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Molecular Constants and Nuclear-Molecular Interactions of Li^7F^{19} by the Molecular Beam Electric Resonance Method*

R. Braunstein† and J. W. Trischka
Syracuse University, Syracuse, New York

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The electric resonance method of molecular beam spectroscopy was used to observe the Li^7F^{19} spectra arising from transitions of the type $(J,m_J) \rightarrow (J,m_{J'})$. Data were taken for the $(1,0) \rightarrow (1, \pm 1)$ and $(2,0) \rightarrow (2, \pm 2)$ transitions for the $v=0$ and $v=1$ vibrational states. The latter transitions were observed by a double-quantum process which occurs by the absorption or stimulated emission of two quanta.

From the analysis of the hyperfine structure, the signs and magnitudes of the Li^7 electric quadrupole constant, (eqQ), the F^{19} and Li^7 spin-rotation constant $c_{F^{19}}$ and c_{Li^7} respectively, and the nuclear dipole-dipole interaction, $g_1g_2(\mu_N)^2/r^3h$, were determined. The internuclear distance was determined from the latter constant. (μ^2A) was determined from the strong-field data, where μ is the permanent electric dipole moment and A is the moment of inertia. The dipole moment was then calculated from (μ^2A) and the internuclear distance.

The nuclear-molecular constants are:

	$v=0$	$v=1$
$(eqQ/h)_{Li^7}$ (kc/sec)	$+412.0 \pm 7.0$	$+412.0 \pm 7.0$
$(c/h)_F$ (kc/sec)	$+32.9 \pm 1.0$	$+32.4 \pm 1.0$
$(c/h)_{Li^7}$ (kc/sec)	$+2.2 \pm 0.6$	$+1.8 \pm 0.6$
$g_1g_2(\mu_N)^2/r^3h$ (kc/sec)	$+12.8 \pm 2.0$	$+11.3 \pm 2.0$

The molecular constants determined for Li^7F^{19} are:

(μ^2A), 10^{-76} cgs units	837.1 ± 0.9	872.3 ± 1.0
r, A	1.51 ± 0.08	1.57 ± 0.08
μ, Debye units	6.6 ± 0.3	6.4 ± 0.3
ω_e, cm^{-1}	646 ± 32	

The $(2,0) \rightarrow (2, \pm 2)$ double-quantum transitions of Li^6F^{19} were also observed, from which the following constants were determined: Li^6F $\omega_e = 756 \pm 38$ cm^{-1}; $(\mu^2A)_0(Li^7F)/(\mu^2A)_0(Li^6F) = 1.120 \pm 0.001$; $(\omega_e)_{Li^6F}/(\omega_e)_{Li^7F} = 1.17 \pm 0.02$.

I. INTRODUCTION

The radio-frequency spectra of Li^7F^{19} were studied by the molecular beam electric resonance method.[1,2] With this method, transitions within specific rotational and vibrational states were observed. This molecule was previously investigated by the magnetic resonance method,[3] where rotational and vibrational states were not distinguished, and consequently, the analysis of the spectra required a calculation of a statistical average over rotational and vibrational states of the molecules in the beam.

From the analysis of the hyperfine structure of the present spectra, it was possible to determine the constants for the electric quadrupole interaction of Li^7, the Li^7 and F^{19} spin-rotation $(\mathbf{I} \cdot \mathbf{J})$ interactions, and the nuclear dipole-dipole interaction.

Although the F spin-rotation interaction constant in Li^7F^{19} can be calculated from the Li^6F^{19} values obtained by Swartz and Trischka,[4] its direct determination affords a check of Foley's[5] theory and model of this interaction. The Li^7 spin-rotation interaction can be estimated from the magnetic resonance data, but since such a value is obtained from consideration of line widths, the present unambiguous determination is more accurate.

The determination of the nuclear magnetic dipole-dipole interaction constant in this experiment together with a measure of the electric dipole moment squared times the moment of inertia allowed a calculation of the internuclear distance and the electric dipole moment which have not been previously measured. Since Rittner[6] and Trischka[7] have discussed the LiF molecule using a classical model, and Benson and van der Hoff[8] have developed a quantum-mechanical model for this molecule, the molecular constants determined in the present experiment serve as a check on these theories.

The molecular and nuclear-molecular constants were calculated from a study of the $(J,m_J) \rightarrow (J,m_J')$ transitions $(1,0) \rightarrow (1, \pm 1)$ and $(2,0) \rightarrow (2, \pm 2)$. The latter spectrum was observed by a double-quantum process. Such a transition occurs by the absorption or stimulated emission of two quanta. Hughes and Grabner[9] reported double-quantum transitions in RbF. Whereas the transitions observed by them were between levels which also allow single-quantum transitions to occur, the transitions observed in Li^7F^{19} occurred between levels which forbid a single-quantum transition. Double-quantum transitions similar to those observed in this molecule have been observed by Kusch[10] in magnetic resonance experiments.

II. APPARATUS

The electric resonance apparatus used in this experiment is the same as that used in the experiments of Luce and Trischka[11] with the modifications incorporated by Swartz and Trischka.[4] The reader is referred to the

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* This research was supported in part by the Office of Naval Research.

† Now at RCA Laboratories, Princeton, New Jersey.

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

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

[3] P. Kusch, Phys. Rev. **75**, 887 (1949).

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

[5] J. M. Foley, Phys. Rev. **72**, 504 (1947).

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

[7] J. W. Trischka, J. Chem. Phys. **20**, 1811 (1952).

[8] G. C. Benson and B. M. E. van der Hoff, J. Chem. Phys. **22**, 469 (1954).

[9] V. Hughes and L. Grabner, Phys. Rev. **79**, 314 (1950); **79**, 829 (1950); **82**, 561 (1951).

[10] P. Kusch, Phys. Rev. **93**, 1022 (1954).

[11] R. G. Luce and J. W. Trischka, J. Chem. Phys. **21**, 105 (1953).

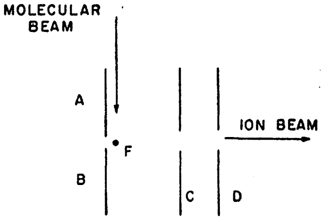

FIG. 1. Cross section of ion gun for mass spectrometer.

aforementioned papers for general information not found in the present description of the modified details of the apparatus. The new features are a new ion gun for the mass spectrometer, a new collimator-buffer field construction, and the use of single crystals for beam material.

A. Ion Gun

A mass spectrometer was used to select Li^7 positive ions produced by surface ionization on a hot oxygenated tungsten wire. The use of a mass spectrometer in these experiments was necessary since positive ion impurities are emitted from the hot wire, and these would have meant a large fluctuating background if the Li^7 ions were collected directly. The separation of Li^6 and Li^7 ions was also especially useful in cases where the spectra of Li^6F^{19} and Li^7F^{19} overlapped.

The geometrical arrangement of the mass spectrometer magnet required that a parallel beam of positive ions be produced normal to the initial direction of the molecular beam. Swartz and Trischka[4] used a gun designed by Thorp[12]; the beam from this ion gun was at times very unstable. The focusing electrodes were at two or three volts with respect to the filament, and consequently, the deposition of a dielectric layer that would become charged might have caused this instability. The positioning of the filament was also very critical in this gun.

The optical analog of electrostatic focusing of charged particles indicates that divergence is produced in a parallel beam of ions on passing through a slit into a field free region. To a first approximation a slit is equivalent to a thin negative lens. However, if there is a field at the point of emergence of the beam from the slit an effective positive lens can be produced and thus a pair of slits can produce a parallel beam of charged particles.

Figure 1 shows a cross section of the two-slit ion gun used in this experiment. The dimensions of the gun were as follows: plates C and D were 0.5 cm apart; plates A and B were 1 cm from C; slits 2.0 cm long and 0.1 cm wide were milled in plates C and D; the filament, F, was placed 0.1 cm from plates A and B which were separated by 0.05 cm. The ratio of F/C potentials was approximately 2 for most of the focusing conditions. Electrodes A and B were approximately 4.5 volts above F with A slightly larger than B. The various electrode potentials were taken off a voltage divider across an electronically stabilized power supply. In this manner, once the gun was focused for one mass peak, other mass peaks could be brought to a focus by changing the accelerating potential while the relative electrode potentials remained the same. With this ion gun, 60 percent of the Li^7 ions formed at the filament arrived at the collector of the mass spectrometer. Although comparable efficiencies were possible with the Thorp gun, the present ion gun gave stable operation.

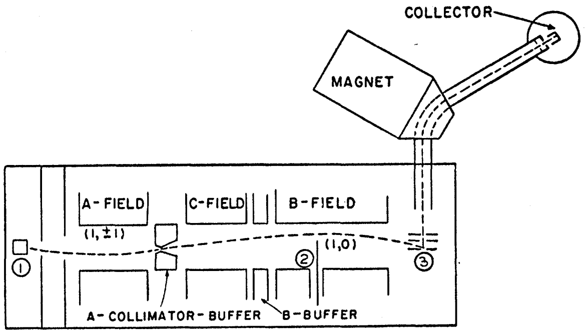

FIG. 2. Schematic diagram of electric resonance apparatus: (1) oven, (2) knife edge for stopping molecules in high rotational states, (3) beam detector and ion gun.

B. Collimator and A-Buffer Field

To refocus a beam in the electric resonance apparatus, it is necessary for molecules to maintain their state of space quantization throughout the electric fields. If an electric field of any magnitude is applied in an adiabatic fashion, it is possible for a molecule to maintain its state identity. It will lose its identity, i.e., undergo a nonadiabatic transition, if an electric field changes too rapidly along the beam path. In this apparatus, when observations were made at low Stark fields, difficulties were often experienced with nonadiabatic transitions which presumably occurred in the regions between the uniform Stark field (C-field) and the inhomogeneous deflecting fields (A and B fields). Figure 2 shows a schematic diagram of the apparatus.

To aid in obtaining a slowly varying field along the beam path, Luce and Trischka[11] placed uniform fields called "buffer-fields" on either side of the C-field and adjusted their strength to minimize the number of nonadiabatic transitions produced by the rapid spatial change of field between the large deflecting fields and the Stark field. Despite the use of these fields, the refocused beam showed erratic fluctuations after appreciable beam material was deposited on the glass collimator slits which were placed between the A-buffer field and the C-field. This was due presumably to changes in the accumulation of charge on the insulator surfaces.

To minimize the above difficulties, a metal collimator which combined the function of collimator and A-buffer

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[12] J. S. Thorp, J. Sci. Instr. **26**, 201 (1949).

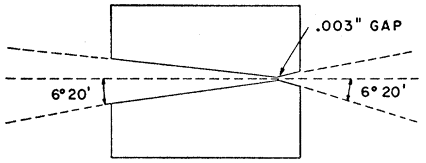

FIG. 3. Collimator and *A*-buffer field.

field was constructed after the design of Swartz and Trischka.[13] The structure of this component is shown in Fig. 3. A taper was arranged in this field to minimize the electric field gradient along the beam axis between the *A*- and the *C*-field region. This structure was mounted from a three point support on the bed plate which supported the *A*-, *B*-, and *C*-fields; this arrangement facilitated the removal of the collimator for cleaning purposes without necessitating the realignment of the collimating slits with respect to the beam path. This collimator-buffer gave satisfactory performance during the weak field runs in this experiment. The weak-field data taken are not reported in this paper. That the buffer fields were effective in controlling nonadiabatic transitions is indicated by the fact that critical settings of the *A*- and *B*-buffer fields were necessary in order to observe spectra at very weak fields.

C. Beam Material

The oven charge of LiF was in the form of single crystals in contrast to the powdered crystals usually used in molecular beam techniques with the alkali halides. This allowed a greater amount of beam charge to be loaded in the oven and also resulted in a decrease in the time required for outgassing of a new charge before a data taking run. The single crystals were cleaved from old LiF windows.[14]

D. Measuring Equipment

The radio-frequency source in this experiment was the General Radio signal generator 805-C; frequencies were measured with a General Radio 620-A heterodyne wave meter calibrated against the Bureau of Standard's station WWV. The random error in frequency determination was 2 parts in 10^4 determined by the least count of the wave-meter dial.

The *C*-field potential was measured using a Leeds and Northrup voltbox a Rubicon potentiometer, and an Eppley standard cell calibrated by the Bureau of Standards. The random error in voltage adjustment during the course of observation of each spectrum was the order of 25 parts in 10^6. Contributions to the uncertainty in the absolute voltage measurements were as follows: the standard cell calibration was known within 1 part in 10^4; the voltbox ratios were known to 2 parts in 10^4; the potentiometer calibration was known within 1 part in 10^4; all contributing to a total possible error in absolute voltage of 4 parts in 10^4. The value of the Stark field was corrected for the residual potential of the *C*-field structure by means of a direct and a reverse field run and an observation of the consequent shift in a line position.

During the course of some of the measurements it was found that the spectra would undergo random drifts of several kilocycles, which were equivalent to voltage changes of 2 parts in 10^4. It was thought that the increased temperature of the voltbox resistors were a contributing element to this difficulty. Wire wound precision resistors, immersed in an oil bath, were compared to those of the voltbox during the course of a run. However, it was found that the voltbox resistances changed by less than 1 part in 10^4 despite the continued drifts in line positions. Regular checks of the 620-A wave-meter calibration made at this time showed no difficulty from this source. Drifts were finally eliminated by applying the proper operating voltage to the *C*-field and its associated voltage measuring equipment for a period of 12 hours prior to a run. It should be noted that when specific lines were repeated from time to time, their absolute positions together with their relative separations agreed well within the error that could be ascribed to the limitations in determining a line position due to the errors in measuring changes in beam intensity. That the drift was not due to the transient charging of the gold film with which the glass *C*-field was coated seems indicated by the observation that when the direction of the Stark field was reversed and the spectra immediately retaken, negligible displacement of a spectral line occurred.

III. THEORY

The Hamiltonian used to explain and to make calculations from the hyperfine structure of the observed spectra of $\mathrm{Li}^7\mathrm{F}^{19}$ is

$$\mathcal{H}=(\hbar^2/2A)\mathbf{J}^2-\boldsymbol{\mu}\cdot\mathbf{E}-(eqQ)_1\frac{[3(\mathbf{I}_1\cdot\mathbf{J})^2+(3/2)(\mathbf{I}_1\cdot\mathbf{J})-\mathbf{I}_1{}^2\mathbf{J}^2]}{2I_1(I_1-1)(2J-1)(2J+3)}+c_1(\mathbf{I}_1\cdot\mathbf{J})+c_2(\mathbf{I}_2\cdot\mathbf{J})$$
$$+(g_1g_2\mu_N{}^2/r^3)\frac{[3(\mathbf{I}_1\cdot\mathbf{J})(\mathbf{I}_2\cdot\mathbf{J})+3(\mathbf{I}_2\cdot\mathbf{J})(\mathbf{I}_1\cdot\mathbf{J})-2(\mathbf{I}_1\cdot\mathbf{I}_2)J(J+1)]}{(2J+3)(2J-1)}. \quad (1)$$

The first term is the rotational energy operator in which *A* is the moment of inertia of the molecule and **J** is the rotational angular momentum. The second term represents the interaction of the external field **E** with the permanent electric dipole moment, $\boldsymbol{\mu}$, of the molecule. The third term gives the interaction between the

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[13] J. C. Swartz and J. W. Trischka (private communication).

[14] Crystals were supplied through the kindness of Dr. Van Zandt Williams of the Perkin-Elmer Company.

electric quadrupole moment of the alkali nucleus, Q_1, and the gradient of the electric field at the position of the alkali nucleus, q_1, produced by the remaining charges in the molecule; eq_1Q_1 is the quadrupole interaction constant defined by Bardeen and Townes.[15] Subscript 1 refers to the nucleus with the strongest nuclear-molecular coupling, which in this case is the Li^7 nucleus, while subscript 2 refers to the F nucleus. The F nucleus has no quadrupole moment since it has a spin of $\frac{1}{2}$. The fourth and fifth terms are the spin-rotation interactions between the nuclear spins and the rotational angular momentum of the molecule, where c_1 and c_2 are the respective interaction constants for the Li^7 and F^{19} nuclei. The last term is the nuclear magnetic dipole-dipole interaction in which g_1 and g_2 are the nuclear gyromagnetic ratios, μ_N is the nuclear magneton, and r is the internuclear distance.

The energy levels and selection rules are discussed in a paper by Hughes and Grabner.[16] The theory of the double-quantum transitions is also given in the above paper. The theory of this type of transition is presented by them as a second-order time-dependent perturbation calculation. For present purposes, the following conclusions of the theory are pertinent. If the radio-frequency field is sufficiently intense, transitions are predicted to occur at half the frequency given by the Bohr condition. These transitions may be considered as occurring by a double-quantum process whereby two quanta supply the energy. At strong static fields (i.e., fields for which the Stark effect is large compared to all internal-molecular interactions), the selection rules allow a $\Delta m_J = \pm 2$ transition to occur at half the frequency that would be necessary for a single quantum transition, thereby allowing the observation of the (2,0) → (2, ±2) transition. It also follows from the theory that the line widths of these transitions should be half as wide as the single quantum line widths.

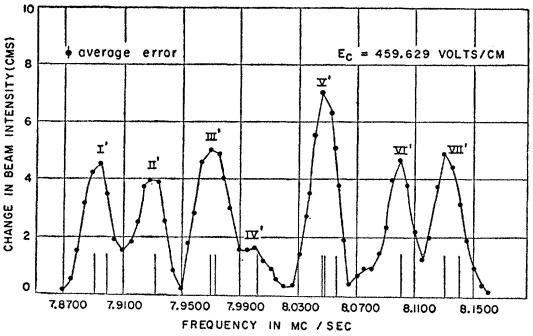

FIG. 4. Single-quantum transitions, (1,0) → (1, ±1), for the $v=0$ vibrational state of Li^7F^{19}. The predicted line positions are indicated by vertical lines under the observed spectra.

IV. SPECTRA AND RESULTS

A consequence of the strong-field theory of the Stark effect for the Hamiltonian, (1), is that to the quadratic term in the field energy, the fine structure produced by terms beyond the second is independent of the value of the electric field; thus the relative separations of the lines are field-independent. By strong field is meant fields where $eq_1Q_1 \ll \mu^2E^2/2A \ll (\hbar^2/2A)J(J+1)$. This is the region where spectra were observed by fixing the C-field voltage and varying the frequency.

Figure 4 shows data for the (1,0) → (1, ±1) transition for the first vibrational state. A preliminary analysis indicated that there were an insufficient number of resolved lines to enable a determination of the value of the four internal interactions from this spectrum alone. The complexity of the spectra is due to the fact that although the quadrupole interaction is the largest interaction, all the other interactions enter in such a significant fashion that the primary quadrupole structure is no longer dominant. An additional complicating feature in the use of the (1,0) → (1, ±1) spectra for the determination of the constants is that the lines have a quadratic dependence on the constants.

Consequently, it was decided to search for the (2,0) → (2, ±2) double-quantum transitions which are allowed at high radio-frequency fields as was previously indicated. This spectrum should be simpler since it is possible to avoid the use of the $m_J = \pm 1$ states, which are always complicated for all J values. Since the direct output voltage of the General Radio signal generator was insufficient, a tuneable resonant circuit, placed in the output of the oscillator, gave as much as 100 volts of rf at resonance. Spectra were found at half the frequency at which the single-quantum (2,0) → (2, ±2) spectra should have been observed were they not forbidden by the selection rules. Figure 5 shows a typical plot of the first vibrational state of the (2,0) → (2, ±2) double-quantum transition. The line widths in this spectrum are seen to be half as wide as for the single quantum transitions, which should indeed be the case for the double-quantum transition. The fact that these were double-quantum transitions and were not due to

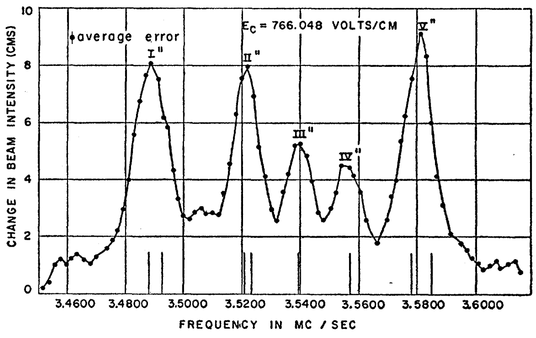

FIG. 5. Double-quantum transitions, (2,0) → (2, ±2), for the $v=0$ vibrational state of Li^7F^{19}. The predicted line positions are indicated by vertical lines under the observed spectra.

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

[16] V. Hughes and L. Grabner, Phys. Rev. 79, 829 (1950).

TABLE I. Nuclear-molecular constants of Li^7F^{19}.

Constant	$v=0$	$v=1$
$(eqQ/h)_{Li^7}$ kc/sec	$+412.0\pm7.0$	$+412.0\pm7.0$
$(c/h)_{F^{19}}$ kc/sec	$+32.9\pm1.0$	$+32.4\pm1.0$
$(c/h)_{Li^7}$ kc/sec	$+2.2\pm0.6$	$+1.8\pm0.6$
$g_1g_2(\mu_N)^2/r^3h$ kc/sec	$+12.8\pm2.0$	$+11.3\pm2.0$

harmonics of the oscillator was shown by the following considerations: (1) A search for spectra at twice the frequency produced negative results. (2) The $(2,0)\rightarrow(2,\pm2)$ single-quantum transitions were found at intermediate fields and were followed to strong fields where they disappeared. (3) In general, to produce resolved lines for single-quantum transitions in Li^7F^{19}, the rf voltage was of the order of 0.4 volts; 30 volts (which was the voltage necessary to produce spectra at the half frequency) would have caused excessive broadening of the lines.

The previous measurements of the nuclear-molecular constants of Li^7F^{19} and Li^6F^{19} [3,4] were used for a preliminary analysis of the $(2,0)\rightarrow(2,\pm2)$ structure. The analysis showed that of the five observed lines only two were single; the rest were unresolved doublets. Four equations involving differences between the five observed lines were necessary to calculate the constants (since initially the position of the unperturbed Stark line was not known). Although a satisfactory theory does not exist for the relative intensities of lines observed in electric resonance experiments, the observed relative intensities in this spectrum indicated that equal weight could be given to each transition. Consequently, the approximation was made that the observed position of a line corresponds to the mean position of the theoretical constituent doublets. Of the four difference equations so formed, only three were linearly independent. However, lines II′ and VI′ of the $(1,0)\rightarrow(1,\pm1)$ spectrum are single and have a linear dependence on the constants so that the required four simultaneous linear equations were formed from a combination of the $J=1$ and $J=2$ spectra. The nuclear-molecular interactions are not expected to vary with rotation for these low rotational states.

The calculated nuclear-molecular interactions are given in Table I. From these constants, the positions of all the lines in $J=1$ and $J=2$ spectra were predicted. These predictions are indicated as vertical lines under the observed spectra in Figs. 4 and 5. The agreement between the observed and predicted line positions justifies the above treatment of the data. It should be noted that giving equal weight to all the possible transitions is not justified in the $J=1$ spectrum since line IV′ which is a single line is much less intense than II′ and VI′ which are also single lines; however, only the single lines II′ and VI′ are used in the calculations of the constants.

TABLE II. Molecular constants of Li^7F^{19}.

Constant	$v=0$	$v=1$
μ^2A, $(J=1)$, 10^{-76} cgs units	$836.8\ \pm1.0$	
μ^2A, $(J=2)$, 10^{-76} cgs units	$837.1\ \pm0.9$	$872.3\ \pm1.0$
r, A	1.51 ± 0.08	1.57 ± 0.08
μ, Debye units	$6.6\ \pm0.3$	$6.4\ \pm0.3$
ω_e, cm^{-1}	646 ± 32	

After the analysis of the fine structure, the position of the unperturbed Stark line was determined, which together with the measurement of the Stark field and a correction made for the contact potential, allowed the product μ^2A to be calculated. The equation due to Lamb for the energy levels of a rigid rotator in an electric field[1] was used for the calculation. The unperturbed Stark line of the $J=2$ spectrum lies at the mean position of the extreme lines I″ and V″. It can be shown that the Stark line for the $J=1$ spectrum lies at $2c_1$ above the mean position of the extreme lines in this spectrum. The values of μ^2A are shown in Table II.

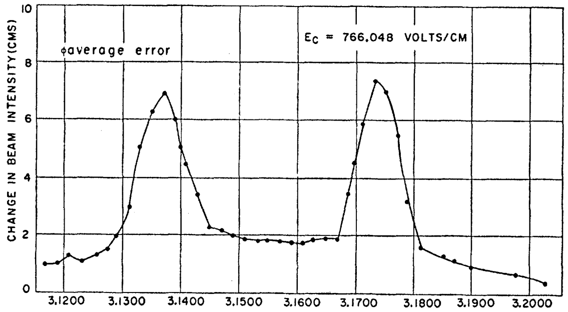

FIG. 6. Double-quantum transitions, $(2,0)\rightarrow(2,\pm2)$, for the $v=0$ vibrational state of Li^6F^{19}.

The μ^2A values determined from both spectra agree within experimental error, thereby lending further justification for the treatment of the data.

The values of μ and A separately can be obtained in some molecules if the departure from quadratic dependency of the unperturbed Stark frequency can be observed. This method requires excessively large fields in the present case because of the smallness of μ^4A^3 in Li^7F^{19}. However, the calculation of μ and A was made possible in this molecule through the measurement of the magnetic dipole-dipole interaction constant. The value of the internuclear distance obtained from this constant was used to obtain A, which in turn was used together with μ^2A to calculate μ. The calculated values of μ and r are given in Table II.

The line shapes of the $J=2$ double-quantum transitions are not understandable on the basis of the ideal line shape calculated by Torrey.[17] The extreme ends of the spectrum seem to indicate secondary maxima. Between lines I″ and II″ there is further indication of

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[17] H. C. Torrey, Phys. Rev. **59**, 293 (1941).

what appears to be an unresolved line which cannot be accounted for since all possible transitions have been considered.

Since no completely isolated line exists in the $(2,0) \rightarrow (2, \pm 2)$ spectra, a study of a line shape was not possible. However, since the spectra of Li^6F^{19} observed by Swartz and Trischka[4] as a single-quantum transition contained only two lines, the double-quantum transitions of this molecule were obtained as a means of comparison. Figure 6 shows the $(2,0) \rightarrow (2, \pm 2)$ spectrum of Li^6F^{19} for $v=0$. This spectrum also shows secondary maxima or at least long tails which are not in keeping with the line shape calculated by Torrey.[17] Figure 7 shows the single-quantum transition observed by Swartz and Trischka[18] for comparison. It should also be noted that the resolution in the $(2,0) \rightarrow (2, \pm 2)$ spectrum of Li^6F is better than in the $(1,0) \rightarrow (1, \pm 1)$ spectrum, permitting a more accurate determination of the F spin-rotation interaction. The prime purpose in obtaining the Li^6F double-quantum transitions was to insure the correct counting of the Li^7F^{19} lines and consequently no further work was done to elucidate the occurrence of these tails.

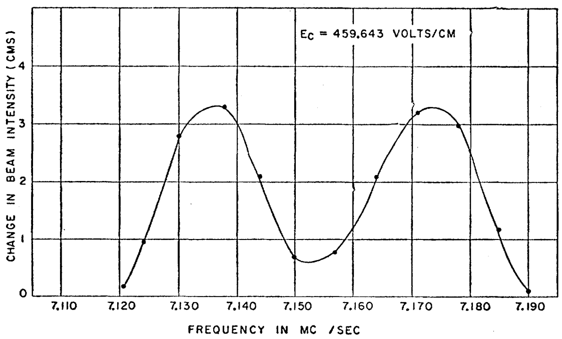

FIG. 7. Single-quantum transitions, $(1,0) \rightarrow (1, \pm 1)$, for the $v=0$ vibrational state of Li^6F^{19}. These line shapes are to be compared with the double-quantum line shapes in Fig. 6.

To provide an additional benefit from the above Li^6F^{19} spectrum, the Li^6F^{19} and Li^7F^{19} spectra were taken at the same field. Consequently, a direct determination of their $\mu^2 A$ ratio, free from systematic errors in voltage was made. The results are shown in Table III.

From the variation in intensity of corresponding lines in vibrational states, the vibrational constants for Li^6F^{19} and Li^7F^{19} were determined. Since the spectra of Li^6F^{19} and Li^7F^{19} were observed under identical conditions, a direct determination of the ratio of their vibrational constants was possible. In view of the fact that the oven temperature was the same during the course of these runs, the uncertainty in the ratio of ω_e's should be due only to the error in measuring relative intensities of lines. Since the location of the peak intensity is unreliable, the ratios of the areas of corresponding lines of the first three vibrational states of each molecule were determined. In Li^7F^{19}, the ratios of the intensities of successive lines were 0.40 ± 0.01 while in Li^6F^{19}, the ratios were 0.34 ± 0.01. The ratio of the ω_e's are given in Table III. The vibrational constants of Li^7F^{19} and Li^6F^{19} are given in Tables II and IV respectively.

TABLE III. Ratios of Li^6F and Li^7F molecular constants.

Quantity	
$(\mu^2 A)_0(Li^7F)/(\mu^2 A)_0(Li^6F)$	1.120 ± 0.001
$(\omega_e)_{Li^6F}/(\omega_e)_{Li^7F}$	1.17 ± 0.02

V. DISCUSSION

The present determination of the quadrupole coupling constant $(eqQ/h)_{Li^7} = +412 \pm 7$ kc/sec can be compared with the value $|eqQ/h| = 408 \pm 12$ kc/sec obtained by Kusch[3,19] from molecular beam magnetic resonance data. The agreement may be taken as an indication that this coupling constant does not vary greatly with vibration or rotation. The positive signs obtained for this interaction are in agreement with the result of Logan *et al.*[20] The fluorine spin-rotation constant $c_2/h = +32.9 \pm 1.0$ kc/sec in Li^7F^{19} is consistent with the value $c_2/h = +37.3 \pm 0.3$ kc/sec found in Li^6F^{19} by Swartz and Trischka,[4] when account is taken of the different reduced masses of the molecules in accordance with Foley's[5] model of this interaction. The Li^7 spin-rotation constant $c_1/h = +2.2 \pm 0.6$ kc/sec differs from the value $c/h = 1.4$ kc/sec calculated by us from Kusch's data.[3] The fact that the electric resonance value is larger than the magnetic resonance value is interesting because the fluorine electric resonance value in CsF and LiF is also larger than the values determined by the magnetic resonance method.

The internuclear distances and dipole moments, determined for the first time in the present experiments, are compared in Table V with values obtained in various theoretical calculations. Benson and van der Hoff[8] made use of a quantum mechanical model of LiF, while Rittner[6] and Trischka[7] utilized a semiclassical, polarized-ion model. It will be noted that agreement between theory and experiment exists for all of the results in Table V except for the value of μ found by Rittner. This value is clearly too low. Although results are listed for two vibrational states, the accuracy of the

TABLE IV. Molecular constants of Li^6F.

Constants	
$(\mu^2 A)_0(J=2)$, 10^{-76} cgs units	747.6 ± 1.0
ω_e, cm^{-1}	756.0 ± 38

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[18] J. C. Swartz and J. W. Trischka (private communication).

[19] The estimated error in this measurement was kindly supplied to the authors by Professor P. Kusch.

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

TABLE V. Comparison of experimental and theoretical values of r and μ. The subscripts on r and μ indicate the vibrational state, where r is in angstrom units and μ in Debye units.

Method	r_0	r_1	μ_0	μ_1
Experimental[a]	1.51 ± 0.08	1.57 ± 0.08	6.6 ± 0.3	6.4 ± 0.3
Theoretical[b]	1.60	1.62	6.35	6.47
Theoretical[c]	1.53		5.04	
Theoretical[d]	$1.44<r<1.65$		6.0	

[a] Present experiments.
[b] G. C. Benson and B. M. E. van der Hoff, J. Chem. Phys. **22**, 469 (1954).
[c] E. S. Rittner, J. Chem. Phys. **19**, 1030 (1951).
[d] J. W. Trischka, J. Chem. Phys. **20**, 1811 (1952).

experimental results is not sufficient to determine how r and μ change from one vibrational state to the next.

The $(\mu^2 A)_0$ of Li^6F (listed in Table IV) obtained from the double-quantum transitions agrees with the value obtained by Swartz and Trischka[4] who observed the single-quantum transitions. The observed ratio of $(\mu^2 A)_0$ given in Table III differs beyond experimental error from the ratio 1.12154 of the reduced masses of these isotopes; this difference may be ascribed to the zero point vibrational difference.

The vibrational constant ω_e of Li^7F^{19} is 646 ± 32 cm^{-1} and for Li^6F^{19} $\omega_e=756\pm38$ cm^{-1}. The absolute values of ω_e are in doubt mainly because of the uncertainty in measuring the temperature of the vapor in the oven, $T=1060$°K, and the error in measuring relative intensities of lines. By measuring the velocity distribution of molecules from an oven similar to the one used in this experiment, Miller[21] has shown that the error in the temperature determined from a thermocouple reading can be ±50°K. Miller also found that the temperature at the slit may be as much as 50° higher than the temperature near the charge, where the thermocouple was located in the oven used in the present experiments. The temperature given above is the measured temperature plus 50°K. The value of ω_e for different isotopic molecules should vary inversely as the square root of the reduced mass. On this basis the ratio of the ω_e's for Li^6F^{19} and Li^7F^{19} should be 1.06, whereas the observed ratio is 1.17 ± 0.02. The reason for this discrepancy is not clear. An explanation may lie in the value of the radiofrequency field used. The observed intensity of a line depends upon the value of the radiofrequency field. The value of the radiofrequency field was selected to give the narrowest line at a given frequency and this value of field was used throughout a given spectrum; this optimum field may be a function of frequency, being appreciably different even in the brief frequency range from the $v=0$ spectra to $v=2$ spectra. It should also be noted that Benson and van der Hoff[8] predicted $\omega_e=1039$ cm^{-1} for Li^6F whereas the observed value is 756 ± 38 cm^{-1}. Rittner[6] predicted that $\omega_e=773$ cm^{-1} for a LiF in which the chemical mass of Li is used. Hence this value is best compared with the experimental result for Li^7F^{19}.

The use of the double-quantum transitions in this experiment enabled considerable simplification of the spectra and their subsequent analysis. This method should prove useful in the study of other molecules if $J\geq2$ states can be refocused.

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[21] R. C. Miller and P. Kusch, Quarterly Report, Columbia Radiation Laboratory, August 31, 1953 (unpublished).