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Molecular Beam Investigation of Rotational Transitions. I. The Rotational Levels of KCl and Their Hyperfine Structure*

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The molecular beam electrical resonance method, which has heretofore been confined to the study of transitions between the $m=0$ and $m=\pm1$ states of diatomic polar molecules in the state $J=1$, has been extended to the study of rotational transitions from $J=0$ to $J=1$. The inhomogeneous electric fields together with a stop wire are so arranged that molecules in the state $J=0$ are selectively refocused on the detector. A transition to the state $J=1$, under the influence of the applied rf field, is observed by a reduction in beam intensity at the detector. The spectra obtained in this way yield more information than with the older method. The hyperfine structure of the state $J=1$ of the molecules $K^{39}Cl^{35}$, $K^{39}Cl^{37}$, and $K^{41}Cl^{35}$ has been investigated at zero field for several vibrational states. The molecular constants obtained for these molecules are:

	$K^{39}Cl^{35}$	$K^{39}Cl^{37}$	$K^{41}Cl^{35}$
Y_{01} (Mc/sec)	3856.370 ± 0.001	3746.583 ± 0.001	3767.394 ± 0.001
$-Y_{11}\approx\alpha_e$ (Mc/sec)	23.680 ± 0.001	22.676 ± 0.002	22.865 ± 0.001
$Y_{21}\approx\gamma_e$ (Mc/sec)	0.050 ± 0.001	0.047 ± 0.001	0.048 ± 0.001
B_e (Mc/sec)	3856.399 ± 0.007	3746.611 ± 0.007	3767.421 ± 0.007

$r_e=2.6666\pm0.0001$A.

The structure of the $J=1$ state was attributable to a nuclear quadrupole interaction for each nucleus. The variations of $(eqQ)_K$ and $(eqQ)_{Cl}$ with vibrational state are

	$v=0$	1	2	3
$(eqQ)_K$ ($K^{39}Cl^{35}$) Mc/sec	-5.656 ± 0.006	-5.622 ± 0.006	-5.571 ± 0.008	-5.511 ± 0.008
$(eqQ)_K$ ($K^{39}Cl^{37}$) Mc/sec	-5.660 ± 0.006	-5.628 ± 0.010		
$(eqQ)_K$ ($K^{41}Cl^{35}$) Mc/sec	-6.899 ± 0.006	-6.840 ± 0.010		
$\lvert(eqQ)_{Cl}\rvert$ ($K^{39}Cl^{35}$) (Mc/sec)	<0.040	0.075 ± 0.010	0.237 ± 0.010	0.393 ± 0.010

The ratios of the quadrupole moments of the potassium isotopes is

$$Q_{K^{41}}/Q_{K^{39}}=1.220\pm0.002.$$

From observation of line shifts in a weak electric field, the molecular dipole moment was determined in two vibrational states. For $v=0$, $\mu=10.48\pm0.05$ Debye, and for $v=2$, $\mu=10.69\pm0.05$ Debye. The ratio of the dipole moments is 1.020 ± 0.004. The mass ratios of the chlorine and potassium isotopes calculated from the molecular constants are

$$Cl^{35}/Cl^{37}=0.9459803\pm0.0000015 \quad\text{and}\quad K^{39}/K^{41}=0.9512189\pm0.0000015.$$

INTRODUCTION

PREVIOUS investigations with the molecular beam electrical resonance method (MBER) were confined to the study of transitions from the state $m_J=0$ to $m_J=\pm1$ of the rotational state $J=1$ of diatomic polar molecules. Although these transitions are forbidden, the presence of even a weak static electric field breaks down this selection rule.

The advantage of this method was that the transition could be studied at low frequencies of the oscillating field. In the state of the art when these experiments were first started, this point was important. The chief disadvantage was that the fine structure of the level arising from nuclear quadrupole and other interactions was complicated by the circumstance that these interactions, as well as the effect of the electric field, vary with vibrational state. The spectrum, therefore, becomes very difficult to unravel. In addition, the molecular constants such as B_e and the electrical dipole moment μ could be determined with only poor precision.

The advance of the microwave art in the last decade makes it possible and convenient to study the transitions between states of different rotational quantum numbers. In this paper the transitions which are studied are between the state $J=0$ to $J=1$ of $K^{39}Cl^{35,37}$, and $K^{41}Cl^{35}$. This is, of course, a clear advantage in the simplification of the spectrum, because the different vibrational states overlap only slightly. More importantly, one may obtain very accurate values for the rotational and vibration-rotational constants of the molecule and therefore very accurate values of the mass ratios of isotopes. In addition, one obtains accurate values of the electric dipole moment of the molecule and its variation with vibrational state. None of the other information of the nuclear interactions with the molecule is lost in the process.

There already exists in the literature an electron diffraction measurement of the internuclear separation of the atoms in KCl. Studies made with the MBER

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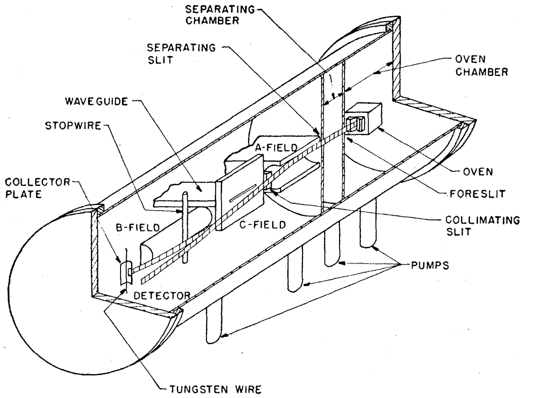

FIG. 1. Schematic of molecular beam electrical resonance apparatus.

method indicate important disagreement with such data in a number of cases. Furthermore, the measurement of Grabner and Hughes[1] on KF made it seem desireable to continue the series with other halide molecules. For these reasons, in addition to the purely technical one that potassium is very easily detected by the hot wire surface ionization detector, it was decided that a careful messurement of KCl would give information of interest and value.

DESCRIPTION OF APPARATUS

The general features of the apparatus used in these experiments are similar to the one described by H. Hughes.[2] The apparatus was originally designed and constructed by V. Hughes of this laboratory and was modified to do the experiments described here.

A cutaway schematic view of the apparatus as modified for these experiments is shown in Fig. 1. The vacuum envelope consisted of a brass cylinder 25$\frac{3}{8}$ in. long and 6$\frac{3}{4}$ in. in diameter. At approximately the center of this cylinder a cylindrical cross piece of somewhat larger diameter was joined for easy access to the C-field region. Two three-stage DPI fractionating diffusion pumps were used to evacuate the observation chamber, a two-stage pump for the separating chamber, and a two-stage pump for the oven chamber. The forevacuum for these pumps was supplied by a booster diffusion pump and a Welch Duo-Seal mechanical pump.

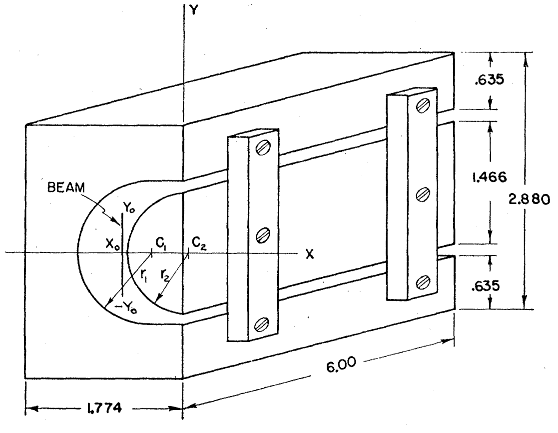

FIG. 2. Oblique projection of deflecting field. (Dimensions in cm.)

The cylindrical surfaces of the inhomogeneous deflecting fields corresponded to the flow lines of a two-wire field, to provide fields which were readily calculable. They were milled from rectangular blocks of duraluminum and polished to allow potentials of 10 000 volts to be applied between the two halves of the fields under vacuum. Figure 2 shows an oblique projection of such a field, and the accompanying Table I gives the design constants for the A and B fields. For mounting in the apparatus, the fields were set on heavy brass blocks which rested on a flat tray fixed in the bottom of the cylindrical envelope. These brass blocks had leveling adjustments and were positioned horizontally by screws through the side of the vacuum envelope. Alignment of these fields was facilitated by mounting knife edges at each end of each field. The position of the deflecting fields relative to the other components of the apparatus, such as the oven, the collimator, the stopwire, and the detector, are shown in Fig. 3.

TABLE I. Design constants of the A and B fields.

	A field	B field
a	0.733 cm	0.458 cm
x_0	0.733 cm	0.688 cm
y_0	0.550 cm	0.500 cm
x_1	1.139 cm	1.261 cm
x_2	0.633 cm	0.588 cm
r_1	0.805 cm	0.714 cm
r_2	0.742 cm	0.473 cm
c_1	0.334 cm	0.547 cm
c_2	−0.109 cm	0.115 cm
x_1-x_2	0.506 cm	0.674 cm
$\Delta V/E$	0.419 cm	0.467 cm
$(\partial E/\partial x)/E$	-1.364 cm^{-1}	-2.014 cm^{-1}
$(\partial E/\partial x)/\Delta V$	3.26 cm^{-2}	4.31 cm^{-2}

Two pairs of slits defined the beam; the slit separation on the iron oven was 1 mil, and the two quartz slits comprising the collimator were 1 mil apart. These quartz slits were waxed to a piece of Micalex which projected into the region between the A field and the C field. The stopwire was a 20-mil tungsten wire which protruded through a hole in the top of the B field into the beam path, and the detector was a heated tungsten filament 3 mils in diameter.

The oven and slit movements on the separating chamber plates were spring loaded pusher devices, with sylphon bellows for vacuum seals. With only a pushing force required, accurate alignment of the internal and external portions of the movement was not necessary. The collimator, stopwire, and detector

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[1] L. Grabner and V. Hughes, Phys. Rev. 79, 819 (1950).
[2] H. Hughes, Phys. Rev. 72, 614 (1947).

movements had dovetail ways restricting the motion to a line in the plane perpendicular to the path of the beam. Here also a sylphon bellows permitted movement under vacuum. The movement with bellows and ways was mounted in a cup-like structure which was waxed in place on top of the vacuum envelope with Apiezon W40. Dial micrometers enabled the position of these movements to be determined to 0.2 mil.

The *C* field consisted of two brass plates lapped on each other and polished. These were clamped together with four quartz spacers (0.6100 ± 0.0002 cm) between the plates at each corner. In the center of the plate was a narrow slit through which microwave energy is fed into the *C* field by a wave guide whose height, in passing through the vacuum envelope to the *C* field, gradually tapered to the narrow dimension of the slit. Since the wave guide transmitted energy in the TE_{01} mode, the long dimension of the slit determined the cut-off wavelength of the guide, and this dimension was constant as the wave guide passed through the vacuum envelope to the *C* field (see Fig. 4). At the flange fitting outside the vacuum envelope, a vacuum seal was made with a 5-mil mica sheet and a Neoprene gasket. Around the edges of the parallel plates of the *C* field a light coating of Aquadag was painted, and across the top and bottom of the plates were clamped sheets of mica with a light coating of Aquadag. We wished by these methods to reduce the amount of energy radiated from the *C*-field structure into the observation chamber. At no time was any effect due to coupling between the klystron and the detector observed. The termination at the end of the wave guide, which represented a considerable reflection, was essentially independent of frequency, or more precisely, was a slowly varying function of frequency compared to the resolution of the apparatus.

This method provided a simple and satisfactory frequency insensitive way of introducing microwave power into a limited region of an extended homogeneous electric field without disturbing this field to any important extent. These conditions were quite necessary for the accurate measurement of the electric dipole moment of the molecule.

FREQUENCY GENERATION AND MEASUREMENT

A reflex klystron was used as a source of microwave energy in the frequency region of 4000 to 8000 Mc/sec supplying a few hundred milliwatts of power. Very little of this power was necessary to induce transitions in the molecules comprising the beam, except in the case where an absorption was intentionally power broadened to facilitate searching. The power required for optimum transition probability in the *C* field 5 cm in length was of the order of a microwatt, which introduces the possibility of using harmonic generation in a frequency region where a direct source is not available.

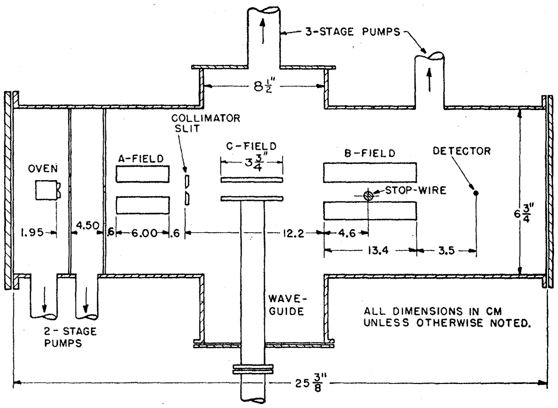

FIG. 3. Dimensions of apparatus.

The band width and stability requirements of the source were determined by the resolution of the apparatus, which in this experiment was prescribed by the length of the *C* field and the thermal velocities of the molecules in the beam. The frequency width of a resonance line is given by the uncertainty relation,

$$\Delta\nu\Delta\tau = 1,$$

where $\Delta\tau$ is the time spent in the radiation field. For KCl this minimum resolution is $\Delta\nu = 18$ kc/sec. The contribution to the width of a resonance due to the natural lifetime of a rotational state is negligible. The high resolution obtainable required a frequency stability of 1 part in 10^8, and for the type of reflex klystron used (2K44) was attainable only by automatic frequency regulation. The klystron source was operated in an oil bath from a regulated (5 parts in 10^6) power supply, and as a reference frequency for stabilization, a harmonic of a secondary standard was used.

In Fig. 5, a block diagram of the apparatus shows the stabilizing and frequency measuring circuits. The secondary standard was a 50-kc quartz bar of the type used for Loran in World War II. The 50-kc signal from this crystal was multiplied by conventional vacuum tube multipliers to a frequency of 240 Mc/sec. Harmonics in the frequency range of the klystron were then obtained by feeding the 240-Mc signal into a harmonic generator of a coaxial type employing a silicon crystal diode. The 35th harmonic of 240 Mc/sec was still sufficiently strong to be used for frequency regulation. It should be emphasized here that although a standard circuit was used for the oscillator employing the quartz bar, and standard multiplier circuits were used, extreme

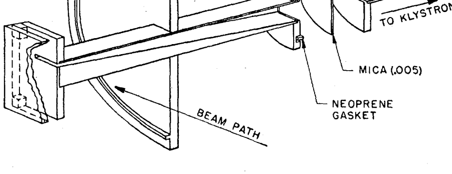

FIG. 4. Isometric section of wave guide which introduces microwave energy into *C* field.

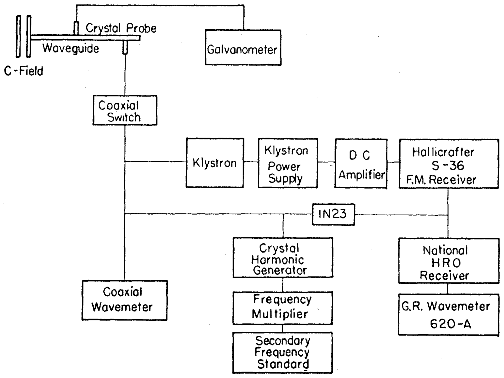

FIG. 5. Schematic of frequency generation and measuring circuit.

care must be used in their construction and operation to keep sideband and hum modulation at a minimum. A signal at 80 Mc/sec may appear to be free of such defects, but a harmonic at several thousand megacycles may show troublesome sidebands and noise modulation.

To obtain an error signal for stabilizing the frequency, the beat frequency between a crystal harmonic and the klystron in the range of 40 to 80 Mc/sec was amplified in an S-36 Hallicrafter receiver. The dc signal from the receiver discriminator was then amplified and used to control the repeller voltage of the klystron. The problem of isolating the high potential of the repeller circuit from the conventional dc amplifiers following the receiver was solved by using, in the last stage of amplification, a cylindrical magnetron diode (GL 2B23) operating in the region of cutoff. The error signal controlled the magnitude of the magnetic field, and the proportional diode current developed a potential across a resistor in series with the repeller lead to the klystron. With the stabilizing circuit in operation, there remained 5 to 10 kc of hum (60, 120) modulation of the klystron signal, but the center frequency was stable to less than 100 cps. The klystron frequency, in addition, was easily varied over a few megacycles by varying the main tuning of the S-36 receiver.

Frequency measurements were made by amplifying the beat frequency between the klystron and a crystal harmonic different from the one used for stabilizing the klystron frequency. By feeding harmonic power from the lower frequency multipliers, in addition to power at 240 Mc, into the crystal multiplier, harmonics in the frequency range of the klystron could be obtained at intervals of 20 mc. This permitted selection of a beat frequency between the klystron and a crystal harmonic in the range 10—30 Mc/sec. Then the signal was amplified by a National HRO receiver, and a zero beat with the radiated signal from a General Radio 620-A heterodyne frequency meter was obtained. The calibration of the receiver did not affect this measurement since the HRO was used only as a selective amplifier for the signal from the klystron (beating against a crystal harmonic), and the signal radiated from the heterodyne frequency meter. A preliminary measurement of the klystron frequency was made with a coaxial wavemeter (0.1 percent accuracy). This helped identify the crystal harmonic with respect to which the beat frequency was measured.

THEORY

A. Molecular Structure

The energy levels of a vibrating rotator have been calculated by Dunham[3] using a WKB method for any potential which can be expanded as a series of powers of $(r-r_e)$ in the neighborhood of the potential minimum, where r_e is defined as the equilibrium internuclear distance.

The equation for the energy levels can be most conveniently written in the following form:

$$F_{v,J}=\sum_{l,j} Y_{lj}(v+\tfrac{1}{2})^l J^j(J+1)^j, \qquad (1)$$

where l and j are summation indices, v and J the vibrational and rotational quantum numbers, respectively, and the Y_{lj} the coefficients.

The connection between some Y's and the ordinary band spectrum constants is shown below:

$$Y_{10}\sim\omega_e,\quad Y_{02}\sim -D_e,\quad Y_{11}\sim -\alpha_e,$$
$$Y_{01}\sim B_e,\quad Y_{20}\sim\omega_e x_e,\quad Y_{21}\sim\gamma_e,$$

where the symbols on the right side refer to the coefficients in the Bohr theory expansion for the molecular energy levels; i.e.,

$$F_{v,J}=\omega_e(v+\tfrac{1}{2})-\omega_e x_e(v+\tfrac{1}{2})^2+\cdots+B_vJ(J+1)$$
$$-D_vJ^2(J+1)^2+\cdots,$$

and

$$B_v=B_e-\alpha_e(v+\tfrac{1}{2})+\gamma_e(v+\tfrac{1}{2})^2+\cdots.$$

$B_v=\hbar^2/2\mu r_v^2$ is the rotational constant for a given vibrational state;

$B_e=\hbar^2/2\mu r_e^2$; α_e is the vibrational-rotational interaction constant;

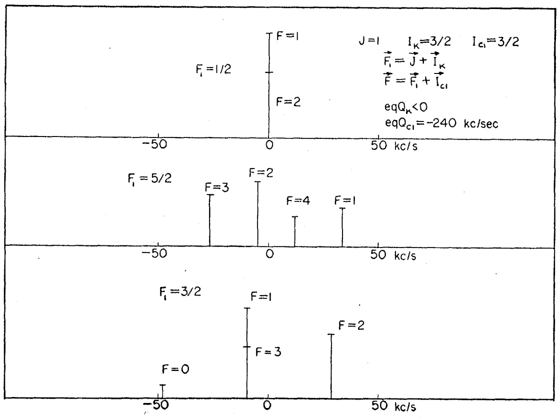

FIG. 6. Theoretical splitting of F_1 levels of the chlorine quadrupole interaction.

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[3] J. L. Dunham, Phys. Rev. 41, 721 (1932).

γ_e is a higher order anharmonic vibrational-rotational interaction term; D_v is the first rotational stretching term.

In this experiment we wished to observe the transition $J=0\rightarrow J=1$ for several vibrational levels. If, for the moment, we neglect hyperfine structure, the frequencies of this rotational transition for the first four vibrational states are given by the following expressions:

$$\begin{aligned} f_0&=2Y_{01}+4Y_{02}+Y_{11}+(1/2)Y_{21},\\ f_1&=2Y_{01}+4Y_{02}+3Y_{11}+(9/2)Y_{21},\\ f_2&=2Y_{01}+4Y_{02}+5Y_{11}+(25/2)Y_{21},\\ f_3&=2Y_{01}+4Y_{02}+7Y_{11}+(49/2)Y_{21}, \end{aligned} \tag{2}$$

where the subscript f_v denotes the vibrational state. It is easily seen that from a knowledge of f_0, f_1, f_2, and f_3 three coefficients may be determined. The smallest coefficient Y_{02}, the rotational stretching term, is calculated from the relation

$$Y_{02}=-4B_e^3/\omega_e^2.$$

B_e is calculated from the relation:

$$Y_{01}=B_e\left[1+\frac{B_e^2}{\omega_e^2}\beta_{01}\right], \tag{3}$$

where

$$\beta_{01}=\frac{Y_{10}^2Y_{21}}{4Y_{01}^3}+16a_1\frac{Y_{20}}{3Y_{01}}-8a_1-6a_1^2+4a_1^3$$

and

$$a_1=\frac{Y_{11}Y_{10}}{6Y_{01}^2}-1\approx-\frac{\alpha_e\omega_e}{6Y_{01}^2}-1.$$

B. HYPERFINE STRUCTURE

The nuclear spins of potassium and chlorine are each $\frac{3}{2}$. The ground state $J=0$ has negligible hfs. What splitting of the ground state that may exist would arise from an interaction that mixes in higher rotational states. However, in KCl such effects are still unobservable with the improved resolution and accuracy of the present experiment.

The fine structure of the $J=1$ state of KCl arises entirely from the interaction of the nuclear quadrupole moments with the rest of the molecule. The Hamiltonian for this interaction consists of two terms, one for each nucleus, and is of the form:

$$\begin{aligned}\mathcal{H}=&-\frac{eqQ_{\mathrm{K}}}{2I(2I-1)(2J-1)(2J+3)}\\ &\times[3(\mathbf{I}\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{I}\cdot\mathbf{J})-\mathbf{I}^2\mathbf{J}^2]\\ &-\frac{eqQ_{\mathrm{Cl}}}{2I(2I-1)(2J-1)(2J+3)}\\ &\times[3(\mathbf{I}\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{I}\cdot\mathbf{J})-\mathbf{I}^2\mathbf{J}^2].\end{aligned}$$

The $\mathbf{I}_k\cdot\mathbf{J}$ interaction between the potassium spin and the rotational angular momentum is too small in KCl to be observable. It is known from experiment that $eqQ_{\mathrm{K}}\gg eqQ_{\mathrm{Cl}}$; therefore, we may consider that the quantum numbers associated with the three energy levels $\mathbf{F}_1=\mathbf{J}+\mathbf{I}_k$ are good quantum numbers. The first interaction term of the Hamiltonian, the potassium quadrupole interaction, is diagonal in this representation. The splitting of the F_1 levels by the chlorine interaction may then be calculated by second-order perturbation theory using an F representation, where $\mathbf{F}=\mathbf{F}_1+\mathbf{I}_{\mathrm{Cl}}$.

$$W(F_1,F)=E_{F_1}+\lambda V_{F_1,F;F_1,F}+\lambda^2\sum_{F_1'\neq F_1}\frac{|V_{F_1F;F_1'F}|^2}{E_{F_1}-E_{F_1'}},$$

where

$$\lambda V_{F_1F;F_1F}=(I_{\mathrm{K}}JF_1I_{\mathrm{Cl}}F|\mathcal{H}_{\mathrm{Cl}}|I_{\mathrm{K}}JF_1I_{\mathrm{Cl}}F),$$

$$F_1'=F_1\pm1,2;$$

and

$$E_{F_1}=(I_{\mathrm{K}}JF_1|\mathcal{H}_{\mathrm{K}}|I_{\mathrm{K}}JF_1),\quad F_1=\tfrac{1}{2},\tfrac{3}{2},\tfrac{5}{2}.$$

The off-diagonal matrix elements of the operator $\mathbf{I}_2\cdot\mathbf{J}$ are given in a paper by Bardeen and Townes.[4] The splitting of the F_1 levels by the chlorine quadrupole interaction is shown in Fig. 6 for an assumed quadrupole interaction constant of $eqQ_{\mathrm{Cl}}=-240$ mc/sec.

A very good determination of the mass ratios of the chlorine and potassium isotopes is possible from a measurement of rotational transitions in the three isotopic species $\mathrm{K^{39}Cl^{35}}$, $\mathrm{K^{39}Cl^{37}}$, and $\mathrm{K^{41}Cl^{35}}$. At least two vibrational states must be measured in each of these molecules to obtain sufficiently accurate values of the coefficients Y_{01}, such that the error in the mass ratio is only a few parts per million. The ratio of the reduced masses is obtained from the expression derived by Dunham,[5]

$$\frac{Y_{01}(\mathrm{K^{39}Cl^{37}})}{Y_{01}(\mathrm{K^{39}Cl^{35}})}=\frac{\mu_{35}}{\mu_{37}}\left[1+\beta_{01}\left(\frac{B_e^2}{\omega_e^2}\right)_{35}\left(\frac{\mu_{35}}{\mu_{37}}-1\right)\right], \tag{4}$$

and the mass ratio from the relation

$$\frac{m_{35}}{m_{37}}=\frac{(\mu_{35}/\mu_{37})(m(\mathrm{K})/m_{37})}{m(\mathrm{K})/m_{37}+1-\mu_{35}/\mu_{37}}, \tag{5}$$

where μ_{35} and μ_{37} are the reduced masses of $\mathrm{K^{39}Cl^{35}}$ and $\mathrm{K^{39}Cl^{37}}$, respectively. The ratio of the masses of $\mathrm{K^{39}}$ to $\mathrm{K^{41}}$ are obtained in a similar manner. The ratio of the mass of $\mathrm{K^{39}}$ to the mass of $\mathrm{Cl^{37}}$, occurring in expression Eq. (5) for the mass ratio of the chlorine isotopes, and the ratio of the mass of $\mathrm{Cl^{35}}$ to the mass of $\mathrm{K^{41}}$ used to obtain the potassium isotope mass ratio, were obtained from precision mass spectrographic measurements of these isotopes given by Collins, Nier, and Johnson.[6]

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[4] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).

[5] J. L. Dunham, Phys. Rev. **41**, 721 (1932).

[6] Collins, Nier, and Johnson, Phys. Rev. **84**, 717 (1951).

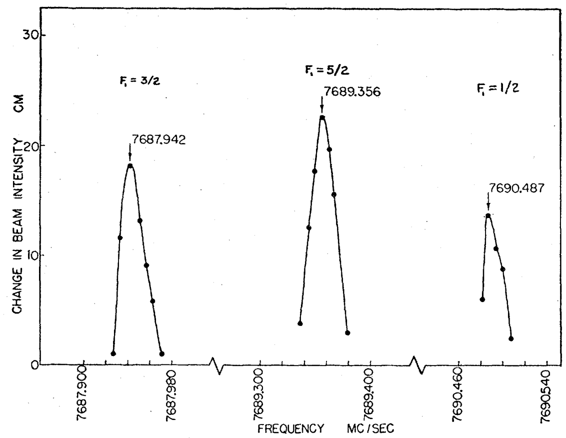

FIG. 7. Observed hfs of $v=0$ state of $K^{39}Cl^{35}$ for the transition $J=0\rightarrow J=1$.

From the frequency shift of the transition $J=0\rightarrow 1$ in a uniform electric field, the electric dipole moment was calculated. A transition from the ground state $J=0$ to an F level of the $J=1$ rotational state which had zero polarizability in very weak fields was observed. Under these circumstances the frequency shift of the line arises only from the relatively large polarizability of the $J=0$ state. The observed frequency shift of the transition, considering only the polarizability of the ground state, is given by

$$f=-\frac{1}{6}\frac{\mu^2E^2}{h\hbar^2/2A},$$

where μ is the permanent dipole moment of the molecule, E the static electric field strength, and A the moment of inertia of the molecule.

The actual transition chosen was from $F=0$, 1, 2, 3 ($J=0$) to $F=1, 2$ ($J=1$, $F_1=\frac{1}{2}$). These two F levels of the upper state, in addition to having zero polarizability in very weak fields, are not split by the chlorine quadrupole interaction. The separation is <500 cps in second-order perturbation.

Relative line intensities were calculated approximately by assuming the fraction of molecules making a transition to a particular excited state, while traversing the C field, was proportional to the number of available ground states consistent with the selection rule $F=0, \pm 1$ ($F=0\rightarrow F=0$ forbidden). Due to lack of precise measurement of the rf amplitude in the C field, and knowledge of the composition of the refocused beam, we could only determine a rough agreement between the observed and calculated intensities.

PROCEDURE

Molecular beams of about 1 500 000 to 5 000 000 cm (where 1 cm$\sim 10^{-15}$ ampere of ion current from the detector) were evaporated from a hot oven source. After one had determined that this total beam was properly collimated, the stopwire was 5 mils beyond the beam center as seen in Fig. 1, the residual beam due to gas scattering was approximately 100 cm. To keep the residual beam low requires a very good vacuum (less than 10^{-6} mm of Hg) and a stable vacuum which requires diffusion pumps which are not subject to "kicking."

The B-field voltage was then set at a predetermined value, which with the proper A-field potential would refocus molecules in the $J=0$ state around the stopwire. For molecules of the most probable velocity in the beam, the deflection at the stopwire for these potentials was 5 mils. As the potential of the A field was varied, a maximum of the refocused beam was observed. However, this was not quite a maximum for refocusing of the $J=0$ state because a small percentage of molecules in the $J=1$, $m=\pm 1$ and $J=2$, $m=\pm 2$ states were refocused at slightly higher potentials, but not high enough to be resolved. Experimentally the difference in the total number of molecules in the $J=0$ state was very slight and for reasons of stability the A field was set at the maximum refocusing potential. Out of a total beam of 2 000 000 cm we would refocus 500 cm of which about 40 to 50 percent would consist of molecules in the $J=0$ state.

The exploration for the spectrum was conducted at zero C-field voltage by varying the frequency of the klystron oscillator. As a starting point for this exploration, a value of B_e was calculated from an electron diffraction measurement of the internuclear distance in KCl. The resonances were initially power broadened to several megacycles which facilitated searching by permitting larger frequency intervals between observations and increasing the intensity of resonances by smearing out the hyperfine structure. At these high power levels spurious responses were observed which presumably were caused by radiation from the C-field structure causing transitions to occur in the interfield region where intense electric fields existed. When changes in beam intensity were observed, a more detailed exploration was made at low power levels. Points on a resonance were made by averaging deflections made by opening and closing a coaxial switch located between the klystron and the wave guide carrying energy to the C field. (See Fig. 5.) These points were taken at frequency intervals of 4 to 10 kc/sec. At low rf power levels and maximum resolution no spurious resonances were observed. Absolute power measurements were not made, but relative power indications were obtained by a pickup probe inserted in the wave guide carrying energy to the C field.

The molecular dipole moment was determined through a measurement of the transition frequencies to the states ($F_1=\frac{1}{2}$, $F=1$, 2) as a function of the potential across the C field from zero up to 7.5 volts. Beyond this point, which represents an electric field intensity of 12.3 volts/cm, the $\mathbf{\mu}\cdot\mathbf{E}$ interaction begins to break up the F_1 representation. There was a contact potential between the C-field plates of 0.087 volt. This was measured by reversing the polarity of the C-field potential at a given point and then readjusting the potential to bring the peak of the resonance back to the same frequency, i.e.,

$$f=f_0+\alpha(V_+ + C),\quad f=f_0+\alpha(V_- - C),$$

where C is the contact potential, $C=\frac{1}{2}(V_- - V_+)$. Measurements of the potential were made with a voltage divider and a Leeds and Northrup type K potentiometer.

DATA AND RESULTS

The spectral patterns of the three isotopic species $K^{39}Cl^{35}$, $K^{39}Cl^{37}$, and $K^{41}Cl^{35}$ are widely separated because of the different moments of inertia. For each molecule the rotational transition $J=0\rightarrow J=1$ consists of a series of lines with a spacing of $\sim 2\alpha_e$ between adjacent vibrational state lines. Since the rotational state zero has negligible hfs, the structure of the rotational transition for a given vibrational state gives directly the hfs of the $J=1$ state. Figure 7 shows the splitting of the rotational transition in the $v=0$ state for $K^{39}Cl^{35}$ due to the potassium quadrupole interaction. In this vibrational state the chlorine quadrupole interaction is negligible. However the chlorine quadrupole interaction increases quite rapidly with vibrational state, and in Fig. 8 for the $v=2$ state, the splitting of the $F_1=\frac{3}{2}$ state by the chlorine interaction is clearly resolved. The theoretical patterns are shown in Fig. 6. In Fig. 9 the progressive splitting of the $F_1=\frac{3}{2}$ state into the various F states by the chlorine interaction for the first four vibrational states is shown. In addition to the increasing chlorine interaction with increasing vibrational state, the potassium quadrupole interaction decreased, but only by 1 percent per vibrational state. These quadrupole interactions are listed in Table II for each molecule, nucleus, and vibrational state.

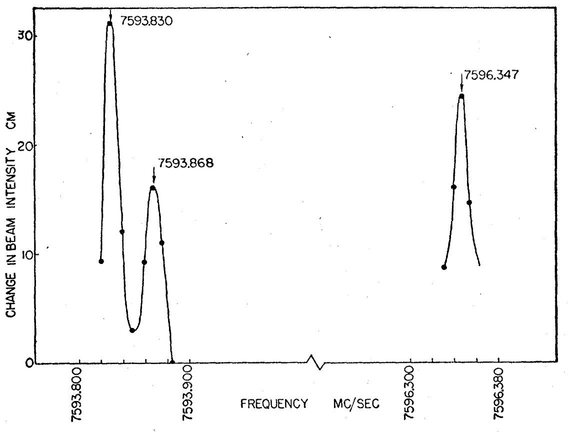

FIG. 8. Observed hfs of $v=2$ state of $K^{39}Cl^{35}$ for the transition $J=0\rightarrow J=1$. (Center line $F_1=5/2$ not shown.)

A considerable body of molecular data was calculable from the observed spectra. Table III shows the Dunham coefficients for the three isotopic species. Here $Y_{02}\approx -D_e$ is calculated from an approximate knowledge of B_e and ω_e. The coefficients Y_{11} and Y_{21} are equal to α_e and γ_e, respectively, within the experimental error. This is not the case for B_e, and the calculation of B_e from Y_{01} must be obtained from Eq. (3). The uncertainty of B_e is considerably greater than Y_{01} because Eq. (3) contains $\omega_e=280\ \text{cm}^{-1}$ and $\omega_e x_e=0.9\ \text{cm}^{-1}$, which were measured by optical spectroscopic observations of vibrational bands[7] and introduce the additional error. The internuclear distance r_e is simply calculated[8] from the relation:

$$B_e=\hbar^2/2\mu r_e^2.$$

Table IV shows the variation of dipole moment and internuclear distance with vibrational state. The error quoted for the dipole moment is equal to twice the error one computes from the deviations of the observed points from a least squares fit of the data. Table V gives the chlorine and potassium mass ratios as calculated from Eqs. (4) and (5). Finally Table VI gives a complete catalog of the frequencies of all the lines observed in KCl. The numbers in parentheses identify the final upper state of the transition.

DISCUSSION

For nuclear physics, the most interesting experimental result of these measurements is the ratio of the nuclear quadrupole moment of K^{41} to that of K^{39}. This value is 1.220 ± 0.0002, and is the only case in the literature for spin $\frac{3}{2}$ when the isotope heavier by two neutrons has the larger quadrupole moment. The other two cases, for which the heavier isotope has the larger quadrupole moment, $Eu^{151,153}$ and $In^{113,115}$ have spins of 5/2 and 9/2 respectively. It is suggestive that K^{39} has 20 neutrons, a magic number, while K^{41} has 22.

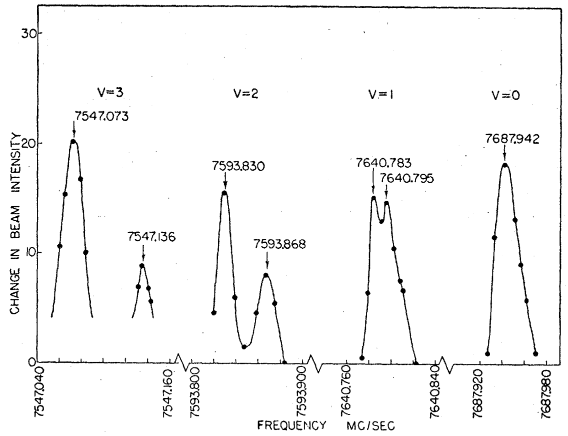

FIG. 9. Variation of hfs due to chlorine quadrupole interaction with with vibrational state. (Upper state $F_1=3/2$.)

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[7] H. Levi, dissertation, Berlin, 1934 (unpublished).

[8] J. W. M. Dumond and E. R. Cohen, U. S. Atomic Energy Commission Special Technical Report No. 1, Nov. 1952 (unpublished).

TABLE II. Variation of the potassium and chlorine nuclear quadrupole interactions with vibrational state.

	$v=0$	1	2	3
$(eqQ)_K$ ($K^{39}Cl^{35}$) Mc/sec	-5.656 ± 0.006	-5.622 ± 0.006	-5.571 ± 0.008	-5.511 ± 0.008
$(eqQ)_K$ ($K^{39}Cl^{37}$) Mc/sec	-5.660 ± 0.006	-5.628 ± 0.010		
$(eqQ)_K$ ($K^{41}Cl^{35}$) Mc/sec	-6.899 ± 0.006	-6.840 ± 0.010		
$\lvert(eqQ)_{Cl}\rvert$ ($K^{39}Cl^{35}$) Mc/sec	<0.040	0.075 ± 0.010	0.237 ± 0.010	0.393 ± 0.010

TABLE III. Molecular constants of KCl.

	$K^{39}Cl^{35}$	$K^{39}Cl^{37}$	$K^{41}Cl^{35}$
Y_{01} Mc/sec	3856.370 ± 0.001	3746.583 ± 0.001	3767.394 ± 0.001
$-Y_{02}\approx D_e$ Mc/sec	0.003	0.003	0.003
$Y_{11}\approx\alpha_e$ Mc/sec	23.680 ± 0.001	22.676 ± 0.002	22.865 ± 0.001
$Y_{21}\approx\gamma_e$ Mc/sec	0.050 ± 0.001	0.047 ± 0.001	0.048 ± 0.001
B_e Mc/sec	3856.399 ± 0.007	3746.611 ± 0.007	3767.421 ± 0.007
$r_e=2.6666\pm0.0001$A			

The sign of the interaction constant eqQ for potassium is quite readily determined from the spectral pattern of the $v=0$ state. The sign of the chlorine quadrupole interaction constant may be inferred if the transitions to the states ($F_1=\frac{3}{2}$, $F=1, 3$) and ($F_1=\frac{3}{2}$, $F=2$) are identified by their relative intensities. The theoretical and experimental plots of these transitions are shown in Figs. 6 and 9. The transition to the state ($F_1=\frac{3}{2}$, $F=0$), which should be much weaker and would have been resolved only in higher vibrational states of reduced population, was never clearly observed. Nevertheless the difference in intensities of the two observed transitions was always distinct and easily measured. Further a negative interaction agrees with the measurement of Logan, Coté, and Kusch[9] ($eqQ=-0.420$ Mc/sec for the chlorine nucleus in KCl). The magnitude is also in qualitative agreement if one remembers that in the magnetic method the chlorine quadrupole interaction constant is an average over vibrational and rotational states excited thermally in the oven source. It is interesting to note the very rapid increase of the chlorine interaction and the rather gradual decrease of the potassium interaction with increasing vibrational state.

TABLE IV. Variation of dipole moment and internuclear distance with vibrational state.

	$K^{39}Cl^{35}$	
	$v=0$	$v=2$
r_v A	2.6707 ± 0.0001	2.6872 ± 0.0001
μ_v Debye	10.48 ± 0.05	10.69 ± 0.05
	$\mu_2/\mu_0=1.020\pm0.004$	

TABLE V. Mass ratios of the potassium and chlorine isotopes.

$Cl^{35}/Cl^{37}=0.9459803\pm0.0000015$
$K^{39}/K^{41}=0.9512189\pm0.0000015$

These very precise measurements of the molecular constants given in Table III permit an evaluation of the mass ratios which is presumably better than the theory allows, because no detailed account is taken of the effects of "L" uncoupling and the fractional error due to electron distribution. It is possible for these effects to be several times the experimental error quoted here. Nevertheless, the calculated values given in Table V agree closely with the mass spectroscopic measurements of Collins, Nier, and Johnson[10] which indicates that these errors may be quite small for the alkali halides. A further development of the theory would make it possible to get mass ratios by means of these molecular beam methods to almost any desired accuracy.

It is interesting that the variation of dipole moment is approximately 1 percent per unit increase in v, while the internuclear distance increases by only 0.3 percent. Comparing this change of the dipole moment with

TABLE VI. Catalog of frequencies of all the lines observed in KCl for the rotational transition $J=0\rightarrow J=1$ in Mc/sec.

Vibrational state	$K^{39}Cl^{35}$	$K^{38}Cl^{37}$	$K^{41}Cl^{35}$	Final state
$v=0$	7690.487	7471.917	7513.659	($F_1=1/2$, $F=1, 2$)
	7689.356	7470.776	7512.280	($F_1=5/2$, $F=1, 2, 3, 4$)
	7687.942	7469.370	7510.555	($F_1=3/2$, $F=0, 1, 2, 3$)
$v=1$	7643.316	7426.754	7468.107	($F_1=1/2$, $F=1, 2$)
	7642.200			($F_1=5/2$, $F=1, 2, 3, 4$)
	7640.783 7640.795			($F_1=3/2$, $F=1, 2, 3$)
$v=2$	7596.347			($F_1=1/2$, $F=1, 2$)
	7593.868 7593.830			($F_1=3/2$, $F=1, 2, 3$)
$v=3$	7549.569			($F_1=1/2$, $F=1, 2$)
	7547.136 7547.073			($F_1=3/2$, $F=1, 2, 3$)

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[9] Logan, Coté, and Kusch, Phys. Rev. 86, 280 (1952).

[10] Collins, Nier, and Johnson, Phys. Rev. 84, 717 (1951).

vibrational quantum number and the corresponding changes of the two quadrupole interaction constants, one must conclude that a simple explanation of these variations in terms of potassium and chlorine moving apart as atoms or ions does not seem likely. In addition, it should be noticed that our value of α_e of 23.680 Mc/sec differs greatly from the Morse potential value of 17.5 Mc/sec.

The comparison of our result for the internuclear distance r_e with the electron diffraction value of Maxwell, Hendricks, and Mosley[11] at 1200°K can be made using the measured variation of r with temperature. When r_e is evaluated from the electron diffraction data we find a value of 2.75A, which is approximately 3 percent larger than our directly measured value of 2.667A. It seems that electron diffraction measurements are consistently high by about the same amount for KBr, CsCl, and NaCl.

In view of the data made available by the techniques described in this paper, it would be desirable to reduce the amount of time required to search and take data. The problem of searching might be solved by automatic frequency sweeping and recording of the beam intensity.

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[11] Maxwell, Hendricks, and Mosley, Phys. Rev. 52, 968 (1937).

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Molecular Beam Investigation of Rotational Transitions. II. The Rotational Levels of KBr and Their Hyperfine Structure*

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The molecular beam electrical resonance method has been used to study the hyperfine structure of the first rotational state in $K^{39}Br^{79}$ and $K^{39}Br^{81}$.

The hyperfine structure arises from the splitting of the $J=1$ state into 10 levels by the quadrupole interactions of potassium and bromine. Molecules in the $J=0$ rotational state were refocused, and transitions to the $J=1$ state were observed by a decrease in beam intensity at the surface ionization detector.

From the structure of the line resulting from the transition $J=0\rightarrow J=1$ in the three lowest vibrational states, the following results were obtained. The molecular constants are

	KBr^{79}	KBr^{81}
Y_{01} Mc/sec	2434.947 ± 0.001	2415.075 ± 0.001
$-Y_{02}$ Mc/sec	0.001	0.001
$-Y_{11}$ Mc/sec	12.136 ± 0.001	11.987 ± 0.001
Y_{21} Mc/sec	0.023 ± 0.001	0.022 ± 0.001
B_e Mc/sec	2434.953 ± 0.007	2415.081 ± 0.007
r_e A	2.8207 ± 0.0001	

The quadrupole interactions and dipole moments in $K^{39}Br^{79}$ in the $v=0$, 1, 2 vibrational states are

	$v=0$	1	2
$(eqQ)_K$ Mc/sec	-5.003 ± 0.003	-4.984 ± 0.003	-4.915 ± 0.003
$(eqQ)_{Br}$ Mc/sec	$+10.244\pm0.006$	$+11.224\pm0.006$	$+12.204\pm0.006$
μ Debye	10.41 ± 0.05		9.93 ± 0.05

The quadrupole interactions in the $v=0$ state of $K^{39}Br^{81}$ are $(eqQ)_K=-5.002\pm0.003$ and $(eqQ)_{Br}=8.555\pm0.006$ Mc/sec.

The mass ratio of the bromine isotopes is $M_{Br^{79}}/M_{Br^{81}}=0.9753088\pm0.0000020$. The ratio of the bromine quadrupole moments is $Q_{Br^{79}}/Q_{Br^{81}}=1.1973\pm0.0006$.

I. INTRODUCTION

THE experiments to be described in this paper deal with measurements of the rotational spectra of $K^{39}Br^{79}$ and $K^{39}Br^{81}$ and form part of a program for a more precise study of the alkali halides by means of the molecular beam electrical resonance method.[1,2] The molecules were studied in the $^1\Sigma$ electronic state and the three lowest vibrational states. All observed resonance lines arise from the rotational transition $J=0\rightarrow J=1$. Each line corresponds to one of the energy levels arising from the hyperfine structure splitting of the first rotational state. The spectrum of these lines is characteristic of a diatomic molecule with two nuclear

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† Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

‡ Predoctoral Fellow of U. S. Atomic Energy Commission.

[1] H. K. Hughes, Phys. Rev. 72, 614 (1947).

[2] Lee, Fabricand, Carlson, and Rabi (preceding paper), Phys. Rev. 91, 1395 (1953). For brevity, this paper will henceforth be referred to as I.