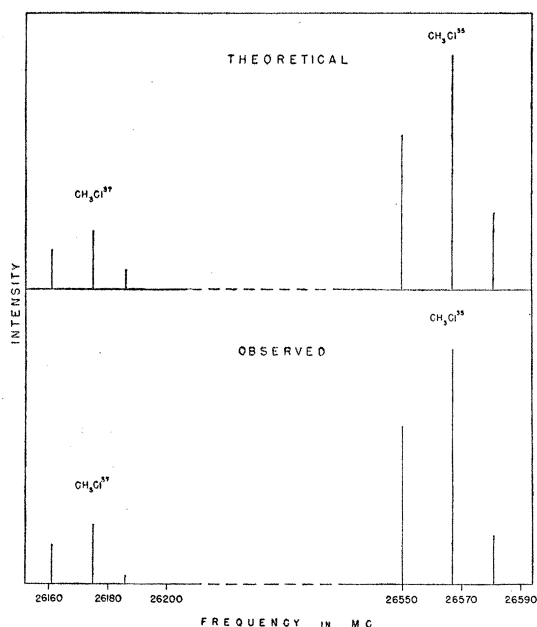


FIG. 1. Calculated and observed hyperfine structure for the $J=0$ to $J=1$ rotational transition of methyl chloride.

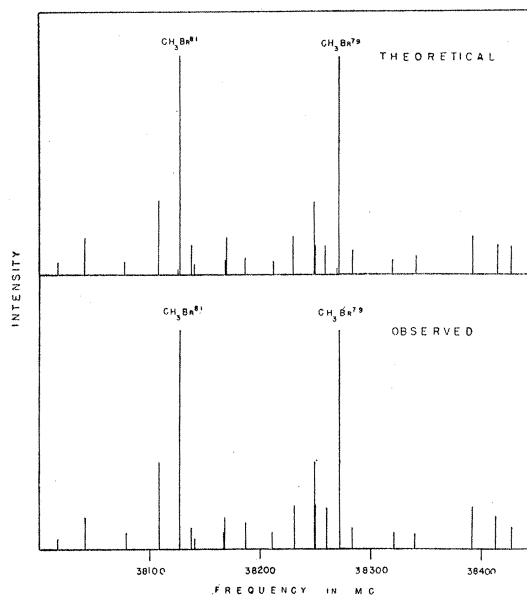


FIG. 2. Calculated and observed hyperfine structure for the $J=1$ to $J=2$ rotational transition of methyl bromide.

where the corresponding coefficients for BrCN and ClCN are given for comparison.

In order to evaluate nuclear quadrupole moments from microwave hyperfine structure the factor $\partial^2V/\partial z^2$ must be determined from other sources. Recently Townes² has suggested that for heavy atoms covalently bonded by p -orbitals this factor can be calculated from atomic fine structure separations by the same formula³ as that used in the determinations of quadrupole moments from atomic spectra. In his evaluation of the quadrupole moments of bromine and chlorine from BrCN and ClCN he assumed that the effects of the double-bond character on $\partial^2V/\partial z^2$ in these molecules can be neglected. The comparisons in Table I indicate that this assumption is hardly justified. Since the almost normal bond length of the methyl halides indicate that they are not complicated by appreciable resonance, the atomic spectra determination of $\partial^2V/\partial z^2$

TABLE I. Quadrupole coupling factors.

Molecule	Nucleus	$\partial^2V/\partial z^2$ (e.s.u.)	Quadrupole coupling $eQ\partial^2V/\partial z^2$	Quadrupole moment (Q in cm^2)
CH_3Cl	Cl^{35}		69	-0.055×10^{-24}
	Cl^{37}		56	-0.045×10^{-24}
ClCN	Cl^{35}	17×10^{15} (a)	84 (a)	-0.067×10^{-24} (a)
	Cl^{37}	17×10^{15} (a)	64 (a)	-0.051×10^{-24} (a)
CH_3Br	Br^{79}		573	0.17×10^{-24}
	Br^{81}		485	0.14×10^{-24}
BrCN	Br^{79}	48×10^{15} (a)	720 (a), (670) (b)	0.21×10^{-24} (a)
	Br^{81}	48×10^{15} (a)	556 (a), (567) (b)	0.16×10^{-24} (a)

^a From C. H. Townes, ref. 2.

^b From W. Gordy, W. V. Smith, A. G. Smith, and H. Ring, Phys. Rev. (to be published).

should be more applicable to them than to the halogen cyanides, in which structures of the type $X^+ = C = N^-$ contribute significantly to the ground state. Hence, we have evaluated the quadrupole moments of the bromine and chlorine nuclei from our measurements on CH_3Br and CH_3Cl , using the $\partial^2 V / \partial z^2$ values as determined by Townes.² These are also listed in the table.

The moments of inertia, I_B , for the lowest vibrational state are: for CH_3Cl ³⁵, 63.1×10^{-40} g-cm²; for CH_3Cl ³⁷, 64.0×10^{-40} g-cm²; for CH_3Br ⁷⁹, 87.5×10^{-40} g-cm²; and for CH_3Br ⁸¹, 87.9×10^{-40} g-cm². The smaller moments of inertia, I_A , in these molecules cannot be determined from pure rotation spectra but have been evaluated to three places from infra-red vibration-rotation spectra. Assuming the CH lengths equal to those in methane and the Hal-C-H angle that determined from the infra-red I_A values, the above I_B values yield 1.79A for the C-Cl length in methyl chloride and 1.94A for the C-Br length in methyl bromide. If a tetrahedral angle, $109^\circ 28'$ is assumed for the angle Hal-C-H, the resulting distances would be 1.78A for C-Cl and 1.93A for C-Br.

* The research described in this report was supported by Contract No. W-28-099-ac-125 with the Army Air Forces, Watson Laboratories, Air Materiel Command.

¹ W. Gordy and M. Kessler, Phys. Rev. **71**, 640 (1947); W. Gordy, A. G. Smith, and J. W. Simmons, Phys. Rev. (to be published).

² C. H. Townes, Phys. Rev. **71**, 909 (1947).

³ H. A. Bethe and R. F. Bacher, Rev. Mod. Phys. **8**, 226 (1936).

Density of Surface States on Silicon Deduced from Contact Potential Measurements

W. H. BRATTAIN AND W. SHOCKLEY

Bell Telephone Laboratories, Murray Hill, New Jersey

July 3, 1947

THE contact potentials of several *N* and *P*-type silicon surfaces have been measured. The respective numbers of donator and acceptor impurities in each sample were determined by measuring the electrical conductivity and Hall constant. A correlation was found between impurity concentration and contact potential. Each surface was ground flat and then sand-blasted lightly with 180 mesh silicon carbide. The contact potential was then measured in air, in vacuum after heat treatment to 400°C, in high purity N_2 and finally in air again. The results are given in Table I. The reference surface was platinum, which probably had a work function between 4 and 5 volts. The data given are averages of several runs and should be accurate to approximately 0.02 volts.

One might expect a contact potential difference between *N* and *P*-type silicon slightly less than the width of the energy gap in silicon (1.2 volts). That this is not the case has already been reported by W. E. Meyerhof.¹ An explanation of the latter result based on surface states has been given by J. Bardeen.² On the basis of the surface state picture one would expect the contact potential between *N* and *P*-type silicon to increase as the respective impurity concentration was increased approaching 1.2 volts as a limit. The data in Table I shows that after heat treatment

in vacuum the contact potential difference between the two types does increase and the difference between *P*-type silicon (5.7×10^{20} acceptors) and *N*-type silicon (1.9×10^{20} donators) is the order of 0.6 volts. From these data one can

TABLE I. Contact potential in volts.

Type	Impurity N/cm^2	In air after sandblast	In vacuum after heat treatment	After letting in N_2	After exposure to air
<i>P</i>	5.7×10^{20}	+0.31	-0.27	-0.19	+0.07
<i>P</i>	1.5×10^{20}	+0.35	-0.18	-0.10	+0.13
<i>P</i>	6.5×10^{18}	+0.30	-0.10	-0.09	+0.17
<i>P</i>	3.1×10^{17}	+0.34	+0.04	+0.14	+0.28
<i>N</i>	6.9×10^{18}	+0.32	+0.16	+0.27	+0.34
<i>N</i>	2.3×10^{19}	+0.37	+0.27	+0.35	+0.39
<i>N</i>	1.9×10^{20}	+0.37	+0.30	+0.37	+0.37

estimate the density of surface states in silicon to be approximately 10^{14} per volt per cm², when the surface has been treated in the above manner. The free silicon surface behaves in air as though the density of surface levels were increased by several orders of magnitude.

¹ W. E. Meyerhof, Phys. Rev. **71**, 727 (1947).

² J. Bardeen, Phys. Rev. **71**, 717 (1947).

Evidence for Surface States on Semiconductors from Change in Contact Potential on Illumination

W. H. BRATTAIN

Bell Telephone Laboratories, Murray Hill, New Jersey

July 3, 1947

ON the basis of the surface state picture¹ one expects a double layer at the free surface of a semiconductor, the excess charge in the surface states being compensated by an equal and opposite space charge in the semiconductor. At low temperatures it should take an appreciable time for this equilibrium to be established between the surface states and the space charge region. Consequently, electrons or holes excited by absorption of light near the surface should upset this equilibrium making the surface state charge more positive for *N*-type semiconductors and more negative for *P*-type semiconductors, thus changing the contact potential when the surface is exposed to light. The experiment suggested has been done on silicon surfaces of both *N* and *P* type and on an *N*-type germanium surface. The contact potential changes due to light exposure at approximately 120°K were +0.12 volts for *N*-type silicon, -0.08 volts for *P*-type silicon, and +0.02 volts for *N*-type germanium. The changes have the predicted sign. The change appeared to be instantaneous on exposure of the surface to light. The return to the equilibrium condition in the dark appeared to have a time constant of the order of a few seconds. No change in contact potential with exposure to light was found at room temperature. The dependence of this effect on temperature, light intensity, and a determination of the time constant are in progress.

¹ J. Bardeen, Phys. Rev. **71**, 717 (1947).