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Microwave Spectra of the Alkali Halides*

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Data from the microwave spectra of all alkali halides excepting LiF, NaF, KF, RbF, and LiCl are given and analyzed in terms of molecular and nuclear constants. These yield internuclear distances and ionic radii for the gaseous alkali halides, molecular dipole moments, potential constants including four constants for some molecules, amount of covalent character from quadrupole coupling constants and from rotational effects, and mass ratios for isotopes of Li, K, Rb, Cl, and Br.

INTRODUCTION

Recent advances in microwave spectroscopy at high temperatures[1,2] have made it possible to obtain the pure rotation spectra of most of the alkali halide molecules. With the exception of LiF, NaF, KF, RbF, and LiCl, which involved certain experimental difficulties, experimental results on all the (stable) alkali halides are given here and discussed in terms of various molecular and nuclear properties.

Past experimental work on the alkali halides in the gaseous state include electron diffraction experiments[3] and molecular beam studies.[4–7] The electron diffraction results yielded internuclear distances with a stated 1 percent error, but these have consistently been found to be about 3 percent too large. Until quite recently, molecular beam experiments on alkali halide molecules utilized radio-frequency resonances. The magnetic resonance experiments[5,6] gave information concerning the nuclear magnetic and electric quadrupole moments, and their interaction with the rotating molecule, and the more recent electric resonance[7] experiments yielded, in addition to the molecular hyperfine structure, information concerning the electric dipole moment and moment of inertia of the molecule. However, these last two quantities are not determined with high accuracy by the electric resonance technique. The very recent molecular beam experiments employing microwave frequencies to study pure rotational transitions[8–10] are most similar in scope to the work described in this paper, although the techniques are greatly different. This type of molecular beam measurement of rotational states has been carried out with KCl,[8] KBr,[9] and RbCl,[10] where it yielded a considerable amount of precise information, some of which is included in this treatment.

The present experiments on the alkali halides in the microwave region provide extremely accurate moments of inertia, internuclear distances, and vibration-rotation interaction constants. Accurate mass ratios for the Cl, Br, Li, K, and Rb isotopes have been obtained. In the lighter molecules, the electric quadrupole hyperfine interactions and the electric dipole moments have been measured. The first part of this paper will deal with the experimental results obtained, and later parts discuss the theoretical significance of some of the results.

APPARATUS AND METHOD

The apparatus for this experiment has been thoroughly described in a previous article.[11] It consists essentially of a gold-plated nickel absorption cell enclosed in a vacuum chamber. This wave guide can be heated to temperatures up to 930°C at present. A thin gold-plated nickel strip, hereafter referred to as a Stark plate, runs the length of the guide parallel to the broad face of the wave guide. An alkali halide salt is placed inside the absorption cell which is then heated until sufficient vapor pressure of the salt is present to produce detectable absorptions of microwave power at the resonant frequencies. Application of an oscillating electric field between the Stark plate and the guide frequency modulates the microwave absorption due to molecular resonances, and greatly increases the sensitivity of the instrument. Application of a steady electric field between the Stark plate and the guide provides a means of measuring the electric dipole moment of the molecule. The details of observing the spectra and measuring the frequency are the same as those employed in conventional microwave spectroscopy at room temperature, and have been thoroughly described in other articles.[12]

Unfortunately temperatures in excess of the 930°C presently attainable are necessary for sufficient vapor pressure of LiF and NaF, so the microwave spectra of these molecules could not be obtained. For LiCl, KF, and RbF, various types of experimental difficulties, some of which are related to the high chemical activity

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[10] R. Braunstein and J. W. Trischka, Quarterly Report, Columbia Radiation Laboratory, August 31, 1953 (unpublished).

[11] Stitch, Honig, and Townes, Rev. Sci. Instr. **25**, 759 (1954).

[12] S. Geschwind, Annals N. Y. Acad. Sci. **55**, 751 (1952).

of these molecules, prevented observation of their spectra. It is hoped that subsequent work will succeed in detection of their spectra.

THEORY

A. Energy of a Rotating Vibrator

The molecular energy levels of a diatomic molecule are based upon the model of a rotating vibrator. If one assumes a Morse potential function of the form[13]

$$V(r-r_e)=D_e(1-e^{-\beta(r-r_e)})^2,$$

the solution of Schrödinger's equation gives the usual energy level expansion:

$$\begin{aligned}W=&\omega_e(v+\tfrac{1}{2})-\omega_e x_e(v+\tfrac{1}{2})^2+\omega_e y_e(v+\tfrac{1}{2})^3+\cdots\\&+B_eJ(J+1)-\alpha_eJ(J+1)(v+\tfrac{1}{2})\\&+\gamma_eJ(J+1)(v+\tfrac{1}{2})^2+\cdots+D_eJ^2(J+1)^2\\&-\beta_eJ^2(J+1)^2(v+\tfrac{1}{2})+\cdots,\end{aligned}$$

where the terms are the familiar band spectra terms[13] and are related to the constants in $V(r-r_e)$. (The third term on the right-hand side is zero for a Morse potential, but is used in the analysis of band spectra.) Since the Morse potential has three independent parameters, only three of the coefficients of the quantum numbers in the energy expansion are independent. Indeed, the agreement of the interrelations between the molecular constants with the experimental values of the constants is a measure of the validity of the Morse potential. For the alkali halides, the high accuracy of the measurements obtained warrants the use of the Dunham potential,[14] which is a power series expansion about the equilibrium internuclear distance r_e of the form

$$V=\sum_{i=2}^{\infty}a_i\left(\frac{r-r_e}{r_e}\right)^i.$$

The Schrödinger equation has been solved for this potential by Dunham and the molecular energy levels are given as

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

The correspondence between the Y_{lm}'s and the ordinary band spectra constants can be obtained by comparing coefficients of identical powers of the quantum numbers in the energy expansions.

For a $J\rightarrow J+1$ pure rotational transition, the frequency of the transition is given by

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

to an approximation required by our experimental accuracy. The Y_{lj}'s with which we are concerned in this present work are:

$$Y_{11}\sim-\alpha_e,\quad Y_{02}\sim D_e,\quad Y_{10}\sim\omega_e,\quad Y_{20}\sim-\omega_ex_e,\quad Y_{21}\sim-\gamma_e,\quad Y_{30}\sim\omega_ey_e,\qquad(2)$$

and Y_{01}, which is related to the rotational constant B_e by

$$Y_{01}=B_e[1+(\beta_{01}B_e^2/\omega_e^2)],$$

where

$$\beta_{01}=(Y_{10}^2Y_{21}/4Y_{01}^3)+(16a_1Y_{20}/3Y_{01})-8a_1-6a_1^2+4a_1^3,$$

and

$$a_1=(Y_{11}Y_{10}/6Y_{01}^2)-1.$$

From a knowledge of Y_{01}, Y_{10}, Y_{20}, Y_{11}, and Y_{21}, the first four coefficients of the power series expansion of the potential can be determined. Expressions relating the Y_{lm}'s to the potential coefficients can be found in Dunham's original paper.

B. Mass Ratios of Isotopes

Under the assumption that the potential function is the same for different isotopic substitutions in a given molecule, very accurate mass ratios can be computed from the experimental data. Denoting the two isotopic species of molecules by M_1X and M_2X, the ratio of the reduced masses is given by

$$\frac{\mu_1}{\mu_2}=\frac{(B_e)_2}{(B_e)_1}=\frac{(Y_{01})_2}{(Y_{01})_1}\left[1+\beta_{01}\frac{B_e^2}{\omega_e^2}\left(\frac{\mu_1}{\mu_2}-1\right)\right]^{-1},\qquad(3)$$

and the mass ratio M_1/M_2 is given by

$$M_1/M_2=\frac{(\mu_1/\mu_2)(X/M_2)}{X/M_2-\mu_1/\mu_2+1},$$

with a fractional error of

$$\pm\left[\delta\left\{\frac{X/M_2+1}{(\mu_1/\mu_2)(X/M_2+1-\mu_1/\mu_2)}\right\}\pm\frac{\Delta(1-\mu_1/\mu_2)}{(X/M_2)(X/M_2+1-\mu_1/\mu_2)}\right],$$

where Δ is the fractional error in the mass X and δ is the fractional error in μ_1/μ_2.

C. Hyperfine Structure

Most of the alkali and halogen nuclei have nonzero electric quadrupole moments. The interaction between the nuclear quadrupole moment and the gradient of the electric field at the nucleus is sufficient to account, within the experimental error, for all molecular hyperfine structure observed in the present experiments. The

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[13] G. H. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (D. van Nostrand Company, Inc., New York, 1952), second edition, p. 101.

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

Hamiltonian for this interaction is

$$H=\frac{-eqQ}{2I(2I-1)(2J-1)(2J+3)J}[3(\mathbf{I}\cdot\mathbf{J})^2+\tfrac{3}{2}\mathbf{I}\cdot\mathbf{J}-I^2J^2],$$

where Q, the quadrupole moment for the particular nucleus concerned, is given by

$$Q=(1/e)\int\rho(3z_n^2-r^2)dxdydz,$$

and q_m is defined as $(d^2V/dz^2)_{\mathrm{Av}}$ at the same nucleus. The z direction lies along the internuclear axis, and V is the electrostatic potential due to all charges outside a small sphere surrounding the nucleus. In cases where both nuclei have sizeable interactions, the Hamiltonian consists of the sum of two expressions of the above form, one for each nucleus.

First-order perturbation theory yields energy levels given by

$$W=W_0+(-eq_mQ)f(I,J,F),$$

$$f(I,J,F)=\frac{\frac{3}{4}C(C+1)-I(I+1)J(J+1)}{2I(2I-1)(2J-1)(2J+3)},$$

$$C=F(F+1)-I(I+1)-J(J+1),$$

in the case of only one nucleus having an appreciable interaction. W_0 represents the unperturbed molecular energy level, and $f(I,J,F)$ is Casimir's function, which has been tabulated in several places.[15] In the few cases where the accuracy of the measurements requires consideration of both nuclear interactions, the energy levels are readily derivable by a technique described by Bardeen and Townes.[16]

In only one case, of all the molecules studied, does second-order perturbation theory seem to be needed. This is in NaI, where the ratio of eqQ_I/B_e is about 1/20. Even here, the magnitude of the contribution of second-order theory just borders on the magnitude of the experimental error. Bardeen and Townes[17] give the matrix elements necessary for computing the appropriate energy levels.

In the heavier molecules, where higher J states were considered due to the low-frequency limit imposed by a given wave-guide size, no hyperfine structure was observed even though eqQ may have been of appreciable magnitude. A glance at relative intensity tables[18] shows that for $J=5$ or higher, $I\leq 5/2$, over 90 percent of the entire line intensity is distributed among $F\rightarrow F+1$ transitions. Also, $f(I,J+1,F+1)-f(I,J,F)$, which is proportional to the frequency shift, becomes smaller with increasing J. Thus, for $J\geq 5$, $I\leq 5/2$, and an eqQ of the order of 100 Mc/sec (this is a large estimate for most of the alkali halides), the total spread of the observable hyperfine components would be of the order of 1 Mc/sec. Several lines within 1 Mc/sec would not be resolved under the conditions of these experiments.

D. Dipole Moments

The energy levels for a diatomic molecule in an electric field have been discussed by Fano.[19] There are three cases into which the calculations naturally fall. Case A: Weak-field case, where $\mu E\ll eqQ$; case B: intermediate-field case where μE is of the same order of magnitude as eqQ, and case C: strong-field case where $\mu E\gg eqQ$. In all of these cases, the quadrupole interaction and electric field energy are small compared to $B_eJ(J+1)$, the rotational energy. All of the molecules for which the dipole moments have been measured in the work described in this paper fall into case A or case C. Case C, the strong-field case, is the simpler one to discuss. Here, J is a good quantum number, and the electric field splits the energy level into $J+1$ levels corresponding to M_J values of 0, ± 1, $\cdots\pm J$. The expression for the energy levels so perturbed is the familiar quadratic Stark effect for molecules:

$$W=W_0+\frac{\mu^2E^2[J(J+1)-3M^2]}{2BJ(J+1)(2J-1)(2J+3)}.$$

These levels may now be perturbed by the electric quadrupole interaction between J and I. In view of the criterion of "strong-field" case, i.e., $eqQ\ll\mu E$ and the fact that the electric field splitting is rarely more than about 10 Mc/sec for the electric fields used in this experiment, the electric quadrupole interaction has not been resolved in these cases.

In the weak field case, I and J combine to form a good quantum number F. The electric field then perturbs the degenerate M_F states. The energy levels in this case are given by

$$W=W_0-\frac{\mu^2E^2}{B}\times\frac{[3M_F^2-F(F+1)][3D(D-1)-4F(F+1)J(J+1)]}{2J(J+1)(2J-1)(2J+3)2F(2F+1)(2F-1)(2F+3)},$$

where

$$D=F(F+1)+J(J+1)-I(I+1).$$

The differences in energy levels divided by h yields the relation between the observed frequency shifts in an electric field and the permanent dipole moment μ of the molecule.

RESULTS

Tables listing measured lines of the molecules whose spectra have been observed are given in Appendix I.

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[15] See, for example, P. Kisliuk and C. H. Townes, J. Research Natl. Bur. Standards **44**, 611 (1950).

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

[17] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 627 (1948).

[18] See H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill Book Company, Inc., New York, 1934), p. 206.

[19] U. Fano, J. Research Natl. Bur. Standards **40**, 215 (1948).

In this section, a discussion of the observed transitions and the information derived from them is given. The actual values of the molecular and nuclear constants appear in the following section, along with other pertinent available data on the alkali halides.

LiBr

The $J=0\rightarrow 1$ transition was observed for Li^7Br^{79}, Li^7Br^{81}, and Li^6Br^{81} at a temperature of about 680°C. Values of Y_{01}, Y_{11}, and Y_{21} have been obtained. The dipole moment of Li^7Br^{79} has been determined for the $v=0$ state. The electric quadrupole coupling constant $(eqQ)_{Br}$ was measured for the $v=0$ states of both Br isotopes and for the $v=1$ state of $LiBr^{81}$.

The calculated reduced mass ratio $\mu(Li^6Br^{81})/\mu(Li^7Br^{81})$ was used to make a rough determination of the percent ionic character of the bond, in a manner identical to that described below for LiI. Since ω_e is not known for LiBr and since it is a quantity necessary for the calculation of Y_{02} and β_{01} which are essential for an accurate mass ratio, it had to be extrapolated from other existing data. The calculation yields a result of 93±35 percent ionic character for the bond.

LiI

The $J=0\rightarrow 1$ transition was measured for both Li^6I and Li^7I at a temperature of about 600°C. Y_{01}, Y_{11}, and Y_{21} for Li^7I, and Y_{01} and Y_{11} for Li^6I have been determined. The dipole moment was measured in the $v=0$ state. The electric quadrupole coupling constant $(eqQ)_I$ has been obtained in the first three vibrational states of Li^7I and in the first two vibrational states of Li^6I.

This molecule is an interesting case for comparison of mass ratio determinations from microwave spectra and from other sources, since this ratio is rather accurately determinable in both cases. Furthermore, since Li is so light, various small effects such as those associated with the position of its valence electron and with L uncoupling of the electrons should be larger than usual and possibly observable.

The mass ratio of the atomic Li isotopes (measured by C. W. Li *et al.*)[20] from nuclear reaction data is 0.8573425±0.0000030. If the Li is in an ionic state in LiI, this gives for the ratio of reduced masses

$$(\mu^6/\mu^7)_{\text{ion}}=0.8637874\pm0.0000030.$$

If the Li carries all its valence electrons as it rotates in the LiI molecule (i.e., it is neutral), the ratio of reduced masses is

$$(\mu^6/\mu^7)_{\text{atom}}=0.8637985\pm0.0000030.$$

It may be seen from Table VII and the discussion below that Li in LiI is approximately 90 percent ionic, so that the ratio of reduced masses to be expected lies between the two values above and is

$$(\mu^6/\mu^7)_{\text{LiI}}=0.8637885\pm0.0000030.$$

The actual ratio obtained from the microwave measurements is

$$(\mu^6/\mu^7)_{\text{measured}}=0.8637888\pm0.0000020,$$

which is in remarkable agreement with the value obtained from nuclear reactions. The experimental uncertainty corresponds to an error in the mass energy of one of the Li isotopes of only about 12 kev.

The above results may be used in reverse to give a measurement of the amount of ionic character of LiI from its mechanical properties. The result is 87±35 percent. Improved measurements of the masses from nuclear reactions should allow improvement of the accuracy of this result.

The above result may be slightly in error because of some L uncoupling in LiI. However, the effect of L uncoupling would be to decrease the apparent amount of ionic character. Since the ionic character is so near 100 percent, it is evident that L uncoupling is not of great importance in this molecule. Hence it probably gives no appreciable errors in mass ratio measurements in the other alkali halides, since their large moments of inertia would make L uncoupling relatively less important.

NaCl[1]

The $J=1\rightarrow 2$ transitions of both $NaCl^{35}$ and $NaCl^{37}$ were observed at a temperature of about 800°C. Values of Y_{01} and Y_{11} for both isotopes were obtained. The ω_e was measured by comparing the relative intensities of the $v=0$ line of $NaCl^{37}$ and the $v=3$ line of $NaCl^{35}$. The lines lie very close together in frequency and hence the standing wave ratio in the wave guide is fairly constant, giving reliability to the relative intensity measurements. The dipole moment μ was assumed to be the same in the two vibration states, which is probably a fair approximation within the accuracy of the intensity measurements.

NaBr

The $J=1\rightarrow 2$, and the $J=2\rightarrow 3$ transitions have been observed for $NaBr^{79}$ and $NaBr^{81}$ at a temperature of about 780°C. In addition to the Y_{01}, Y_{11}, and Y_{21}, quantities, the Y_{02}, or D_e was obtained from the two J transitions. The quadrupole coupling constant $(eqQ)_{Br^{79}}$ was measured in the $v=0$ state. The $(eqQ)_{Na}$, although a factor of about 10 smaller than $(eqQ)_{Br^{79}}$, was taken into account in interpretation of the observed hyperfine pattern. Accurate measurement of $(eqQ)_{Br}$ for excited vibrational states or for Br^{81} were not made because of difficulty with the overlap of lines of the two Br isotopic species.

NaI

The $J=2\rightarrow 3$ transition was observed at a temperature of approximately 650°C. The Y_{01}, Y_{11}, and Y_{21}

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[20] Li, Whaling, Fowler, and Lauritsen, Phys. Rev. 83, 512 (1951).

were obtained. The $F \rightarrow F+1$ and $F \rightarrow F$ hyperfine components of the transition were completely resolved. The quadrupole coupling constants of I for four different vibrational states were obtained. Effects of second order perturbation theory on the hyperfine levels were of the same order of magnitude as the experimental error, and hence the quadrupole coupling constants were determined by a least square fit to first-order theory.

KCl

The $J=0 \rightarrow 1$ transition of KCl was observed, but no very precise measurements were made because extensive data was already available from molecular beam experiments.[8]

KBr

The $J=0 \rightarrow 1$ transition of KBr had already been accurately measured by the method of molecular beams,[9] and hence no further measurements were made of the spectrum of this molecule.

KI

Lines from the $J=4 \rightarrow 5$, $5 \rightarrow 6$, and $6 \rightarrow 7$ transitions of $K^{39}I$, and a single line from the $J=5 \rightarrow 6$ transition of $K^{41}I$ have been observed at a temperature of about 690°C. The mass ratio of the potassium isotopes was calculated. Hyperfine structure was evident in the $J=4 \rightarrow 5$ transition, but only a rough measurement of $(eqQ)_I$ could be made due to the incomplete resolution.

RbCl

The $J=0 \rightarrow 1$ transition of RbCl had already been accurately measured by the method of molecular beams,[10] and hence no further measurements were made of the spectrum of this molecule.

RbBr

The $J=8 \rightarrow 9$ transition was observed at a temperature of about 730°C for $Rb^{85}Br^{79}$, $Rb^{85}Br^{81}$, and $Rb^{87}Br^{79}$. Y_{01}, Y_{11}, and Y_{21} were determined for $Rb^{85}Br^{79}$, and Y_{01} and Y_{11} for $Rb^{85}Br^{81}$, and $Rb^{87}Br^{79}$. A line was also measured for the $J=7 \rightarrow 8$ transition yielding a value of Y_{02}. The relative intensities of the three neighboring lines $v=0$ of $Rb^{87}Br^{79}$, $v=0$ of $Rb^{85}Br^{81}$, and $v=3$ of $Rb^{85}Br^{79}$ were compared and used in conjunction with the known value of ω_e to indicate how the dipole moment varies with vibration state. The mass ratios of the isotopes of both Br and Rb were calculated from the frequencies for isotopic species.

RbI

The $J=10 \rightarrow 11$, $11 \rightarrow 12$, and $12 \rightarrow 13$ transitions were observed at a temperature of about 660°C. For $Rb^{85}I$, the values of Y_{01}, Y_{11}, Y_{21} and Y_{02} were obtained; for $Rb^{87}I$, the values of Y_{01} and Y_{11}. Relative intensity measurements of the $v=0$ $Rb^{87}I$ and the $v=4$ $Rb^{85}I$ pair of lines, and of the corresponding $v=1$, $v=5$ pair of lines indicate how the dipole moment varies with vibration state. The mass ratio of the Rb isotopes was determined.

CsF

The $J=1 \rightarrow 2$ transition was observed[2] at a temperature of about 700°C and the constants Y_{01}, Y_{11}, and Y_{21} evaluated. The dipole moment was measured in the $v=0$ state.

CsCl

The $J=5 \rightarrow 6$ transition was observed[2] at a temperature of about 720°C. For $CsCl^{35}$, the Y_{01}, Y_{11}, and Y_{21} were determined. For $CsCl^{37}$, Y_{01} and Y_{11} were obtained. Measurement of the two isotopic species allowed a determination of the mass ratio of the two Cl isotopes.

CsBr

The $J=9 \rightarrow 10$, $10 \rightarrow 11$, and $11 \rightarrow 12$ transitions were observed[2] at a temperature of about 690°C. For both $CsBr^{79}$ and $CsBr^{81}$, Y_{01}, Y_{11}, and Y_{21} were determined. Y_{02} was determined for $CsBr^{79}$, using some of the information from the $CsBr^{81}$ spectra and allowing for the dependence of Y_{02} on $1/\mu^2$. ω_e was obtained very roughly from relative intensity measurements assuming no variation of dipole moment with vibration state.

CsI

The $J=15 \rightarrow 16$, $16 \rightarrow 17$, and $17 \rightarrow 18$ transitions were observed at a temperature of about 640°C. Values of Y_{01}, Y_{11}, Y_{21}, and Y_{02} were obtained.

MOLECULAR AND NUCLEAR CONSTANTS OF THE ALKALI HALIDES

In Tables I and II, most of the available molecular data on the alkali halides is included.[1–13, 21–30] Quantities in parentheses ( ) were derived from simple theoretical relations using directly measured quantities. Those in brackets [ ] were obtained by extrapolation of other information in the tables. For some quantities, such as dipole moments, there have been several determinations made by different experimenters. The most accurate value is listed in the tables, and other values are given in the notes accompanying the tables.

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

[22] P. A. Tate, Massachusetts Institute of Technology Quarterly Progress Report, July 15, 1953 (unpublished).

[23] R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) **A219**, 120 (1953).

[24] J. W. Trischka, Phys. Rev. **76**, 1365 (1949).

[25] R. G. Luce and J. W. Trischka, Phys. Rev. **83**, 851 (1951).

[26] J. W. Trischka, Phys. Rev. **74**, 718 (1948).

[27] J. C. Schwartz and J. W. Trischka, Phys. Rev. **88**, 1085 (1952).

[28] Logan, Cote, and Kusch, Phys. Rev. **86**, 280 (1952).

[29] L. Grabner and V. Hughes, Phys. Rev. **79**, 819 (1950).

[30] V. Hughes and L. Grabner, Phys. Rev. **79**, 314 (1950).

TABLE I. Molecular constants. Quantities in parentheses ( ) were derived from simple theoretical relations using directly measured quantities. Those in brackets [ ] were obtained by extrapolation of other information in the tables.

	Y_{01} Mc/sec	B_e Mc/sec	$(-Y_{11})$ α_e Mc/sec	Y_{21} γ_e kc/sec	Y_{02} D_e kc/sec	(Y_{10}) ω_e cm^{-1}	(Y_{20}) $\omega_e x_e$ cm^{-1}	(Y_{30}) $\omega_e y_e$ cm^{-1}	I_e	r_e(A)	r_e el. diff.	μ_e debye
Li^{7}F												
Li^{7}Cl^{35}												
Li^{7}Cl^{37}												
Li^{6}Br^{81}	19 161.511 ±0.07	19 162.316 ±0.07	(208.75)	(868)	[109]							
Li^{7}Br^{79}	16 650.570 ±0.05	16 651.186 ±0.05	169.09 ±0.08	(656±40)	[82]	[480]	[1.7]		30.36012	2.1704 ±0.0001		6.19 ±0.15
Li^{7}Br^{81}	16 650.002 ±0.05	16 617.617 ±0.05	168.58 ±0.08	653±40	[82]							
Li^{6}I	15 381.448 ±0.08	15 381.986 ±0.08	152.59 ±0.10	(610±20)	(69.0)							
Li^{7}I	13 286.386 ±0.08	13 286.785 ±0.08	122.62 ±0.10	455 ±50	(51.5)	450[a]	1.5[a]	0.0017[a]	38.04799	2.3919 ±0.0001		6.25 ±0.20
NaF												
NaCl^{35}	6536.86 ±0.10	6537.07 ±0.10	48.28	[145]	(8.60)	380[a]	1.0[a]		77.3331	2.3606 ±0.0001	2.48	8.5 ±0.4[b]
NaCl^{37}					(8.24)							
NaBr^{79}	4534.51 ±0.10	4534.52 ±0.10	28.25 ±0.10	85 ±30	7±3	315[a]	1.15[a,f]	0.0008[a]	111.486	2.5020 ±0.0001	2.61	
NaBr^{81}	4509.34 ±0.10	4509.35 ±0.10	28.06 ±0.10	[84]	(4.13)							
NaI	3531.759 ±0.035	3531.778 ±0.040	19.439 ±0.030	46.9 ±6.0	(2.39)	286[a]	0.75[a]	0.001[a]	143.138	2.7115 ±0.0001	2.87	
K^{39}F						405[c]	1.45[c,d]					8.62[e]
K^{39}Cl^{35} [f]	3856.370 ±0.007	3856.399 ±0.007	23.680 ±0.001	50 ±1		305[c,d]	0.9[c,d]		131.08913	2.6666 ±0.0001	2.76	10.48[g]
K^{39}Cl^{37} [f]	3746.583 ±0.007	3746.611 ±0.007	22.676 ±0.002	47 ±1								
K^{41}Cl^{35} [f]	3767.394 ±0.007	3767.421 ±0.007	22.865 ±0.001	48 ±1								
K^{39}Br^{79} [h]	2434.947 ±0.007	2434.953 ±0.007	12.136 ±0.001	23 ±1		230[c,d]	0.7[c,d]		203.4372	2.8207 ±0.0001	2.91	10.41[g]
K^{39}Br^{81} [h]	2415.075 ±0.007	2415.081 ±0.007	11.987 ±0.001	22 ±1								
K^{39}I	1825.006 ±0.030	1825.012 ±0.030	8.0337 ±0.0018	12.21 ±0.25	1.03 ±0.3	200[c,d,i]	0.5		277.00945	3.0478	3.19	11.05[e]
K^{41}I	1756.903 ±0.030											
Rb^{85}F						390[c,j]	1.3[c]					
Rb^{87}F												
Rb^{85}Cl^{35} [k]		2627.400 ±0.003	13.6008 ±0.0035	21 ±3		270[c]	0.7[c]		192.4077	2.7868 ±0.0001	2.86	
Rb^{35}Cl^{37} [k]												
Rb^{87}Cl^{35} [k]												
Rb^{85}Br^{79}	1424.8342 ±0.02	1424.840 ±0.02	5.5782 ±0.0056	7.9 ±1.1	0.45 ±0.20	181[i]	0.35[c]		354.8006	2.9448 ±0.0001	3.02	
Rb^{85}Br^{81}	1406.5944 ±0.02		5.461 ±0.011									
Rb^{87}Br^{79}	1409.0573 ±0.02		5.4744 ±0.0085									
Rb^{85}I	984.3137 ±0.012	984.3166 ±0.012	3.2806 ±0.0012	2.98 ±0.20	−0.234 ±0.035	147[i]	0.25[c]		513.5883	3.1769 ±0.0001	3.22	
Rb^{87}I	970.7601 ±0.012		3.2135 ±0.0030									
CsF	5527.27 ±0.04	5527.34 ±0.04	33.13 ±0.05	9 ±12		385[c,l]	1.23[c]		91.4603	2.3453 ±0.0001		7.874[m,n]
CsCl^{35}	2161.195 ±0.015	2161.208 ±0.015	10.085 ±0.004	7.1 ±0.7		240[c]	0.6[c]		233.9118	2.9062	3.02	10.40[o]
CsCl^{37}	2068.761 ±0.015		9.46 ±0.03									
CsBr^{79}	1081.3392 ±0.02	1081.3429 ±0.02	3.7175 ±0.0029	3.1 ±0.4	−0.27 ±0.08	171[c,i]	0.3[c]		467.5039	3.0720 ±0.0001	3.10	
CsBr^{81}	1064.5853 ±0.02		3.6313 ±0.0024	3.1 ±0.5								
CsI	708.3568 ±0.02	708.3579 ±0.02	2.0441 ±0.0020	1.45 ±0.40	−0.152 ±0.025	120[c,i]	0.2[c]		713.6686	3.3150 ±0.0001	3.36	12.1[e]

[a] See reference 21.
[b] See reference 22.
[c] See reference 23.
[d] Levi (see reference 21) gives the following values for the potassium halides:

	ω_e (cm^{-1})	$\omega_e x_e$	$\omega_e y_e$
KCl	280	0.9	0.0011
KBr	231	0.7	0.0011
KI	212	0.7	0.001.

[e] See reference 4.
[f] See reference 8.
[g] Reference 4 gives values 9.53 and 10.85 debye for the respective dipole moments of KCl and KBr.
[h] See reference 9.
[i] For the molecules NaBr, KI, RbBr, RbI, CsBr, and CsI, values of ω_e were obtained from the experimental value of Y_{02}, or D_e. These values in cm^{-1} are:

NaBr	235±60,	KI	165±35,
RbBr	169±40,	RbI	134±15,
CsBr	143±25,	CsI	103±18.

[j] Hughes and Grabner (see reference 28) obtain $w_e = 340 \pm 68$ cm^{-1}.
[k] See reference 10.
[l] Trischka (see reference 26) reports $\omega_e = 270 \pm 30$ cm^{-1} from relative intense measurements.
[m] See reference 24.
[n] The present work yielded a value of 7.85±0.25 for the dipole moment of CsF.
[o] See reference 25.

TABLE II. Electric quadrupole coupling constants and dipole moments.

Molecule	Nucleus and ref.	eqQ/h (Mc/sec)					μ_{el}(debye)		
		$v=0$	$v=1$	$v=2$	$v=3$	Av. over vib. state	$v=0$	$v=1$	$v=2$
Li^{6}F	[a]						$\left(\frac{450.2}{I_{v=0}}\right)^{\frac{1}{2}}$	$\left(\frac{469.6}{I_{v=1}}\right)^{\frac{1}{2}}$	
Li^{7}F	Li[b]					+0.408			
Li^{7}Cl	Li[b]					+0.192			
Li^{7}Br^{79}	Li[b]					+0.184			
Li^{7}Br^{79}	Br	+37.20 ±0.45					6.19 ±0.15		
Li^{7}Br^{81}	Br	+30.71 ±0.40	+33.19 ±0.20						
Li^{7}I	Li[b]					+0.172			
Li^{7}I	I	−198.15 ±0.30	−206.5 ±0.30	−212.6 ±1.5			6.64 ±0.20		
Li^{6}I	I	−199.43 ±0.30	−206.8 ±2.0						
NaF	Na[b]					−8.12			
NaCl	Na[b]					−5.40	8.5		
NaBr	Na[b]					−4.68			
NaBr^{79}	Br	+58±2							
NaI	Na[b]					−3.88			
NaI	I	−259.87 ±0.60	−264.52 ±0.65	−267.59 ±0.40	−271.03 ±0.20				
K^{39}F	K[c]	−7.938	−7.828	−7.744	−7.658		7.33	Increase of about 0.8% per vibration	
K^{39}Cl^{35}	K[d]	−5.656	−5.622	−5.571	−5.511		10.48		10.69
K^{39}Cl^{35}	Cl[d]	<0.040	+0.075	+0.237	+0.393				
K^{39}Br^{79}	K[e]	−5.003	−4.984	−4.915			10.41		9.93
K^{39}Br^{79}	Br[e]	+10.244	+11.244	+12.204					
K^{39}I	I[f]	−60±10					11.05		
Rb^{85}F	Rb[g]	−70.31	−69.54	−68.71	−67.99				
Rb^{85}Cl^{35}	Rb[h]	−52.675	−52.306	−51.903					
Rb^{85}Cl^{35}	Cl[h]	+0.774	+0.612	+0.470					
CsF	Cs[i]	+1.240					7.874	7.945	
CsCl	Cs[j]	<4					10.40		
CsCl	Cl[j]	<3							
CsI	[f]						12.1		

[a] See reference 27.
[b] See reference 28.
[c] See reference 29.
[d] See reference 8.
[e] See reference 9.
[f] See reference 4.
[g] See reference 30.
[h] See reference 10.
[i] See reference 24.
[j] See reference 25.

GENERAL CONSIDERATIONS CONCERNING TREATMENT OF DATA AND THE NUMERICAL RESULTS

The quantities $[Y_{01}+2Y_{02}(J+1)^2]$, Y_{11}, and Y_{21} for the molecules investigated in this paper were obtained from least square fits to Eq. (1), for lines of a given J transition. Since in most of the molecules, more than three vibrational states were measured, these three molecular parameters could be determined somewhat more accurately than indicated by the errors involved in individual measurements. The Y_{02} and Y_{01} values were also obtained from least square fits to Eq. (1) for lines from different J transitions but the same vibration state.

In general, the accuracy with which Y_{02} is determined is quite poor, and in many cases it gives rise to the principle error in Y_{01}. In calculating the mass ratio of two isotopic species, A and B, the ratio $Y_{01}{}^A/Y_{01}{}^B$ enters, and this ratio is quite insensitive to the error in Y_{02}. Hence, in Table III, more significant figures in the values of Y_{01} may be listed than might at first glance appear warranted, in view of the quoted errors. Use of the theoretical dependence of Y_{11} and Y_{21} on $1/\mu^{\frac{3}{2}}$ and $1/\mu^2$, respectively, also helps to decrease errors in the ratio $Y_{01}{}^A/Y_{01}{}^B$ and hence in the mass ratio. Here μ is the reduced mass.

From the values of Y_{02}, the vibration frequencies ω_e can be calculated via the relation $\omega_e=[4B_e{}^3/D_e]^{\frac{1}{2}}$. Thus, values of ω_e have been determined having approximately one-half the percentage error of D_e. In all but one of the cases where this determination was made, the ω_e agrees within the experimental error with the vibration frequencies recently determined by Barrow and Caunt.[23] Nevertheless, our vibration frequencies are consistently lower than those obtained by Barrow and Caunt. Since their method is much more prone to large *systematic* errors than that used here, the results obtained by the above method are of value.

TABLE III. Mass ratios of isotopes obtained from the microwave spectra of alkali halides. An asterisk indicates data from measurements by molecular beam techniques.

	Ratio	Molecule
Cl^{35}/Cl^{37}	0.9459781 ± 0.0000030	CsCl
Cl^{35}/Cl^{37}	0.9459803 ± 0.0000015	$K^{39}Cl$ [a]*
Br^{79}/Br^{81}	0.9753068 ± 0.0000045	CsBr
Br^{79}/Br^{81}	0.9752999 ± 0.0000065	$Rb^{85}Br$
Br^{79}/Br^{81}	0.9753088 ± 0.0000020	$K^{39}Br$ [b]*
Li^{6}/Li^{7}	0.8573423 ± 0.0000020	LiI
K^{39}/K^{41}	0.9512250 ± 0.0000070	KI
K^{39}/K^{41}	0.9512189 ± 0.0000015	KCl^{35} [a]*
Rb^{85}/Rb^{87}	0.9770177 ± 0.0000045	RbI
Rb^{85}/Rb^{87}	0.9770146 ± 0.0000055	$RbBr^{79}$

[a] See reference 3.
[b] See reference 4.

In the cases of RbBr and RbI, relative intensities of rotational transitions for various vibrational states were used to determine roughly the change of dipole moment μ with vibration. The relative intensity for vibration states of excitation v_1 and v_2 is given by $[(u_{v1})^2/(u_{v2})^2]\exp[-h\omega_e(v_1-v_2)/kT]$, so that the dipole moment ratio can be determined if ω_e and T are known. For both RbBr and RbI the data indicate a decrease of u with increasing vibration state.

A. The Potential Coefficients

The vibration frequency ω_e and the first anharmonic term in the vibration spectra, $\omega_e x_e$, are known for most of the alkali halides to within an accuracy of about 10 percent. These constants, in conjunction with the Y_{01}, Y_{11}, and Y_{21} values afford sufficient information for the computation of the first four potential coefficients in the Dunham expansion. The potential energy has been expressed by Dunham in the form

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

where $\xi=(r-r_e)/r_e$, $a_0=\omega_e^2/4B_e$, and both B_e and ω_e are expressed in cm^{-1}.

The dependence of all the a_i's on the value of ω_e limits the accuracy with which the potential coefficients are known. In addition, the errors increase as one goes to successively higher terms. Table IV gives the coefficients a_0, a_1, a_2, and a_3. The quantities $\mathcal{A}_1$, $\mathcal{A}_2$, and $\mathcal{A}_3$ appearing beside the corresponding a's are explained in the following section. Rough estimates of the reliability of the a's would be as follows:

	Error due to uncertainty in ω_e	Error due to uncertainty in $\omega_e x_e$
a_0	±20%	
a_1	± 7%	
a_2	±20%	± 8%
a_3	±50%	±25%

The values of ω_e and $\omega_e x_e$ used were those given by Barrow and Caunt for the K, Rb, and Cs halides, and those given by Levi for the Na halides and for LiI. The ω_e and $\omega_e x_e$ for LiBr were estimated to be 480 cm^{-1}, and 1.7 cm^{-1}, respectively. Even in cases such as CsF and CsBr where Barrow and Caunt's values appear to be too high, they were none the less used for the sake of uniformity.

The potential constants can be related to the physical properties of the molecules. Rittner[31] has recently used an expression for the energy of a completely ionic diatomic molecule of the form,

$$W(r)=\varphi+Ae^{-r/\rho}-c'/r^6+\tfrac{1}{2}h\nu_0+(h\nu_0/e^{h\nu_0/kT}-1)-\tfrac{1}{2}kT,$$

where

$$\varphi=-\frac{e^2}{r}-\frac{e^2(\alpha_1+\alpha_2)}{2r^4}-\frac{2e^2\alpha_1\alpha_2}{r^7},$$

and A is a repulsion constant. Here φ is the electrostatic contribution to the potential energy, α_1 and α_2 are the polarizabilities[32] of the alkali and halogen ions, respectively, ρ is a repulsion constant, and c' is a measure of Van der Waal's attractive force between ions. If $W(r)$ is expanded about r_e, the resulting expression is

$$W(r-r_e)=C+hc\mathcal{A}_0\left(\frac{r-r_e}{r_e}\right)^2+hc\mathcal{A}_1\mathcal{A}_0\left(\frac{r-r_e}{r_e}\right)^3+hc\mathcal{A}_2\mathcal{A}_0\left(\frac{r-r_e}{r_e}\right)^4+hc\mathcal{A}_3\mathcal{A}_0\left(\frac{r-r_e}{r_e}\right)^5,$$

where C is a constant term of no importance to the potential coefficients, and

$$\mathcal{A}_0=-\frac{1}{hc}\left\{\frac{e^2}{r_e}+\frac{5e^2(\alpha_1+\alpha_2)}{r_e^4}+\frac{21c'}{r_e^6}+\frac{56e^2\alpha_1\alpha_2}{r_e^7}-\frac{r_e^2A}{2\rho^2}e^{-r_e/\rho}\right\},$$

$$\mathcal{A}_1=\frac{1}{hc\alpha_0}\left\{\frac{e^2}{r_e}+\frac{10e^2(\alpha_1+\alpha_2)}{r_e^4}+\frac{56c'}{r_e^6}+\frac{168e^2\alpha_1\alpha_2}{r_e^7}-\frac{r_e^3A}{6\rho^3}e^{-r_e/\rho}\right\},$$

$$\mathcal{A}_2=-\frac{1}{hc\alpha_0}\left\{\frac{e^2}{r_e}+\frac{17.5e^2(\alpha_1+\alpha_2)}{r_e^4}+\frac{126c'}{r_e^6}+\frac{420e^2\alpha_1\alpha_2}{r_e^7}-\frac{r_e^4A}{24\rho^4}e^{-r_e/\rho}\right\},$$

$$\mathcal{A}_3=\frac{1}{hc\alpha_0}\left\{\frac{e^2}{r_e}+\frac{28e^2(\alpha_1+\alpha_2)}{r_e^4}+\frac{252c'}{r_e^6}+\frac{924e^2\alpha_1\alpha_2}{r_e^7}-\frac{r_e^5A}{120\rho^5}e^{-r_e/\rho}\right\}.$$

The agreement of the quantities $\mathcal{A}_1$, $\mathcal{A}_2$, and $\mathcal{A}_3$ with the experimentally determined coefficients a_1, a_2, and a_3 is a measure of the applicability of Rittner's expression for the energy. For the purpose of calculating $\mathcal{A}_1$, $\mathcal{A}_2$, and $\mathcal{A}_3$, the experimental values of α_1 and α_2 can be used. London[33] has shown how the Van der Waal's constant c' can be estimated with the aid of the

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[31] E. S. Rittner, J. Chem. Phys. **19**, 1030 (1951).

[32] Values used are those of L. Pauling, Proc. Roy. Soc. (London) **A114**, 181 (1927). See also reference 31.

[33] F. London, Z. Physik **63**, 245 (1930).

optically determined energy levels of the alkali ions and the electron affinities of the halogen ions.

From the experimental values of ω_e and r_e, both A and ρ can be determined from the equations,

$$(dW/dr)_{r_e}=0,$$

$$(d^2W/dr^2)_{r_e}=\text{force constant.}$$

This determination of course makes $\mathcal{A}_0$ identical to a_0. The values computed for $\mathcal{A}_1$, $\mathcal{A}_2$ and $\mathcal{A}_3$ are listed in parenthesis in Table IV for comparison with the experimental values.

The agreement must be considered quite satisfactory with the exception of LiBr and LiI.

B. Electron Diffraction Values of Internuclear Distances

On comparing the r_e values obtained by microwave spectroscopy with those obtained from electron diffraction measurements (corrected for the average over vibration states[31]), it is seen that the electron diffraction measurements are consistently larger, in most cases by amounts exceeding the experimental error. The magnitude of the discrepancy appears to vary systematically, being of the order of four percent for the lighter molecules, and decreasing progressively for the heavier molecules. (See Table I.) A possible reason for this discrepancy is a small percentage of dimerization of the vapors. This would not affect any of the spectroscopic results, but would make the electron diffraction values larger, since in a dimer, one would expect the average internuclear distance to be larger than that for a monomer.

TABLE IV. Potential coefficients a_0, a_1, a_2, and a_3 are determined from the experimental data. $\mathcal{A}_1$, $\mathcal{A}_2$, and $\mathcal{A}_3$ are obtained from Rittner's theoretical expressions.

	a_0	a_1	$(\mathcal{A}_1)$	a_2	$(\mathcal{A}_2)$	a_3	$(\mathcal{A}_3)$
LiF							
LiCl							
LiBr	1.02	−2.45	(−1.71)	5.5	(+1.18)	−14	(+ 1.54)
LiI	1.14	−2.56	(−1.75)	6.0	(1.68)	−15	(+ 0.28)
NaF							
NaCl	1.66	−3.14	(−3.01)	9.2	(5.71)	−31	(− 8.0)
NaBr	1.64	−3.16	(−3.09)	7.4	(6.0)	−16	(− 8.2)
NaI	1.74	−3.23	(−3.32)	8.8	(7.0)	−26	(−11.0)
KF	1.41						
KCl	1.81	−3.43	(−3.46)	10.0	(7.7)	−32	(−12.8)
KBr	1.63	−3.35	(−3.35)	9.1	(7.4)	−26	(−11.5)
KI	1.64	−3.41	(−3.50)	9.1	(7.9)	−25	(−13.4)
RbF	1.78						
RbCl	2.08	−3.66	(−3.92)	11.8	(10.0)	−42	(−19.1)
RbBr	1.73	−3.49	(−3.53)	10.3	(8.1)	−33	(−13.7)
RbI	1.64	−3.49	(−3.55)	10.2	(8.0)	−32	(−13.6)
CsF	2.01	−3.21	(−3.35)	8.4	(7.0)	−26	(−10.8)
CsCl	2.00	−3.59	(−3.83)	10.6	(9.5)	−35	(−17.6)
CsBr	2.03	−3.72	(−4.03)	11.7	(10.5)	−41	(−20.8)
CsI	1.53	−3.45	(−3.53)	9.2	(7.9)	−26	(−13.2)

TABLE V. Internuclear distances and additivity of ionic radii. All distances are in angstrom units.

	F Inter-nuclear distance	XCl-XF differ-ence	Cl Inter-nuclear distance	XBr-XCl differ-ence	Br Inter-nuclear distance	XI-XBr differ-ence	I Inter-nuclear distance
Li					2.1704	0.2215	2.3919
NaH-LiH difference					0.3316		0.3196
Na			2.3606	0.1414	2.5020	0.2095	2.7115
KH-NaH difference			0.3060		0.3187		0.3363
K			2.6666	0.1541	2.8207	0.2271	3.0478
RbH-KH difference			0.1202		0.1241		0.1291
Rb			2.7868	0.1580	2.9448	0.2321	3.1769
CsH-RbH difference			0.1194		0.1272		0.1381
Cs	2.3453	0.5609	2.9062	0.1658	3.0720	0.2430	3.3150

C. Ionic Radii

It has been found that the sum of assigned ionic radii in alkali halide crystals can satisfactorily account for the observed internuclear distances in the crystals[34] if certain factors concerning the crystal environment are taken into account. This might suggest a similar degree of constancy of ionic bonding radii in the vapors. In a former paper,[2] this has been investigated for the molecules KCl, KBr, CsCl, and CsBr. Table V gives a more complete picture of how constant the ionic radii are. Variations in the differences $r_e(XH_1)$ minus $r_e(XH_2)$ for various alkalis (X's) or $r_e(X_1H)$ minus $r_e(X_2H)$ for various halogens indicate deviation from the so-called "additivity rule."

Schomaker and Stevenson[35] have modified the additivity criterion by allowing the bond distance to be sensitive to the relative amounts of ionic and covalent character present. Their modification of the internuclear distance depends linearly upon the electronegativity difference, and hence does not affect the departure from additivity present in Table V. A quadratic dependence on the electronegativity difference would affect the additivity departure. However, the alkali bromide-iodide sequence is inconsistent with any simple scheme for modifying the internuclear distances that involves only the relative electronegativities. This might be expected, since the polarization of the atomic electrons plays an important role in determining the structure of alkali halide molecules in the vapor state, and the polarizabilities vary greatly from one alkali or halogen to the next.

Undoubtedly similar deviations from the additivity rule as large as 0.01A or 0.02A exist for other types of bonds. However, the alkali halides afford a particularly clear case for examination of these deviations, since

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[34] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1944), second edition, p. 343.

[35] V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. **63** 37 (1941).

TABLE VIa. Ionic radii in angstrom units.

Ion	Diatomic molecule set No. 1	Diatomic molecule with allowance made for polarization and bond type set No. 2	Solid crystal
Li^+	0.478	0.498	0.607
Na^+	0.825	0.786	0.958
K^+	1.131	1.091	1.331
Rb^+	1.251	1.217	1.484
Cs^+	1.371	1.358	1.656
F^-	0.974	1.100	1.341
Cl^-	1.535	1.485	1.806
Br^-	1.689	1.600	1.951
I^-	1.917	1.778	2.168

they are a large group of molecules with essentially the same simple type of bond.

It is of course the great accuracy of microwave determinations of internuclear distances which allows the relatively small deviations from additivity of ionic radii to be examined in detail. If precision of only about 1 percent is required for internuclear distances, a set of ionic radii can be constructed which satisfactorily gives internuclear distances for the alkali halides. If a standard radius is chosen by Pauling's method[36] for KCl, for example, the ionic radii listed in set No. 1 of Table VIa are obtained. The internuclear distances given by the radii are compared with measured values in Table VIb.

If internuclear distances are determined simply by an attractive Coulomb potential A/r and a repulsive potential B/r^n, it can be shown that the internuclear distance should be $r=(nB/A)^{1/(n-1)}$. In most crystalline alkali halides $A=e^2$ times the Madelung constant 1.748, and the repulsion is due to six nearest neighbors. In an isolated molecule, $A=e^2$, and the repulsion is due to only one nearest neighbor. To a rough approximation, r is, in fact, given by $(nB/A)^{1/(n-1)}$, where n and B are obtained from available information on solids. However, good agreement cannot be expected, since the values of r in isolated molecules are considerably different from those in solids, and the appropriate values of n may be different. In an isolated molecule, there is an additional attractive potential due to the polarizability of each ion. Allowing for this attractive interaction, the internuclear distance should be approximately $r=[nB/A]^{1/(n-1)}-[4(\alpha_1+\alpha_2)/(n-1)r^2]$, where α_1 and α_2 are the polarizabilities of the two ions involved. Allowing for the term $-4(\alpha_1+\alpha_2)/(n-1)r^2$ lessens the agreement between experimental measurements and predictions of internuclear distance from this simple extrapolation of information about the solid alkali halides.

TABLE VIb. Internuclear distances for the gaseous alkali halides.

Molecule	Observed internuclear distance in angstrom units	Sum of ionic radii from set No. 1 of Table VIa	Calculated internuclear distance from ionic radii of set No. 2, Table VIa
LiF		1.452	1.527
LiCl		2.013	2.022
LiBr	2.1704	2.167	2.166
LiI	2.3919	2.395	2.392
NaF		1.799	1.840
NaCl	2.3606	2.361 (standard)	2.356
NaBr	2.5020	2.514	2.500
NaI	2.7115	2.742	2.727
KF	2.55[a]	2.105	2.129
KCl	2.6666	2.666 (standard)	2.666 (standard)
KBr	2.8207	2.821 (standard)	2.815
KI	3.0478	3.048 (standard)	3.051
RbF		2.225	2.246
RbCl	2.7868	2.787 (standard)	2.793
RbBr	2.9448	2.941	2.944
RbI	3.1769	3.168	3.182
CsF	2.3453	2.345 (standard)	2.346
CsCl	2.9062	2.906 (standard)	2.911
CsBr	3.0720	3.060	3.065
CsI	3.3150	3.288	3.307

[a] Measured roughly by resonance between Stark components with molecular beam techniques. (See reference 29.)

A useful empirical expression for internuclear distances of these molecules can be constructed which fits the experimental data to an accuracy of about 0.005 A. Such an expression is

$$r=r_1+r_2-0.410[(\alpha_1+\alpha_2)/r^3]+0.175[(X_F-X_{Cs})-(X_2-X_1)],$$

where X_1 and X_2 are the electro negatives of atoms 1 and 2, respectively. The values of r_1 and r_2 in this expression are taken equal to those for the crystal ionic radii obtained by Pauling[34] multiplied by the factor 0.820. From the discussion above, the ratio of distances in the vapor and crystalline phases may be expected to be

$$\frac{r\text{ (vapor)}}{r\text{ (crystal)}}=\left[\frac{nB}{(6nB/1.748)}\right]^{1/(n-1)}=(0.29)^{1/(n-1)}.$$

This ratio equals 0.820 when n is between 7 and 8, which is a reasonable average value for n in the solid alkali halides. As is expected, the polarization term shortens the internuclear distance. The term involving the electronegativities is somewhat similar to that introduced by Schomaker and Stevenson. It has little theoretical justification, especially since the alkali halides are almost entirely ionic. However, its introduction does allow an improved fit to experimentally determined internuclear distances.

Table VIa lists the set of radii (No. 2) which are 0.820 times Pauling's radii[37] for solid alkali halides, and Table VIb allows comparison between calculated and measured internuclear distances. These radii are not of great interest in themselves, but they should allow fairly accurate estimation of internuclear distances of the alkali halides which have not yet been measured.

D. Electric Quadrupole Coupling Constants

In "ionic" substances such as the alkali halides the quadrupole coupling constant is the resultant of several

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[36] L. Pauling, reference 34, p. 344.

[37] L. Pauling, reference 34, p. 64.

small terms of different signs, and hence it is particularly difficult to predict theoretically.

Quadrupole coupling constants of the halogens are most easily treated, since for a covalently bonded halogen, the single *p* electron missing from the valence shell of the halogen produces a large coupling constant,[38] and in some of the alkali halides the covalent character is large enough (although quite small) to make this source of coupling dominant. An isolated negative halogen ion has zero quadrupole coupling. For covalent bonds, coupling constants near −110.4 Mc/sec, 769.8 Mc/sec, and −2292.4 Mc/sec are to be expected for Cl^{35}, Br^{79}, and I^{127}, respectively (F has zero quadrupole moment). Coupling constants for these atoms in the alkali halides are very much less than the above numbers, but are always of the same sign. In some cases (such as NaI) the coupling constants are large enough to indicate fairly clearly that the relatively small covalent character produces the dominant contribution to the coupling constant. In others (such as KCl), the coupling constants are so small that other effects are surely of importance. These include contributions due to the electric field of the neighboring alkali, and that due to distortions of the valence shell of electrons by polarization.

The quadrupole coupling constants of the halogens probably give the clearest available evidence on the amount of covalent character in the structure of the alkali halides. If the measured coupling constants are devided by the coupling constant given above for purely covalent bonds, one obtains the results listed in Table VII. The covalent character of the alkali halide bonds is given approximately by these numbers.[38] It may be noted that in accordance with expectations the covalent character obtained from Table VII decreases with increasing electronegativity of the halogens I, Br, and Cl. However, LiI appears to be slightly less covalent than NaI from this table in spite of the fact that the electronegativity difference between Li and I is less than that between Na and I. This may be due to effects of polarization or other contributions to the coupling constant in the two molecules, or it may simply be due to the fact that covalent character depends on other variables in addition to the electronegativity difference. The small size of Li, for example, can be expected to lower the energy of the ionic state of LiI by comparison with that of NaI.

The results listed in Table VII give further evidence that the alkali halides are almost purely ionic. They also show, however, that some of the alkali halides involving the least electronegativity differences have a small amount of covalent character.

Quadrupole coupling constants for the alkalis are more difficult to understand than those for the halogens because both the ionic and the atomic states of the alkali elements have spherical distributions of electrons and hence zero quadrupole coupling constants. The coupling constants observed in the molecule are evidently due to distortions or excitations of the electron shells about the alkali atoms, and to charges on the adjacent halogens.

TABLE VII. Ratio of quadruple coupling constant for the halogens to that due to a single *p* electron.

Molecule	Ratio
KCl	0.0004
KBr	0.013
KI	0.026
NaBr	0.075
NaI	0.113
LiBr	0.048
LiI	0.086

E. Electric Dipole Moments

Table VIII lists the values of the dipole moments calculated from Rittner's[31] expression,

$$\mu = er_e - \frac{[r_e^4 e(\alpha_1+\alpha_2)+4er_e\alpha_1\alpha_2]}{r_e^6-4\alpha_1\alpha_2},$$

where α_1 and α_2 are the ionic polarizabilities. The experimental dipole moments obtained by molecular beams or microwave spectroscopy are also listed, for comparison. The calculated values are consistently lower, even for the LiBr and LiI, which have considerable covalent character. The polarizabilities may possibly be in error, but it seems more likely that the disagreement is primarily because the classical model used is not adequate for computing reliable induced dipole moments.

TABLE VIII. Comparison of dipole moments calculated from polarized ion model with experimental values.

	μ calculated	μ experimental
LiF		
LiCl		
LiBr	5.139	6.25 ±0.15
LiI	5.375	6.64 ±0.20
NaF		
NaCl	7.770	8.5 ±0.4
NaBr	7.959	
NaI	7.993	
KF		
KCl	9.180	10.48 ±0.03
KBr	9.576	10.41 ±0.02
KI	9.922	(11.05)
RbF		
RbCl	9.450	
RbBr	9.925	
RbI	9.762	
CsF	7.278	7.874±0.012
CsCl	9.363	10.40 ±0.10
CsBr	9.974	
CsI	10.612	(12.1)

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[38] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

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APPENDIX I. MEASURED FREQUENCIES IN MC/SEC FOR MICROWAVE TRANSITIONS OF THE ALKALI HALIDES

LiBr: $J=0\rightarrow 1$.

Transition	$v=0$ state	$v=1$	$v=2$
	Li^{7}Br^{79}		
$F=3/2\rightarrow 5/2$	33 130.30±0.10		32 461.52±0.10
$F=3/2\rightarrow 3/2$	33 139.50±0.10		
$F=3/2\rightarrow 1/2$	33 122.44±0.30		
	Li^{7}Br^{81}		
$F=3/2\rightarrow 5/2$	33 063.96±0.10	32 729.14±0.10	32 397.13±0.10
$F=3/2\rightarrow 3/2$	33 071.53±0.10	32 737.53±0.10	
$F=3/2\rightarrow 1/2$	33 057.54±0.25	32 722.60±0.10	
	Li^{6}Br^{81}		
$F=3/2\rightarrow 5/2$	38 112.72±0.10		

LiI: $J=0\rightarrow 1$.

Transition	$v=0$	$v=1$	$v=2$
	Li^{7}I		
$F=5/2\rightarrow 7/2$	26 460.14±0.10	26 217.11±0.10	25 975.62±0.20
$F=5/2\rightarrow 5/2$	26 418.44±0.10	26 173.72±0.10	25 931.21±0.20
$F=5/2\rightarrow 3/2$	26 477.88±0.10	26 235.65±0.10	25 995.48±0.40
	Li^{6}I		
$F=5/2\rightarrow 7/2$	30 620.17±0.10	30 317.79±0.20	
$F=5/2\rightarrow 5/2$	30 578.28±0.10		
$F=5/2\rightarrow 3/2$	30 638.10±0.15	30 336.40±0.40	

NaCl: $J=1\rightarrow 2$.

$v=0$	$v=1$	$v=2$	$v=3$
	NaCl^{35}		
26 051.1±0.75	25 857.6±0.75	25 666.5±0.75	25 473.9±0.75
	NaCl^{37}		
25 493.9±0.75	25 307.5±0.75	25 120.3±0.75	

NaBr

Rotational transition	Hyperfine transition	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$
			NaBr^{79}			
$J=1\rightarrow 2$	$F=5/2\rightarrow 7/2$ $3/2\rightarrow 5/2$	18 080.13±0.10	17 968.42±0.20	17 856.57±0.10		
	$F=1/2\rightarrow 3/2$ $5/2\rightarrow 5/2$	18 095.95±0.15[a]	17 082.5±0.8[a]			
	$F=3/2\rightarrow 3/2$	18 070.07±0.10				
$J=2\rightarrow 3$	$F=7/2\rightarrow 9/2$ $5/2\rightarrow 7/2$	···	26 952.98±0.10[a]	26 785.63±0.10[a]	26 621.8±0.8[a]	26 455.8±0.8[a]
	$F=3/2\rightarrow 5/2$ $1/2\rightarrow 3/2$	···	26 956.30±0.30[a]	26 789.51±0.30[a]	···	···
			NaBr^{81}			
$J=1\rightarrow 2$	$F=5/2\rightarrow 7/2$ $3/2\rightarrow 5/2$	17 980.48±0.20[a]	17 868.49±0.10			
	$F=3/2\rightarrow 3/2$	17 971.0±0.5[a]				
$J=2\rightarrow 3$	$F=7/2\rightarrow 9/2$ $5/2\rightarrow 7/2$	···	26 803.55±0.10[a]	26 639.9±0.8[a]	26 475.0±0.8[a]	
	$F=3/2\rightarrow 5/2$ $1/2\rightarrow 3/2$	···	26 806.32±0.40[a]	26 643.2±0.8[a]	···	

[a] Due to overlap of neighboring lines, the above figures do not necessarily represent true line positions, but rather maxima corresponding to the designated transition. The true line positions can be calculated from these.

NaI: $J=2\rightarrow 3$.

Transition	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$
$F=9/2\rightarrow 11/2$	21 135.35±0.20	···	20 903.62±0.20	20 788.73±0.20	20 674.43±0.2
$F=7/2\rightarrow 9/2$	21 137.49±0.20	21 021.50±0.20	20 906.05±0.20	20 791.24±0.20	20 676.96±0.2
$F=5/2\rightarrow 7/2$	21 124.58±0.20	21 008.40±0.20	20 892.92±0.20	20 777.70±0.20	20 663.68±0.2
$F=3/2\rightarrow 5/2$	21 111.67±0.20	···	20 879.61±0.20	20 764.43±0.40	···
$F=1/2\rightarrow 3/2$	21 108.64±0.20	···	···	···	···
$F=9/2\rightarrow 9/2$	···	20 970.52±0.20	20 854.59±0.20	20 738.98±0.20	···
$F=7/2\rightarrow 7/2$		same frequencies as $7/2\rightarrow 9/2$ transitions			
$F=5/2\rightarrow 5/2$	21 148.85±0.20	···	20 917.89±0.20	20 803.00±0.20	···
$F=3/2\rightarrow 3/2$	21 141.93±0.20	···	···	···	···
$F=1/2\rightarrow 1/2$	···	···	···	···	···

KI

v	$J=4\rightarrow 5$	$J=5\rightarrow 6$	$J=6\rightarrow 7$
		$K^{39}I$	
0	18 209.77±0.10[a]	21 851.32±0.10	25 492.81±0.15
1	18 129.61±0.20	21 755.19±0.10	25 380.71±0.15
2	···	21 659.38±0.10	25 268.95±0.15
3	···	21 563.91±0.10	25 157.04±0.30
5	···	21 373.63±0.10	···
6	···	21 279.07±0.10	···
7	···	21 184.73±0.10	···
		$K^{41}I$	
0		21 036.78±0.10	

[a] The shape of this line was used to obtain $(eqQ)_I$. The frequency given is the peak of the line. A secondary maximum occurred at a frequency 18 208.97 ±0.10 Mc/sec.

RbBr

Rotational transition	Vibration state	$Rb^{85}Br^{79}$	$Rb^{87}Br^{79}$	$Rb^{85}Br^{81}$
$J=8\rightarrow 9$	0	25 596.03±0.10	25 312.99±0.10	25 268.84±0.10
	1	25 495.98±0.10	25 214.65±0.10	25 170.56±0.10
	2	25 396.14±0.10	25 116.57±0.10	25 072.63±0.10
	3	25 296.52±0.10		
	4	25 197.32±0.10		
$J=7\rightarrow 8$	0	22 752.29±0.10		

RbI

Rotational transition	Vibration state	$Rb^{85}I$	$Rb^{87}I$
$J=12\rightarrow 13$	0	25 547.52±0.10	25 196.01±0.10
	1	25 462.28±0.10	25 112.84±0.10
	2	25 377.33±0.10	25 029.38±0.10
	3	25 292.65±0.10	
	4	25 207.88±0.20	
	5	25 123.45±0.10	
	6	25 038.99±0.10	
$J=11\rightarrow 12$	1	23 503.98±0.10	
	2	23 425.51±0.10	
$J=10\rightarrow 11$	0	21 617.58±0.10	

CsF: $J=1\rightarrow 2$.

Vibration state	Frequency
0	22 038.51±0.20
1	21 898.21±0.40
2	21 757.58±0.60
3	21 617.09±0.60
4	21 477.5±1.0

CsCl: $J=5\rightarrow 6$.

Vibration state	$CsCl^{35}$	$CsCl^{37}$
0	25 873.11±0.10	24 767.86±0.10
1	25 752.16±0.20	24 654.86±0.30
2	25 631.58±0.20	24 541.40±0.50
3	25 511.25±0.20	
4	25 390.36±0.40	
5	25 270.0 ±0.6	
6	25 150.1 ±0.6	
7	25 031.0 ±0.6	
8	24 911.2 ±0.6	

CsBr

Isotopic species	Vibration state	$J=9\rightarrow 10$	$J=10\rightarrow 11$	$J=11\rightarrow 12$
$CsBr^{79}$	0	21 588.57±0.10	23 747.17±0.10	···
	1	21 514.48±0.20	23 665.60±0.20	25 816.53±0.20
	2	21 440.65±0.20	23 583.87±0.20	25 648.95±0.20
	3	21 366.36±0.20	23 502.95±0.20	25 550.22±0.20
	4	21 292.40±0.20	···	···
	5	21 218.66±0.20	23 340.26±0.20	
	6	···	23 259.19±0.20	
	7		23 178.25±0.20	
	8		23 097.97±0.20	
$CsBr^{81}$	0	21 254.44±0.10	23 379.53±0.10	25 504.69±0.10
	1	···	23 299.79±0.20	···
	2		23 220.22±0.20	
	3		23 140.61±0.20	
	4		23 061.38±0.20	

CsI

Vibration state	$J=15\rightarrow 16$	$J=16\rightarrow 17$	$J=17\rightarrow 18$
0	22 632.26±0.10	24 046.40±0.10	25 460.53±0.10
1	22 567.02±0.10	23 976.96±0.10	25 387.04±0.10
2	···	23 907.70±0.10	25 313.66±0.10
3		23 838.47±0.10	···

APPENDIX II. DATA FOR DETERMINATION OF DIPOLE MOMENTS.

LiBr

Data on $J=0\rightarrow 1$, $F=3/2\rightarrow 5/2$, $v=0$, Li^7Br^{79} line.

Voltage (volts)	Frequency (Mc/sec)
+ 4.0	33 130.30±0.10
+27.0	33 132.02±0.10
+50.2	33 136.96±0.10

LiI

Data on $J=0\rightarrow 1$, $F=5/2\rightarrow 7/2$, $v=0$, Li^7I line.

Voltage (volts)	Frequency (Mc/sec)
0	26 460.14±0.10
23.3	26 462.23±0.10
47.0	26 468.60±0.20
70.3	26 478.56±0.20

CsF

Data on $J=1\rightarrow 2$, $v=0$, line.

Voltage (volts)	Frequency (Mc/sec)	
	$M=0$ component	$M=1$ component
0	22 038.51±0.20	22 038.51±0.20
25[a]	22 034.05±0.30	22 039.89±0.30
50[a]	22 026.63±0.40	22 047.31±0.40
75[a]	22 013.68±0.50	22 056.21±0.50

[a] These are not the true voltages, but the dipole moment was determined by direct comparison with the OCS molecule. The actual voltage is within 10 percent of the stated values.

Calibration of electric field strength in guide *vs* voltage on Stark plate, using CH_3Cl^{37} ($J=0\rightarrow 1$, $F=3/2\rightarrow 5/2$, $K=0$ line).

Voltage (volts)	Frequency (Mc/sec)
−4.0	26 179.22±0.05
19.3	26 179.35±0.05
43.0	26 179.78±0.05
66.3	26 180.53±0.10
89.5	26 181.58±0.10
136.6	26 184.79±0.10