Millimeter-Wave Molecular-Beam Spectroscopy: Alkali Chlorides*

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The pure rotational spectra of the alkali chlorides were investigated in the 0.96- to 3-mm range of the microwave region with the molecular-beam spectrometer earlier developed at Duke University. Introduction of Teflon microwave lenses and high-pass microwave filters improved this spectrometer so that measurements into the submillimeter region were possible, to an accuracy of better than one part in 10^6. Dunham's solution for the diatomic molecule was applied in interpretation of data. Improved values for B_e, α_e, and γ_e were obtained for most molecules studied. The centrifugal distortion constants D_e and β_e were obtained from the rotational spectra for the first time for all molecules measured. From the latter two constants, accurate values of ω_e and $\omega_e x_e$ were derived. Other derived quantities are: potential coefficients, isotopic mass ratios, moments of inertia, and internuclear distances. For most of these quantities, the accuracies obtained surpass those from previous measurements.

INTRODUCTION

AN earlier designed, high-temperature, molecular-beam, microwave spectrometer[1,2] for operation in the shorter millimeter-wave range of the spectrum has been improved and extended in frequency coverage and has been used for extensive measurements of the alkali chlorides. Unlike the rf molecular-beam spectrometers,[3–5] which detect deflected molecules, this spectrometer detects the loss in radiation which results from the absorption of radiation by a beam of molecules simply sprayed across the radiation path. Since no deflection of the beam is necessary, this spectrometer can be used at the very high millimeter- or submillimeter-wave frequencies, at which molecules generally become insensitive to the deflection fields required for operation of the molecular-beam electric-resonance spectrometers. It has the advantage over the latter of employing a microwave detector which does not depend on the type of molecules being investigated. Because of the weak absorption of molecules in the centimeter or longer wave rf region, the present instrument, which we shall designate as a molecular-beam absorption spectrometer, is not generally applicable at these frequencies. It becomes applicable and effective in the shorter millimeter- and submillimeter-wave regions, where the absorption coefficients of most molecules become large. Because molecules generally become less sensitive to electric and magnetic fields with increase of rotational frequency, the molecular-beam resonance methods become ineffective in the millimeter-wave region, where the present spectrometer operates best. Thus, the molecular-beam absorption spectrometer is complementary to the electric- and magnetic-resonance spectrometers.

Before development of our molecular-beam spectrometer, the microwave group at Columbia University designed a hot-cell microwave spectrometer[6,7] which, like ours and like the conventional microwave spectrometer for gases, employs a microwave radiation detector. With it, they measured rotational transitions in the centimeter wave region for most of the alkali halides. More recently, Lide, Cahill, and Gold[8] have improved the hot-cell spectrometer and have extended its range to 45 kMc/sec for the measurement of the $J=0\rightarrow 1$ transition of LiCl. The principal disadvantage of the hot-cell spectrometer is the pronounced pressure and Doppler broadening of the spectral lines in a gas heated to high temperature. Also, the microwave-transmission losses in a hot cell are large for the high millimeter-wave frequencies. The molecular-beam spectrometer used here eliminates most of the pressure and Doppler broadening, and its microwave-transmission losses are sufficiently low that it can be used in the submillimeter-wave region. Introduction of dielectric lenses for the focusing of the millimeter waves through the absorption cell has significantly reduced its transmission losses over those of the earlier design.

As was demonstrated in the study of alkali bromides and iodides[2] and as is evident from this study of the alkali chlorides, a precise measurement of the millimeter-wave rotational spectra allows a more complete and more accurate evaluation of the molecular constants of these molecules than is possible from either infrared or centimeter-wave measurements. The millimeter-wave measurements are needed because the effects of centrifugal distortion on the molecular structure can be significant and because these effects of distortion may be

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[1] A. K. Garrison and W. Gordy, Phys. Rev. **108**, 899 (1957).
[2] J. R. Rusk and W. Gordy, Phys. Rev. **127**, 817 (1962).
[3] H. K. Hughes, Phys. Rev. **72**, 614 (1947).
[4] C. A. Lee, B. P. Fabricand, R. O. Carlson, and I. I. Rabi, Phys. Rev. **91**, 1395 (1953).
[5] B. P. Fabricand, R. O. Carlson, C. A. Lee, and I. I. Rabi, Phys. Rev. **91**, 1403 (1953).
[6] M. L. Stitch, A. Honig, and C. H. Townes, Rev. Sci. Instr. **25**, 759 (1954).
[7] A. Honig, M. Mandel, M. L. Stitch, and C. H. Townes, Phys. Rev. **96**, 629 (1954).
[8] D. R. Lide, P. Cahill, and L. P. Gold, J. Chem. Phys. **40** (1964).

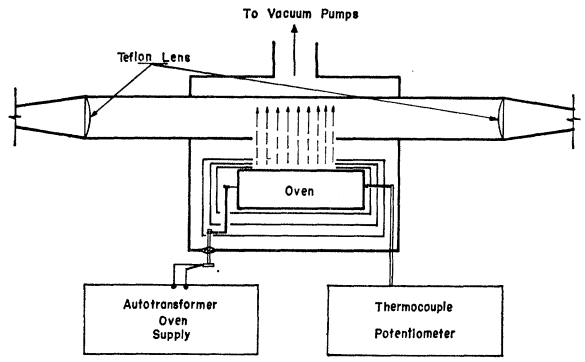

FIG. 1. Schematic diagram of molecular beam absorption cell.

accurately evaluated only by measurements at the higher microwave frequencies, at which frequencies this distortion significantly alters the rotational spectra.

EXPERIMENTAL CONSIDERATIONS

In its systems for microwave-power generation, detection, control, and measurement, the spectrometer used in this study is similar to most of those employed for video detection in the Duke microwave laboratory.[9] The principal difference between this spectrometer and conventional microwave spectrometers is in the absorption cell itself, which is specialized for the generation and utilization of high-temperature molecular beams.

Since the molecular-beam spectrometer has been described in earlier papers of this series,[1,2] only the present modifications of it will be described here. The absorption cell is shown in schematic arrangement in Fig. 1. It consists of a 60-cm section of S-band waveguide (3- $\times 1\frac{1}{2}$-in. cross section), into which the output of a harmonic generator operating from a 32–39 kMc/sec reflex klystron is matched by means of a 30-cm G- to S-band transition section.[9] The power is matched to the G-band waveguide of the detector by an identical S- to G-band transition section. A 6-in. slit is cut in the bottom of the S-band waveguide which is the absorption cell so that a beam of molecules can pass into it from a separate oven located just below the slit. The spectrometer has been modified from the earlier design[2] by the addition of high-pass microwave filters which reduce detector-crystal noise in order to give higher harmonics and the addition of Teflon lenses which increase the efficiency of transmission through the slotted waveguide section. These modifications have made possible detection into the submillimeter region. The filters, which operate by means of a short constriction in the E-field direction in an otherwise straight section of rectangular waveguide, are located at the output guide of the harmonic generator. Three high-pass microwave filters were made with cutoff wavelengths corresponding to the fourth, fifth, and sixth harmonics of the klystron frequency at the low end of its frequency band. These cutoff wavelengths were 1.87 mm, 1.56 mm, and 1.17 mm, respectively.

The lenses were placed at the large ends of the G- to S-band transition sections, as shown in Fig. 1. They are identical, planoconvex types designed upon assumption of a point source of radiation about one centimeter from the apex of the input transition section. Y. Y. Hu[10] shows that for sectoral E- or H-plane horns of less than a five-degree half-angle, the formula $d/\lambda=5$ gives the location of the phase center or "equivalent point source" of the horn for the design of parabolic reflectors. That the theory should follow for transmission lenses is evident. The distance d into the horn from its apex for the wavelength for which the lenses were designed ($\lambda=2$ mm) was approximately a centimeter and was not at all critical. The "equivalent point source" appears to be actually a sphere with a radius of about 1 cm for the small-angle horn used here, as is noted in Hu's work. However, with the lens 29 cm from the equivalent source, the point-source approximation is a good one.

By use of the equivalent point source, two lenses were designed by means of the thin-lens equation normally employed in the design of optical lenses. Since the wavelength of 2 mm is small as compared with the 76-$\times$38-mm lenses, the thin-lens equation is a reasonable approximation from consideration of diffraction effects. Teflon was used for fabrication of the lenses because of its high softening temperature. Its index of refraction was taken to be 1.35. A focal length of 29 cm causes the lens to collimate the output beam of the horn. This collimated beam of microwave power is refocused by its mate at the receiving horn so that it matches this power into the G-band waveguide of the detector. Brown's monograph on microwave lenses[11] offers further information on this subject.

The errors in measurement with the present spectrometer compare favorably with those obtained with the methods of molecular-beam resonance. The accuracy of measurement is limited only by the observer's ability to ascertain the center of an absorption line. Six measurements were made on each line, with directions of the electronic sweep of the klystron alternated so that time delays in the amplifier are canceled. This gives three measurements for which the dispersion usually lies between 1 and 5 parts in 10^7.

No very difficult problems were encountered in the measurement of the rotational transitions in the more abundant chlorides of Na, K, Rb, and Cs. Difficulties with line strength in most of the less abundant chlorine and rubidium isotopes precluded measurements over the three vibrational states necessary for resolution of B_v into the three structural constants Y_{01}, α_e, and γ_e.

[9] W. Gordy, W. V. Smith, and R. F. Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, New York, New York, 1953), Chap. I.

[10] Y. Y. Hu, J. Franklin Inst. **271**, 31 (1961).

[11] J. Brown, *Microwave Lenses* (Methuen and Company Ltd., London, 1953).

The spectra of LiCl were not observed because of the high degree of dimerization in the molecular beam. Lide, Cahill, and Gold[8] have reported measurements of the $J=0\rightarrow 1$ transition of LiCl made with a heated Stark modulation cell.

Cesium chloride, the heaviest molecule investigated in this study has significant populations in the first four vibrational states. This division of population among vibrational states causes the rotational absorption lines for the ground vibrational state of this molecule to be weaker than those of the lighter chlorides, but allows measurement of rotational transitions in four of the vibrational states for $CsCl^{35}$.

All the isotopes of rubidium chloride studied have significant nuclear quadrupole couplings and at the lower J values show an absorption line splitting of several megacycles per second. Nevertheless, for the high J transitions measured in this work, the nuclear quadrupole splitting is negligible. For example, the line splitting is less than a tenth of a megacycle at 190 kMc/sec and is thus within the experimental error of our measurements. The rotational absorption lines in the third vibrational state were very weak; only one was measurable.

The spectral frequencies of $NaCl^{35}$ were measured over a wide range extending into the submillimeter-wavelength region. A cathode-ray oscilloscopic display of one of the submillimeter lines obtained for $NaCl^{35}$ is shown in Fig. 2. The signal is weak because it is near the upper frequency end of the operating range of the present spectrometer. Much stronger signals were, of course, observed in the one- to three-mm range.

Approximate oven temperatures at which the spectral lines appeared for each molecule are shown in Table I.

TABLE I. Oven temperatures.

Molecule	Temperature (°K)
NaCl	1022
KCl	1010
RbCl	970
CsCl	889

No attempt was made to measure these temperatures with strict accuracy. Care was taken only to obtain reproducible temperature measurements, since these measurements were used to predict the temperature at which spectral lines should appear at subsequent observations.

THEORETICAL CONSIDERATIONS

Dunham's theory[12] for the diatomic molecule has been applied in the analysis of the data obtained for the alkali halides. The part of this treatment which is required to make the derived results meaningful is outlined below.

[12] J. L. Dunham, Phys. Rev. **41**, 713 (1932); **41**, 721 (1932).

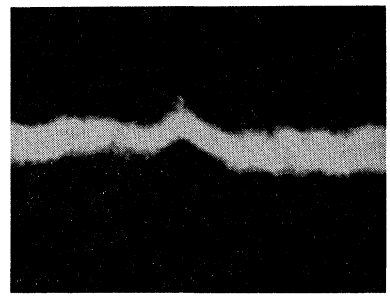

FIG. 2. Cathode-ray oscilloscopic display of the $J=23\rightarrow 24$, $v=0$, transition of $NaCl^{35}$ occurring at 312 109.88 Mc/sec (wavelength 0.97 mm). The width of the line is approximately 100 kc/sec.

The time-dependent, Schrödinger equation for the diatomic vibrating rotor may be written as

$$d^2\psi/d\xi^2+(2\mu r_e^2/h^2)\times[(E-U)-J(J+1)/(1+\xi)^2]\psi=0, \quad (1)$$

where $\xi=(r-r_e)/r_e$, where E is the energy value, and J is the rotational quantum number. The term $J(J+1)/(1+\xi)^2$ may be considered as a "centrifugal potential" and μ as a reduced mass in the equivalent, one-dimensional problem. The term U is dependent on the separation distance of the nuclei and represents the interatomic potential caused by the nuclear and electronic charges. For solution of this equation, the form of the potential function U must be known.

Many potential functions of the closed formula type have been examined by Varshni[13] and by other investigators.[14–16] Probably the most successfully and widely used of these functions is the Morse potential.[14] However, the best fit to the microwave data is obtained by use of a potential function expressed as a power series in ξ, valid only near a minimum and used first by Dunham.[12] This potential is

$$U(\xi)=hca_0^2\xi^2(1+a_1\xi+a_2\xi^2+a_3\xi^3+\cdots), \quad (2)$$

where the a's are constant coefficients.

Dunham applied this power series expansion of the potential in Eq. (1), expanded the centrifugal term as a power series, and solved the resulting equation about a minimum by the Wentzel-Kramers-Brillouin method.[12] The formula which he thus obtained for the energy levels is

$$F_{v,j}=\sum_{lj} Y_{lj}(v+1/2)^l J^j(J+1)^j, \quad (3)$$

where the Y_{lj} are the spectral constants to be obtained from the frequency measurements, J is the rotational quantum number, and v is the vibrational quantum number. If the units of the Y_{lj} are defined as Mc/sec, $F_{v,j}$ becomes a power series for the energy levels in the same units.

Dunham's approach has been reviewed by Sandeman[15] and has been extended slightly to include those Y_{lj}

[13] Y. P. Varshni, Rev. Mod. Phys. **29**, 664 (1957).
[14] P. M. Morse, Phys. Rev. **34**, 57 (1929).
[15] I. Sandeman, Proc. Roy. Soc. (Edinburgh) **60**, 210 (1940).
[16] J. E. Kilpatrick, I. Chem. Phys. **30**, 801 (1959).

expressions which would be needed if measurements of the present accuracy could be made on vibrational transitions as well. Kilpatrick,[16] using a perturbation approach different from that of Dunham, has arrived at the same results as Sandeman and Dunham, in different form, except for his equation for Y_{00}, which includes D, a term for the dissociation energy. The term for the dissociation energy does not appear in the Dunham solution because this solution considers only the form of the potential in a restricted region near the minimum of the potential function. Sandeman has pointed out that the Dunham potential can be valid only over a limited region because of difficulty with convergence of the series potential for large ξ. Dunham's formulation, or Kilpatrick's, seems to be the only one, however, which can be used with the precise spectral data obtainable in the microwave region. It is satisfactory for the microwave measurements probably because the energy levels accessible to our microwave spectrometer lie sufficiently near the minimum of the potential curve for the formulation to apply. This theory was applied by Honig *et al.*[7] to their centimeter-wave measurements of the alkali halides made with their hot-cell spectrometer and by Rusk and Gordy[2] to their measurements of the alkali bromides and iodides made with their high-temperature molecular-beam spectrometer.

By applying the Bohr frequency condition,

$$\nu=(W_2-W_1)/h,$$

and the pure rotational absorption selection rules, $\Delta J=+1$, $\Delta v=0$, to the energy-level formula, one obtains the equation relating frequency ν, quantum numbers v, J, and structural constants Y_{lj}. The equation given below expresses this frequency in terms of those Dunham constants which have a measurable effect on the energy levels. The rotational quantum number for the lower level of the transition is represented by J.

$$\begin{aligned}\nu=&2Y_{01}(J+1)+2Y_{11}(v+\tfrac{1}{2})(J+1)\\&+2Y_{21}(v+\tfrac{1}{2})^2(J+1)+4Y_{02}(J+1)^3\\&+4Y_{12}(v+\tfrac{1}{2})(J+1)^3+Y_{03}(J+1)^3(J+2)^3.\end{aligned}\quad(4)$$

The relation of Y_{03} to other well-known structural constants is given by

$$Y_{03}=(2D_2/3\omega_e^2)(12B_e^2-\alpha_e\omega_e).\quad(5)$$

Subtraction of this term, in frequency units, from each measured line frequency ν, gives a corrected frequency ν'. The corrected frequencies ν_i' are used in the calculation of the five remaining constants with a least-square technique. The derived constants are calculated from the Y values with the following relations given by Dunham[12]:

$$Y_{10}=\omega_e=2(B_e^3/Y_{02})^{1/2},\quad(6)$$

$$a_0=\omega_e^2/4B_eC,\quad(7)$$

$$a_1=Y_{11}\omega_e/6B_e^2-1,\quad(8)$$

$$a_2=Y_{12}\omega_e^3/48B_e^4+2.375+2.25a_1+1.125a_1^2,\quad(9)$$

$$a_3=\omega_e^2Y_{21}/30B_e^3-1-2a_1+6a_2+2.6a_1a_2-1.5(a_1^2+a_1^3),\quad(10)$$

$$Y_{20}=-\omega_ex_e=-1.5B_e(a_2-1.25a_1^2),\quad(11)$$

$$Y_{00}=B_e(3a_2-1.75a_1^2)/8,\quad(12)$$

$$Y_{03}=16B_e^5(3+a_1)/\omega_e^4,\quad(13)$$

$$Y_{04}=-(64B_e^7/\omega_e^6)(13+9a_1-a_2+2.25a_1^2),\quad(14)$$

$$\beta_{01}=7.5+7a_1-4.5a_2+7.5a_3-11.5a_1a_2+5.25(a_1^2+a_1^3),\quad(15)$$

$$B_e=Y_{01}/(1+B_e^2\beta_{01}/\omega_e^2).\quad(16)$$

$$I_e=h/8\pi^2B_e,\quad(17)$$

$$\mu=M_1M_2/(M_1+M_2),\quad(18)$$

$$r_e=(I_e/\mu)^{1/2},\quad(19)$$

where B_e is set as equal to Y_{01} on the right-hand side of all equations except Eq. (16).

The probable error limits in the evaluated Y values were obtained by use of a statistical method[2] designed to produce a 99% confidence in the stated errors. The limits of error for the derived constants are based on these errors and have a 99% confidence level or better. The bulk of the data analysis was performed on the IBM-7072 digital computor available in the Duke University Digital Computing Laboratory.

Except for Y_{01}, the observed Dunham constants Y are related to the more familiar spectral constants for diatomic molecules, as follows:

$$\begin{aligned}&Y_{01}\simeq B_e \quad Y_{21}=\gamma_e \quad Y_{12}=-\beta_e\\&Y_{11}=-\alpha_e \quad Y_{02}=-D_e \quad Y_{03}=H_e.\end{aligned}\quad(20)$$

Similarly,

$$Y_{10}=\omega_e \quad Y_{20}=-\omega_ex_e.\quad(21)$$

The first of these relations, $Y_{01}\simeq B_e$, is only approximate, but the other relationships hold with sufficient accuracy for the results described here. For a further description of these spectral constants, see Herzberg's monograph.[17]

Because of the high J values involved in the transitions observed in the present work, no nuclear hyperfine structure was resolved. A negligible broadening of some of the lines by nuclear quadrupole interactions were the only hyperfine effects which could be observed. Thus we shall not outline the theory of nuclear interactions here. A treatment of these effects, which are resolvable at lower frequencies, is given by Honig *et al.*[7]

[17] G. Herzberg, *Molecular Structure and Molecular Spectra* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1959), 2nd ed., Vol. I, p. 144.

TABLE II. Observed and calculated microwave frequencies of the alkali halides.

Transition	Measured (Mc/sec)	Calculated (Mc/sec)
$NaCl^{35}$		
$v=0$, $J=7 \rightarrow 8$	104 189.74±0.10	104 189.66
$v=0$, $J=11 \rightarrow 12$	156 248.60±0.10	156 248.63
$v=0$, $J=13 \rightarrow 14$	182 262.89±0.10	182 262.86
$v=0$, $J=14 \rightarrow 15$	195 265.39±0.10	195 265.38
$v=0$, $J=16 \rightarrow 17$	221 260.15±0.10	221 260.11
$v=0$, $J=17 \rightarrow 18$	234 251.83±0.10	234 251.87
$v=0$, $J=20 \rightarrow 21$	273 202.04±0.15	273 202.04
$v=0$, $J=23 \rightarrow 24$	312 109.88±0.20	312 109.84
$v=1$, $J=13 \rightarrow 14$	180 907.78±0.10	180 907.81
$v=1$, $J=14 \rightarrow 15$	193 813.63±0.10	193 813.59
$v=1$, $J=17 \rightarrow 18$	232 509.95±0.10	232 509.89
$v=1$, $J=23 \rightarrow 24$	309 787.82±0.10	309 787.79
$v=2$, $J=14 \rightarrow 15$	192 371.05±0.10	192 371.02
$NaCl^{37}$		
$v=0$, $J=8 \rightarrow 9$	114 701.33±0.10	114 701.35
$v=0$, $J=14 \rightarrow 15$	191 091.62±0.10	191 091.57
$v=0$, $J=16 \rightarrow 17$	216 531.44±0.10	216 531.48
$v=1$, $J=8 \rightarrow 9$	113 858.03±0.10	113 857.97
$v=1$, $J=11 \rightarrow 12$	151 783.57±0.10	151 783.62
$v=1$, $J=14 \rightarrow 15$	189 686.13±0.10	189 686.11
KCl^{35}		
$v=0$, $J=12 \rightarrow 13$	99 929.54±0.10	99 929.52
$v=0$, $J=19 \rightarrow 20$	153 677.48±0.10	153 677.46
$v=0$, $J=24 \rightarrow 25$	192 023.49±0.10	192 023.48
$v=0$, $J=29 \rightarrow 30$	230 320.56±0.10	230 320.56
$v=0$, $J=34 \rightarrow 35$	268 558.98±0.15	268 558.94
$v=1$, $J=12 \rightarrow 13$	99 316.44±0.10	99 316.40
$v=1$, $J=24 \rightarrow 25$	190 844.49±0.10	190 844.53
$v=1$, $J=29 \rightarrow 30$	228 905.95±0.10	228 905.90
$v=2$, $J=24 \rightarrow 25$	189 670.52±0.10	189 670.51
KCl^{37}		
$v=0$, $J=21 \rightarrow 22$	164 220.00±0.10	164 220.01
$v=0$, $J=23 \rightarrow 24$	179 121.98±0.10	179 121.92
$v=0$, $J=35 \rightarrow 36$	268 363.84±0.15	268 363.80
$v=1$, $J=18 \rightarrow 19$	140 997.10±0.10	140 997.03
$v=1$, $J=23 \rightarrow 24$	178 038.18±0.10	178 038.10
$Rb^{85}Cl^{35}$		
$v=0$, $J=33 \rightarrow 34$	177 967.57±0.10	177 967.52
$v=0$, $J=34 \rightarrow 35$	183 187.48±0.10	183 187.53
$v=0$, $J=41 \rightarrow 42$	219 690.65±0.10	219 690.65
$Rb^{85}Cl^{35}$		
$v=0$, $J=48 \rightarrow 49$	256 120.42±0.10	256 120.44
$v=1$, $J=20 \rightarrow 21$	109 440.74±0.10	109 440.77
$v=1$, $J=33 \rightarrow 34$	177 045.49±0.10	177 045.50
$v=1$, $J=34 \rightarrow 35$	182 238.38±0.10	182 238.39
$v=1$, $J=41 \rightarrow 42$	218 551.58±0.10	218 551.62
$v=1$, $J=48 \rightarrow 49$	254 791.36±0.10	254 791.47
$v=2$, $J=33 \rightarrow 34$	176 126.30±0.10	176 126.30
$v=2$, $J=34 \rightarrow 35$	181 292.02±0.10	181 292.14
$v=3$, $J=33 \rightarrow 34$	175 209.82±0.10	175 209.90
$v=3$, $J=34 \rightarrow 35$	180 348.70±0.10	180 348.78
$Rb^{87}Cl^{35}$		
$v=0$, $J=29 \rightarrow 30$	156 025.06±0.10	156 025.05
$v=0$, $J=33 \rightarrow 34$	176 777.46±0.10	176 777.45
$v=0$, $J=40 \rightarrow 41$	213 046.83±0.10	213 046.82
$v=1$, $J=27 \rightarrow 28$	144 890.88±0.10	144 890.87
$v=1$, $J=37 \rightarrow 38$	196 490.65±0.10	196 490.64
$Rb^{85}Cl^{37}$		
$v=0$, $J=34 \rightarrow 35$	176 196.16±0.10	176 196.15
$v=0$, $J=35 \rightarrow 36$	181 216.30±0.10	181 216.30
$v=0$, $J=41 \rightarrow 42$	211 311.17±0.10	211 311.15
$v=1$, $J=34 \rightarrow 35$	175 300.90±0.10	175 300.90
$v=1$, $J=35 \rightarrow 36$	180 295.47±0.10	180 295.470
$v=2$, $J=34 \rightarrow 35$	174 408.33±0.10	174 408.260
$CsCl^{35}$		
$v=0$, $J=35 \rightarrow 36$	155 062.73±0.10	155 062.72
$v=0$, $J=44 \rightarrow 45$	193 699.77±0.10	193 699.74
$v=0$, $J=53 \rightarrow 54$	232 250.96±0.10	232 250.92
$v=1$, $J=44 \rightarrow 45$	192 790.44±0.10	192 790.44
$v=1$, $J=53 \rightarrow 54$	231 159.53±0.10	231 159.46
$v=1$, $J=62 \rightarrow 63$	269 425.24±0.15	269 425.25
$v=2$, $J=44 \rightarrow 45$	191 883.04±0.10	191 883.03
$v=2$, $J=53 \rightarrow 54$	230 070.34±0.10	230 070.29
$v=3$, $J=44 \rightarrow 45$	190 977.56±0.10	190 977.53
$CsCl^{37}$		
$v=0$, $J=42 \rightarrow 43$	177 224.90±0.10	177 224.89
$v=0$, $J=59 \rightarrow 60$	246 912.71±0.10	246 912.69
$v=1$, $J=42 \rightarrow 43$	176 411.12±0.10	176 411.12
$v=1$, $J=46 \rightarrow 47$	192 760.59±0.10	192 760.52
$v=1$, $J=59 \rightarrow 60$	245 776.61±0.10	245 776.61

ROTATIONAL CONSTANTS

The measured frequencies for each of the alkali chlorides studied are listed in Table II. In the same table are given for comparison the theoretical values of the frequencies as calculated with the spectral constants given in Table III.

The six constants (Y_{01}, α_e, γ_e, D_e, β_e, and H_e) were calculated directly from the measurements for the isotopic species $CsCl^{35}$, $RbCl^{35}$, KCl^{35}, $NaCl^{35}$, and $Rb^{85}Cl^{37}$. For the species $CsCl^{37}$, KCl^{37}, $NaCl^{37}$, and $Rb^{87}Cl^{37}$, these measurements yielded only four constants (B_0, B_1, D_e, β_e) because observations of rotational transitions for only two vibrational states were made. For the latter, Y_{01} and α_e were derived from B_0 and B_1 by use of a value of γ_e calculated with the isotopic mass ratio formulas. These six structural constants for each molecule are shown in Table III.

Comparison of the RbCl and KCl data with previous results[4] obtained with molecular-beam electric resonance shows that the three constants making up $B_v(Y_{01},\alpha_e,\gamma_e)$ have comparably small errors for the two types of measurement and that they agree well within these errors. This experiment shows no improvement in B_v over that obtained from low J transitions accurately measured with molecular-beam, electric-resonance techniques because the fractional error in the measured frequencies for both experiments is comparable.

A comparison of the present data for CsCl and NaCl with those of the previously made hot-cell measurements[7] shows a significant improvement in accuracy in the values for the three constants making up B_v. The greatest improvement of the present study over the previous results arises in the measurement of the centrifugal distortion constants D_e and β_e and in the evaluation of other constants which are influenced by these constants. The earlier microwave measurements,

TABLE III. Observed rotational constants.

Molecule	Y_{01} Mc/sec	α_e $-Y_{11}$ Mc/sec	γ_e Y_{21} Mc/sec	D_e $-Y_{02}$ Kc/sec	β_e $-Y_{12}$ Kc/sec	H_e Y_{03} cps$\times 10^{-3}$
$NaCl^{35}$	6537.367±0.006	48.711±0.009	0.154±0.008	9.3540±0.0050	−0.0250±0.0050	−1.020 ±0.010
$NaCl^{37}$	6397.287±0.006	47.151±0.009	0.147±0.008	8.9630±0.0060	−0.0190±0.0060	−0.950 ±0.010
KCl^{35}	3856.373±0.009	23.681±0.013	0.049±0.004	3.2600±0.0030	−0.0025±0.0003	−0.623 ±0.008
KCl^{37}	3746.578±0.009	22.678±0.013	0.047±0.004	3.0780±0.0040	−0.0041±0.0040	−0.571 ±0.008
$Rb^{85}Cl^{35}$	2627.393±0.004	13.599±0.004	0.021±0.001	1.4830±0.0010	0.0007±0.0004	−0.248 ±0.002
$Rb^{87}Cl^{35}$	2609.774±0.004	13.458±0.006	0.020±0.001	1.4610±0.0010	0.0019±0.0010	−0.243 ±0.002
$Rb^{85}Cl^{37}$	2526.856±0.004	12.826±0.005	0.019±0.002	1.3710±0.0010	0.0003±0.0010	−0.221 ±0.002
$CsCl^{35}$	2161.246±0.002	10.119±0.002	0.011±0.002	0.9791±0.0004	0.0015±0.0002	−0.1413±0.0006
$CsCl^{37}$	2068.813±0.002	9.476±0.003	0.010±0.002	0.8974±0.0005	0.0014±0.0005	−0.1239±0.0007

which were performed at lower frequencies, did not yield these constants.

The slight effects of Y_{03} or H_e on the observed frequencies were obtained from values of the other structural constants with the equation

$$Y_{03}=H_e=2D_e(12B_e^2-\alpha_e\omega_e)/3\omega_e^2). \qquad (22)$$

Only one pass through the computor was required for reduction of the measured frequencies to structural constants when this calculated value was used. The values of H_e as calculated from previous constants and as calculated from the constants derived from the first passage through the computor agreed within the limits of the effect of the H_e's on the measured frequencies. Values for H_e, listed in Table III, show about two more significant figures than would have been obtained if the value for H_e had been extraced directly from the measured frequencies.

The measured constants under consideration have been found to be consistent under the mass ratio transformation within the experimental errors. The values for Y_{00} and Y_{04} (Table IV) have a number of significant figures and thus provide some check for the Dunham theory. Derived values for Y_{00} and Y_{04} are consistent for different isotopic species of the same molecule, as are all the derived constants presented in the following sections.

Equation (16) was used for derivation of B_e from Y_{01}. The equilibrium moment of inertia and equilibrium nuclear distance, I_e and r_e, were derived from B_e by use of Eqs. (17) and (19), respectively. These values are listed with two-figure errors to allow for adequate comparison between isotopes. If, at a later date, a more accurate value of Planck's constant h should become available, these values may be calculated from the data with greater absolute accuracy. Values for I_e and r_e both agree within their experimental errors with previous measurements because the five-figure accuracy of h masks the differences between these and the hot-cell measurements. All conclusions reached by Honig *et al.*[7] regarding I_e and r_e remain unaffected. Values for these constants are listed in Table V.

TABLE IV. Derived values of Y_{00} and Y_{04}.

Molecule	Y_{00} (kMc/sec)	Y_{04}
$NaCl^{35}$	2.30±0.20	−0.003 ±0.002
$NaCl^{37}$	2.10±0.20	−0.004 ±0.002
KCl^{35}	1.29±0.08	−0.0010 ±0.0002
KCl^{37}	1.40±0.40	−0.0006 −0.0007
$Rb^{85}Cl^{35}$	0.73±0.08	−0.00033−0.00005
$Rb^{87}Cl^{35}$	0.80±0.20	−0.00040±0.00010
$Rb^{85}Cl^{37}$	0.80±0.20	−0.00026±0.00009
$CsCl^{35}$	0.40±0.04	−0.00020±0.00002
$CsCl^{37}$	0.40±0.10	−0.00017±0.00003

TABLE V. Molecular structural constants.

Molecule	B_e (Mc/sec)	β_{01}	I_e[a] (amu-Å)	r_e[a] (Å)
$NaCl^{35}$	6537.406±0.006	−17±2	77.3376±0.0030	2.360898±0.000046
$NaCl^{37}$	6397.320±0.006	−15±3	79.0311±0.0031	2.360898±0.000046
KCl^{35}	3856.385±0.009	−15±1	131.1040±0.0053	2.666772±0.000054
KCl^{37}	3746.592±0.009	−18±7	134.9459±0.0054	2.666771±0.000054
$Rb^{85}Cl^{35}$	2627.397±0.004	−10±2	192.4290±0.0076	2.786865±0.000055
$Rb^{87}Cl^{35}$	2609.776±0.004	−6±4	193.7282±0.0077	2.786869±0.000055
$Rb^{85}Cl^{37}$	2526.860±0.004	−12±5	200.0852±0.0079	2.786864±0.000055
$CsCl^{35}$	2161.247±0.002	−4±1	233.9332±0.0091	2.906411±0.000057
$CsCl^{37}$	2068.814±0.003	−3±4	244.3852±0.0096	2.906408±0.000057

[a] $h=(1.05443\pm0.00004)\times10^{-27}$ erg-sec, 1 g $=(6.02486\pm0.00016)\times10^{23}$ amu, from J. W. Dumond and E. R. Cohen, in *Handbook of Physics*, edited by E. U. Condon and H Odishaw (McGraw-Hill Book Company, Inc., New York, 1958), pp. 7–168.

VIBRATIONAL CONSTANTS

The vibrational constants ω_e and $\omega_e x_e$ were derived from the experimentally observed Y's by use of the Dunham theory, Eqs. (6)–(20). Values thus obtained are compared in Table VI with the values obtained from infrared measurements by Rice and Klemperer.[18] The present values of ω_e agree within experimental error with those from their infrared data, but are an order of magnitude more accurate if one can trust the Dunham theory to hold within the limits of our experimental error. It is worthy of note that the ω_e values of Rice and Klemperer are in much better agreement with our ω_e values, and also with those of Rusk and Gordy on the alkali bromides and iodides than are any other previous values from infrared or optical spectroscopy. Through an oversight their excellent infrared values were not listed for comparison in the earlier paper.[2]

TABLE VI. Derived vibrational constants of alkali chlorides.

Molecule	ω_e Microwave[a] cm^{-1}	ω_e Infrared[b] cm^{-1}	$\omega_e x_e$ Microwave[a] cm^{-1}	$\omega_e x_e$ Infrared[b] cm^{-1}
$NaCl^{35}$	364.60±0.10	366±4	1.755±0.030	2.05
$NaCl^{37}$	360.60±0.10		1.740±0.030	
KCl^{35}	279.80±0.10	281±6	1.167±0.005	1.30
KCl^{37}	275.80±0.20		1.113±0.005	
$Rb^{85}Cl^{35}$	233.34±0.08	228±6	0.856±0.008	0.92
$Rb^{87}Cl^{35}$	232.67±0.08		0.870±0.020	
$Rb^{85}Cl^{37}$	228.88±0.08		0.810±0.040	
$CsCl^{35}$	214.22±0.05	209±6	0.740±0.004	0.75
$CsCl^{37}$	209.55±0.06		0.710±0.020	

[a] From present data calculated with Dunham's theory.
[b] Infrared results of Rice and Klemperer (Ref. 18).

There is an interesting regularity evident in the comparison of the theoretical values of $\omega_e x_e$ from the Dunham equations, from a formula derived by Pekeris,[19] and the experimental values of Rice and Klemperer.[18] Pekeris' formula, shown below, gives better agreement with the $\omega_e x_e$ values of Rice and Klemperer than does the Dunham expression for the lighter molecules, particularly NaCl (see Table VII). The agreement of infrared data with the Dunham or Pekeris formula shows a regular variation with increasing molecular mass.

TABLE VII. Comparison of microwave and infrared $\omega_e x_e$'s for alkali chlorides and bromides.

Molecule	$\omega_e x_e$ Microwave[a] cm^{-1}	$\omega_e x_e$ Infrared[b] cm^{-1}	$\omega_e x_e$ Microwave[c] cm^{-1}
$NaCl^{35}$	1.755	2.05	2.0640
$NaBr^{79}$	1.160[d]	1.50	1.4040[d]
KCl^{35}	1.167	1.30	1.3390
NaI	0.965[d]	1.08	1.0720[d]
$Rb^{85}Cl^{35}$	0.856	0.92	0.9530
KBr^{79}	0.758[d]	0.80	0.8534[d]
$CsCl^{35}$	0.740	0.75	0.7940

[a] Calculated with Dunham's Theory.
[b] Infrared measurements, Rice and Klemperer (Ref. 18).
[c] Calculated with Pekeris's theory (Morse potential).
[d] Rusk and Gordy (Ref. 2).

The Pekeris formula for $\omega_e x_e$ follows from one for α_e, which was derived from a perturbation treatment with the Morse potential[14] as a basis.

$$\alpha_e = (2\omega_e x_e B_e/\omega_e)[3(B_e/\omega_e x_e)^{1/2} - 3(B_e/\omega_e x_e)]. \quad (23)$$

This equation may be solved for $\omega_e x_e$ to give

$$\omega_e x_e = B_e[(\alpha_e \omega_e/6B_e^2)+1]^2, \quad (24)$$

which in terms of Dunham's constant a_1 is

$$\omega_e x_e = B_e a_1^2. \quad (25)$$

Formula (25) may also be obtained from Dunham's relations if Y_{00} is equated to zero in Eq. (12) and the expression thus obtained for a_2 is substituted into Dunham's Eq. (11) for Y_{20}. By Eq. (11), Y_{20} equals $-\omega_e x_e$. The constant Y_{00} is invariant between isotopic species and is independent of the nuclear mass of a given molecule. Therefore, Y_{00} must be dependent on the nature of the potential function. It cannot arbitrarily be set to zero because its value is determined by the potential coefficients a_1 and a_2, whose values depend on the measured rotational constants. Table IV shows that the value for Y_{00} obtained from the rotational constants is definitely not zero.

The only spectral quantity which shows any possibly significant discrepancy within the Dunham theory is the anharmonicity constant, $\omega_e x_e$. This possible discrepancy should be examined further. Although Rice and Klemperer did not give estimates of the limits of error for their $\omega_e x_e$ values, the good agreement between their ω_e values and those of the present study gives credence to their $\omega_e x_e$ values. The Dunham theory is based upon an expansion of the potential function in a power series around the equilibrium position. The Morse potential function upon which the Pekeris formula is based should give a better representation than does the Dunham potential for regions not so near the equilibrium position. This might explain the better agreement of the Pekeris formula with the $\omega_e x_e$ values from the infrared measurement of the lighter molecules with their higher vibrational energies. Varshni and Sukla[20] compare these and other observed constants of the alkali halides with values calculated from a number of different potential functions. It is of interest to compare their different values for $\omega_e x_e$ (see their Table IV) with those obtained here.

MASS RATIOS

The mass ratios between Cl^{35} and Cl^{37}, also those between Rb^{85} and Rb^{87}, were calculated for all the molecules measured. All mass ratios are shown in Table VIII, along with some previously obtained values for

[18] S. A. Rice and W. Klemperer, J. Chem. Phys. **27**, 573 (1957).
[19] C. L. Pekeris, Phys. Rev. **45**, 98 (1934).
[20] Y. P. Varshni and R. C. Shukla, J. Chem. Phys. **35**, 582 (1961).

TABLE VIII. Isotopic mass ratios.

Chlorine (Cl^{35}/Cl^{37})			Rubidium (Rb^{87}/Rb^{85})		
Molecule	Method	Ratio	Molecule	Method	Ratio
NaCl	Present	0.9459780±0.0000045	$RbCl^{35}$	Present	0.9770086±0.0000112
KCl	Present	0.9459783±0.0000089	RbI	Present[d]	0.9770162±0.0000093
RbCl	Present	0.9459768±0.0000047	RbCl	MBER[e]	0.9770163±0.0000045
CsCl	Present	0.9459785±0.0000028	RbF	MBER[e]	0.9770148±0.0000052
CsCl	Hot Cell[a]	0.9459781±0.0000030	RbI	Hot cell[a]	0.9770177±0.0000045
$K^{39}Cl$	MBER[b]	0.9459803±0.0000015	RbBr	Hot cell[a]	0.9770146±0.0000055
	Mass spectroscopy[c]	0.9459759±0.0000035	RbBr	Mass spectroscopy[c]	0.9770191±0.0000022

[a] See Ref. 7.
[b] L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, Phys. Rev. **52**, 968 (1937).
[c] W. H. Johnson, K. S. Quisenberry, and A. O. Nier, *Handbook of Physics*, edited by E. U. Condon and H. Odishaw (McGraw-Hill Book Company, Inc., New York, 1958), pp. 9–55.
[d] See Ref. 2.
[e] See Ref. 4.

comparison. These quantities were calculated from the ratios B_e/B_e', as described by Honig *et al.*[7]

POTENTIAL COEFFICIENTS

The coefficients in the Dunham potential series, Eq. (2) up to and including a_3, are listed in Table IX

TABLE IX. Potential coefficients.

Molecule	a_0 cm^{-1}	a_1	a_2	a_3
$NaCl^{35}$	152 400±90	−3.076±0.001	6.47±0.09	−11.0±1.0
$NaCl^{37}$	152 320±100	−3.076±0.001	6.39±0.10	−11.0±1.0
KCl^{35}	152 100±100	−3.226±0.002	6.96±0.04	−12.0±0.8
KCl^{37}	152 100±200	−3.226±0.003	7.10±0.30	−13.0±3.0
$Rb^{85}Cl^{35}$	155 300±100	−3.297±0.001	7.08±0.08	−11.5±0.8
$Rb^{87}Cl^{35}$	155 500±100	−3.297±0.002	6.90±0.20	−10.0±2.0
$Rb^{85}Cl^{37}$	155 400±100	−3.297±0.002	7.14±0.20	−12.0±2.0
$CsCl^{35}$	159 100±70	−3.317±0.002	6.92±0.04	−10.0±0.8
$CsCl^{37}$	159 090±90	−3.318±0.001	6.89±0.20	−10.0±2.0

for each individual molecule. They were obtained with Eqs. (6)–(20). The potential coefficients between isotopic species are equal (within the stated errors) as should be expected.

Table X, which includes results for the bromides and iodides by Rusk and Gordy,[2] compares values of a_0, a_1, a_2, and a_3 for three different halides of the same alkali metals. The coefficients a_1 are shown to be approximately the same between the iodide, the bromide, and the chloride for a given alkali metal, except for cesium, where the relationship is one of slightly increasing absolute value of a_1 with decreasing mass. The coefficients a_0 also show a regularity in that a_0 increases smoothly with decreasing halide mass for the same alkali metal. These regularities were noted in the results on the iodides and bromides previously reported from this laboratory.[2] This chloride work extends and confirms them. They had not been shown before the development of our millimeter-wave, molecular-beam spectrometer, apparently because values of D_e and β_e were not available to sufficient accuracy for precise calculation of the potential coefficients. For comparison, we have given in parentheses the potential coefficients earlier obtained by Honig *et al.*[7] It will be noted that in many instances there are rather wide discrepancies between our values and theirs.

TABLE X. Comparison of potential coefficients.[a]

Molecule	a_0 $cm^{-1}\times10^{-5}$	a_1	a_2	a_3
LiBr	1.42 (1.02)	−2.71 (−2.45)	6.8 (5.5)	−19 (−14)
LiI	1.35 (1.14)	−2.70 (−2.56)	5.0 (6.0)	−8 (−15)
NaCl	1.52 (1.66)	−3.07 (−3.14)	6.4 (9.2)	−11 (−31)
NaBr	1.48 (1.64)	−3.05 (−3.16)	6.5 (7.4)	−12 (−16)
NaI	1.42 (1.74)	−3.02 (−3.23)	5.9 (8.8)	−8 (−26)
KCl	1.52 (1.81)	−3.22 (−3.43)	7.0 (10.0)	−12 (−32)
KBr	1.48 (1.63)	−3.24 (−3.35)	6.9 (9.1)	−11 (−26)
KI	1.43 (1.64)	−3.25 (−3.41)	6.9 (9.1)	−11 (−25)
RbCl	1.55 (2.08)	−3.30 (−3.66)	7.0 (11.8)	−11 (−42)
RbBr	1.53 (1.73)	−3.33 (−3.49)	7.3 (10.3)	−13 (−33)
RbI	1.44 (1.64)	−3.34 (−3.49)	7.2 (10.2)	−11 (−32)
CsCl	1.59 (2.00)	−3.32 (−3.59)	7.0 (10.6)	−10 (−35)
CsBr	1.55 (2.03)	−3.38 (−3.72)	7.6 (11.7)	−14 (−41)
CsI	1.50 (1.53)	−3.43 (−3.45)	7.6 (9.2)	−13 (−26)

[a] Data for bromides and iodides come from Rusk and Gordy (Ref. 2), those for chlorides from the present study. Values given in parentheses are those of Honig *et al.* (Ref. 7).

FUTURE WORK

Modifications of the oven are being made which will permit measurements to be made on substances which vaporize at higher temperatures than do the alkali chlorides. Millimeter-wave rotational transitions of NaF in different vibrational states have already been detected,[21] and it is hoped that a series similar to these on bromides, iodides, and chlorides can soon be reported from this laboratory on the alkali fluorides.

[21] S. E. Veazey and W. Gordy (to be published).

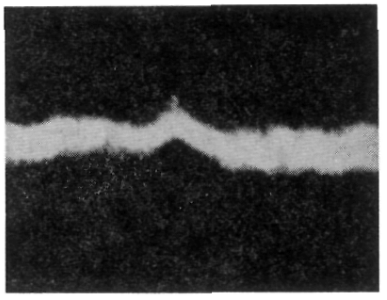

FIG. 2. Cathode-ray oscilloscopic display of the $J=23 \rightarrow 24$, $v=0$, transition of $NaCl^{35}$ occurring at 312 109.88 Mc/sec (wavelength 0.97 mm). The width of the line is approximately 100 kc/sec.