UCRL-17916
cy. 2

University of California

Ernest O. Lawrence Radiation Laboratory

THE MOLECULAR-BEAM ELECTRIC RESONANCE SPECTRA OF NaCl AND NaBr

C. A. Melendres, A. J. Hebert and K. Street Jr.

November 1967

RECEIVED
RADIAT
FE
LIB
DOCUM

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545

UCRL-17916
cy. 2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-17916
UC-4 Chemistry
TID-4500 (51st Ed.)

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

THE MOLECULAR-BEAM ELECTRIC RESONANCE SPECTRA OF NaCl AND NaBr

C. A. Melendres, A. J. Hebert and K. Street Jr.

November 1967

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy $3.00; Microfiche $0.65

I. INTRODUCTION

Over the past years, the molecular beam electric resonance technique of radio-frequency spectroscopy[1,2] has become established as a very accurate method for determining molecular dipole moments and studying interactions between nuclear moments and the molecular fields. The work described here forms part of a series of investigations on the radio-frequency spectra of the alkali halides. More accurate values of dipole moments and quadrupole coupling constants provide the test for a polarizable ion model for these molecules.[3]

The radio-frequency Stark spectra of $Na^{23}Cl^{35}$ has been studied by Gold.[4] He obtained values of dipole moments for the first three vibrational states of the molecules. The quality of the spectra, however, did not permit an accurate determination of the hyperfine interaction constants. An approximate value of 5.6 MHz was given for the quadrupole coupling constant (eqQ) of both the Na^{23} and Cl^{35} nucleus.

A number of studies have been conducted to determine hyperfine interactions in $Na^{23}Cl^{35}$ by the molecular beam magnetic resonance (MBMR) method.[5,6,7,8] The widely different values of the Na^{23} coupling constant in $Na^{23}Cl^{35}$, however, lead one to doubt the accuracy of the method.

Up until the present work, the spectra of the isotopic molecule $Na^{23}Cl^{37}$ have not been studied. The radio-frequency Stark spectra of $Na^{23}Br^{79}$ and $Na^{23}Br^{81}$ have not been studied before. Microwave measurements[9] gave a value of 58 ± 2 MHz for $(eqQ)_{Br}79$ and magnetic (MBMR) measurements[7,10] indicate a value of 4.7 to 4.9 MHz for $(eqQ)_{Na}23$ in $Na^{23}Br^{79}$.

The incorporation of a signal averaging system to the molecular beam spectrometer in this laboratory has permitted the re-examination of the radio-frequency spectra of these molecules. From an analysis of the hyperfine

components of the Stark spectra, more accurate values of dipole moments and (eqQ)'s have been obtained as a function of vibrational state. An assignment of the (eqQ)'s in $Na^{23}Cl^{35}$ to the respective nuclei was made possible after a determination of $(eqQ)_{Cl^{37}}$ from the $Na^{23}Cl^{37}$ spectra. Values of dipole moments of the two NaBr isotopes have been measured for the first time together with the (eqQ) of the various nuclei.

II. EXPERIMENTAL APPARATUS AND PROCEDURES

A. Molecular Beam Spectrometer

The experimental apparatus used in this work is that built by Hebert[11] and has been used in a number of previous investigations carried out in this laboratory.[3,12] Since it has been described in detail before, only a brief summary will be given here.

The spectrometer consists essentially of four high vacuum chambers which house an oven, a state-selecting inhomogeneous electric field (A-field), an extremely homogeneous electric field (C-field), a refocusing inhomogeneous electric field (B-field), a surface ionization detector, a 60° sector magnet mass spectrometer and a 14-stage electron multiplier. A schematic diagram of the apparatus is shown in Fig. 1.

The source ovens used in these experiments were 3/8" diam × 0.010" wall × 6-1/2" long tubes of Platinum-Iridium alloy (80%-20%), with 0.25" long by 0.005" wide slit at the middle. Sample is placed in the oven and heated to about 850°C for NaCl and 800°C for NaBr by resistance heating. Sample effuses from the source to a buffer chamber and on to a main chamber which houses the deflecting fields and the detector. The inhomogeneous A and B fields are of the

THE MOLECULAR-BEAM ELECTRIC RESONANCE SPECTRA OF NaCl AND NaBr*

C. A. Melendres, A. J. Hebert, and K. Street Jr.

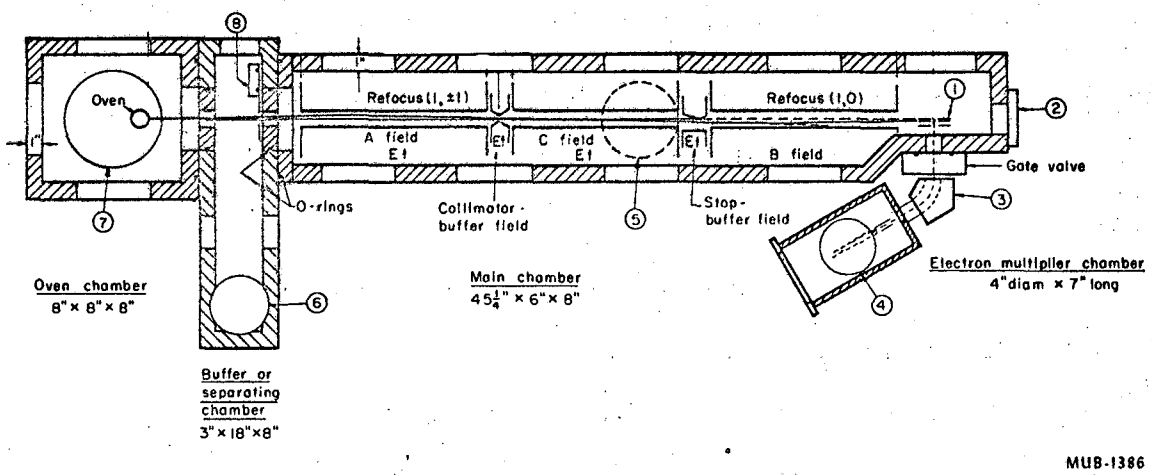
Lawrence Radiation Laboratory and
Department of Chemistry
University of California
Berkeley, California

November 1967

ABSTRACT

The radio-frequency Stark spectra of $Na^{23}Cl^{35}$, $Na^{23}Cl^{37}$, $Na^{23}Br^{79}$ and $Na^{23}Br^{81}$ have been observed by the molecular beam electric resonance method of molecular spectroscopy. Analysis of spectral lines obtained by observing transitions of the type $J = 1, M_J = \pm 1 \rightarrow J = 1\ M_J = 0$ at strong electric fields yielded molecular dipole moments and nuclear hyperfine interaction constants for the different vibrational states of the molecules.

*This work was done under auspices of the U. S. Atomic Energy Commission.



l_0 = 12.3 cm l_4 = 7 cm l_A = 30.5 cm

l_1 = 20.6 cm l_5 = 55 cm l_B = 30.5 cm

l_2 = 4 cm l_6 = 69 cm l_C = 25.4 cm

l_3 = 5 cm

Fig. 1. Schematic diagram (top view) of the electric resonance apparatus. Field lengths and chambers are to scale. Field gaps and beam displacements are exaggerated. Unshaded areas in chamber walls represent access ports. (Dimensions refer to internal chamber sizes.)

(1) Hot wire and ion accelerator
(2) Glass port cover for optical alignment
(3) Permanent magnet, 60°, 1-cm gap
(4) Outlet, 4 in. diam, to liquid nitrogen trap and oil-diffusion pump
(5) Outlet, 5 in. diam, to liquid nitrogen trap and oil-diffusion pump
(6) Outlet, 4 in. diam, to gate valve, liquid nitrogen trap, and oil-diffusion pump
(7) Outlet, 6 in. diam, to gate valve, liquid nitrogen trap, and oil-diffusion pump
(8) Gate valve and beam flag.

dipole type, 30.5 cm long, and permit the selection of a certain (J,M_J) quantum state and refocusing of the same state ("flop-out" experiments) or another ("flop-in" experiment).[1] J is the rotational angular momentum quantum number for the molecule and M_J is its component in the direction of the electric field. The homogeneous Stark field (C-field) consists of 2 parallel plate electrodes 25.4 cm long and separated by 1.000001 ± 0.000001 cm at 20°C. Field homogeneity is within 7 ppm. Field measurement is made via a Guildline ratio box with a Leeds and Northrup Guarded Potentiometer calibrated with a bank of unsaturated standard cells. Uncertainty in the C-field voltage measured is about 2 parts in 10^5. Radiofrequency voltage is introduced in the C-field region in a manner first introduced by Trischka.[13] The ribbon beam is detected by surface ionization on a 0.010" wide × 0.001" thick Tungsten filament heated to about 1650°K. The ions evaporating from the hot filament are accelerated, mass analyzed using a 60° sector magnet and focussed on a 14-stage electron multiplier. The ion current is then amplified to drive a chart recorder for visual display of the spectra or the ion pulses from the multiplier amplified and counted for a digitalized output.

B. Signal Averaging System

Spectra of sufficient quality to enable the accurate determination of dipole moments and coupling constants for the sodium halides were made possible only by the incorporation of a signal averaging system for the recovery of weak signals buried in noise. The resonance signals from both NaCl and NaBr molecules are considerably weaker compared to that of the lighter alkali halides. This is due to an intrinsic reduction in beam intensity brought about by the size or

mass of the molecule[14] and the large residual noise level due to Na impurities evaporating from the hot wire detector. With NaCl, line measurements obtained without using the signal averaging system have at best a signal to noise ratio of 3:1; for NaBr, about 1:1. With signal averaging, considerable enhancement of the signal to noise ratio is obtained.

A block diagram of the signal averaging system used is shown in Fig. 2. This system will be described in greater detail elsewhere[15] and only a brief description will be given here. A list of the electronic equipment used is given in Table A-I of the Appendix. The principle of the method is based on the fact that in counting statistics, the fluctuation about the average number of counts is equal to the square root of the number of counts, for one standard deviation. The signal, on the other hand, grows in time in direct proportion to the number of counts accumulated. Thus if one could repeatedly scan the region of the spectrum in which a resonance line appears, store and average the signal intensities over long periods, one in effect obtains an enhancement of the signal to noise ratio over that obtainable by just a single sweep.

The system shown is used to produce a linear frequency or voltage sweep to scan the spectral region of interest several times a second. Basically, a synchronizer (Hewlett Packard 8708A) is used to phase lock the frequency of the signal generator (Hewlett Packard 608F) and a ramp voltage of variable frequency and amplitude used to sweep over a certain frequency range by modulating the signal generator view the synchronizer. With this mode of operation, sweep widths of a few hundred KHz were obtained. In exact step with this repetitive frequency sweep, is an "intensity counts" sweep provided by a switch programmed time base oscillator. This "intensity vs. time" sweep is designed to store and accumulate the count information in a multi-channel analyzer (Norther Scientific NS-610).

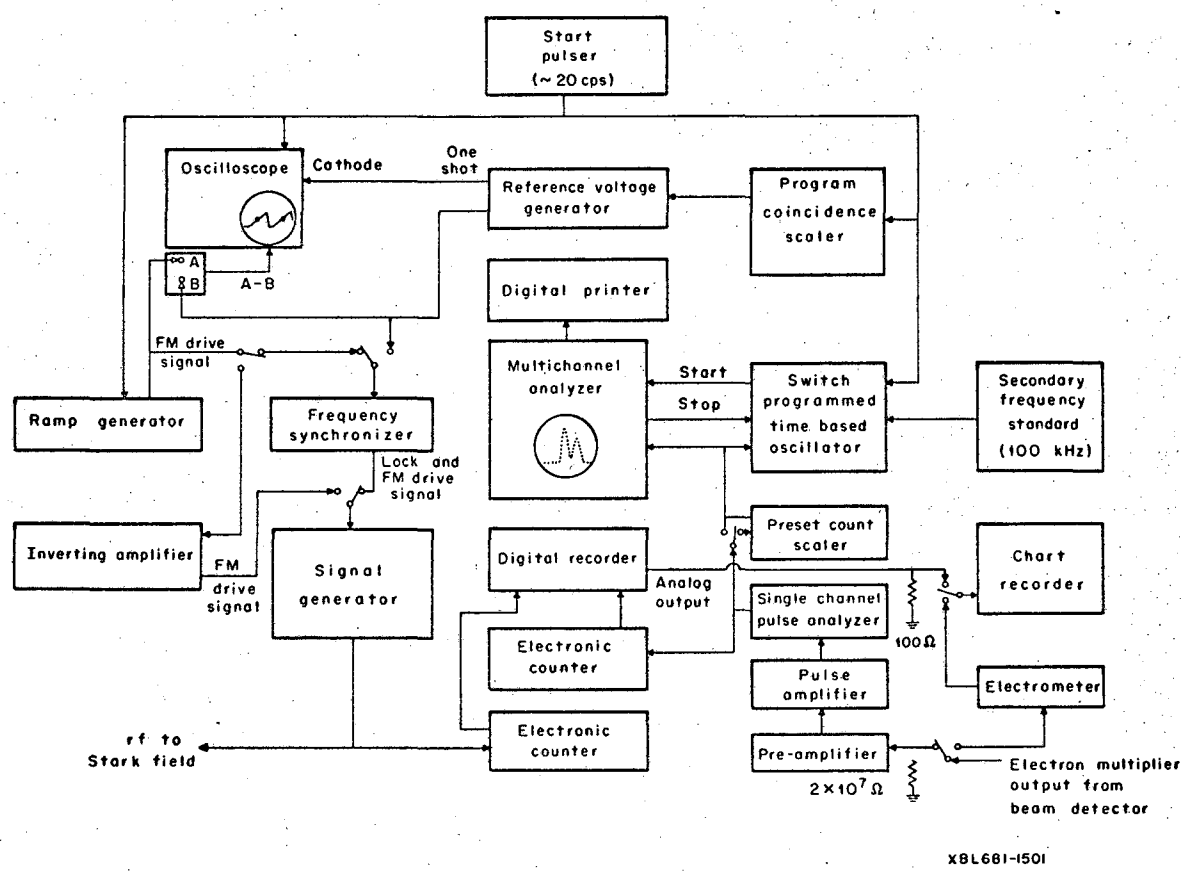


Fig. 2. Block diagram of signal averaging system.

A triggering signal from the pulse generator (Electronics Inc., Model 301) starts both the frequency and multi-channel analyzer sweeps and ensures their synchronization.

A frequency vs. channel number correlation is then made using the program coincidence scaler in conjunction with the reference voltage generator and oscilloscope. This gives the frequency corresponding to any desired channel of the multi-channel analyzer.

By operating the system for about 1.5 to 2.5 hours a signal to noise ratio of about 5:1 was obtained for most of the lines measured.

C. Radio-frequency Spectra of NaCl and NaBr.

The spectral lines observed were produced by transitions of the type $(J = 1, M_J = \pm 1) \rightarrow (J = 1, M_J = 0)$. The $J = 1$ level is three-fold degenerate in the absence of external fields and nuclear hyperfine interactions. However, due to the spin of 3/2 in both the Na and Cl nuclei, the rotational angular momentum of the molecule is coupled to the spin angular momenta of the nuclei through the nuclear electric quadrupole and spin-rotation interactions. The application of an electric field causes further splitting of the energy levels due to the Stark effect. At a field of 600 v/cm, in which the spectra were taken, the Stark effect is the dominant interaction (Strong field)[16] and the hyperfine interactions can be treated as perturbations on the Stark levels. An energy level diagram for $Na^{23}Cl^{35}$ at strong fields is shown in Fig. 3.

The hyperfine components of the $(J = 1, M_J = \pm 1) \rightarrow (J = 1, M_J = 0)$ transition were also investigated in the NaBr molecules at a field strength

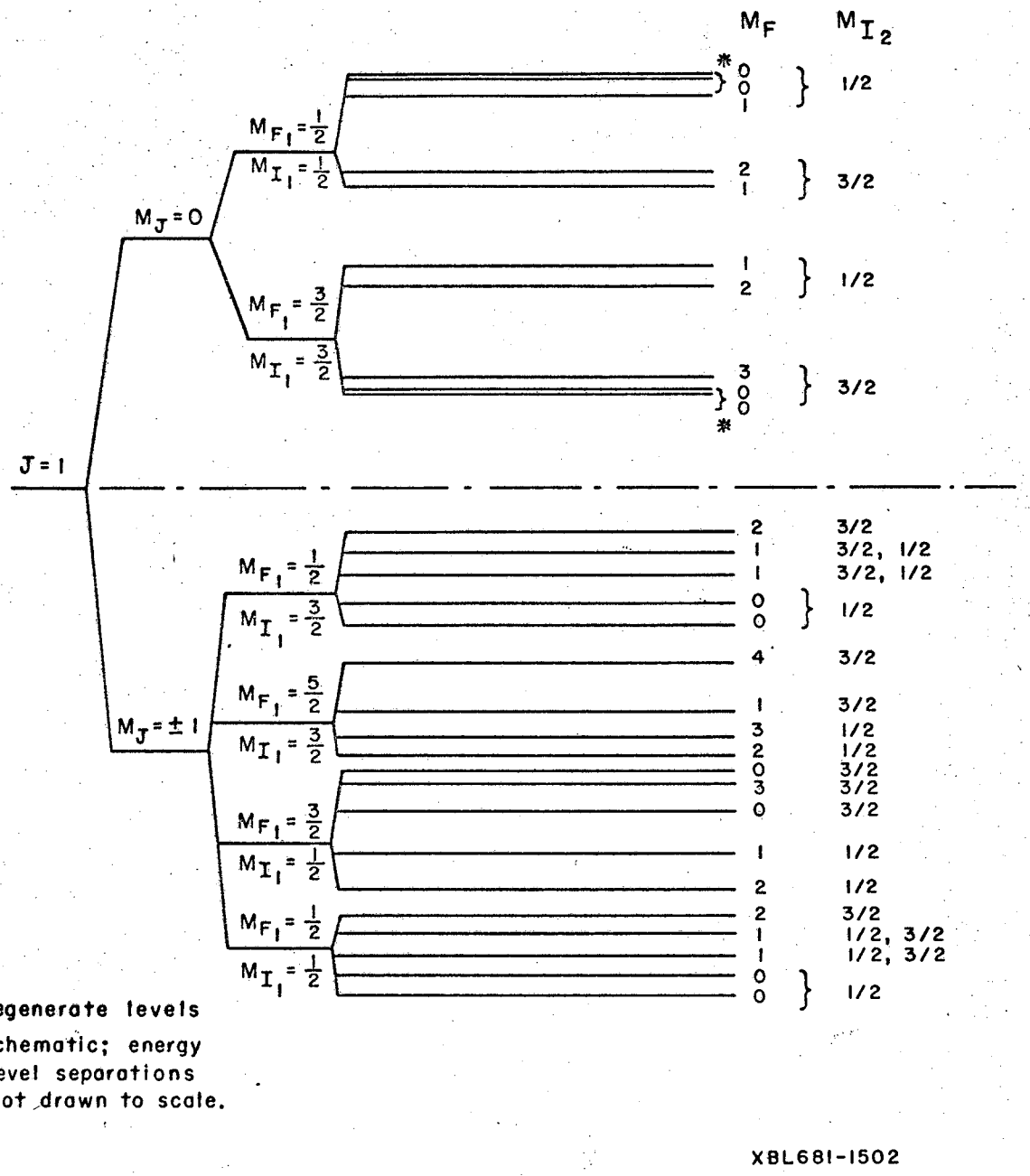


Fig. 3. Energy level diagram[a] for $Na^{23}Cl^{35}$ at strong fields.

of 600 v/cm. The two Br isotopes have spins equal also to 3/2. A radio-frequency voltage of about 1 volt rms was used to induce transitions between the various levels of the molecules.

III. RESULTS AND DISCUSSION

The spectra of the molecules were interpreted using the Hamiltonian:[17,18]

$$H = B\underline{J}^2 - \underline{\mu}\cdot\underline{E} - eq_1Q_1 \frac{[3(\underline{I}_1\cdot\underline{J})^2 + 3/2\,(\underline{I}_1\cdot\underline{J}) - (\underline{I}_1^2\underline{J}^2)]}{2I_1(2I_1-1)(2J-1)(2J+3)}$$

$$-eq_2Q_2 \frac{[3(\underline{I}_2\cdot\underline{J})^2 + 3/2(\underline{I}_2\cdot\underline{J}) - (\underline{I}_2^2\underline{J}^2)]}{2I_2(2I_2-1)(2J-1)(2J+3)} + c_1(\underline{I}_1\cdot\underline{J}) + c_2(\underline{I}_2\cdot\underline{J})$$

$$+ c_3 \frac{[3(\underline{I}_1\cdot\underline{J})(\underline{I}_2\cdot\underline{J}) + 3(\underline{I}_2\cdot\underline{J})(\underline{I}_1\cdot\underline{J}) - 2(\underline{I}_1\cdot\underline{I}_2)\,J(J+1)]}{(2J-1)(2J+3)} + c_4(\underline{I}_1\cdot\underline{I}_2)$$

The first term in the above expression represents the rotational energy of the molecule, where B is the rotational constant and $\underline{J}$ the rotational angular momentum operator. The second term represents the interaction of the permanent electric dipole moment $\underline{\mu}$ with the externally applied electric field $\underline{E}$. The third and fourth terms represent the interaction of the nuclear quadrupole moments (Q_1 and Q_2) with the field gradients at the nuclei (q_1 and q_2). I_1 and I_2 are the nuclear spins, e is the electronic charge and eq_1Q_1 and eq_2Q_2 are the quadrupole coupling coupling constants. The fifth and sixth terms represent the magnetic coupling of the nuclear spins with the molecular angular momentum, where c_1 and c_2 are the spin-rotation interaction constants. The seventh and eighth terms represent the tensor and scalar spin-spin interactions respectively, with c_3 and c_4 the respective interaction constants.[19]

A computer program was used to calculate the matrix elements of the above Hamiltonian using a $(J, I_1, I_2, M_J, M_{I_1}, M_{I_2})$ representation, where M_J, M_{I_1} and M_{I_2} are the projections of J, I_1 and I_2 respectively in the direction of the field E. The program calculates the energy eigenvalues by diagonalizing this matrix and then calculates the spectral line positions and intensities, corresponding to the given set of input parameters B, J, I_1, I_2, eq_1Q_1, eq_2Q_2, c_1, c_2, c_3, c_4 and μ, according to the selection rules $\Delta M_F = 0, \pm 1, \pm 2 \ldots$ where M_F is the projection of the total angular momentum in the direction of the field. The line intensities are calculated from the matrix elements of the dipole moment operator using the calculated wave functions. The unknown interaction constants are varied to obtain the best fit to the observed spectra.

A. Spectra of $Na^{23}Cl^{35}$ and $Na^{23}Cl^{37}$

The spectra of $Na^{23}Cl^{35}$ at 600 v/cm consist of 13 groups of lines for each vibrational state. All of these were observed for the v = 0,1, and 2 vibrational states and a few for the v = 3 state. Each group is a composite of several overlapping lines giving a full width at half maximum (FWHM) of about 30 to 60 KHz. Some separation of the components of these lines was evident as the vibrational state increased. The compound lines appear somewhat broader than that calculated based on the average transit time of the molecules in the C-field region and taking into account C-field inhomogeneities. This is probably due to power broadening of the lines cause by using a radio-frequency voltage of about 1 volt rms. The spectra for the v = 0 state of $Na^{23}Cl^{35}$ is shown in Fig. 4. The observed line positions are shown in

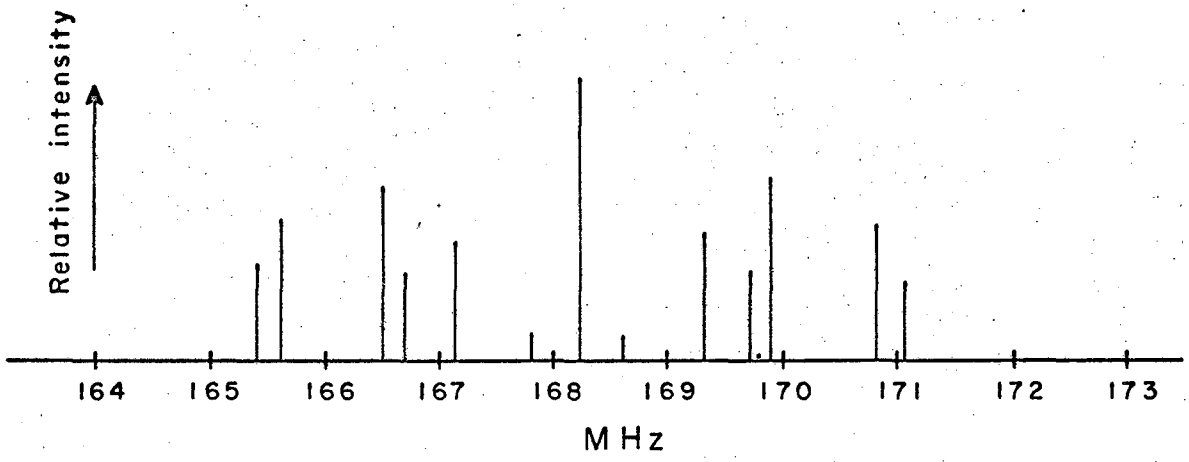
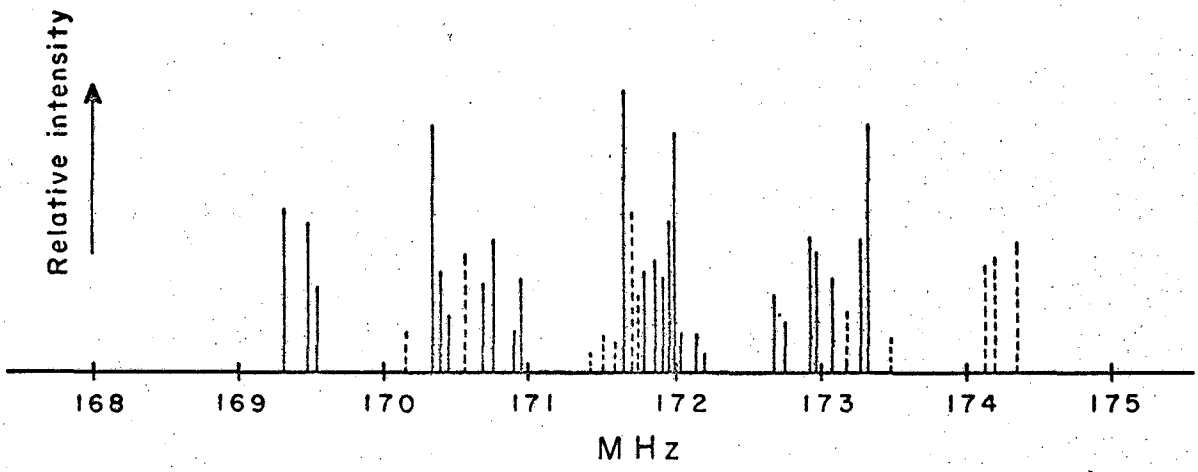


Fig. 4. V = 0 spectra of $Na^{23}Cl^{35}$.



XBL681-1503

Fig. 5. V = 0 spectra of $Na^{23}Cl^{37}$.

N.B.-Dotted lines have been overlapped by $Na^{23}Cl^{35}$ lines or have not been observed inadvertently.

Tables A-II, A-III, A-IV and A-V of the Appendix. The predicted or calculated line frequencies are also given. Most of the lines have been measured individually. The observed line positions for the v = 0 state represent an average of two or more measurements. The NaCl beam was very stable for long periods of time. Fluctuations in beam intensity and oven bursts, as experienced by Gold, have been eliminated by using as oven material sticks of NaCl obtained from previous runs.

In fitting the observed unresolved multiplets, calculated composite line positions were obtained by graphically adding component lines of Gaussian line shapes, with FWHM = 25 KHz and having the calculated frequencies and relative intensities. The centers of these calculated compound lines were then compared with the observed lines until a best fit was obtained. Values of rotational constants used in fitting the spectra were derived from the data of Clouser and Gordy.[29] A sufficiently good fit was obtained using only the dipole moments and the (eqQ)s of the two nuclei. The accuracy of the line measurements did not warrant the use of the small magnetic interaction constants. Magnetic resonance experiments indicate $c_{Na^{23}}$ to be approximately 1 KHz.[6] $c_{Cl^{35}}$ is probably of the same order of magnitude as that of Cl^{35} in TlCl i.e. about 1.4 KHz.[6] This would cause shifts in the spectral lines of 1 to 1.5 KHz at 600 v/cm, which are indeed small, compared to the observed spectral frequencies which ranged from 165 to 171 MHz for the v = 0 state.

Values of the dipole moments and quadrupole coupling constants obtained for a best fit are given in Tables I and II respectively. The dipole moments obtained in the present work are an order of magnitude more accurate than those of Gold. They agree with those of the latter within his error limits. The variation of μ with vibrational state for $Na^{23}Cl^{35}$ has been fitted with a

Table I. Dipole Moments of $Na^{23}Cl^{35}$ and $Na^{23}Cl^{37}$

$Na^{23}Cl^{35}$

	Present Work	Gold[4]
μ_0 =	9.00195 ± 0.00045 D	9.000 ± 0.004 D
μ_1 =	9.06190 ± 0.00046 D	9.061 ± 0.004 D
μ_2 =	9.12226 ± 0.00050 D	9.122 ± 0.004 D
μ_3 =	9.18290 ± 0.00097 D	

μ_e = 8.97208 ± 0.00065 D

μ_I = 0.05963 ± 0.00020 D

μ_{II} = 0.00017 ± 0.00010 D

$Na^{23}Cl^{37}$

μ_0 = 9.0017 ± 0.00069 D

μ_1 = 9.0610 ± 0.00071 D

μ_e = 8.97205 ± 0.00130 D

μ_I = 0.05930 ± 0.00060 D

Table II. Quadrupole Coupling Constants in $Na^{23}Cl^{35}$

Na^{23}	Present Work	Gold[4]	Cachs et al.[8]	Nierenberg[5] and Ramsey	Zeiger[6] and Bolef	Cote[7] and Kusch
$(eqQ)_0$	$= -5.720 \pm 0.020$ MHz	-5.6 ± 0.1 MHz	-5.328 ± 0.08* MHz	-5.400* MHz	-5.520 ± 0.02* MHz	-5.670* MHz
$(eqQ)_1$	$= -5.590 \pm 0.020$ MHz					
$(eqQ)_2$	$= -5.470 \pm 0.025$ MHz					
$(eqQ)_3$	$= -5.350 \pm 0.030$ MHz					
$(eqQ)_e$	$= -5.785 \pm 0.025$ MHz				-5.608 ± 0.02 MHz	
$(eqQ)_I$	$= 0.133 \pm 0.005$ MHz					
$(eqQ)_{II}$	$= -0.003 \pm 0.001$ MHz					
Cl^{35}						
$(eqQ)_0$	$= -5.575 \pm 0.020$ MHz					
$(eqQ)_1$	$= -5.820 \pm 0.020$ MHz					
$(eqQ)_2$	$= -6.060 \pm 0.025$ MHz					
$(eqQ)_3$	$= -6.300 \pm 0.030$ MHz					
$(eqQ)_e$	$= -5.452 \pm 0.025$ MHz					
$(eqQ)_I$	$= -0.247 \pm 0.003$ MHz					
$(eqQ)_{II}$	$= 0.001 \pm 0.001$ MHz					

Values obtained by Molecular Beam Magnetic Resonance method; except for those of Zeiger and Bolef, these values are averaged over the vibrational states of the molecule.

Table III. Quadrupole Coupling Constants in $Na^{23}Cl^{37}$

Na^{23}

$(eqQ)_0$	=	- 5.720	±	0.010	MHz
$(eqQ)_1$	=	- 5.590	±	0.010	MHz
$(eqQ)_e$	=	- 5.785	±	0.016	MHz
$(eqQ)_I$	=	0.130	±	0.015	MHz

Cl^{37}

$(eqQ)_0$	=	- 4.370	±	0.010	MHz
$(eqQ)_1$	=	- 4.565	±	0.010	MHz
$(eqQ)_e$	=	- 4.273	±	0.016	MHz
$(eqQ)_I$	=	- 0.195	±	0.015	MHz

quadratic equation in the vibrational quantum number[11] i.e.

$$\mu_v = \mu_e + \mu_I(v + 1/2) + \mu_{II}(v + 1/2)^2$$

The coefficients μ_e, μ_I and μ_{II} were obtained by the method of least squares.

Observation of the spectra of $Na^{23}Cl^{37}$ permitted the assignment of the coupling constants in $Na^{23}Cl^{35}$ to the respective nuclei. Since the values (eqQ) in $Na^{23}Cl^{35}$ are significantly different, that which gives a ratio of $(eqQ)_{Cl^{35}}$ to $(eqQ)_{Cl^{37}}$ closest to the value of 1.268, observed in many chlorine substituted molecules,[20] corresponds to the Cl^{35} coupling.

Results of magnetic resonance measurements, themselves at variance with each other, are somewhat lower than $(eqQ)_{Na^{23}}$ observed in this work. Oachs' value for $(eqQ)_{Cl^{35}}$ is in agreement with the present work. Gold indicated that his V = 0 spectra is best fitted with coupling constants of 5.5 and 5.7 MHz, with no assignment to the respective nucleus. Within accuracy of his data, however, he concluded that a value of 5.6 ± 0.1 MHz was more likely after making an examination of the calculated values of field gradients in Na^{23} and Cl^{35} in various molecules.

Spectra of only the v = 0 and 1 vibrational states of $Na^{23}Cl^{37}$ were obtained. Most of the lines were overlapped by the $Na^{23}Cl^{35}$ lines. The lines observed were mostly singlets, the (eqQ) of the two nuclei being now sufficiently different to cause large separations between the components of each unresolved multiplet line in $Na^{23}Cl^{35}$. The intensities compared with those of the $Na^{23}Cl^{35}$ lines correspond to that expected for the 25% natural abundance of Cl^{37}. The observed spectrum for the v = 0 state of $Na^{23}Cl^{37}$ is shown schematically in Fig. 5.

Dipole moments derived from the spectra are shown in Table I. These are somewhat smaller than those of $Na^{23}Cl^{35}$. These were fitted with the equation $\mu = \mu_e + \mu_I(v + 1/2)$. The equilibrium dipole moments are in excellent agreement. The coefficients μ_I in the dipole moment function for both molecules follow the isotopic dependence as predicted by theory,[19] being proportional to B_e/ω_e.

The coupling constants for Na^{23} in $Na^{23}Cl^{37}$ are essentially the same as those in $Na^{23}Cl^{35}$. This attests to the correctness of the (eqQ) assignment discussed already. After correcting the chlorine coupling in both NaCl molecules to a common vibrational state the ratio obtained is:

$$\frac{(eqQ_e)_{Cl^{35}}}{(eqQ_e)_{Cl^{37}}} = 1.2761 \pm 0.0075$$

This value if in good agreement with the observed coupling constants in molecules containing chlorine.[22,23,24,25] It is, however, somewhat higher than more recent microwave measurements[26] on CH_3Cl, ClCN, GeH_3Cl and the measurements by Wang et al.[27] These give an average value of 1.268. A much closer comparison, however, cannot be made in view of our large error limits brought about by the fact that our spectra had been obtained at strong fields where the line positions are rather insensitive to small changes in the values of the quadrupole interactions.

A weak field experiment whould permit a much more accurate determination of these quantities. This will probably be undertaken in this laboratory in the near future.

B. Spectra of $Na^{23}Br^{79}$ and $Na^{23}Br^{81}$

The radio-frequency spectra for the J = 1 and different vibrational states were obtained for $Na^{23}Br^{79}$ and $Na^{23}Br^{81}$. The spectra for each vibrational state consisted of 12 groups of lines as shown in Figs. 6 and 7. Each group is again a composite of a number of lines giving total widths at half maximum of 60 to 80 KHz. Measurements of the line positions are given in Tables A-VIII to A-XIV of the Appendix. Fitting of these spectra was done in the same manner as that of NaCl. Rotational constants used were derived from the data of Rusk and Gordy.[28] Values of dipole moments obtained from an analysis of the spectra are given in Table IV. Quadrupole coupling constants are given in Tables V and VI for $Na^{23}Br^{79}$ and $Na^{23}Br^{81}$ respectively. No essential differences could be observed between the dipole moments of the two isotopic molecules. The low signal to noise level of about 2:1 to 3:1 after two hours run time limited the accuracy of the line frequency measurements. The variation of dipole moment with vibrational state is linear within experimental errors. No values for the dipole moments of these molecules have been reported before and no comparison could be made here. The values are, however, what may be expected on the basis of the dipole moments of the other Na-halides. $(eqQ)_{Na^{23}}$ are the same in both $NaBr^{79}$ and $NaBr^{81}$. Our values are fairly close to those obtained by Magnetic resonance (MBMR) methods[7,10] as shown in Table V. The values found for $(eqQ)_{Br^{79}}$ are in excellent agreement with those obtained by microwave spectroscopy.[9] We have obtained more accurate values, however, and determined the variation of (eqQ) with vibrational state. A linear variation is obtained. This is also true for $(eqQ)_{Br^{81}}$ in $Na^{23}Br^{81}$. From the equilibrium values of this quantity we obtain:

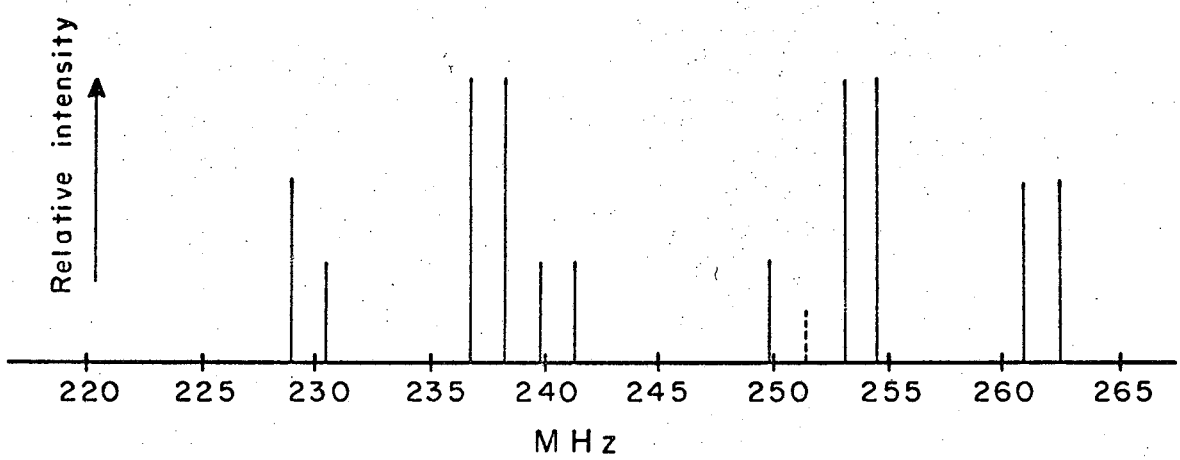
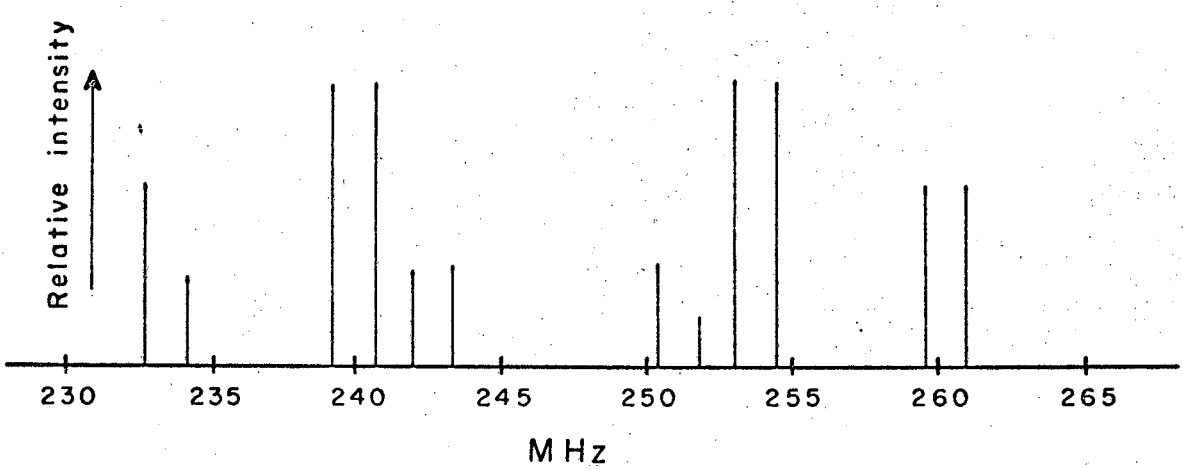


Fig. 6. V = 0 spectra of $Na^{23}Br^{79}$.



XBL681-1504

Fig. 7. V = 0 spectra of $Na^{23}Br^{81}$.

Table IV. Dipole Moments of $Na^{23}Br^{79}$ and $Na^{23}Br^{81}$

$Na^{23}Br^{79}$

$\mu_0 = 9.1183 \pm 0.00056$ D

$\mu_1 = 9.1715 \pm 0.00062$ D

$\mu_2 = 9.2246 \pm 0.00063$ D

$\mu_3 = 9.2779 \pm 0.0007$ D

$\mu_e = 9.09177 \pm 0.00127$ D

$\mu_I = 0.05308 \pm 0.00070$ D

$\mu_{II} = -0.0001 \pm 0.0004$ D

$Na^{23}Br^{81}$

$\mu_0 = 9.1183 \pm 0.00059$ D

$\mu_1 = 9.1715 \pm 0.00060$ D

$\mu_2 = 9.2245 \pm 0.00082$ D

$\mu_e = 9.01978$ D

$\mu_I = 0.05310$ D

$\mu_{II} = -0.0001$ D

Table V. Quadrupole Coupling Constants in $Na^{23}Br^{79}$

	Present Work	Others
Na^{23} in $Na^{23}Br^{79}$		
$(eqQ)_0$ =	-4.820 ± 0.078 MHz	-4.880 MHz (Mol. Beam Mag. Resonance)[7]
		-4.680 MHz (" " " ")[10]
$(eqQ)_1$ =	-4.770 ± 0.078 MHz	
$(eqQ)_2$ =	-4.720 ± 0.090 MHz	
$(eqQ)_3$ =	-4.670 ± 0.100 MHz	
$(eqQ)_e$ =	-4.845 MHz	
$(eqQ)_I$ =	0.050 MHz	
$(eqQ)_{II}$ =	0.0 MHz	
Br^{79} in $Na^{23}Br^{79}$		
$(eqQ)_0$ =	58.060 ± 0.080 MHz	58.000 ± 2.000 MHz (Microwave)[9]
$(eqQ)_1$ =	59.160 ± 0.110 MHz	
$(eqQ)_2$ =	60.300 ± 0.100 MHz	
$(eqQ)_3$ =	61.400 ± 0.150 MHz	
$(eqQ)_e$ =	57.498 ± 0.130 MHz	
$(eqQ)_I$ =	1.116 ± 0.037 MHz	
$(eqQ)_{II}$ =	0.0 ± 0.009 MHz	

Table VI. Quadrupole Coupling Constants in $Na^{23}Br^{81}$

Na^{23} in $Na^{23}Br^{81}$

$(eqQ)_0$	=	- 4.820	±	0.065	MHz
$(eqQ)_1$	=	- 4.770	±	0.075	MHz
$(eqQ)_2$	=	- 4.720	±	0.080	MHz
$(eqQ)_e$	=	- 4.845			MHz
$(eqQ)_I$	=	0.050			MHz
$(eqQ)_{II}$	=	0.0			MHz

Br^{81} in $Na^{23}Br^{81}$

$(eqQ)_0$	=	48.550	±	0.090	MHz
$(eqQ)_1$	=	49.700	±	0.090	MHz
$(eqQ)_2$	=	50.850	±	0.110	MHz
$(eqQ)_e$	=	47.975			MHz
$(eqQ)_I$	=	1.150			MHz
$(eqQ)_{II}$	=	0.0			MHz

$$\frac{(eqQ)_{Br^{79}}}{(eqQ)_{Br^{81}}} = 1.1985 \pm 0.0039$$

This is in agreement, within our experimental error, with values of the ratio observed previously.[30]

The accuracy of the line position measurements did not warrant including the magnetic interactions in fitting the spectra. Line shifts due to these are expected to be insignificant.

APPENDIX

Table A-I.	Electronic Equipment for Signal Averaging System.
Table A-II.	V = 0 Spectra of $Na^{23}Cl^{35}$
Table A-III.	V = 1 Spectra of $Na^{23}Cl^{35}$
Table A-IV.	V = 2 Spectra of $Na^{23}Cl^{35}$
Table A-V.	V = 3 Spectra of $Na^{23}Cl^{35}$
Table A-VI.	V = 0 Spectra of $Na^{23}Cl^{37}$
Table A-VII.	V = 1 Spectra of $Na^{23}Cl^{37}$
Table A-VIII.	$Na^{23}Br^{79}$ Spectra V = 0
Table A-IX.	$Na^{23}Br^{79}$ Spectra V = 1
Table A-X.	$Na^{23}Br^{79}$ Spectra V = 2
Table A-XI.	$Na^{23}Br^{79}$ Spectra V = 3
Table A-XII.	$Na^{23}Br^{81}$ Spectra V = 0
Table A-XIII.	$Na^{23}Br^{81}$ Spectra V = 1
Table A-XIV.	$Na^{23}Br^{81}$ Spectra V = 2

Table A-I. Electronic Equipment for Signal Averaging System.

Unit	Model No.	Manufacturer
Transistorized linear pulse amplifier		LRL[a] Plan No. 15X4845
Inverting amplifier (gain 1-10X, zero offset)		LRL[a] Plan No. 13X1450
Frequency or pulse scaler (0 to 10^8 counts per second; with 5253A and 5253B plug-ins the counting range is extended to 500 MHz.)	5245L	Hewlett-Packard Co., Palo Alto, Calif.
Radio frequency signal generators: a) 50 kHz to 65 MHz. b) 10 MHz to 455 MHz.	 606B 608F	Hewlett-Packard Co., Palo Alto, Calif.
Digital recorder with analog output	562A	Hewlett-Packard Co., Palo Alto, Calif.
Frequency synchronizer (locks 606B and 608F signal generators and allows modulation)	8708A	Hewlett-Packard Co., Palo Alto, Calif.,
Frequency mixer (50 kHz to 450 MHz.)	10514A	Hewlett-Packard Co.,
Stark field voltage supply (1-6000V at 20 mA)	HV-1556	Power Designs Pacific, Inc., Palo Alto, Calif.
Reference voltage supply (0-10 volts)		LRL[a] Plan No. 13X1470
Ramp voltage generator		LRL[a] Plan No. 13X1430
Start pulse function generator	301	Electronics, Inc. Portland, Oregon
Single channel analyzer	NC-11	Hammer Electronics Co. Inc., Princeton, New Jersey
Multichannel analyzer (1024 channels in quadrants, 2×10^{-5} sec dead time per channel)	NS-610	Northern Scientific Madison, Wisconsin
Data processor	460	Northern Scientific Madison, Wisconsin
Switch programed time based oscillator		LRL[a] Plan No. 15X8410
Programed coincidence scaler (0-9999 channels)		LRL[a] Plan No. 13X1310

Table A-II. V = 0 Spectra of $Na^{23}Cl^{35}$
E = 600 v/cm

Observed Line[a] Positions	Calculated Line Positions			Difference
	Calc'd Freq.	Intensity	Composite Line Frequency	
1. 165,433.7 KHz	165433.3 KHz	59.85	165,433.5 KHz	-0.2 KHz
2. 165,634.2	165.628.7	23.84		
	165,628.7	24.09	165,632.0	-2.2
	165,635.4	23.37		
	165,635.4	23.41		
3. 166,548.8	166,531.7	19.71		
	166,546.5	20.41	166,550.0[b]	1.2
	166,559.5	100.00		
4. 166,736.5	166,725.2	4.25		
	166,731.9	38.89	166,737.5	1.0
	166,743.8	38.40		
	166,750.4	4.25		
5. 167,115.2	167,089.9	15.53		
	167,096.6	15.49		
	167,104.7	14.44		
	167,110.7	26.48	167,116.0[b]	0.8
	167,110.7	17.37		
	167,111.5	14.39		
	167,137.4	16.65		
	167,137.4	25.33		
6. 167,835.9	167,840.3	4.71		
	167,840.3	4.67	167,843.5	7.6
	167,846.9	5.07		
	167,846.9	4.98		
7. 168,230.6	168,203.2	20.01		
	168,207.2	13.51		
	168,209.8	20.10		
	168,213.6	98.64		
	168,219.5	51.43		
	168,219.8	24.27		
	168,227.6	1.35		
	168,230.9	24.27		
	168,232.1	1.34	168,230.0	-0.6
	168,234.3	48.55		
	168,234.6	25.72		
	168,245.8	25.71		
	168,246.1	98.63		
	168,252.5	13.51		
	168,253.2	40.13		

Table A-II. (cont'd)

Observed Line[a] Positions	Calculated Line Positions			Difference
	Calc'd Freq.	Intensity	Composite Line Frequency	
8. 168,616.6 KHz	168,612.7 KHz	4.98		
	168,612.7	5.07	168,616.0 KHz	-0.6
	168,619.4	4.67		
	168,619.4	4.72		
9. 169,346.7	169,322.3	25.32		
	169,322.3	16.64		
	169,349.0	17.36	169,343.5[b]	-3.2
	169,349.0	26.47		
	169,351.6	28.84		
	169,366.4	31.02		
10. 169,723.5	169,709.3	4.26		
	169,715.9	38.41	169,721.5	-2.0
	169,727.8	38.89		
	169,734.4	4.25		
11. 169,916.6	169,900.2	99.95		
	169,911.0	10.19		
	169,915.4	10.23	169,905.5[b]	-7.1
	169,925.8	9.83		
	169,930.2	9.88		
12. 170,826.4	170,824.3	23.40		
	170,824.3	23.37	170,827.5	1.1
	170,830.9	24.09		
	170,830.9	23.84		
13. 171,025.5	171,024.2	29.97		
	171,028.6	29.88	171,026.0	0.5

[a]Average error in observed line positions = 2.4 KHz

[b]Center of composite line, does not necessarily coincide with peak.

Table A-III. V = 1 Spectra of $Na^{23}Cl^{35}$
E = 600 v/cm

Observed Line[a] Positions	Calculated Line Positions			Difference
	Calc'd Freq.	Intensity	Composite Line Frequency	
1. 168,868.1 KHz	168,870.5 KHz	59.86	168,870.5 KHz	2.4 KHz
2. 169,072.7	169,066.0	24.02		
	169,066.0	24.24	169,071.5	-1.2
	169,076.3	23.17		
	169,076.3	23.25		
3. 169,969.0	169,971.4	19.51	169,971.4	2.4
170.006.8	170,002.3	20.61		
	170,008.3	100.00	170,007.5	0.7
4. 170,185.2[b]	170,165.9	1.25		
	170,176.2	42.06		
	170,198.8	41.26	170,187.5	2.3
	170,209.1	1.25		
5. 170,563.5[b]	170,534.9	15.85		
	170,541.7	25.11		
	170,557.3	19.27	170,570.0[c]	6.5
	170,565.9	14.12		
	170,572.6	14.06		
	170,599.6	18.03		
	170,599.6	23.43		
6. 171,299.1	171,298.7	4.62		
	171,298.7	4.57	171,304.5	5.4
	171,309.0	5.16		
	171,309.0	5.08		
7. 171,668.6	171,657.2	13.99		
	171,666.8	20.01		
	171,667.4	99.79		
171,693.2(ctr)	171,673.5	20.10	171,671.5	2.9
	171;676.1	52.28		
	171,677.0	23.84		
	171,688.1	23.85	171,695.0(ctr)	1.8(ctr)
171,724.2[b]	171,707.0	47.70		
	171,707.9	26.15	171,718.5	-5.7
	171,719.0	26.13		
	171,719.5	40.13		
	171,722.3	99.78		
	171,732.3	14.00		

Table A-III. (cont'd)

Observed Line[a] Positions	Calculated Line Positions Calc'd Freq.	Intensity	Composite Line Frequency	Difference
8. 172,090.6 KHz	172,080.5 KHz	5.09		
	172,080.5	5.17	172,085.5	-5.1
	172,090.8	4.58		
	172,090.8	4.63		
9. 172,818.5	172,790.0	23.43		
	172,790.0	18.01		
	172,820.4	28.19	172,819.5[c]	1.0
	172,832.3	19.27		
	172,832.3	25.10		
	172,851.3	31.67		
10. 173,209.3[b]	173,180.5	1.25		
	173,190.8	41.27	173,202.5	-6.8
	173,213.3	42.06		
	173,223.6	1.25		
11. 173,383.4[d]	173,381.3	99.95		
	173,385.1	10.29	173,382.5	-0.9
	173,389.5	10.33		
	173,416.0	9.73	173,416.5[b]	
	173,420.4	9.78		
12. 174,314.6	174,313.3	23.24		
	174,313.3	23.18	174,318.5	3.9
	174,323.5	24.23		
	174,323.5	24.02		
13. 174,513.8	174,516.9	29.97	174,519.0	5.2
	174,521.3	29.88		

[a]Average line error = 3.2 KHz

[b]Overlaps with V = 0 $Na^{23}Cl^{37}$ lines.

[c]Center of composite line(s) does not necessarily coincide with peak(s).

[d]Fitted main peak; smaller peak overlaps with V = 0 $Na^{23}Cl^{37}$ line.

Table A-IV. V = 2 Spectra of $Na^{23}Cl^{35}$
E = 600 v/cm

Observed Line Positions	Calculated Line Positions: Calc'd Freq.	Calculated Line Positions: Intensity	Composite Line[a] Frequency	Difference
1. 172,376.1 KHz	173,377.5 KHz	59.87	172,377.5 KHz	1.4 KHz
2. 172,584.5	172,576.1	24.72		
	172,567.1	24.88	172,579.5	-5.0
	172,592.7	22.36		
	172,592.7	22.49		
3. 173,539.2[b]	173,454.3	18.67		
	173,527.9	100.00	173,538.5[2]	-0.7
	173,555.0	21.42		
4. 173,670.4	173,669.2	43.87	173,669.2	-1.2
173,739.3	173,744.9	41.79	173,744.9	5.6
5. 174,048.5	174,021.2	17.23		
	174,027.7	17.21	174,037.5	-11.0
	174,049.7	24.55		
	174,049.7	22.16		
174,110.6[c]	174,121.9	12.77	174,125.5	14.9
	174,128.5	12.69		
174,155.4[c]	174,158.3	18.64	174,158.3	12.9
	174,158.3	20.60		
6. 174,830.3	174,821.5	4.25		
	174,821.5	4.19	174,835.0	4.7
	174,847.0	5.60		
	174,847.0	5.53		
7. 175,180.1	175,126.2	14.03		
	175,151.7	99.98		
	175,174.9	55.84		
	175,181.2	22.04	175,171.5	-8.6
	175,192.2	22.06		
	175,198.7	19.98		
	175,205.3	20.07		
175,231.1(ctr)			175,231.0(ctr)	-0.1
175,277.7	175,260.4	40.08		
	175,275.7	44.10		
	175,281.9	27.94	175,290.5	12.8
	175,292.9	27.90		
	175,310.7	99.97		
	175,336.2	14.04		

Table A-IV. (cont'd)

Observed Line Positions	Calculated Line Positions: Calc'd Freq.	Calculated Line Positions: Intensity	Composite Line[a] Frequency	Difference
8. 175,633.6	175,615.3 KHz	5.53		
	175,615.3	5.61	175,627.0	-6.6
	175,640.9	4.19		
	175,640.9	4.25		
9. --[d]	176,304.1	20.60	176,319.0[a]	--
	176,304.1	18.63		
	176,337.2	25.47		
176,413.3	176,412.7	22.15	176,424.0[a]	10.7
	176,412.7	24.54		
	176,437.9	34.45		
10. 176,718.1	176,717.4	41.81	176,717.4	-0.7
176,791.2[c]	176,793.2	43.88	176,793.2	2.0
11. 176,921.3[f]	176,905.2	10.69	176,925.0[a]	3.7
	176,909.5	10.74		
	176,934.4	99.95		
177,011.3	177,005.9	9.31	177,007.5	-3.6
	177,010.3	9.36		
12. 177,877.7	177,869.7	22.48		
	177,869.7	22.36	177,882.5	4.8
	177,895.2	24.88		
	177,895.2	24.72		
13. 178,082.9	178,082.7	29.98	178,084.5	1.6
	178,087.1	29.89		

Average line error = 5.1 KHz

[a]Composite line center does not necessarily coincide with peak(s).

[b]Smaller peak overlapped by V = 0 $Na^{23}Cl^{37}$ line.

[c]Overlap with V = 0 $Na^{23}Cl^{37}$ lines.

[d]Overlap with V = 3 $Na^{23}Cl^{35}$ line.

[e]Overlap with V = 1 $Na^{23}Cl^{35}$ line.

[f]Overlap with V = 1 $Na^{23}Cl^{37}$ line.

Table A-V. V = 3 Spectra of $Na^{23}Cl^{35}$
E = 600 v/cm

Observed Line Positions	Calculated Line Positions: Calc'd Freq.	Calculated Line Positions: Intensity	Composite Line Frequency[a]	Difference
1. 175,959.2 KHz	175,951.8 KHz	59.91	175,951.8 KHz	-7.4 KHz
2. 176,155.7[b]	176,135.2	25.35		
	176,135.2	25.49	176,155.0	-0.7
	176,175.8	21.54		
	176,175.8	21.68		
3. 177,013.6	177,004.5	17.85	177,004.5	-9.1
177,138.0	177,115.6	100.00	177,115.6	-22.4
177,170.3	177,174.9	22.22	177,174.9	4.6
4. 177,251.6	177,228.3	44.68	177,228.3	-23.3
177,359.3	177,358.6	41.35	177,358.6	-0.7
5. -- [c]				
6. --				
7. --				
8. --				
9. --				
10. 180,315.9	180,312.1	41.36	180,312.1	-3.8
180,441.5	180,442.4	44.68	180,442.4	0.9
11. 180,493.4	180,493.6	11.10	180,495.5	2.1
	180,497.9	11.13		
180,556.9	180,555.2	99.95	180,555.2	-1.7
180,664.9	180,664.0	8.89	180,666.0	1.1
	180,668.4	8.95		
12. 181,491.9	181,494.9	21.67	181,494.9	3.0
	181,494.9	21.54		
--	181,535.5	25.49	181,535.5	--
	181,535.5	25.34		
13. 181,713.2	181,716.8	29.99	181,719.0	5.8
	181,721.2	29.90		

Average line error = 6.5 KHz

[a]Composite line center does not necessarily coincide with peak(s).

[b]Overlap with V = 1 $NaCl^{37}$ line.

[c]Lines have not been observed; calculated line positions have thus been omitted.

Table A-VI. V = 0 Spectra of $Na^{23}Cl^{37}$
E = 600 v/cm

Observed Line[a] Positions	Calculated Line Positions Calc'd Freq.	Intensity	Composite Line Frequency	Difference
1. 169,303.0 KHz	169,302.1 KHz	60.01	169,302.1 KHz	-0.9 KHz
2. 169,450.6	169,448.4 169,448.4	26.33 26.45	169,448.4	-2-2
3. 169,501.8	169,504.9 169,504.9	20.03 20.16	169,504.9	3.1
4. -- [b]	170,162.5	16.41	170,162.5	
5. 170,316.9	170,313.3	100.00	170,313.3	-3.6
6. 170,365.4	170,354.3	46.06	170,365.3	-0.1
7. 170,407.0	170,413.9	23.56	170,413.9	6.9
8. --	170,560.4	40.55	170,560.4	
9. 170,649.1	170,643.1 170,647.9	20.74 20.77	170,645.5	-3.6
10. 170,708.2	170,693.7 170,693.7	27.05 26.13	170,693.7	-14.5
11. 170,889.9	170,894.6 170,899.3	9.42 9.33	170,897.0	7.1
12. 170,931.7	170,940.5 170,940.5	16.47 17.01	170,940.5	8.8
13. -- [c]	171.420.8 171,420.8	3.34 3.29	171.420.8	
14. -- [c]	171,477.3 171,477.3	6.89 6.83	171,477.3	
15. -- [c]	171,554.1	13.33	171,554.1	
16. 171,607.7	171,610.6	99.98	171,610.6	2.9
17. -- [b]	171,656.7	64.82	171,656.7	
18. -- [b]	171,694.4 171,702.5	17.43 17.48	171,698.5	
19. 171,762.9	171,754.9 171,759.8	19.82 19.89	171,757.5	-5.4
20. 171,850.8	171,849.2	39.72	171,849.2	-1.6
21. 171,908.9	171,908.2	34.91	171,908.2	-0.7

Table A-VI. (cont'd)

Observed Line Positions	Calculated Line Positions: Calc'd Freq.	Calculated Line Positions: Intensity	Composite Line Frequency	Difference
22. 171,951.4 KHz	171,945.8 KHz 171,953.9	32.43 32.38	171,950.0 KHz	-1.4 KHz
23. 171,993.5	171,996.1	99.97	171,996.1	2.6
24. 172,042.0	172,052.5	13.33	172,052.5	10.5
25. 172,133.7	172,129.3 172,129.3	6.83 6.70	172,129.3	-4.4
26. 172,194.3	172,185.8 172,185.8	3.29 3.34	172,185.8	-8.5
27. 172,674.3	172,666.0 172,666.0	17.01 16.46	172,666.0	-8.3
28. 172,715.3	172,709.6	18.76	172,709.6	-5.7
29. 172,903.5	172,912.9 172,912.9	26.13 27.03	172,912.9	9.4
30. 172,961.7	172,961.1	41.51	172,961.1	-0.6
31. 173,051.2	173,046.2	40.56	172,046.2	-5.0
32. -- [b]	173,190.9 173,194.3	11.77 11.79	173,192.5	
33. 173,245.9	173,241.3	46.07	173,241.3	-4.6
34. 173,294.1	173,293.3	99.96	173,293.3	-0.8
35. -- [b]	173,442.4 173,445.8	8.18 8.23	173,444.0	
36. -- [d]	174,101.7 174,101.7	20.15 20.02	174.101.7	
37. -- [d]	174,158.1 174,158.2	26.45 26.32	174,158.2	
38. -- [b]	174,302.9 174,306.2	30.04 29.96	174,304.5	

[a]Average line error = 8.8 KHz.

[b]Lines overlap with V = 1 $Na^{23}Cl^{35}$ lines.

[c]Lines have not been observed, inadvertently.

[d]Overlap with V = 2 $Na^{23}Cl^{35}$ lines.

Table A-VII. V = 1 Spectra of $Na^{23}Cl^{37}$
E = 600 v/cm

Observed Line Positions	Calculated Line Positions: Calc'd Freq.	Calculated Line Positions: Intensity	Composite Line Frequency	Difference
1. -- [a]	172,785.8 KHz	59.95	172,785.8 KHz	
2. -- [f]	172,941.1 172,941.1	25.73 25.86	172,941.1	
3. -- [f]	172,984.6 172,984.6	20.99 21.12	172,984.6	
4. -- [b]	173,684.3	17.31	172,684.3	
5. 173,795.1	173,801.5	100.00	173,801.5	6.4
6. 173,870.4	173,871.7 173,882.9	22.72 45.19	173,879.0	8.6
7. -- [b]	174,027.0	41.05	174,027.0	
8. -- [b]	174,175.9 174,180.8	19.38 19.39	174,178.5	
9. 174,212.2	174,214.4 174,214.4	25.85 24.71	174,214.4	2.2
10. -- [c]	174,363.2 174,368.2	10.70 10.61	174,366.0	
11. 174,407.6	174,402.6 174,402.6	17.49 18.26	174,402.6	-5.0
12. -- [d]	174,925.4 174,925.4	3.68 3.63	174,925.4	
13. -- [d]	174,968.9 174,968.9	6.35 6.29	174,968.9	
14. -- [b]	175,112.8	13.68	175,112.8	
15. -- [b]	175,156.3	99.98	175,156.3	
16. -- [b]	175,194.1	61.36	175,194.1	
17. -- [b]	175,224.0 175,215.7	19.26 19.21	175,219.0	
18. -- [b]	175,261.7 175,266.6	19.90 19.97	175,264.0	
19. -- [b]	175,337.1	39.89	175,337.1	
20. -- [b]	175,381.4	38.47	175,381.4	

Table A-VII. (cont'd)

Observed Line Positions	Calculated Line Positions: Calc'd Freq.	Calculated Line Positions: Intensity	Composite Line Frequency	Difference
21. 175,406.1 KHz	175,403.1 KHz 175,411.3	30.69 30.66	175,407.0 KHz	0.9
22. 175,439.0	175,445.0	99.98	175,445.0	6.0
23.	175,488.5	13.69	175,488.5	-8.3
24. -- [a]	175,632.4 175,632.4	6.29 6.36	175,632.4	
25. -- [d]	175,675.9 175,675.9	3.63 3.68	175,675.9	
26. 176,192.7	176,198.7 176,198.7	18.26 17.48	176,198.7	6.0
27. 176,235.4	176,235.6	21.31	176,235.6	0.2
28. -- [b]	176,386.8 176,386.8	24.70 25.84	176,386.8	
29. -- [b]	176,422.9	38.79	176,422.9	
30. 176,570.2	176,574.2	41.06	176,574.2	4.0
31. -- [b]	176,718.3 176,727.9 176,731.3	45.19 11.35 11.38	176,721.0	
32. -- [b]	176,799.7	99.96	176,799.7	
33. -- [b]	176,915.3 176,918.6	8.63 8.68	176,917.0	
34. -- [e]	177,616.6 177,616.6	21.12 20.99	177,616.6	
35. -- [e]	177,660.1 177,660.1	25.86 25.73	177,660.1	
36. 177,812.9	177,813.7 177,817.1	30.01 29.93	177,815.5	2.6

Average line error = 7.3 KHz

[a]Overlap with V = 1 $Na^{23}Cl^{35}$ line(s).

[b]Overlap with V = 2 $Na^{23}Cl^{35}$ line(s).

[c]Overlap with V = 1 $Na^{23}Cl^{35}$ and V = 0 $Na^{23}Cl^{37}$ lines.

[d]Lines have not been observed.

[e]Overlap with V = 3 $Na^{23}Cl^{35}$ line(s).

[f]Overlap with V = 0 $Na^{23}Cl^{37}$ line(s).

Table A-VIII. $Na^{23}Br^{79}$ Spectra V = 0

$(J=1,\ M_J=\pm 1,\ V=0 \xrightarrow{E=600\ v/cm} J=1,\ M_J=0,\ V=0)$

Observed Line[a] Positions	Calculated Line Positions Calc'd Freq.	Intensity	Composite Line Frequency	Difference
1. 228,954 KHz	228,952 KHz	63.99	228,970 KHz	16 KHz
	228,988	64.03		
2. 230,357	230,352	31.93	230,375	18
	230,395	31.96		
	230,398	31.98		
	230,398	32.01		
3. 236,706	236,694	100.00	236,720	14
	236,734	49.53		
	236,745	49.49		
4. 238,121	238,106	99.98	238,123	2
	238,139	49.64		
	238,139	49.54		
5. 239,924	239,915	17.64	239,933	9
	239,915	17.62		
	239,951	35.73		
6. 241,339	241,315	17.56	241,338	- 1
	241,322	17.58		
	241,361	35.73		
7. 249,964	249,937	36.08	249,958	- 6
	249,980	35.49		
8. --[b]	251,345	18.03	251,364	
	251,349	18.03		
	251,383	17.78		
	251,383	17.81		
9. 253,156	253,158	49.53	253,175	19
	253,158	49.63		
	253,191	99.97		
10. 254,566	254,559	98.98	254,581	15
	254,604	99.95		
11. 260,934	260,899	31.93	260,921	-13
	260,899	31.91		
	260,941	63.73		
12. 262,330	262,308	31.93	262,327	- 3
	262,312	31.92		
	262,346	63.80		

[a]Average line error = 19 KHz.

[b]Line has not been observed inadvertently.

Table A-IX. $Na^{23}Br^{79}$ Spectra V = 1

$(J=1,\ M_J=\pm 1,\ V=L \xrightarrow{E=600\ v/cm} J=1,\ M_J=0,\ V=1)$

Observed Line[a] Positions	Calculated Line Positions: Calc'd Freq.	Calculated Line Positions: Intensity	Composite Line Frequency	Difference
1. 232,931 KHz	232,944 KHz	63.99	232,962 KHz	31 KHz
	232,979	64.04		
2. 234,312	234,329	31.93	234,351	39
	234,337	31.97		
	234,373	31.99		
	234,373	32.01		
3. 240,841	240,830	100.00	240,855	14
	240,868	49.56		
	240,879	49.52		
4. 242,232	242,227	99.98	242,243	10
	242,259	49.66		
	242,259	49.56		
5. 244,084	244,099	17.65	244,117	33
	244,099	17.63		
	244,134	35.73		
6. 245,485	245,484	17.59	245,507	22
	245,491	17.59		
	245,528	35.73		
7. 254,369[b]	254,321	36.08	254,341	-28
	254,361	35.53		
8. 255,701	255,714	18.04	255,732	31
	255,717	18.03		
	255,749	17.79		
	255,749	17.82		
9. 257,582	257,589	49.55	257,606	24
	257,589	49.64		
	257,621	99.96		
10. 258,981	258,977	99.03	258,998	17
	259,019	99.94		
11. 265,464	265,476	31.93	265,496	32
	265,476	31.91		
	265,516	63.74		
12. -- [c]	266,869	31.93	266,887	
	266,872	31.92		
	266,905	63.81		

[a]Average line error = 30 KHz.

[b]Overlap with V = $Na^{23}Br^{81}$ line.

[c]Line has not been observed inadvertently

Table A-X. $Na^{23}Br^{79}$ Spectra V = 2

$(J=1,\ M_J=\pm1,\ V=2 \xrightarrow{E=600\ v/cm} J=1,\ M_J=0,\ V=2)$

Observed Line[a] Positions	Calculated Line Positions: Calc'd Freq.	Calculated Line Positions: Intensity	Composite Line Frequency	Difference
1. 236,965 KHz	236,976 KHz	64.00	236,993 KHz	28 KHz
	267,009	64.04		
2. 238,411	238,346	31.94	238,368	-43
	238,353	31.97		
	238,389	31.99		
	238,389	32.01		
3. 245,014	245,011	100.00	245,035	21
	245,048	49.59		
	245,058	49.55		
4. 246,423	246,393	99.98	246,408	-15
	246,424	49.68		
	246,424	29.58		
5. -- [b]	248,331	17.66	248,347	
	248,331	17.64		
	248,364	35.72		
6. -- [b]	249,701	17.60	249,722	
	249,708	17.61		
	249,743	35.73		
7. 258,797[c]	258,759	36.08	258,778	-19
	258,798	35.57		
8. 260,140	260,136	18.04	260,154	14
	260,140	18.04		
	260,171	17.81		
	260,171	17.83		
9. 262,086	262,078	49.57	262,093	7
	262,078	49.66		
	262,109	99.96		
10. 263,462	263,450	99.08	263,471	9
	263,491	99.94		
11. -- [b]	270,113	31.93	270,133	
	270,113	31.91		
	270,152	63.75		
12. 271,503	271,491	31.93	271,508	5
	271,494	31.92		
	271,526	63.82		

[a]Average line error = 26 KHz.

[b]Line has not been observed, inadvertently or sufficiently well.

[c]Overlap with V = 1 $Na^{23}Br^{81}$ line.

Table A-IX. $Na^{23}Br^{79}$ Spectra V = 3

$(J=1, M_J=\pm 1, V=3 \xrightarrow{E=600\ v/cm} J=1, M_J=0, V=3)$

Observed Line[a] Positions	Calculated Line Positions: Calc'd Freq.	Calculated Line Positions: Intensity	Composite Line Frequency	Difference
1. 241,097 KHz	241,086 KHz	64.01	241,102 KHz	5 KHz
	241,118	64.05		
2. 242,459	242,441	31.95	242,462	3
	242,448	31.98		
	242,481	31.99		
	242,482	32.02		
3. -- [b]	249,265	100.00	249,288	
	249,300	49.61		
	249,310	49.58		
4. -- [b]	250,631	99.98	250,646	
	250,661	49.69		
	250,661	49.61		
5. 252,654	252,631	17.67	252,647	- 7
	252,631	17.65		
	252,663	35.72		
6. -- [b]	253,987	17.62	254,007	
	253,993	17.62		
	254,027	35.72		
7. -- [b]	263,260	36.09	263,278	
	263,297	35.60		
8. 264,652	264,623	18.04	264,639	-13
	264,626	18.04		
	264,656	17.82		
	264,656	17.86		
9. 266,619	266,626	49.59	266,641	22
	266,626	49.67		
	266,656	99.95		
10. 268,010	267,984	99.12	268,004	- 6
	268,023	99.93		
11. -- [b]	274,805	31.94	274,824	
	274,805	31.92		
	274,842	63.77		
12. -- [b]	276,168	31.94	276,185	
	276,171	31.93		
	276,201	63.82		

[a] Average line error = 39 KHz.

[b] Line has not been observed inadvertantly or sufficiently well.

Table A-XII. $Na^{23}Br^{81}$ Spectra V = 0

$(J=1,\ M_J=\pm 1,\ V=0 \xrightarrow{E=600\ v/cm} J=1,\ M_J=0,\ V=0)$

Observed Line[a] Positions	Calculated Line Positions Calc'd Freq.	Intensity	Composite Line Frequency	Difference
1. 232,800 KHz	232,765 KHz	63.84	232,786 KHz	-14 KHz
	232,807	63.78		
2. 234,187	234,162	31.79	234,190	3
	234,169	31.83		
	234,217	31.88		
	234,217	31.91		
3. 239,254	239,242	100.00	239,272	18
	239,291	49.32		
	239,302	49.27		
4. 240,676	240,654	99.98	240,674	- 2
	240,693	49.49		
	240,693	49.36		
5. 241,956	241,927	17.61	241,948	- 8
	241,927	17.58		
	241,969	35.86		
6. 243,370	243,324	17.51	243,352	-18
	243,332	17.52		
	243,379	35.87		
7. 250,367	250,332	36.14	250,358	- 9
	250,383	35.30		
8. 251,755	251,740	18.07	251,762	7
	251,744	18.06		
	251,784	17.71		
	251,784	17.74		
9. 253,020	253,018	49.34	253,036	16
	253,018	49.46		
	253,057	99.94		
10. 254,425	254,416	98.51	254,443	18
	254,470	99.92		
11. 259,512	259,495	31.85	259,521	9
	259,495	31.82		
	259,546	63.51		
12. 260,934	260,902	31.86	260,924	-10
	260,906	31.85		
	260,946	63.65		

[a]Average line error = 25 KHz.

Table A-XIII. $Na^{23}Br^{81}$ Spectra V = 1

$(J=1,\ M_J=\pm1,\ V=1 \xrightarrow{E=600\ v/cm} J=1,\ M_J=0,\ V=1)$

Observed Line[a] Positions	Calculated Line Positions: Calc'd Freq.	Calculated Line Positions: Intensity	Composite Line Frequency	Difference
1. 236,706[b] KHz	236,691 KHz	63.80	236,711 KHz	5 KHz
	236,731	63.86		
2. 238,121[b]	238,073	31.81	238,100	-21
	238,080	31.85		
	238,126	31.89		
	238,126	31.92		
3. 243,370[c]	243,318	100.00	243,347	-23
	243,364	49.36		
	243,375	49.32		
4. -- [d]	244,715	99.98	244,734	--
	244,752	49.52		
	244,752	49.40		
5. -- [d]	246,058	17.63	246,078	--
	246,058	17.60		
	246,098	35.86		
6. -- [d]	247,440	17.53	247,465	--
	247,447	17.55		
	247,493	35.86		
7. 254,718	254,667	36.14	254,692	-26
	254,716	35.36		
8. 256,100	256,060	18.07	256,081	-19
	256,063	18.06		
	256,102	17.73		
	256,102	17.76		
9. 257,443	257,408	49.38	257,427	-16
	257,408	49.49		
	257,445	99.93		
10. 258,797[e]	258,791	98.60	258,817	20
	258,843	99.91		
11. 264,049	264,034	31.86	264,059	10
	264,034	31.83		
	264,083	63.54		
12. 265,464[f]	265,427	31.87	265,448	-16
	265,430	31.85		
	265,469	63.67		

[a]Average line error = 25 KHz.

[b]Overlap with V = 0 $Na^{23}Br^{79}$ line.

[c]Overlap with V = 0 $Na^{23}Br^{81}$ line.

[d]Line has not been observed sufficiently well.

[e]Overlap with V = 2 $Na^{23}Br^{79}$ line.

[f]Overlap with V = 1 $Na^{23}Br^{79}$ line.

Table A-XIV. $Na^{23}Br^{81}$ Spectra V = 2

$(J=1,\ M_J=\pm1,\ V=2 \xrightarrow{E=600\ v/cm} J=1,\ M_J=0,\ V=2)$

Observed Line[a] Positions	Calculated Line Positions: Calc'd Freq.	Calculated Line Positions: Intensity	Composite Line Frequency	Difference
1. 240,636 KHz	240,589 KHz	63.82	240,609 KHz	-27 KHz
	240,628	63.87		
2. 241,956	241,957	31.82	241,981	25
	241,964	31.86		
	242,007	31.90		
	242,007	31.92		
3. 247,322	247,366	100.00	247,393	71
	247,410	49.41		
	247,834	49.37		
4. 248,738	248,747	99.98	248,765	27
	248,783	49.55		
	248,783	49.44		
5. -- [b]	250,160	17.64	250,179	
	250,160	17.62		
	250,198	35.85		
6. -- [b]	251,529	17.56	251,553	
	251,535	17.57		
	251,578	35.85		
7. 258,981[c]	258,974	36.14	258,998	17
	259,021	35.41		
8. 260,314	260,352	18.07	260,372	58
	260,355	18.06		
	260,392	17.74		
	260,392	17.78		
9. -- [b]	261,769	49.40	261,787	
	261,769	49.51		
	261,805	99.93		
10. -- [b]	263,138	98.68	263,163	
	263,188	99.91		
11. 268,522	268,545	31.87	268,568	46
	268,545	31.84		
	268,592	63.57		
12. 270,018	269,923	31.87	269,943	-75
	269,926	31.86		
	269,963	63.68		

[a] Average line error = 30 KHz

[b] Line has not been observed inadvertantly or sufficiently well.

[c] Overlap with V = 1 $Na^{23}Br^{79}$ line.

REFERENCES

1. P. Kusch and V.W. Hughes, in Handbuch der Physik (Springer-Verlag, Berlin, 1959) vol 37/1

2. J.W. Trischka, in Methods of Experimental Physics (Academic Press, New York, 1962) vol 3, p.589

3. C.D. Hollowell, The Molecular Beam Electric Resonance Spectra of LiF, NaF and KCl,(Ph.D. Thesis),UCRL 17019, Nov. 1966

4. L.P.Gold, The Molecular Beam Electric Resonance Spectra of Some Alkali Halides,(Ph.D. Thesis),Harvard University, Cambridge, Mass, Nov. 1961

5. W.A. Nierenberg and N.F. Ramsey, Phys. Rev. 72, 1075 (1947)

6. H.J. Zeiger and D. I. Bolef, Phys. Rev. 85, 788 (1952)

7. R.E. Cote and P. Kusch, Phys. Rev. 90, 103 (1953)

8. S.A. Oachs, R. E. Cote, and P. Kusch, J. Chem. Phys. 21, 459 (1953)

9. A. Honig, M. Mandel, M. Stitch and C. H. Townes, Phys. Rev. 96, 269 (1954)

10. R. A. Logan, R.E. Cote and P. Kusch, Phys. Rev. 86, 280 (1952)

11. A.J. Hebert, "A Molecular Beam Electric Resonance Spectrometer and the Radiofrequency Spectra of LiF,(Ph.D. Thesis),UCRL 10482, Sept.1962

12. F.W. Breivogel, The Radiofrequency and Microwave Spectra of LiBr and LiI,(Ph.D. Thesis),UCRL 11665, Sept. 1964

13. R. Braunstein and J. W. Trischka, Phys. Rev. 98, 1092 (1955)

14. F. Lovas, (University of California, Berkeley), Private Communication, June 1967

15. F. Lovas, Radiofrequency Stark Spectra of RbF, RbCl, CsF, CsCl and NaI, (Ph.D. Thesis), UCRL 17909, Nov. 1967

16. C.H. Townes and A.L. Schawlow, Microwave Spectroscopy,(McGraw-Hill Book Co., New York, 1955) Ch. 10

17. G. Graff, W. Paul and Ch. Schlier, Z. Physik 153, 38, (1958)

18. N.F. Ramsey, Molecular Beams, (Clarendon Press, Oxford, 1956)

19. N.F. Ramsey, Phys. Rev. 91, 303,(1953)

20. V. Jaccarino and J. King, Phys. Rev. 81,471, (1951)

21. N.A. Schuster and G.E. Pake, Phys. Rev. 81, 157 (1951)

22. Davis, Feld, Zabel and Zacharias, Phys. Rev. 76, 1076 (1949)

23. Gordy, Simmons and Smith, Phys. Rev. 74, 243 (1948)

24. Gilbert, Roberts and Griswold, Phys. Rev. 76, 1723 (1948)

25. Smith, Tidwell and Williams, Phys. Rev. 79, 1007(1950)

26. S. Geshwind, R. Gunther-Mohr and C. H. Townes, Phys. Rev. 81, 288 (1951)

27. T. C. Wang, C.H. Townes, A. L .Schawlow, and A. N. Holden, Phys. Rev. 86, 809 (1952)

28. J. R. Rusk and W. Gordy, Phys. Rev. 127, 817 (1962)

29. P.L. Clouser and W. Gordy, Phys. Rev. 134, A863 (1964)

30. A.J. Hebert, F.W. Breivogel Jr., and K. Street Jr., J.Chem. Phys. 41, 2368 (1964)

31. Ch. Schlier, Z. Physik, 154, 460, (1959)

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.