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THE RADIO-FREQUENCY AND MICROWAVE SPECTRA OF Li^6I^{127} BY THE MOLECULAR BEAM ELECTRIC RESONANCE METHOD*

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ABSTRACT

The radio-frequency and microwave spectra of Li^6I^{127} have been observed by the molecular-beam electric-resonance method of molecular spectroscopy. Spectra of Li^6I^{127} in the first two vibrational states were obtained. From the J=1 radio-frequency Stark spectra values were obtained for the electric dipole moment μ, the iodine nuclear quadrupole interaction eqQ_I, and the iodine spin-rotation constant c_I. The values of these constants are:

	v=0	v=1
μ (D)	7.4285 ± 0.001	7.5120 ± 0.001
eqQ_I (Mc/sec)	-198.780 ± 0.005	-207.453 ± 0.010
c_I (kc/sec)	7.7 ± 0.4	7.8 ± 0.6

The observation of J=1 → J=0 microwave transitions yielded the following rotational constants:

B_0 = 15,304.895 ± 0.005 Mc/sec

B_1 = 15,153.316 ± 0.009 Mc/sec.

I. INTRODUCTION

The molecular-beam electric-resonance (MBER) method of radio-frequency spectroscopy has proven to be very useful in determining accurate values for the electric dipole moments and nuclear hyperfine interaction constants of many of the alkali halides.[1,2] In the present work on Li^6I^{127} we have used the MBER technique to determine the electric dipole moment μ, the I^{127} quadrupole interaction eqQ_I, and the I^{127} spin-rotation interaction c_I, in the v=0 and v=1 vibrational states.

The MBER method has also been used to study the J=1→ J=0 microwave transition in Li^6I^{127}. The microwave absorption spectra of LiI 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 I^{127} quadrupole constants and the electric dipole moment of Li^7I. Rusk and Gordy report slightly different values of Y_{01} and B_e and they were also able to report a value for 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] In the present work we obtained values for Y_{01} and B_e which are in excellent agreement with the values of Rusk and Gordy. Our dipole moments are considerably larger than those reported by Honig et al.

II. EXPERIMENTAL

A. Technique

The experimental apparatus used in this work is the same as that used in previous work[7,8] on Li^6Br and NaF. The apparatus and techniques used have been described elsewhere[7,8,9] and will not be discussed here.

The Li^6I was prepared by dissolving 95% enriched Li^6 in distilled water and adding HI. The solution was evaporated and the LiI sample was dried in a furnace at 500°C.

B. Radio-Frequency Spectra

The radio-frequency spectral lines observed were produced by transitions of the type $(J=1, m_J=0) \rightarrow (J=1, m_J=\pm 1)$ where J is the rotational angular momentum quantum number and m_J gives the projection of J on the direction of the electric field. The J=1 level, which is three-fold degenerate in the absence of external fields and nuclear hyperfine interaction, is split into two levels by the application of an electric field of 600.00 volts/cm. The I^{127} nucleus has a spin of 5/2 which couples with the rotational angular momentum through nuclear electric quadrupole and spin-rotation interactions to split the J=1, $m_J=0$ level into 3 levels and the J=1, $m_J=\pm 1$ level into 6 levels. It was found that the spectra could be interpreted without the use of the nuclear hyperfine interactions arising from the Li^6 nucleus which were expected to be much smaller than those of the I^{127} nucleus.

The selection rules are $\Delta m_F=0, \pm 1$, where $m_F = m_J + m_I$ and m_I is the projection of the nuclear spin of I^{127} on the electric field direction. These selection rules predict that 13 lines should be observed in the spectrum (see Fig. 1). Since μ, eqQ_I, and c_I, are functions of the internuclear distance, a separate set of spectral lines is expected for each vibrational state which is sufficiently populated. In this work a complete v=0 spectrum and 5 lines of the v=1 spectrum were obtained, where v is the vibrational quantum number. One line of the v=0 spectrum is shown in Fig. 2.

The full width at half maximum of the spectral lines was approximately 4 kc. This is consistent with the expected uncertainty principle line width considering the average velocity of the molecules and the length of the transition region, and a small broadening due to the unresolved Li^6 quadrupole interaction. The signal-to-noise ratio for the v=0 spectrum was approximately 10 to 1.

Spectra were taken with both polarities of the electric field so that a correction for a small contact potential that is present in the Stark C-field circuit could be made. This correction amounted to 1 part in 10^4 of the line position. The reproducibility of the line maxima was approximately 0.5 kc/sec. The principle source of error in these experiments is the uncertainty in the absolute value of the electric field strength which amounts to ±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 Spectra

In obtaining the microwave spectrum of Li^6I the C-field was set at 50 volts/cm and the radio-frequency was set to produce the peak corresponding to Line 5 in Fig. 1. The microwave frequency was then swept and a resonance was indicated by a decrease in the radio-frequency peak due to a depopulation of the upper level by microwave transition of the type $J=1 \rightarrow J=0$. The decrease amounted to a more than 50% reduction in the "flop-in" Stark signal. The observed microwave lines had a full width at half maximum of approximately 25 kc/sec.

III. RESULTS AND DISCUSSION

A. Radio-Frequency Spectra

The Hamiltonian necessary for interpreting the spectra of Li^6I^{127} is:

$$\mathcal{H} = B\,\underline{J}^2 - \underline{\mu}\cdot\underline{E} - eqQ_I \frac{3(\underline{I}\cdot\underline{J})^2 + 3/2\,(\underline{I}\cdot\underline{J}) - (\underline{I}^2\,\underline{J}^2)}{2I(2I-1)\,(2J-1)\,(2J+3)} + c_I\,\underline{I}\cdot\underline{J}$$

where B is the rotational constant and $\underline{E}$ is the electric field. In fitting the spectra a computer program was used which calculated the matrix elements of $\mathcal{H}$ in a representation described by the quantum numbers J, I, m_J, m_I. The program diagonalized this matrix to give the energy eigenvalues. This program has been described in more detail previously.[7] The unknown input parameters to the program were μ, eqQ_I, and c_I. The program calculated the eigenvalues and transition frequencies corresponding to these parameters, which were adjusted until a best fit to the observed spectra was obtained. The observed and predicted lines are listed in Table I. The observed relative intensities given in the table are only accurate to ±20% since the lines were not all taken at the same beam intensity. The molecular constants which give a best fit to the spectra are given in Table II along with earlier results.

The values obtained for eqQ_I are in agreement with previous results. In the present work the experimental error has been reduced by 2 orders of magnitude. The spin-rotation constant, c_I, is reported here for the first time.

The present dipole moment is higher than the previously reported value[3] and is considerably outside of the combined experimental errors. Our dipole moments should be accurate to ±1 part in 10^4; the major source of error here being due to uncertainty in the electric field voltage. The precision or reproducibility of the dipole moments is nearly an order of magnitude better. Discrepancies between dipole moments measured by MBER and microwave absorption

spectroscopy have been noted previously in the case of LiBr[3,7] and NaCl.[3,10] In all three cases the MBER value for the dipole moment is higher than the microwave value.

B. Microwave Spectra

The observed microwave frequencies were corrected for Stark and nuclear hyperfine energies. The electric dipole moments and nuclear hyperfine constants obtained from the radio-frequency spectra were used in making these corrections. Table III gives these corrections and the zero field frequencies, ν_o. The values of Y_{01} and Y_{11} were calculated from the equation

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

Since we were able to measure the frequencies in only the two lowest vibrational states, we used the value 610 ± 70 kc/sec given by Honig et al.[3] for Y_{21}. The values for D_v were calculated from the results of Rusk and Gordy[4] for Li^7Br by making isotope corrections.[6]

Table IV lists the values of Y_{01}, Y_{11}, B_v, and B_e for Li^6I^{127} and compares them with the values of Honig et al. Table IV also compares the present results with the previous values for Li^7I using isotope corrections.

Table I. Observed and predicted radio-frequency line positions for Li^6I^{127} at an electric field of 600.00 volts/cm.

J=1 v=0				J=1 v=1			
Line No.	Observed (Mc/sec)	Predicted (MC.sec)	Observed relative intensity	Line No.	Observed (Mc/sec)	Predicted (Mc/sec)	Observed relative intensity
1	18.5006	18.5006	100	1	18.8931	18.8932	30
2	28.3275	28.3276	70				
3	40.8378	40.8372	70	3	42.1634	42.1639	20
4	41.7682	41.7680	40				
5	47.6687	47.6683	40				
6	48.5993	48.5991	40	6	50.2200	50.2210	33
7	49.0616	49.0621	60	7	50.8575	50.8569	37
8	63.4503	63.4492	80				
9	71.3968	71.3989	90				
10	85.7859	85.7858	70	10	89.0826	89.0825	27
11	91.7161	91.7167	60				
12	92.6151	92.6169	80				
13	98.5488	98.5478	70				

Table II. Dipole moments, quadrupole-coupling constants, and spin-rotation constants of Li^6I^{127}.

	Present results	Previous results[3]
μ (D)		
v=0	7.4285 ± 0.001[a]	6.64 ± 0.20
v=1	7.5120 ± 0.001[a]	- - -
eqQ_I (Mc/sec)		
v=0	-198.780 ± 0.004	-199.43 ± 0.30
v=1	-207.453 ± 0.010	-206.8 ± 2.0
c_I (kc/sec)		
v=0	7.7 ± 0.4	- - -
v=1	7.8 ± 0.6	- - -

[a] Precision of the results is ±0.0002D.

Table III. Observed microwave transition frequencies and corrections at E = 50.00 V/cm.

Vibrational state	Observed frequency ν (Mc/sec)	J=1 and J=0 Stark and hyperfine corrections (Mc/sec)	Zero field frequencies ν_o (Mc/sec)
0	30,637.8480±0.0071	28.2200±0.0030	30,610.0235±0.010
1	30,336.312 ±0.014	29.4457±0.0030	30,306.866 ±0.017

Table IV. Calculated microwave results and comparisons.
All constants are in Mc/sec.

	Rusk and Gordy[5]	Honig et al.[4]	Present results
		Li^6I^{127}	
B_e	--	15,381.986±0.08	15,381.013±0.10
Y_{01}	--	15,381.448±0.08	15,381.144±0.10
$-Y_{11}(\approx\alpha_e)$	--	152.59 ±0.10	152.799±0.15
$Y_{21}(\approx\gamma_e)$	--	0.610±0.070	--
B_0	--	--	15,304.895±0.005
B_1	--	--	15,153.316±0.009
		Li^7I^{127}	
B_e	13,286.15 ±0.10	13,286.785±0.08	13,286.110±0.10[a]
Y_{01}	13,286.262±0.07	13,286.386±0.08	13,286.217±0.10[a]
$-Y_{11}(\approx\alpha_e)$	--	122.62 ±0.10	122.670±0.15[a]
$Y_{21}(\approx\gamma_e)$	--	0.455±0.50	--

[a] For comparison with previous Li^7I^{127} results our Li^6I^{127} measurements were corrected for isotope effects.

FOOTNOTES AND REFERENCES

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FIGURE CAPTIONS

Fig. 1. The energy levels of Li^6I^{127} with respect to electric field strength. The numbered vertical lines correspond to the observed transitions between the indicated M_F levels. $M_F = m_J + m_I$.

Fig. 2. A typical v=0 line for Li^6I^{127} at E = 600.00 V/cm. This line corresponds to line 4 (uncorrected for contact potential) in Fig. 1. The line maximum corresponds to a counting rate of 6200 counts/sec over a background of 7000 counts/sec.

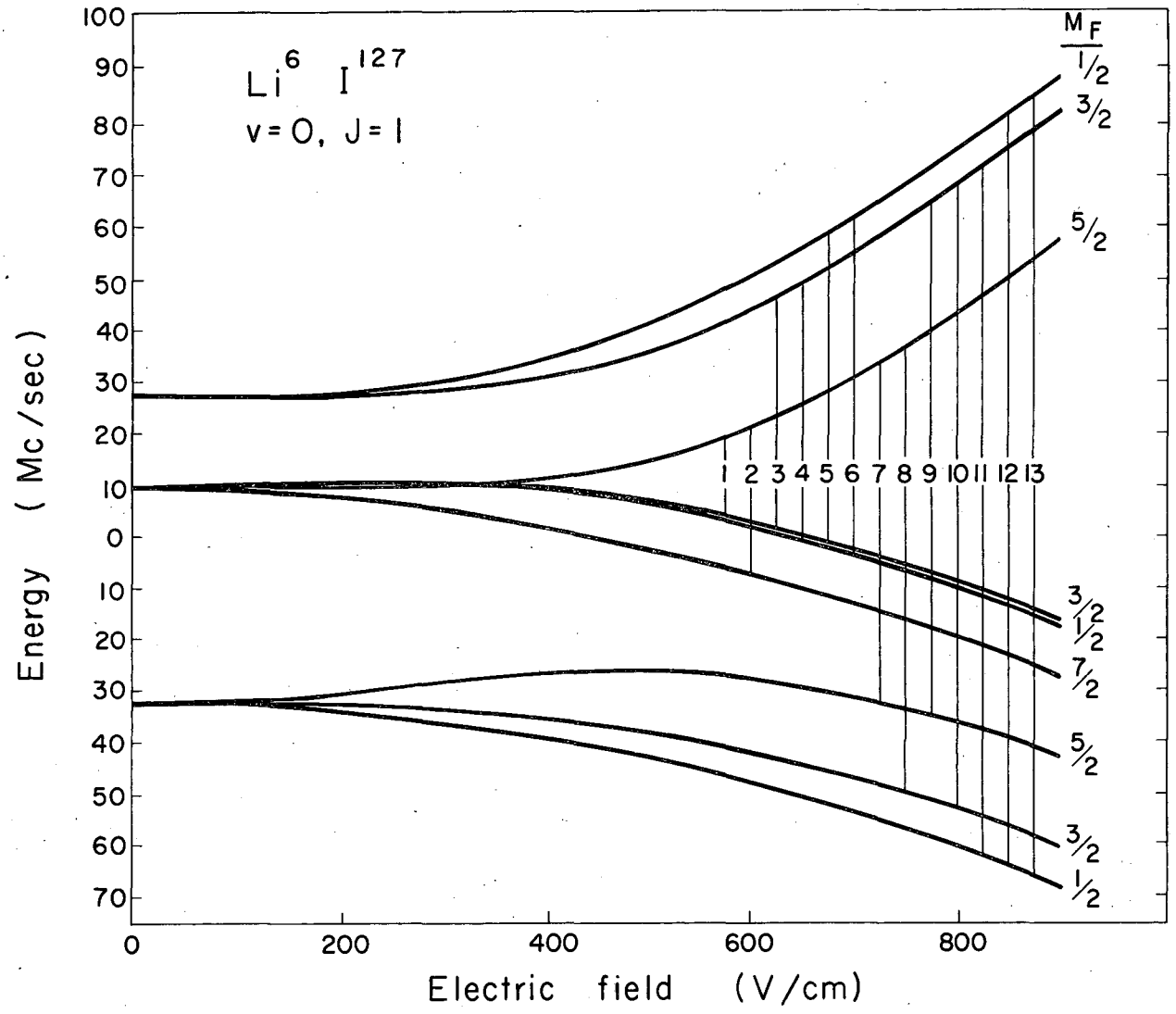
Li 6 I 127
v = 0, J = 1
Energy (Mc/sec)
Electric field (V/cm)
M F
1/2
3/2
5/2
3/2
1/2
7/2
5/2
3/2
1/2
1 2 3 4 5 6 7 8 9 10 11 12 13
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
0
200
400
600
800
MUB-2849

Fig. 1

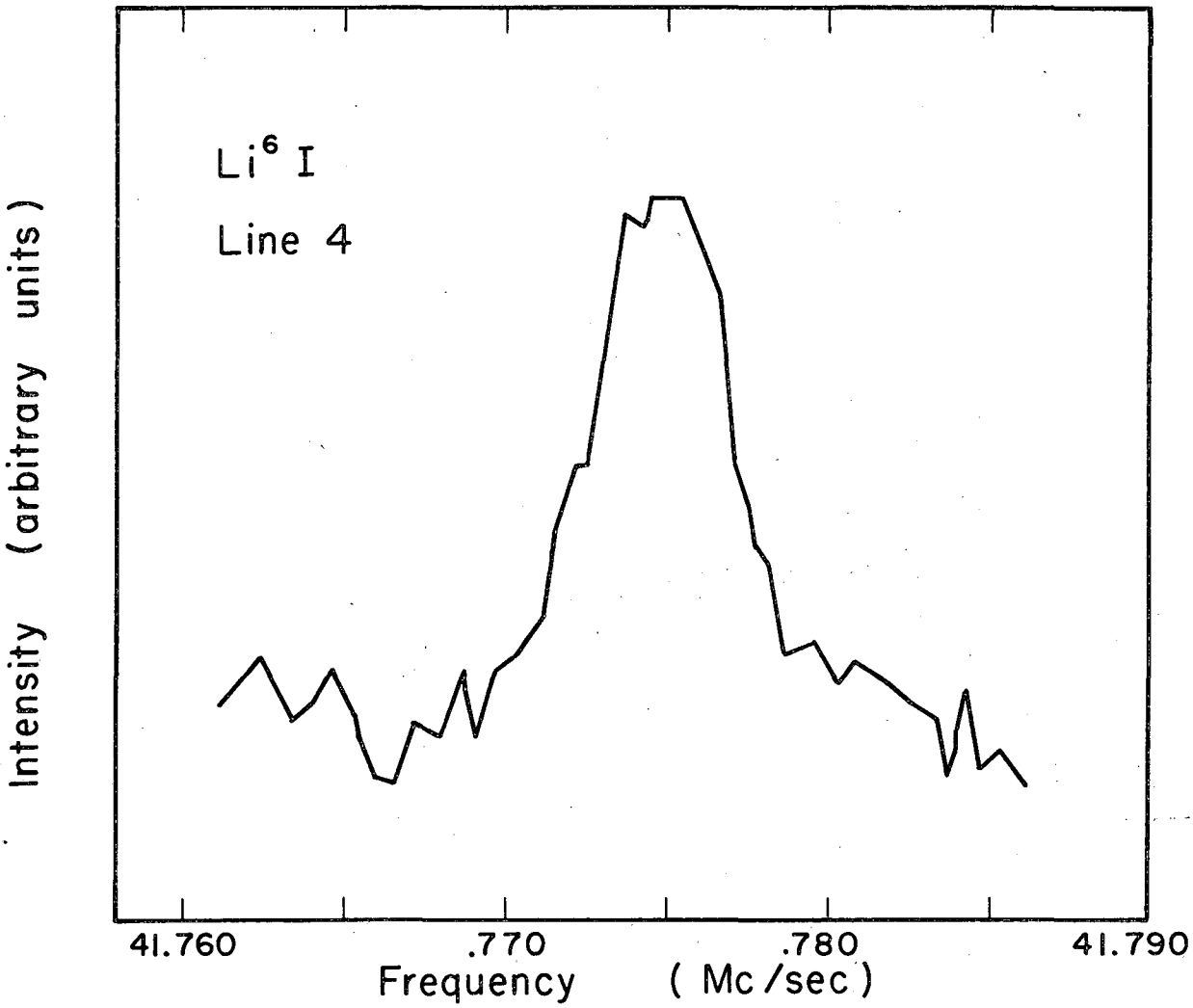
Li⁶ I
Line 4
Intensity (arbitrary units)
41.760
.770
.780
41.790
Frequency (Mc/sec)
MUB-3867

Fig. 2