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A. J. Hebert, F. W. Breivogel, Jr., and K. Street, Jr.

April 21, 1964

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

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ERRATUM

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Please make the corrections shown on the attached sheet.

ERRATUM: RADIO-FREQUENCY AND MICROWAVE SPECTRA OF LiBr BY THE MOLECULAR-BEAM ELECTRIC-RESONANCE METHOD

[J. Chem. Phys. 41, 2368 (1964)]

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A numerical error has been found in the calculation of the quadratic expression for the variation of the quadrupole coupling constant of $^{6}Li^{81}Br$ with vibrational state. If one uses the data as given in Table IV, the entries under $^{6}Li^{81}Br$ at the bottom of Table IV, page 2374 should read:

$$(eqQ)_e = 30.916 \pm 0.002 \text{ Mc/sec}$$

$$(eqQ)_I = 2.438 \pm 0.002 \text{ Mc/sec}$$

$$(eqQ)_{II} = -0.03286 \pm 0.002 \text{ Mc/sec}$$

This in turn effects the second equation in Section C, page 2375, which should now read:

$$[(eqQ)_e]^{79}Br/[(eqQ)_e]^{81}Br = 1.19728 \pm 0.00008$$

This change is of some significance since Bonczyk and Hughes[1] have used this data along with that of King and Brown[2] to deduce a value for the anisotropy of the nuclear polarizability of bromine.

We wish to thank Dr. Thomas C. English[3] for alerting us to an inconsistency in the reported ratios.

1. P. A. Bonczyk and V. W. Hughes, Bull. Am. Phys. Soc. 12, 132 (1967).
2. J. G. King and H. H. Brown, Phys. Rev. 142, 53 (1966).
3. T. C. English, private communication.

The Radio-Frequency and Microwave Spectra Of LiBr By The Molecular-Beam Electric-Resonance Method*

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April 21, 1964

ABSTRACT

The molecular-beam electric-resonance technique has been used to obtain dipole moments, μ_v, quadrupole interaction constants of bromine $(eqQ)_v$, spin-rotation interaction constants, c_{Br}, and rotational constants for Li^6Br^{79} and Li^6Br^{81} in several of the lower vibrational levels. The observation of $J = 1$ radio-frequency spectra for three or more vibrational states led to the following values:

Li^6Br^{79}

$$\mu_v = 7.22624 + 0.08318\,(v + 1/2) + 0.00057\,(v + 1/2)^2 \pm 0.001 \text{ debye}$$

$$(eqQ)_v = 37.015 + 2.918\,(v + 1/2) - 0.039\,(v + 1/2)^2 \pm 0.005 \text{ Mc}$$

$$c_{Br} = 9.2 \pm 0.2 \text{ kc}$$

Li^6Br^{81}

$$\mu_v = 7.22611 + 0.08312\,(v + 1/2) + 0.00060\,(v + 1/2)^2 \pm 0.001 \text{ debye}$$

$$(eqQ)_v = 30.912 + 2.442\,(v + 1/2) - 0.034\,(v + 1/2)^2 \pm 0.005 \text{ Mc}$$

$$c_{Br} = 9.9 \pm 0.2 \text{ kc}$$

The observation of $J = 1 \rightarrow J = 0$ microwave transitions yielded the following rotational constants:

$\underline{Li^6Br^{79}}$

$B_0 = 19\,090.296 \pm 0.006$ Mc

$B_1 = 18\,882.800 \pm 0.009$ Mc

$B_2 = 18\,677.242 \pm 0.055$ Mc

$\underline{Li^6Br^{81}}$

$B_0 = 19\,057.005 \pm 0.006$ Mc

$B_1 = 18\,850.050 \pm 0.020$ Mc

$B_2 = 18\,645.035 \pm 0.217$ Mc.

I. INTRODUCTION

The molecular-beam electric-resonance method[1] has been used to investigate the radio-frequency and microwave spectra of Li^6Br^{79} and Li^6Br^{81}. The radio-frequency transitions observed were of the type $(J, m_J) \rightarrow (J, m_J \pm 1)$, J being the rotational quantum number and m_J the magnetic quantum number. The microwave transitions observed were of the type $J = 1 \rightarrow J = 0$.

Values for the electric dipole moments, μ_v, the quadrupole interaction constants of bromine, $(eqQ)_v$, and spin-rotation interaction constants of bromine, c_{Br}, have been obtained for several of the lower vibrational levels. Observations of three or more vibrational states of Li^6Br^{79} and of Li^6Br^{81} have enabled us to derive expressions that indicate nonlinear variations of quadrupole-coupling constants and electric dipole moments with vibrational state.

Fitting of the observed radio-frequency Stark spectra required the use of a recently completed computer program that includes provisions for second-order quadrupole and Stark-quadrupole effects.[2]

The microwave spectra of LiBr have been observed previously by Honig et al.[3] and by Rusk and Gordy.[4] Honig et al. have reported values for the rotational constants, the bromine quadrupole interaction constants of Li^7Br in the $v = 0$ and $v = 1$ vibrational states, and the electric dipole moment of Li^7Br. Rusk and Gordy report somewhat different values for Y_{01} and B_e, and the first experimentally derived values for D_0 and D_e. The Y_{ij}'s refer to the coefficients in the Dunham expansion,[5] and the other symbols to the usual band-spectra constants.[6] The present results agree with those of Rusk and Gordy. Observations of rotational transitions for the $v = 0$, 1, and 2 vibrational states of Li^6Br^{79}--in conjunction with the Rusk and Gordy values for D_e, ω_e, and $\omega_e x_e$--have allowed accurate calculations of Y_{01}, Y_{11}, Y_{21} and the rotational

constants, B_v, for the low vibrational states of all isotopic species of LiBr. The use of these rotational constants with our radio-frequency spectra have allowed us to calculate the bromine quadrupole interaction constants and dipole moments of Li^6Br. Values for the bromine spin-rotation interaction constants in Li^6Br^{79} and Li^6Br^{81} are reported for the first time.

II. EXPERIMENTAL

A. Apparatus

The electric-resonance apparatus used in these experiments is similar to that evolved by Trischka,[7] although differing in dimensions and some details. As these details are available elsewhere,[8] only a brief description is given here. The apparatus, shown schematically in Fig. 1, consists of a differentially pumped four-chamber high-vacuum system, a tungsten ribbon and ion accelerator for surface-ionization detection, a 5-cm-radius permanent-magnet mass analyzer with separate electron-multiplier chamber, 30-cm-long dipole (or two-wire analog) inhomogeneous electric deflecting fields, and a homogeneous electric Stark "C" field region 25 cm long. The Stark field is produced by parallel electrodes made by evaporating a gold film on glass optical flats ground to produce surfaces parallel to within one quarter wavelength of helium light (1300 Å).

The source oven is a tube 6 in. long and 3/8 in. in diameter, made of a (20% iridium)-(80% platinum) alloy. The tube has a beam slit 0.005-inch wide by 0.25 inch high and is heated by passing current from a 1.5-Vac line transformer through it.

Figure 2 indicates the path of a molecule with effective dipole moment μ_e and dipole moment μ under the influence of a force $F = \mu_e \frac{\partial E}{\partial X}$, as it passes through the apparatus. This type of experiment yields signals commonly

referred to as "flop-in" signals, since the molecule must undergo a transition to be detected.

B. Voltage Measurements

The value of the electric field is calculated from the known spacing of the homogeneous C field electrodes (0.50000 ± 0.00001 cm) and the applied voltage. The voltage is measured with a resistance bridge and a Rubicon potentiometer in conjunction with an Eppley standard cell. All measurements are performed in the molecular-beam laboratory where temperature variations are < 1° C per day under good conditions. The potentiometer was calibrated with a bank of standard cells, which were calibrated by the National Bureau of Standards at 5 parts in 10^6, and cross checked against a Dauphinee potentiometer certified at 3 parts in 10^6. The resistance-bridge ratio used to calculate the voltage applied to the C field was determined with a Leeds and Northrup Guarded Wheatstone Bridge certified at 1 part in 10^4. Thus, the uncertainty in the absolute value of the electric-field strength is expected to be 1 part in 10^4. The reproducibility of the field is an order of magnitude better than this and can be maintained constant to within 1 part in 10^5 while measuring relative Stark splittings.

C. Microwave Equipment

Transitions from the $J = 1$ to the $J = 0$ rotational states of Li^6Br were induced with approximately 10^{-6} W of microwave power at frequencies near 38 Gc. The microwave signals were obtained by using the third-harmonic output of a Hewlett Packard 940 A frequency doubler set modified by removing the low-pass filter. The fundamental frequency of 12.6 Gc at a power level of 10^{-1} W was generated by a Varian X-12 klystron. The klystron was phase locked with a Hewlett Packard DY2650A-M5 oscillator synchronizer to a Hewlett Packard 608 C signal generator. The 608 C signal generator was found to have a short-term stability of approximately 5 parts in 10^8.

The fundamental frequency was monitored roughly with a wavemeter whereas more accurate readings were made with a Hewlett Packard 540 B transfer oscillator and a HP 5245L-5253A frequency counter. Final frequency determinations were made from the frequency-counter readings of the 608 C signal-generator output at approximately 210 Mc.

The frequency counter was calibrated with a signal from station WWVB and set at A-1 (the atomichron standard) with an accuracy of 1 part in 10^9. The counter was observed to have a stability of 4 parts in 10^{10} per day and was continuously checked against signals from WWVB during these experiments.

Microwave power was introduced into the 0.5-cm gap of the electric-field transition region by means of a sectoral horn with a length of 14 in. and an apex of 20°. The mouth of the horn, which measures 0.5 cm by 14 cm, is located along the last 15 cm of the 25-cm long transition region, 2.5 inches above the beam axis. Thus, microwave signals in the TE_{10} mode would have their electric field parallel to the Stark field. This orientation produces transitions in which $\Delta m_J = 0$. The microwave-beam angle between half-power points for this horn is expected to be approximately 20°.[9]

D. Radio-Frequency Equipment

Hewlett-Packard 606 A and 608 C rf generators are used to produce signals from 50 kc to 65 Mc, and from 10 Mc to 480 Mc, respectively. The 606 A has been observed to have a short-term stability of approximately 1 part in 10^7, whereas the 608 C has a short-term stability of approximately 5 parts in 10^8. The radio-frequency signals are monitored with a Hewlett-Packard 524 D electronic counter that has been calibrated against signals from WWVB and referenced to A-1, the atomichron standard, with an accuracy of 1 part in 10^9. The counter was observed to have a stability of better than 5 parts in 10^8 per week.

Permanent rf spectral records are obtained through the use of a Hewlett-Packard 560 A 11-channel digital recorder with analog output. The rf count from the 524 D counter is fed into the first seven channels of the digital recorder. Pulses from the electron multiplier, which are a direct measure of beam intensity, are amplified and fed into a second 524 D counter. The resultant-beam-intensity count is fed into the remaining four channels of the digital recorder. The first three digits of the beam-intensity count can be converted to a voltage (analog output), and fed into a Leeds and Northrup chart recorder for graphic representation of the spectrum.

Radio frequency is fed into the molecular-beam transition region at a fixed frequency and counted for 1 sec while a 1-sec beam-intensity count is being taken; both signals are then recorded simultaneously during the first 0.1 sec of a 1-sec counter "dead time," and the frequency is increased by approximately 300 cps. The remaining 0.9 sec of dead time allows the signal generator ample time to stabilize at the new frequency while also allowing time for the hot-tungsten-filament beam ionizer to equilibrate at the new beam intensity before the next count is taken.

E. Beam Material

Li^6Br crystals were prepared by adding small pieces of 95%-enriched Li^6 metal to distilled water, and then adding reagent-grade HBr to the solution. The solution was then evaporated and the crystals were further dried in a vacuum desiccator.

III. THEORY

The spectra obtained in these experiments were analyzed by means of a high-speed digital-computer program.[10] The Hamiltonian, $\mathcal{H}$, used in the computer program is:[11, 12]

$$\mathcal{H} = B\underset{\sim}{J}^2 - \underset{\sim}{\mu} \cdot \underset{\sim}{E} - eq_1Q_1 \frac{\left[3(\underset{\sim}{I}_1 \cdot \underset{\sim}{J})^2 + \frac{3}{2}(\underset{\sim}{I}_1 \cdot \underset{\sim}{J}) - (\underset{\sim}{I}_1^2 \underset{\sim}{J}^2)\right]}{2I_1(2I_1 - 1)(2J - 1)(2J + 3)}$$

$$- eq_2Q_2 \frac{\left[3(\underset{\sim}{I}_2 \cdot \underset{\sim}{J})^2 + \frac{3}{2}(\underset{\sim}{I}_2 \cdot \underset{\sim}{J}) - (\underset{\sim}{I}_2^2 \underset{\sim}{J}^2)\right]}{2I_2(2I_2 - 1)(2J - 1)(2J + 3)} + c_1(\underset{\sim}{I}_1 \cdot \underset{\sim}{J})$$

$$+ c_2(\underset{\sim}{I}_2 \cdot \underset{\sim}{J}) + \frac{g_1 g_2 \mu_N^2}{r^3} \frac{\left[3(\underset{\sim}{I}_1 \cdot \underset{\sim}{J})(\underset{\sim}{I}_2 \cdot \underset{\sim}{J}) + 3(\underset{\sim}{I}_2 \cdot \underset{\sim}{J})(\underset{\sim}{I}_1 \cdot \underset{\sim}{J}) - 2(\underset{\sim}{I}_1 \cdot \underset{\sim}{I}_2) J(J+1)\right]}{(2J - 1)(2J + 3)}.$$

The first term in the above expression gives the rotational energy, where B is the molecular rotational constant and J is the rotational angular-momentum operator. The second term gives the interaction of the permanent electric-dipole moment, μ, of the molecule with the external electric field, E. The third and fourth terms give the interaction of the nuclear electric-quadrupole moments (Q_1 and Q_2) with the electric-field gradients at the nuclei (q_1 and q_2), e is the electronic charge, I_1 and I_2 are the nuclear spins, and the subscripts distinguish between the two nuclei. The fifth and sixth terms give the magnetic coupling of the nuclear spins with the molecular angular momentum, where c_1 and c_2 are constants. The seventh term is the magnetic dipole-dipole interaction between the two nuclei, where g_1 and g_2 are the gyromagnetic ratios for the two nuclei, r is the internuclear distance, and μ_N is one nuclear magneton.

The computer program calculates the matrix elements of $\mathcal{H}$ in a J, I_1, I_2, m_J, m_{I_1}, m_{I_2} representation, where m_J, m_{I_1}, and m_{I_2} are the projections of $\underset{\sim}{J}$, $\underset{\sim}{I}_1$, and $\underset{\sim}{I}_2$ respectively on the direction of the field E. The program computes the energy eigenvalues by diagonalizing this matrix and then calculates the spectral-line positions corresponding to the given set of input parameter

according to the selection rules $\Delta m_F = 0, \pm 1$, where m_F is the projection of the total angular momentum on the field direction. Input to the program consists of the parameters J, B, μ, eq_1Q_1, eq_2Q_2, c_1, c_2, and $g_1g_2\mu_N^2/r^3$ for each vibrational state. The matrix is diagonal in m_F and the program utilizes this fact to reduce computing time. The first term in $\mathcal{H}$ is, of course, diagonal in this representation. The last three terms are very small in general and only matrix elements diagonal in J are included for them.

The quadrupole terms have matrix elements diagonal in J as well as ones connecting J with $J \pm 2$. The quadrupole operator in the Hamiltonian given above can be used only to calculate matrix elements diagonal in J; therefore, in order to include the off-diagonal elements, a more general expression is needed.[13] Formulae derived by Fano[14] were used in calculating these matrix elements.

The nonzero matrix elements of the second term in the Hamiltonian, the Stark interaction, are of the form $(J, m_J \left| \underset{\sim}{\mu} \cdot E \right| J \pm 1, m_J)$. Since J may take any positive integer value, the matrix is infinite in extent. However, in calculating $J = 1$ eigenvalues, only the first four J states are included in the matrix; for $J = 2$ calculations, the first five J states are included, and so on. For the Stark energy this is equivalent to a fourth-order perturbation treatment, whereas for the quadrupole energy it is equivalent to a second-order perturbation treatment.

IV. RESULTS AND DISCUSSION

A. Radio-Frequency Spectra

The radio-frequency voltages necessary to observe Li^6Br spectra corresponding to optimum resolution for the transitions $(1, \pm 1) \rightarrow (1, 0)$ were from 0.03 to 0.07 V rms. Slightly higher values were necessary for optimal observations involving $J = 2$. The observed-natural-line widths were

approximately 5 kc at half-maximum intensity for most lines, in agreement with the expected theoretical uncertainty broadening for a 25-cm transition region.[15] The signal-to-noise ratio was approximately 25 to 1 for observed transitions of the $v = 0$ vibrational state. At 50 mc this would indicate a precision of 4 parts in 10^6.

Both weak- and intermediate-field spectra were observed. Weak-field spectra correspond to fields such that μE is much less than eqQ, whereas in the immediate field case μE is comparable to eqQ. The observed weak-field spectra yielded lines for the first six vibrational states of Li^6Br^{79} and for the first five vibrational states of Li^6Br^{81}. The intermediate-field spectra yielded useful results for $v = 0$, 1, and 2 for both isotopes. Several complete sets of spectra were observed at 666.782 V/cm and at 400.00 V/cm.

Zero-field spectra were observed only in the case of multiple quantum transitions.[16] A Stark field of 5 V/cm was found to be necessary for the observation of weak-field single-quantum transitions.

Figure 3 shows some representative observed lines for $J = 1$ transitions. The maximum signal for a typical spectral line of LiBr in the first vibrational state corresponds to approximately 2400 counts/sec above a background of 1700 counts/sec. The expected statistical fluctuations in this case are in fair agreement with the observed signal-to-noise ratio of approximately 25 to 1. Figure 4 shows the energy levels of Li^6Br^{79} with respect to electric-field strength.

The lithium quadrupole interaction constant, $(eqQ)_{Li^6}$, was not determined since the small line splitting expected from this interaction could not be resolved. A few initial calculations with the computer program also confirmed that the inclusion of the magnetic dipole-dipole interaction, $g_1 g_2 \mu_N^2 / r^3$, and the lithium spin-rotation interaction, c_{Li^6}, would also be unnecessary. The

exclusion of these terms resulted in an appreciable conservation of computer time and no observable loss in accuracy. Thus, subsequent inputs to the program for intermediate-field calculations were the two known values, E and B_v, and the unknown parameters $(eqQ)_{Br}$, μ_v, and c_{Br}. The two lines observed for each weak-field vibrational state and isotope were used to calculate values for $(eqQ)_{Br}$ and c_{Br}.

Tables I and II show the observed and calculated intermediate-field spectra for Li^6Br^{79} and Li^6Br^{81}, respectively. All observed frequencies are corrected for a contact potential corresponding to approximately one part in 10^4 of the field voltage. This was done by obtaining spectra with both polarities of the Stark field.[17, 18] The calculated spectra were derived by using the values for the molecular constants μ_v, $(eqQ)_v$, and c_{Br} as given in Tables III and IV and discussed below.

B. Dipole Moments

Table III lists the dipole moments for Li^6Br^{79} and Li^6Br^{81}, as determined from the intermediate-field data. The observed dipole moments for the two isotopic species of Li^6Br can be fitted to expressions of the form

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

The values for the constants are summarized in Table III.

Similar nonlinear variations have been observed in the dipole moment of Li^6F^{19} by Wharton et al.,[19] and have also been observed by us for Li^6F^{19}, Li^7F^{19}, and NaF.[20]

The discrepancy of approximately 1 debye (D) between these dipole moments and the value previously reported for the Li^7Br^{79} dipole moment from microwave data[3] (6.19 ± 0.15 D) is quite unexpected. The accuracy stated for the present values is quite in line with our theoretical and experimental expectations; in addition, our LiF and NaF dipole-moment

results are in good agreement with those of other workers.[19, 21] Our higher value for the dipole moment further increases the disagreement between the value (5.139 D) calculated from Rittners' polarized-ion model[3, 22] and the experimental value.

C. Quadrupole-Coupling Constants

Table IV lists the calculated quadrupole-coupling constants for Li^6Br. The internal consistency of the weak-field values is attested to by the negligible variation of the ratio

$$(eqQ)_{Br^{79}} / (eqQ)_{Br^{81}} = 1.19726 \pm 0.00008$$

for all observed vibrational states. When corrected to a common vibrational energy, the ratio becomes

$$\left[(eqQ)_e\right]_{Br^{79}} / \left[(eqQ)_e\right]_{Br^{81}} = 1.19743 \pm 0.00008 .$$

This ratio is in excellent agreement with the previously observed bromine quadrupole ratio of 1.1973 ± 0.0006.[23] Quadradic equations for the variation of quadrupole-coupling constants with vibrational quantum number have been derived from the more complete weak-field data and are also shown in Table IV. These values are significantly higher (even when corrected for the Li-isotope effect) than those reported previously for $v = 0$ and 1 of Li^7Br.[3]

Attempts to fit the intermediate-field spectra observed at various voltages with a computer program[10] that did not have provisions for Stark-quadrupole and second-order quadrupole effects resulted in quadrupole-coupling constants that changed linearly with field voltage and extrapolated quite accurately to the weak-field values at zero field.

D. Spin-Rotation Interaction Constants

The intermediate-field spectra and the weak-field spectra yielded the same bromine spin-rotation constants, within experimental error. Neither isotope showed any significant change in this constant for the first five

vibrational states. The observed values are directly proportional to the nuclear g values and inversely proportional to the moment of inertia, as expected from theory.[24] The values from the intermediate-field data are as follows:

$$c_{Br^{79}} = 9.2 \pm 0.2 \text{ kc}$$

$$c_{Br^{81}} = 9.9 \pm 0.2 \text{ kc}.$$

E. Microwave Results

The $J = 1 \rightarrow J = 0$ microwave transitions were observed by setting the Stark field and the radio frequency to give a maximum signal for a prominent line in the reorientation spectrum, i.e. a $J = 1$, $m_J = \pm 1 \rightarrow J = 1$, $m_J = 0$ transition. The microwave frequency was then swept and the resonant frequency observed as a decrease in the radio-frequency "flop-in" signal due to depletion of the final state by rotational transition of the type $J = 1$, $m_J = 0 \rightarrow J = 0$, $m_J = 0$. The decrease amounted to a more than 80% reduction in the "flop-in" Stark signal. The microwave line widths at half maximum were approximately 50 kc, in excellent agreement with the expected Doppler and uncertainty[12] broadening for the sectoral horn described above. The lowest frequency transition we attempted to observe was for Li^6Br^{81}, $v = 2$. This transition was not observed due to a sharp decrease in klystron power output in going from 12.45 to 12.43 Gc. The Li^6Br^{79} $v = 2$ transition was observed at a 12.45 Gc fundamental. Sufficient power was not available to power broaden any of the observed lines.

The observed transition frequencies were corrected for Stark and hyperfine splitting by use of the dipole moments and coupling constants determined in the radio-frequency experiments. Table V lists the observed

transition frequencies, ν, Stark-field and hyperfine corrections, and zero-field transition frequencies, ν_0, for the observed transitions.

Table VI lists the values of D_v for Li^6Br^{79} calculated from the results of Rusk and Gordy[4] for Li^7Br by making the Li isotope correction.[6] Our resultant values for Y_{01}, Y_{11}, Y_{21}, B_v and B_e are also given. The values of Y_{01}, Y_{11}, and Y_{21} were calculated from the equation

$$\nu_0 = 2Y_{01} + 2Y_{11}(v + 1/2) + 2Y_{21}(v + 1/2)^2 - 4D_v,$$

and the frequencies observed for the three lowest vibrational states. The values for B_v were calculated by means of the equation

$$B_v = Y_{01} + Y_{11}(v + 1/2) + Y_{21}(v + 1/2)^2.$$

The equations and additional molecular constants used to calculate D_v and B_e are as given by Rusk and Gordy.

Table VII lists the spectroscopic constants calculated for LiBr from the present Li^6Br^{79} results corrected for isotopic effects and compares them with previously reported values. In general our values lie between those given by Honig et al.[3] and those given by Rusk and Gordy.[4] The agreement between our values and those of Rusk and Gordy is good. The reason for the differences between these results and those of Honig et al. is not known. A high degree of internal consistency in the present results is indicated by a comparison of the observed spectroscopic constants for Li^6Br^{81} and those calculated from the Li^6Br^{79} results, as shown in Table VIII. The listed errors for the present values are expected to be conservative.

The B_e values reported here have not been corrected for the wobble-stretch effect,[25] since the agreement between our calculated B_e for Li^7Br^{79} and that given by Rusk and Gordy is within the combined experimental errors.

FOOTNOTES AND REFERENCES

* This work was supported by the U. S. Atomic Energy Commission.

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Table I. Observed and calculated line positions for the intermediate-field radio-frequency spectra of $Li^{6}Br^{79}$.

Line No.	Observed (kc)	Calculated (kc)
$(1, \pm 1) \rightarrow (1, 0)$, V = 0, E = 400.00 V/cm, B_0 = 19090.296 Mc/sec		
1	8 728.2	8 728.6
2	13 858.5	13 858.5
3	15 834.5	15 834.2
4	20 964.6	20 964.1
5	22 330.1	22 330.1
6	23 689.3	23 689.1
7	29 435.6	29 435.7
$(1, \pm 1) \rightarrow (1, 0)$, V = 1, E = 400.00 V/cm, B_1 = 18882.800 Mc/sec		
1	8 884.5	8 884.5
2	14 355.7	14 355.6
3	16 453.3	16 453.2
4	21 924.4	21 924.4
5	23 438.2	23 438.3
6	24 815.1	24 815.0
7	31 007.2	31 007.2
$(1, \pm 1) \rightarrow (1, 0)$, V = 2, E = 400.00 V/cm, B_2 = 18677.242 Mc/sec		
1	9 079.3	9 079.2
2	14 878.5	14 878.7
3	17 095.3	17 095.1
4	22 895.1	22 894.6
5	24 554.3	24 555.6
6	25 946.5	25 946.7
7	32 571.8	32 571.5
$(2, \pm 2) \rightarrow (2, \pm 1)$, V = 0, E = 666.782 V/cm		
	5 710.7	5 710.7
	7 648.6	7 648.5
	8 576.1	8 576.0
	10 269.0	10 268.7
	12 686.9	12 686.3
	12 851.0	12 851.0
	13 613.6	13 613.9
	14 788.7	14 788.9
	17 166.3	17 166.9
	17 409.3	17 409.0

Table II. Observed and calculated line positions for the intermediate-field radio-frequency spectra of Li^6Br^{81}.

Line No.	Observed (kc)	Calculated (kc)
$(1, \pm 1) \rightarrow (1, 0)$, V = 0, E = 400.00 V/cm, B_0 = 19057.005 Mc/sec		
1	9 562.3	9 562.3
2	13 939.0	13 939.1
3	15 673.9	15 673.9
4	20 050.4	20 050.7
5	21 067.6	21 067.5
6	22 454.7	22 454.6
7	27 179.1	27 179.1
$(1, \pm 1) \rightarrow (1, 0)$, V = 1, E = 400.00 V/cm, B_1 = 18850.050 Mc/sec		
1	9 706.7	9 706.5
2	14 393.4	14 393.1
3	16 237.8	16 237.8
4	20 924.2	20 924.5
5	22 036.5	22 036.5
6	23 479.4	23 479.2
7	28 567.9	28 567.9
$(1, \pm 1) \rightarrow (1, 0)$, V = 2, E = 400.00 V/cm, B_2 = 18645.035 Mc/sec		
1	9 887.6	9 887.7
2	14 873.5	14 873.6
3	16 824.4	16 824.9
4	21 812.1	21 810.9
5	23 016.9	23 016.9
6	24 511.9	24 512.4
7	29 954.4	29 954.3
$(2, \pm 2) \rightarrow (2, \pm 1)$, V = 0, E = 666.782 V/cm		
	6 324.0	6 323.9
	8 121.0	8 121.6
	8 790.0	8 790.1
	10 761.6	10 762.1
	12 093.8	12 093.7
	12 133.3	12 132.7
	12 762.1	12 762.2
	13 930.5	13 930.3
	15 957.0	15 957.2
	16 570.6	16 570.7

Table III. Dipole moments for Li^6Br.

Li^6Br^{79}	$\mu(\pm 0.001\ D)^a$	Li^6Br^{81}	$\mu(\pm 0.001\ D)^a$
J = 1; v = 0	7.26797	J = 1; v = 0	7.26782
v = 1	7.35228	v = 1	7.35213
v = 2	7.43772	v = 2	7.43763
J = 2; v = 0	7.26789	J = 2; v = 0	7.26777
μ_e = 7.22624 ± 0.0016 D		μ_e = 7.22611 ± 0.0016 D	
μ_I = 0.08318 ± 0.0010 D		μ_I = 0.08312 ± 0.0010 D	
μ_{II} = 0.00057 ± 0.0003 D		μ_{II} = 0.00060 ± 0.0003 D	

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

[a] Precision of the results is ±0.0001 D.

Table IV. Bromine quadrupole-coupling constants, $(eqQ)_v$.

	Li^6Br^{79} (±0.005 Mc)			Li^6Br^{81} (±0.005 Mc)	
v	Weak field	Intermediate field	v	Weak field	Intermediate field
0	38.463	38.464	0	32.127	32.130
1	41.304	41.306	1	34.500	34.504
2	44.067	44.070	2	36.805	36.810
3	46.751		3	39.046	
4	49.355		4	41.222	
5	51.883				
	$(eqQ)_e$ = 37.015 ± 0.003 Mc			$(eqQ)_e$ = 30.912 ± 0.002 Mc	
	$(eqQ)_I$ = 2.918 ± 0.002 Mc			$(eqQ)_I$ = 2.442 ± 0.002 Mc	
	$(eqQ)_{II}$ = -0.039 ± 0.002 Mc			$(eqQ)_{II}$ = -0.034 ± 0.002 Mc	

$$(eqQ)_v = (eqQ)_e + (eqQ)_I \left(v + \frac{1}{2}\right) + (eqQ)_{II} \left(v + \frac{1}{2}\right)^2$$

Table V. Observed transition frequencies and Stark-field corrections.

All transitions were observed at E = 400.00 V/cm.

Vibrational state	Observed transition frequencies ν (Mc/sec)	J = 1 and J = 0 Stark shift and hyperfine corrections (Mc/sec)	Zero field frequencies ν_0 (Mc/sec)
	----- Li^6Br^{79} -----		
0	38194.147 ± 0.012	13.8993	38180.248 ± 0.012
1	37779.628 ± 0.018	14.3747	37765.253 ± 0.018
2	37369.002 ± 0.040	14.8662	37354.136 ± 0.040
	----- Li^6Br^{81} -----		
0	38127.585 ± 0.012	13.9184	38113.667 ± 0.012
1	37714.156 ± 0.040	14.4031	37699.753 ± 0.040

Table VI. Spectroscopic constants of $Li^{6}Br^{79}$.

D_0	$= 86.19 \pm 0.37$ kc
D_1	$= 86.58 \pm 0.45$ kc
D_2	$= 86.97 \pm 0.53$ kc
B_e	$= 19194.592 \pm 0.055$ Mc
$Y_{01} (\approx B_e)$	$= 19194.7741 \pm 0.050$ Mc
$Y_{11} (\approx -\alpha_e)$	$= -209.4415 \pm 0.077$ Mc
$Y_{21} (\approx \gamma_e)$	$= 0.9725 \pm 0.030$ Mc
B_0	$= 19090.296 \pm 0.006$ Mc
B_1	$= 18882.800 \pm 0.009$ Mc
B_2	$= 18677.242 \pm 0.020$ Mc

Table VII. Calculated microwave results and comparisons.

	Honig et al.[3] (Mc)	Rusk and Gordy[4] (Mc)	Data calculated[a] from present Li^6Br^{79} results (Mc)
	----- Li^7Br^{79} -----		
B_e	16 651.186 ± 0.05	16 650.179 ± 0.10	16 650.287 ± 0.048
Y_{01}	16 650.570 ± 0.05	16 650.318 ± 0.06	16 650.444 ± 0.043
$-Y_{11} \approx a_e$	169.09 ± 0.08	-----	169.210 ± 0.062
$Y_{21} \approx \gamma$	0.656 ± 0.040	-----	0.731 ± 0.022
	----- Li^7Br^{81} -----		
B_e	16 617.617 ± 0.05	16 616.622 ± 0.13	16 616.721 ± 0.048
Y_{01}	16 617.002 ± 0.05	16 616.780 ± 0.07	16 616.878 ± 0.043
$-Y_{11} \approx a_e$	168.58 ± 0.08	-----	168.699 ± 0.062
$Y_{21} \approx \gamma_e$	0.653 ± 0.040	-----	0.729 ± 0.022
	----- Li^6Br^{81} -----		
B_e	19 162.316 ± 0.07	-----	19 161.026 ± 0.055
Y_{01}	19 161.511 ± 0.07	-----	19 161.206 ± 0.050
$-Y_{11} \approx a_e$	208.75	-----	208.895 ± 0.077
$Y_{21} \approx \gamma_e$	0.868	-----	0.970 ± 0.030

[a] For comparison with previous LiBr results, our Li^6Br^{79} measurements were corrected for isotope effects.

Table VIII. Observed and calculated spectroscopic constants for Li^6Br^{81}.

Vibrational state	Observed values (Mc)	Values calculated from present Li^6Br^{79} results (Mc)
0	B_0 = 19 057.005 ± 0.006	19 057.003 ± 0.093
1	B_1 = 18 850.050 ± 0.020	18 850.051 ± 0.227
2	B_2 = -----	18 645.035 ± 0.217 [a]

[a] This value was calculated from the observed B_0 and B_1 for Li^6Br^{81} and a Y_{21} calculated from that given for Li^6Br^{79}.

FIGURE CAPTIONS

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

(1) Hot wire and ion accelerator

(2) Glass port cover for optical alignment

(3) Permanent magnet, 60°, 1-cm gap

(4-7) Outlets to liquid nitrogen traps and oil-diffusion pumps

(8) Gate valve and beam flag.

Fig. 2. A schematic diagram of the apparatus. The beam displacements are exaggerated and the field gaps are not to scale.

Fig. 3. A set of typical lines of Li^6Br^{79} for $v = 0$, 1, and 2 at $E = 400.000$ V/cm. These lines correspond to line 1 (uncorrected for contact potential) in Fig. 4.

Fig. 4. The energy levels of Li^6Br^{79} with respect to electric-field strength. The numbered vertical lines correspond to observed transitions between the indicated M_F levels. $M_F = m_J + m_{I_{Br}}$.

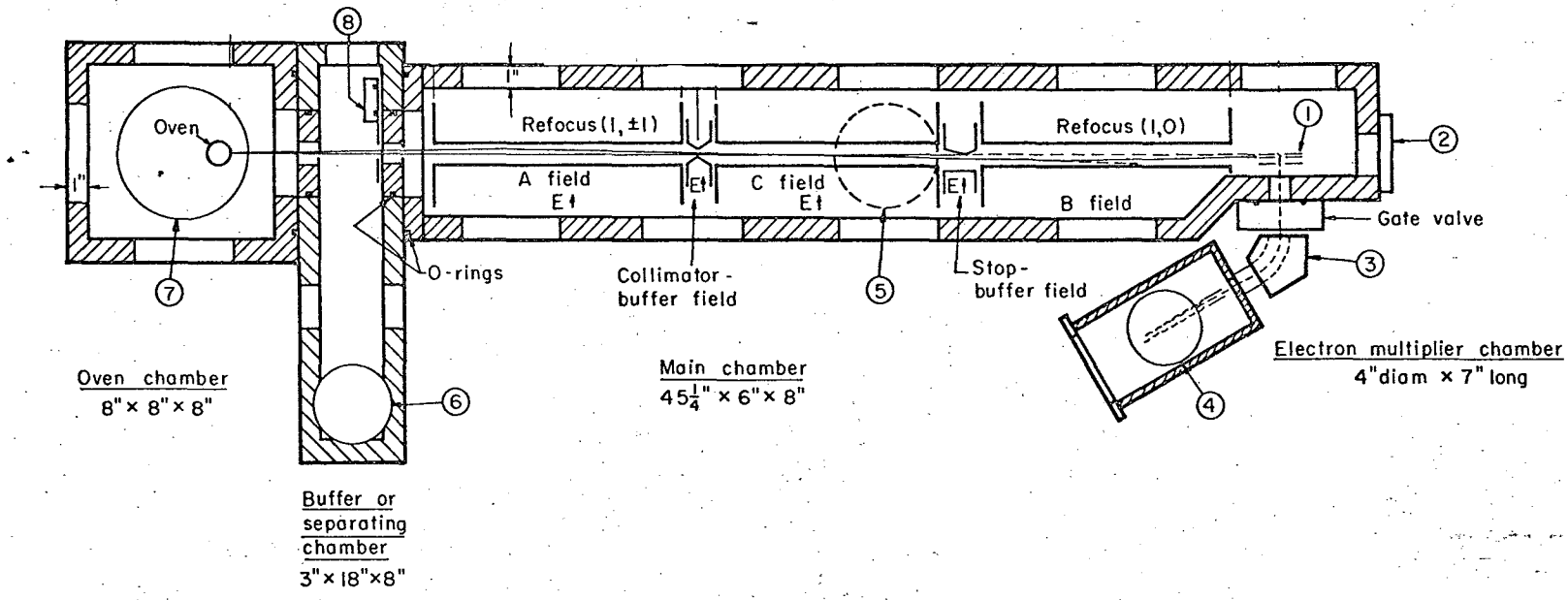

Fig. 1.

UCRL-11012

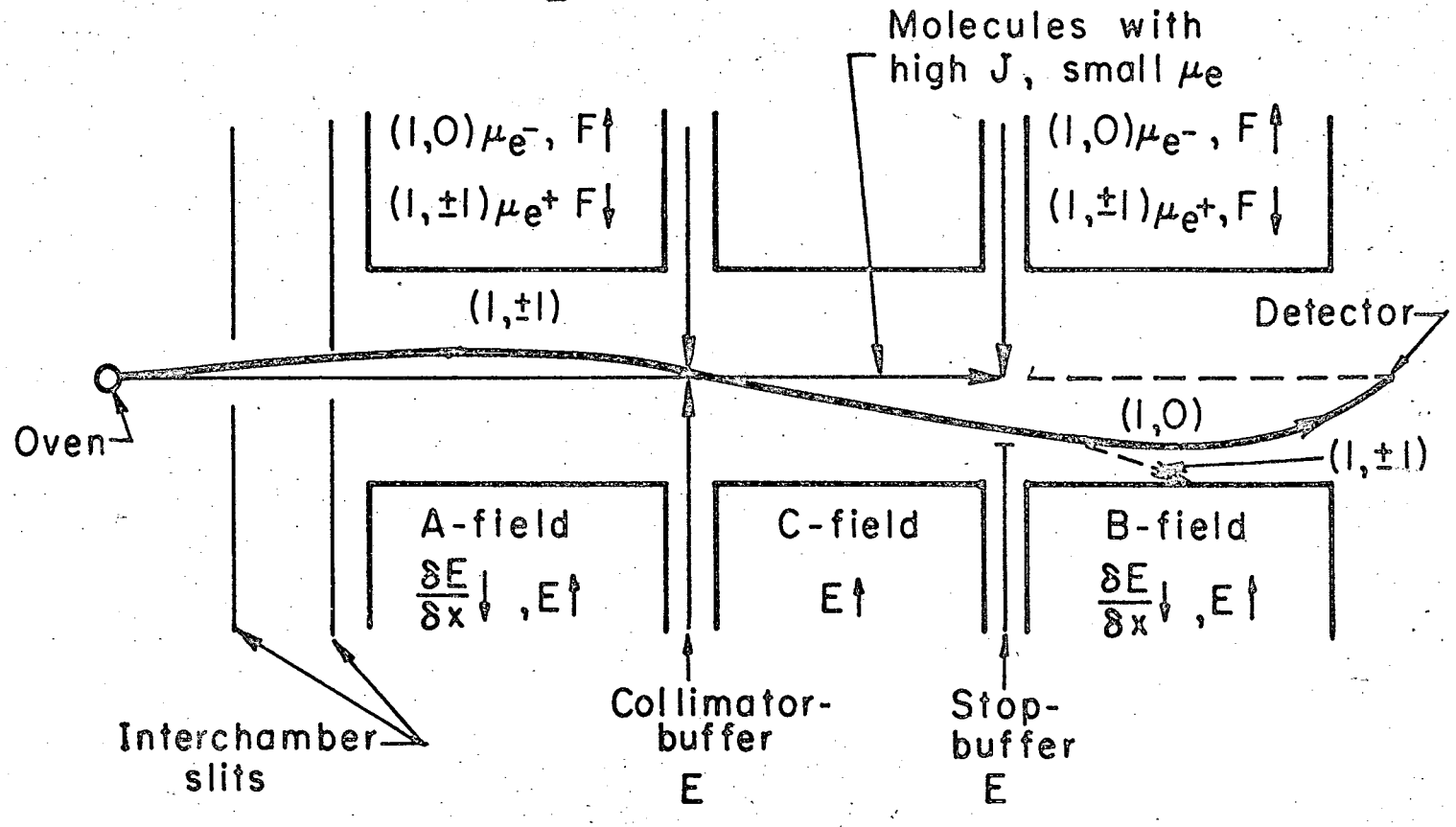
Molecules with
high J, small μ_e
$(1,0)\mu_{e^-}$, F↑
$(1,\pm1)\mu_{e^+}$ F↓
$(1,0)\mu_{e^-}$, F↑
$(1,\pm1)\mu_{e^+}$, F↓
$(1,\pm1)$
Detector
Oven
$(1,0)$
$(1,\pm1)$
A-field
$\frac{\delta E}{\delta x}$↓, E↑
C-field
E↑
B-field
$\frac{\delta E}{\delta x}$↓, E↑
Interchamber
slits
Collimator-
buffer
E
Stop-
buffer
E
MU-28374

Fig. 2.

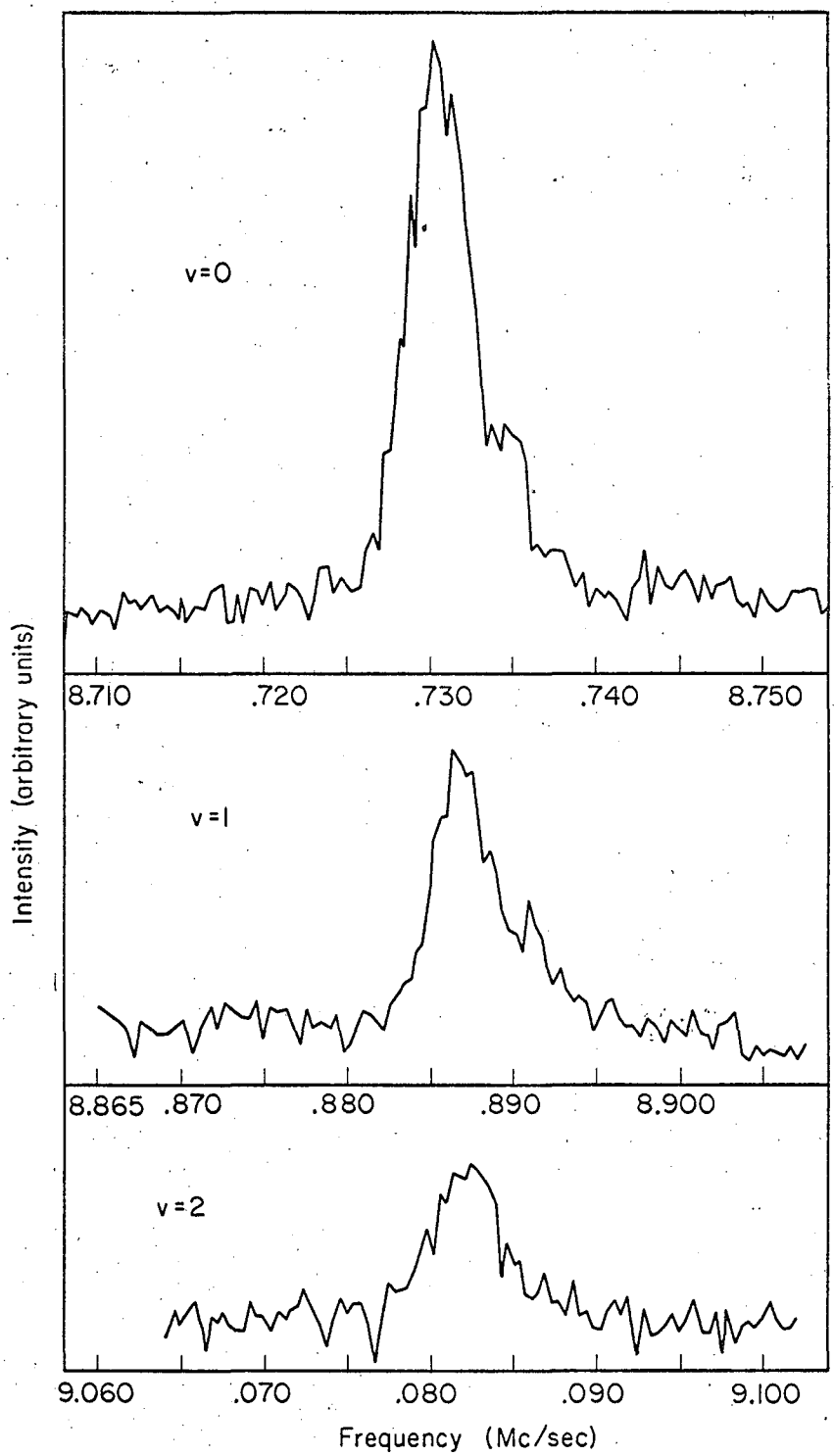
v=0
8.710
.720
.730
.740
8.750
v=1
8.865
.870
.880
.890
8.900
v=2
9.060
.070
.080
.090
9.100
Intensity (arbitrary units)
Frequency (Mc/sec)
MUB-2479

Fig. 3.

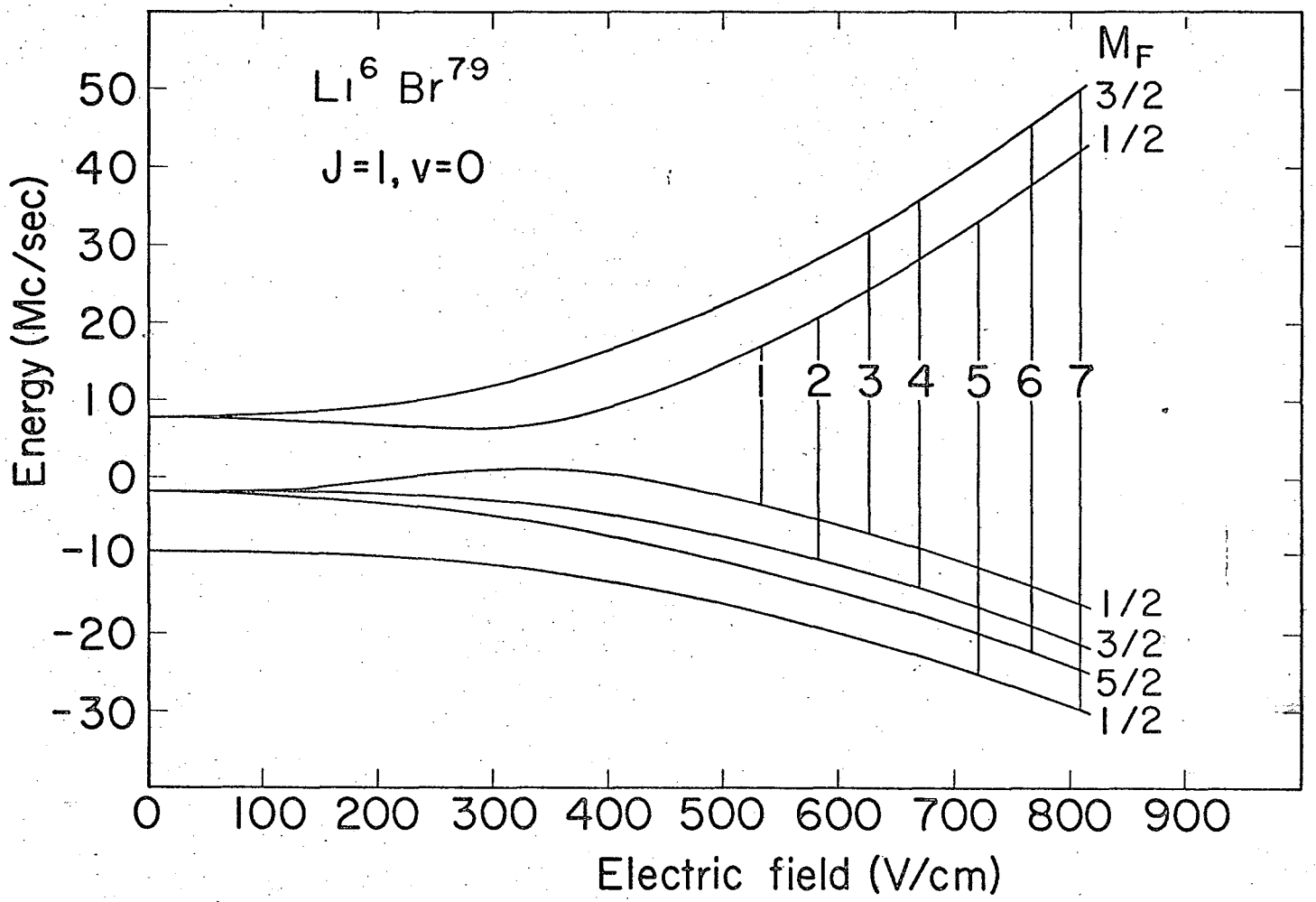
Li⁶ Br⁷⁹
J=1, v=0
Energy (Mc/sec)
50
40
30
20
10
0
-10
-20
-30
0
100
200
300
400
500
600
700
800
900
Electric field (V/cm)
M_F
3/2
1/2
1
2
3
4
5
6
7
1/2
3/2
5/2
1/2
MUB-2478

Fig. 4.