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

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

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

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

PHYSICAL REVIEW VOLUME 91, NUMBER 6 SEPTEMBER 15, 1953

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

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

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

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

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

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

	$v=0$	1	2
$(eqQ)_K$ Mc/sec	−5.003±0.003	−4.984±0.003	−4.915±0.003
$(eqQ)_{Br}$ Mc/sec	+10.244±0.006	+11.224±0.006	+12.204±0.006
μ Debye	10.41 ±0.05		9.93 ±0.05

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

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

I. INTRODUCTION

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

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

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

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

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

	4,5/2	3,5/2	3,3/2	2,5/2	2,3/2	2,1/2	1,5/2	1,3/2	1,1/2	0,3/2
4,5/2	$-.05A$ $-.05B$ $-E$									
3,5/2		$-.05A$ $+.11B$ $-E$	$+.12B$							
3,3/2		$+.12B$	$+.20A$ $+.04B$ $-E$							
2,5/2				$-.05A$ $+.02B$ $-E$	$-\frac{3\sqrt{14}}{100}B$	$-\frac{3\sqrt{35}}{100}B$				
2,3/2				$-\frac{3\sqrt{14}}{100}B$	$+.20A$ $-.12B$ $-E$	$-\frac{\sqrt{10}}{100}B$				
2,1/2				$-\frac{3\sqrt{35}}{100}B$	$-\frac{\sqrt{10}}{100}B$	$-.25A$ $-E$				
1,5/2							$-.05A$ $-.14B$ $-E$	$-\frac{7\sqrt{6}}{100}B$	$-\frac{\sqrt{3}}{100}B$	
1,3/2							$-\frac{7\sqrt{6}}{100}B$	$+.20A$ $+.04B$ $-E$	$+\frac{\sqrt{2}}{20}B$	
1,1/2							$-\frac{\sqrt{3}}{20}B$	$+\frac{\sqrt{2}}{20}B$	$-.25A$ $-E$	
0,3/2										$+.20A$ $+.20B$ $-E$

$A=(eqQ)_1$

$B=(eqQ)_2$

FIG. 1. Matrix of the quadrupole interaction operators in KBr.

electric quadrupole interactions each associated with a nucleus of spin 3/2. In this molecule, as contrasted with KCl, the quadrupole interactions of potassium and of bromine are of comparable magnitudes.

From the experimental data were obtained the molecular constants of the molecules, the electric dipole moment, the quadrupole interactions, the ratios of the quadrupole moments and masses of the bromine isotopes. Of great interest are the variations with vibrational state of the electric dipole moment and the bromine quadrupole interaction in light of the extraordinary variations of these quantities in KCl given in reference I.

The apparatus and the general experimental procedure are described in I. For the molecules used in this experiment, a beam is obtained from a hot oven source at a temperature of approximately 900°K. At this temperature, a large number of rotational states are excited. The molecules in the $J=0$ state, about one part in 8000, are selected for refocusing. Transitions to the $J=1$ state are observed by a decrease in beam intensity at the surface ionization detector. A 2K43 klystron supplied the necessary microwave power for exciting these transitions (around 4800 Mc/sec). The details of frequency measurements, frequency stabilization, and the procedure used in locating and resolving the spectra are given in I.

Since only a small fraction of the molecules are in the $J=0$ state and the number of hyperfine structure and vibrational levels in the $J=1$ state is large, the intensity change for any one transition is small. To obtain the necessary signal-to-noise ratio, very intense molecular beams had to be employed. With a galvanometer sensitivity of 10^{-15} amp/cm, the direct beam was about 10^7 centimeters of which 2000 centimeters were refocused. For the lines arising from the

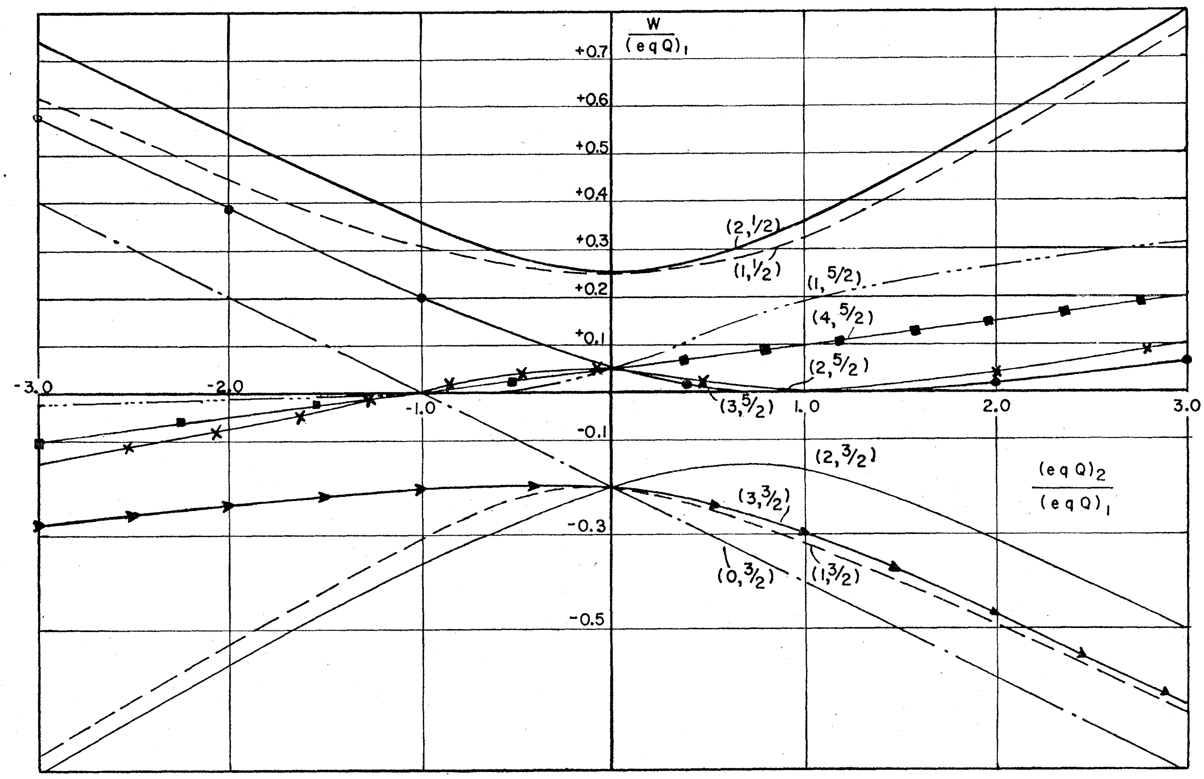

FIG. 2. Plot of the energy levels in the $J=1$ state in units of $(eqQ)_1$ against the ratio $(eqQ)_2/(eqQ)_1$.

zeroth vibrational state, the intensity was approximately 0.7 percent of the refocused beam and 0.2 percent for the second vibrational state. In all cases, the line intensity relative to the refocused beam was half the expected value as calculated from the line intensities observed in KCl.

II. THEORY

In this paper, the energy levels which arise from the splitting of the first rotational state by two nuclear electric quadrupole interactions will be calculated exactly.

The part of the Hamiltonian dealing with the hyperfine structure is

$$-eq_1Q_1\frac{[3(\mathbf{I}_1\cdot\mathbf{J})^2+\frac{3}{2}\mathbf{I}_1\cdot\mathbf{J}-\mathbf{I}_1^2\mathbf{J}^2]}{2I_1(2I_1-1)(2J-1)(2J+3)}$$

$$-eq_2Q_2\frac{[3(\mathbf{I}_2\cdot\mathbf{J})^2+\frac{3}{2}\mathbf{I}_2\cdot\mathbf{J}-\mathbf{I}_2^2\mathbf{J}^2]}{2I_2(2I_2-1)(2J-1)(2J+3)}.$$

The subscripts 1 and 2 refer to the two nuclei. q is the gradient of the electric field at the nucleus along the internuclear axis produced by all charges outside the nucleus, and Q is the nuclear quadrupole moment. In KBr, both nuclei have spins of 3/2. The matrix of the quadrupole operators in the $I_1JF_1I_2FM$ representation is shown in Fig. 1. In this representation, the spin of nucleus 1 is coupled to J through the quadrupole interaction, giving three energy states characterized by $F_1=I_1+J=1/2$, 3/2, and 5/2. The quadrupole interaction of nucleus 2 splits these F_1 states into 10 states labeled by $(F=I_2+F_1, F_1)=(2, 1/2)$, (1, 1/2), (3, 3/2), (2, 3/2), (1, 3/2), (0, 3/2), (4, 5/2), (3, 5/2), (2, 5/2), (1, 5/2). The quadrupole operator of nucleus 1 is diagonal in this representation, but off-diagonal elements occur for the quadrupole operator of nucleus 2. The matrix elements were taken from Bardeen and Townes.[3]

TABLE I. Frequencies of all observed lines in Mc/sec. The numbers in parentheses represent the hyperfine structure levels (F, F_1) of the $J=1$ state to which the transitions take place.

Vibrational state	$K^{39}Br^{79}$		$K^{39}Br^{81}$	
0	4860.523	(2, 1/2)	4820.613	(2, 1/2)
			4820.130	(1, 1/2)
	4859.740	(3, 5/2)	4819.815	(3, 5/2)
			4818.143	(1, 5/2)
	4857.502	(4, 5/2)	4817.992	(4, 5/2)
	4857.383	(2, 5/2)	4817.909	(2, 5/2)
	4856.588	(3, 3/2)	4817.056	(3, 3/2)
			4815.884	(1, 3/2)
	4854.856	(2, 3/2)	4815.635	(2, 3/2)
1	4836.530	(2, 1/2)	4794.062	(2, 1/2)
	4835.743	(3, 5/2)	4793.140	(3, 5/2)
	4833.270	(4, 5/2)		
	4833.143	(2, 5/2)		
	4832.362	(3, 3/2)		
	4830.463	(2, 3/2)		
2	4812.622	(2, 1/2)		
	4811.835	(3, 5/2)		
	4809.129	(4, 5/2)		
	4808.990	(2, 5/2)		
	4808.247	(3, 3/2)		
	4806.153	(2, 3/2)		

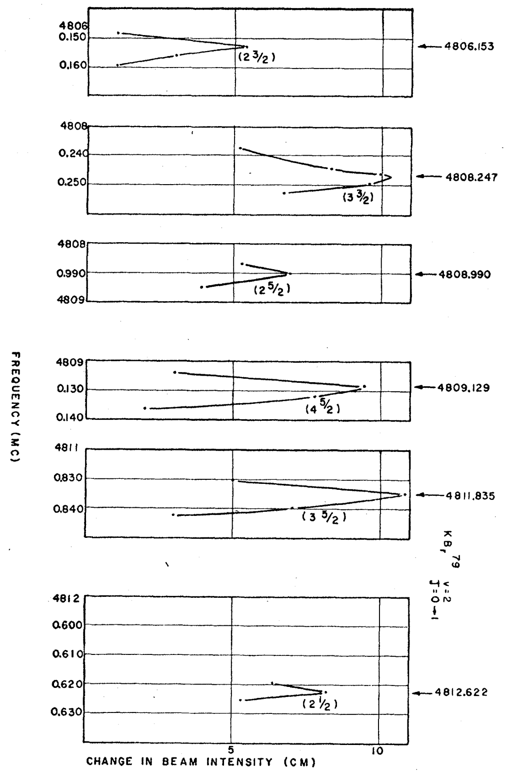

FIG. 3. Spectrum of the rotational transition $J=0\rightarrow J=1$ in the vibrational state $v=2$ in KBr^{79}.

Diagonalization of the matrix yields the 10 energy levels of the first rotational state in terms of the quadrupole interactions of the two nuclei. Figure 2 is a plot of the energy of the levels in units of the quadrupole interaction of nucleus 1 against the ratio $(eqQ)_2/(eqQ)_1$. The right side of Fig. 2 gives the energy levels for a positive ratio, and the left side for a negative ratio.

III. EXPERIMENTAL DATA

The spectrum of KBr differs from that of KCl described in I in that the lines are much further apart in frequency and are, therefore, well resolved. The separations of the lines are of the order of one or two Mc/sec. Because KBr is heavier, the molecules of KBr spend more time in the radiation field, and the theoretical half-width of the lines are less than in KCl. Actual half-widths were about 15 kc/sec, the theoretical about 10 kc/sec.

In the zeroth vibrational state, nine of the ten lines resulting from the rotational transition $J=0\rightarrow J=1$ were observed. Figure 3, which is typical of the spectra

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

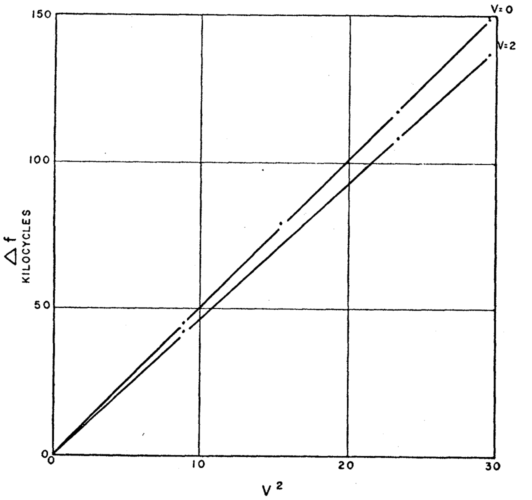

FIG. 4. Frequency shift of the transition $(J=0)\rightarrow(J=1, F_1=1/2, F=2)$ with the square of the applied voltage in the vibrational states $v=0$ and $v=2$ in KBr^{79}.

observed for both $K^{39}Br^{79}$ and $K^{39}Br^{81}$ in the several vibrational states, shows six of the lines in the vibrational state, $v=2$, of $K^{39}Br^{79}$. The line spacings are markedly different for different vibrational states, because of the variation of the quadrupole interactions with internuclear distance. In Table I are listed the frequencies of all observed lines.

The electric dipole moment was obtained by observing the shift in frequency of one of the transitions, $(J=0)\rightarrow(J=1, F_1=1/2, F=2)$, in very small electrostatic fields, of the order of one or two volts per centimeter. For these small fields, the $J=1$ state is unshifted in energy, and the increase in frequency of this transition is due to the energy decrease of the more easily polarized $J=0$ state. This energy decrease is given by $\frac{1}{6}\mu^2E^2/(\hbar^2/2A)$, where μ is the dipole moment and A the moment of inertia. Figure 4 shows a plot of frequency shift *versus* the square of the applied voltage for the zeroth and second vibrational states in $K^{39}Br^{79}$. The slope of the lines is proportional to the product μ^2A. Since A is known from the zero field data, μ is easily calculated.

In addition to the sharp line spectra described above, there appeared in certain frequency regions resonance bands which were approximately ten to twenty Mc/sec wide. These bands appeared in the regions centered, approximately, about the following frequencies: 5230 Mc/sec, 5170 Mc/sec, 4980 Mc/sec, 4780 Mc/sec. The frequency region searched extended from 4400 to 5300 Mc/sec, so that there is the possibility of the occurrence of other bands in other regions. The intensity of the bands depended markedly on the microwave power input. At powers comparable to those used in resolving the sharp line spectra, the band intensity was about 1/5 the line intensity. The origin of these bands is not known. In view of the low intensity of the diatomic lines, it is possible that these bands arise from other forms of molecular aggregates of potassium and bromine, such as polymers of the KBr molecule.[4]

TABLE II. Potassium and bromine quadrupole interaction constants in KBr.

Quantity	$K^{39}Br^{79}$	$K^{39}Br^{81}$
$(eqQ)_K$ $(v=0)$ Mc/sec	-5.003 ± 0.003	-5.002 ± 0.003
$(v=1)$	-4.984 ± 0.003	
$(v=2)$	-4.915 ± 0.003	
$(eqQ)_{Br}$ $(v=0)$ Mc/sec	$+10.244\pm0.006$	$+8.555\pm0.006$
$(v=1)$	$+11.224\pm0.006$	
$(v=2)$	$+12.204\pm0.006$	

IV. RESULTS

By comparing the splitting of the observed lines in each vibrational state with the theoretical energy level pattern shown in Fig. 2, the potassium and bromine quadrupole interactions in each vibrational state were calculated. These values are listed in Table II. The observed line spacings do not correspond to the theoretical pattern for any other values of the quadrupole interactions, so that these values are unique. The uncertainties given for each quantity arise from a 2-kc/sec uncertainty in the determination of the peak of each line. The accuracy of these interactions is greater than for the corresponding quantities in KCl because (1) the splitting of the lines is greater in KBr, and (2) there are more resolved lines.

To calculate the molecular constants one must know the frequencies of the lines arising from the pure rotational transitions $J=0\rightarrow J=1$ for the different vibrational states, apart from the influence of the quadrupole interactions. Since the quadrupole interactions are known from the spectrum, the frequencies of the unperturbed lines are readily calculated from the theory. The constants are listed in Table III. The relationships of the Y's, the Dunham coefficients, to the spectra are discussed in I. All the Y's listed were obtained from the spectra except Y_{02}, which was calculated from the relationship $-Y_{02}=4B_e^3/\omega_e^2$. Table IV gives the internuclear distances and electric dipole moments in the zeroth and second vibrational states.

The mass ratio of the bromine isotopes was calculated from the formula:

$$\frac{M_1}{M_2}=\frac{(M/M_2)(Y_{01}{}^{81}/Y_{01}{}^{79})}{1+M/M_2-Y_{01}{}^{81}/Y_{01}{}^{79}},$$

where M_1 is the mass of Br^{79}, M_2 the mass of Br^{81}, and M the mass of K^{39}. The result is

$$M_{Br^{79}}/M_{Br^{81}}=0.9753088\pm0.0000020.$$

The ratio of the nuclear quadrupole moments of the bromine isotopes was calculated from the ratio of the

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[4] Ochs, Coté, and Kusch, J. Chem. Phys. 21, 459 (1953).

bromine quadrupole interactions in the zeroth vibrational state in KBr^{79} and KBr^{81}. The result is

$$Q_{\mathrm{Br}^{79}}/Q_{\mathrm{Br}^{81}}=1.1973\pm0.0006.$$

V. DISCUSSION

A proof that the potassium quadrupole interaction, $(eqQ)_{\mathrm{K}}$, is negative and the bromine interaction, $(eqQ)_{\mathrm{Br}}$, is positive follows. The ratio of the quadrupole interactions, $(eqQ)_2/(eqQ)_1$, is negative, since the observed line pattern does not fit the theoretical pattern for positive values. This can be seen from the energy level diagram (Fig. 2), which has been plotted by assigning a negative value to the denominator of the ratio, $(eqQ)_1$. From the experimental data, the values of the ratios of the quadrupole interactions in KBr^{79} and KBr^{81} are -2.048 and -1.170, respectively. These values of the ratios were assigned once the values of the rotational constants for both isotopic species were calculated, since the rotational constant, being inversely proportional to the reduced mass of the molecule, is larger for KBr^{79}. Now,

$$\frac{(eqQ)_{\mathrm{Br}^{79}}/(eqQ)_{\mathrm{K}}}{(eqQ)_{\mathrm{Br}^{81}}/(eqQ)_{\mathrm{K}}}=\frac{Q^{79}}{Q^{81}}=1.2 \text{ if } (eqQ)_{\mathrm{Br}} \text{ is } (eqQ)_2,$$

$$\frac{(eqQ)_{\mathrm{K}}/(eqQ)_{\mathrm{Br}^{81}}}{(eqQ)_{\mathrm{K}}/(eqQ)_{\mathrm{Br}^{79}}}=\frac{Q^{79}}{Q^{81}}=0.85 \text{ if } (eqQ)_{\mathrm{Br}} \text{ is } (eqQ)_1.$$

Here the assumption is apparently made that $(eqQ)_{\mathrm{K}}$ is the same in both molecular species. However, since the ratio of the quadrupole interactions for the bromine isotopes is known to be 1.2, and the spacings of the spectra for the two isotopes fit Fig. 2 with the same scale factor, $(eqQ)_1$, one of the interactions must be constant in both molecular species. The common interaction, $(eqQ)_1$, must therefore be $(eqQ)_{\mathrm{K}}$, and the sign of its interaction negative. The ratio 1.2 for the quadrupole moments of the bromine isotopes is then in agreement with the observations of Townes,[5] Dehmelt and Kruger,[6] and King and Jaccarino.[7]

The signs of the K^{39} quadrupole interactions in KF,[8] KCl, and KBr are also all negative. The absolute magnitudes decrease from 7.938 Mc/sec in KF to 5.656 Mc/sec in KCl to 5.003 Mc/sec in KBr. Similar behavior has been observed for the Na^{23} quadrupole interaction constants in the sodium halides by Logan, Coté, and Kusch.[9]

The change with vibrational state of $(eqQ)_{\mathrm{K}^{39}}$ in KBr and KCl does not remain constant, but becomes larger for higher vibrational states. In $\mathrm{K}^{39}\mathrm{Cl}^{35}$, the change in this interaction increased from 0.8 percent for $v=0\rightarrow v=1$ to 1.1 percent for $v=2\rightarrow v=3$. In KBr^{79}, the decrease in $(eqQ)_{\mathrm{K}}$ for $v=0\rightarrow v=1$ is about 1/3 that for $v=1\rightarrow v=2$. This shift corresponds to percentage decreases of 0.4 percent and 1.4 percent, respectively. In $\mathrm{K}^{39}\mathrm{F}$, $(eqQ)_{\mathrm{K}}$ decreases by about 1.3 percent for unit change in the vibrational quantum number. The potassium interaction decreases with vibrational state in the potassium halides thus far studied.

TABLE III. The molecular constants of KBr.

Quantity	$\mathrm{K}^{39}\mathrm{Br}^{79}$	$\mathrm{K}^{39}\mathrm{Br}^{81}$
Y_{01} Mc/sec	2434.947 ± 0.001	2415.075 ± 0.001
$-Y_{02}$	0.001	0.001
$-Y_{11}$	12.136 ± 0.001	11.987 ± 0.001
Y_{21}	0.023 ± 0.001	0.022 ± 0.001
B_e	2434.953 ± 0.007	2415.081 ± 0.007
r_e A	2.8207 ± 0.0001	

In both KCl and KBr the quadrupole interaction constants for the halogen show large changes with vibrational state. The change in the bromine interaction is to larger values and appears to be a constant amount of about one Mc/sec, 10 percent of the interaction, for the lowest vibrational states. This change is in contrast to the erratic changes with vibrational state exhibited by the chlorine interaction in KCl.

The value obtained for the ratio of the quadrupole moments of the bromine isotopes has been corrected to take into account the fact that the gradient of the electric field at the bromine nucleus, which enters into the experimentally measured quadrupole coupling, is not the same for two isotopes in the same molecule because of different zero point vibration for the two isotopic species. This effect amounts to about one part in 6000 in the quadrupole moment ratio.

In calculating the mass ratio of the bromine isotopes from the mass ratio formula, the Y_{01}'s were obtained from the spectra. The mass of Br^{81} used was that given by Ogata,[10] and the mass of K^{39} that given by Collins, Nier, and Johnson.[11] The ratio of the Y_{01}'s was corrected by small terms of the order of B_e^2/ω_e^2 given by Dunham,[12] since Y_{01} is not exactly inversely proportional to the reduced mass of the molecule.

The theory on which the mass ratio formula is based assumes a vibrating rotator model diatomic molecule. Any deviations from this model would result in inaccuracies in the mass ratio. Such deviations can arise

TABLE IV. Internuclear distances and electric dipole moments in the vibrational states $v=0$ and $v=2$ in $\mathrm{K}^{39}\mathrm{Br}^{79}$.

Quantity	$v=0$	$v=2$
r A	2.8243 ± 0.0001	2.8384 ± 0.0001
μ Debye	10.41 ± 0.05	9.93 ± 0.05
	$\mu_0/\mu_2=1.048\pm0.004$	

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[5] C. H. Townes, Phys. Rev. **71**, 909 (1947).

[6] Dehmelt and Kruger, Z. Physik **129**, 401 (1951).

[7] J. G. King and V. Jaccarino (private communication).

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

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

[10] K. Ogata, Phys. Rev. **75**, 200 (1949).

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

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

from the following causes: (1) interaction between electronic and nuclear motions which leads to a mixing of the ground electronic state with the excited Π state, and hence a slight change in the rotational energy; (2) the moment of inertia of the electrons which is calculated in the above model on the assumptions that each atom has the proper number of electrons to make it neutral and that the entire mass of the atom is concentrated at the nucleus. These effects cannot be precisely evaluated because the electronic wave functions are not known. The error quoted in the mass ratio is experimental error.

The values of the internuclear distances in KCl and KBr are about 3 percent lower than the values given by electron diffraction methods after correction for the vibrational state distribution has been made. Similar discrepancies have been observed in CsCl by Luce and Trischka,[13] and in NaCl by Stitch, Honig, and Townes.[14]

As can be seen from Table IV, the electric dipole moment of KBr decreases with increasing vibrational quantum number. The percentage decrease in the dipole moment is about 5 percent for the change from the zeroth to the second vibrational state. The percentage increase in the internuclear distance for this change in vibrational state is about 0.5 percent. Hence, a small increase in the internuclear distance causes a large decrease in the dipole moment.

The experimental value of the vibration-rotation interaction constant, $\alpha_e = -Y_{11}$, is 12.136 Mc/sec. The theoretical value, computed on the assumption of a Morse potential for KBr, is 10.0 Mc/sec.

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

[14] Stitch, Honig, and Townes, Phys. Rev. 86, 813 (1952).

PHYSICAL REVIEW VOLUME 91, NUMBER 6 SEPTEMBER 15, 1953

A Self-Consistent Calculation of the Dissociation of Oxygen in the Upper Atmosphere. II. Three-Body Recombinations*

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The dissociation region of oxygen molecules is treated in the same "self-consistent" manner described in previous papers, except that now the densities of atomic and molecular oxygen have been calculated as functions of the altitude, on the assumption that the main recombination process between oxygen atoms is a three-body nonradiative process. The result of the present work indicates that dissociation occurs at an altitute about 5 km higher than the corresponding previous calculation. Furthermore, the region of dissociation is broader than in the previous model. The maximum atomic density is 0.5 to $1\times10^{13}/\text{cm}^3$.

I. INTRODUCTION

In two previous papers[1,2] the densities of atomic and molecular oxygen in the upper atmosphere were calculated in terms of two different models. Both of these models were carried out in a "self-consistent" manner, that is, no *a priori* assumptions were made as to the distribution of molecular or atomic oxygen. (Such assumptions have been made by previous authors in the field.[1,2])

In the first model it was possible to calculate the distribution of temperature as well as the distribution of the atomic and the molecular oxygen densities. In the second model, a temperature distribution was assumed in order to avoid the necessity of imposing a severe assumption, used in the first model, with respect to energy balance.

In both of these models the principal recombination process was assumed to be a two-body radiation process. The present paper is to be regarded as a direct extension of reference 2; the assumption of two-body recombinations is replaced by the assumption that the oxygen atoms recombine in a three-body process. Therefore, instead of repeating the various details of the model of reference 2 and of the method of solution of the equations for the densities, we shall merely indicate the modifications.

II. THE THREE-BODY RECOMBINATION PROCESS

The principal modification of reference 2 which we introduce in the present work is to replace the two-body recombination process (11) there by the three-body recombination process (10). The rate of recombination of the oxygen atoms is taken to be $Cn_Mn_p^2$ where C is the three-body recombination coefficient

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[1] H. E. Moses and T. Y. Wu, Phys. Rev. 83, 109 (1951).

[2] H. E. Moses and T. Y. Wu, Phys. Rev. 87, 628 (1952).