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A MOLECULAR-BEAM ELECTRIC-RESONANCE
SPECTROMETER AND THE RADIO-FREQUENCY
SPECTRA OF LITHIUM FLUORIDE

Berkeley, California

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AND THE RADIO-FREQUENCY SPECTRA OF LITHIUM FLUORIDE

Alvin Joseph Hebert
(Ph. D. Thesis)

September 26, 1962

A MOLECULAR-BEAM ELECTRIC-RESONANCE SPECTROMETER
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A MOLECULAR-BEAM ELECTRIC RESONANCE SPECTROMETER AND THE RADIO-FREQUENCY SPECTRA OF LITHIUM FLUORIDE

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September 26, 1962

ABSTRACT

The construction and operation of a radio-frequency electric resonance molecular beam apparatus are described. The resolution of the apparatus is consistent with theoretical expectations. A simple mass spectrograph and an automated counting-recording scheme allow the procurement of spectra from signals that correspond to as few as one hundred detected transitions per second.

The experimental results obtained for lithium fluoride are presented and discussed. Spectra were observed for the first three vibrational states of Li^6F^{19} and Li^7F^{19} . A value for the lithium quadrupole coupling constant, the spin-rotation constant, the Stark-effect constant, and the dipole moment is reported for each vibrational state. Results for the $V = 2$ vibrational state of Li^7F^{19} are reported for the first time.

An analysis of the Li^7F^{19} spectra has resolved an uncertainty in the rotational and vibrational constants previously reported. This in turn has allowed a much more accurate determination of the dipole moments of LiF .

I. INTRODUCTION

This thesis deals with the design and operation of a high-resolution molecular beam electric resonance (MBER) apparatus. The unit is designed for studies of the radio-frequency spectra of dipolar molecules in an electric field. The experimental results obtained for the molecules Li^6F^{19} and Li^7F^{19} are presented and discussed.

The apparatus follows the same basic design as that used in the first unit of this type, which was constructed by H. K. Hughes and reported in 1947.¹ A mass-spectrometer detection system incorporated in the unit is similar to the one first used in a MBER by Trischka and others.^{2, 3, 4}

The following section presents a brief discussion of the theory of operation for a radio-frequency MBER apparatus. The reader is referred to the aforementioned papers, a book by N. F. Ramsey⁵, and a review article by P. Kusch and V. W. Hughes⁶ for more detailed treatments.

A. Theory of Operation

A molecular beam is produced by effusion from a source slit that is narrower than the mean free path of the molecules. A collimator near the center of the apparatus defines the beam. In the case of alkali halide beams, a salt is heated in a small oven which is provided with a slit 5 mils (0.005 inch) wide by 0.5 cm high. The beam travels in a vacuum sufficient to make the mean free path of the molecules much greater than the distance between the oven and the detector.

1. H. K. Hughes, Phys. Rev. 72, 614 (1947).
2. J. C. Swartz and J. W. Trischka, Phys. Rev. 88, 1085 (1952).
3. R. G. Luce and J. W. Trischka, J. Chem. Phys. 21, 105 (1953).
4. R. Braunstein and J. W. Trischka, Phys. Rev. 98, 1092 (1955).
5. N. F. Ramsey, Molecular Beams (Clarendon Press, Oxford, 1956).
6. P. Kusch and V. W. Hughes, in Handbuch der Physik (Springer-Verlag, Berlin, 1959), Vol. 37/1.

Two inhomogeneous electric fields, designated A and B, allow the selection of a given rotational quantum state in the beam for study. The rotational state of interest will be designated by the angular momentum quantum number J ; the electric quantum number m_J corresponds to the projection of J on the field direction. Figure I-1 shows a plot of the ratio μ_e/μ versus the dimensionless parameter λ for various states (J, m_J) of a linear polar diatomic molecule,⁷ where $\lambda = \mu E/(\hbar^2/2A)$, μ_e is the effective dipole moment, μ is the permanent dipole moment, A is the moment of inertia of the molecule, and E is the electric field value. A schematic diagram of the apparatus is also shown in Fig. I-1. Molecules in the beam experience a force, $F = \mu_e \partial E/\partial x$, where $\partial E/\partial x$ is the gradient of the field in the x direction. Thus, the proper selection of E and $\partial E/\partial x$ in the A and B fields can result in a refocusing of molecules that leave the source slit at a slight angle to the axis between the source and detector.

Experiments can be performed in which a single rotational state is refocused, i. e., $(1, 0)_A \rightarrow (1, 0)_B$, and a transition induced by rf in the region between the A and B fields, $(1, 0) \rightarrow (1, \pm 1)$, will result in a decrease in the signal at the detector. A stop is normally placed in the B field to prevent molecules with high J (and thus small μ_e) from reaching the detector. Experiments of this type are often called "flop-out" experiments. Similarly, experiments of the "flop-in" type may be performed in which only those molecules that undergo a transition, i. e., $(1, \pm 1) \rightarrow (1, 0)$, are refocused and detected. Fig. I-2 shows a schematic diagram of the apparatus and the path of a molecule that has undergone a transition in the C-field region and is subsequently detected. Molecules that have not undergone a transition are deflected away from the detector by the B field.

The experiments reported in this thesis are of the "flop-in" type. Both types of experiments yield the same results. One advantage of the "flop-in" experiment is the lower deflecting-field voltages

7. H. K. Hughes, Phys. Rev. 72, 618 (1947).

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Fig. I-1. The effective electric moments of a rotating polar molecule in an electric field (reference 7), and a schematic diagram of the apparatus.
(Note: Beam displacements are exaggerated; field gaps are not to scale.)

MUB-1386

Fig. I-2. 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. (Dimensions refer to internal chamber sizes.)

- (1) Hot wire and ion accelerator
- (2) Glass port cover for optical alignment
- (3) Permanent magnet, 60°, 1-cm gap
- (4) Outlet, 4 in. diam, to liquid nitrogen trap and oil-diffusion pump
- (5) Outlet, 5 in. diam, to liquid nitrogen trap and oil-diffusion pump
- (6) Outlet, 4 in. diam, to gate valve, liquid nitrogen trap, and oil-diffusion pump
- (7) Outlet, 6 in. diam, to gate valve, liquid nitrogen trap, and oil-diffusion pump
- (8) Gate valve and beam flag.

necessary for refocusing when the sigmoid-path technique shown in Fig. I-2 is used. Another advantage is the better signal-to-noise ratio that is usually obtained.

The equation stating the condition for refocusing a beam onto the detector is analogous to the molecular- or atomic-beam magnetic resonance case discussed by Ramsey,⁸ and is given as follows:

$$\mu_{eA}(\partial E/\partial x)_A \ell_A (\ell_A + 2\ell_1) \ell_6 / \ell_5 + \mu_{eB}(\partial E/\partial x)_B \ell_B (\ell_B + 2\ell_4) = 0. \quad (I-1)$$

Inserting the values for ℓ_A , ℓ_B , ℓ_1 , ℓ_4 , ℓ_5 , and ℓ_6 as defined in Fig. I-2, Eq. (I-1) becomes

$$2\mu_{eA}(\partial E/\partial x)_A + \mu_{eB}(\partial E/\partial x)_B = 0. \quad (I-2)$$

The method and field strengths used to obtain refocused beams of LiF molecules with $J = 1$ are discussed in Section II of this paper.

The magnitude and direction of the electric field may change so rapidly in the interfield regions that molecules lose their state of space quantization. This type of nonadiabatic transition allows the detection of molecules that have not undergone transitions induced by rf in "flop-in" experiments. The buffer fields, shown in Fig. I-2, reduce variations in the electric field along the beam path so that only those changes in m_J which are induced by an rf signal in the homogeneous electric C field region result in an increase in the number of molecules that reach the detector.

In the absence of nuclear-molecular interactions, the frequency (Stark frequency) corresponding to the transition $(1, \pm 1) \leftrightarrow (1, 0)$ is given, to a close approximation, by the expression⁹

$$\nu = 6/20(\mu^2 A / h\hbar^2)E^2 - 0.086144(\mu^4 A^3 / h\hbar^6)E^4, \quad (I-3)$$

where ν is the frequency in cycles per second, and E is the field strength in esu. When the second term in Eq. (I-3) is not too small

8. N. F. Ramsey, Molecular Beams (Clarendon Press, Oxford, 1956), p. 90.

9. H. K. Hughes, Phys. Rev. 76, 1675 (1949).

compared with the first, μ and A can be determined by fitting the above relation to spectra taken at different field strengths. H. K. Hughes first used this method to obtain the dipole moment and moment of inertia of CsF .^{1,9} Equation (I-3) is also used to determine μ when A is known.

The method used to analyze the spectra obtained for Li^6F and Li^7F is given in Section III.

Transitions involving a change of J can also be induced with microwave signals. The apparatus is not equipped for this type of experiment at present.

The beam is detected by means of hot-wire ionization and a mass-spectrometer system. The detection system is discussed in Section II of this paper.

The main factors that determine the resolution of the apparatus are the length of the C-field transition region, the homogeneity of the C field, and the amplitude of the rf signal used to induce transitions. The last factor is easily dealt with by selecting an rf amplitude that gives rise to a maximum spectral line intensity while maintaining a minimum line width. The importance of the first factor is demonstrated by an equation for the natural line width as derived from the Heisenberg uncertainty principle,¹⁰

$$\Delta\nu \approx v/L, \quad (\text{I-4})$$

where $\Delta\nu$ is the natural width of a single line at half the maximum intensity, L is the length of the transition region, and v is the most probable velocity for the molecules of interest. The length of the C-field transition region is 20 cm; therefore a molecular beam with $v = 5 \times 10^4$ cm/sec would result in a theoretical line width of approximately 2.5 kilocycles.

The need for C-field homogeneity is demonstrated if one considers observing a single 2-kc-wide line at a transition frequency of 50 megacycles. Since the transition frequency is roughly proportional

10. P. Kusch and V. W. Hughes, in Handbuch der Physik (Springer-Verlag, Berlin, 1959), Vol. 37/1, pp. 54-60.

to the square of the electric field, a C-field homogeneity of one part in 50,000 would be required for adequate resolution.

B. Some Features and Limitations of the Apparatus

Some of the design features incorporated in the apparatus are as follows.

1. The source oven has a large sample capacity and satisfactory temperature stability up to 900°C . The oven construction permits ease in sample changing, while an accurate repositioning system eliminates lengthy realignment procedures.

2. The 10-in.-long by 4-in.-high C field is homogeneous to better than 2 parts in 10^5 . The C-field design eliminates the need for electrode surface contact clips, which tend to fail when the voltage is changed rapidly.

3. The inhomogeneous deflecting fields are capable of producing gradients of 3×10^5 volts/cm². These fields should prove useful in the study of molecules with small effective dipole moments. The field lengths allow the use of lower applied voltages for adequate deflection, thus reducing field variations along the beam path.

4. A combination beam-stop and B-C buffer field eliminates the large variations in field strength that may occur when the beam stop is located in the center of the B field.

5. A relatively simple permanent-magnet mass-spectrographic detection system is used which allows adequate isotopic resolution of K^{39} and K^{41} and has been satisfactory in detecting Cs^{133} .

6. The automatic frequency-recording and detection system provides accurately recorded spectral lines from signals corresponding to as low as a few hundred detected transitions during a 3-second counting period.

The use of hot-wire ionization for beam detection seriously limits the versatility of the apparatus, since only those elements which have a first ionization potential close to or below the work function of oxidized tungsten can be detected with adequate efficiency. This limitation may be overcome in the future through the addition of an electron-bombardment ionizer.

II. CONSTRUCTION AND OPERATION OF THE APPARATUS

A. Vacuum System

The oven, buffer, and main vacuum chambers, shown in Figs. II-1 and I-2, are made of 1-in.-thick aluminum plate. An accurate smooth machine finish is applied to the tops and sides of the chambers after welding. This finish provides a surface for seating the vacuum-seal O rings as well as accurate mounting surfaces for the port covers. Access ports are located at every place possible for convenience and adaptability. O rings provide a vacuumtight fit between the chambers.

The electron multiplier chamber was made from a standard 4-in. iron "welding tee." The chamber was nickel plated, after the soft iron connecting flanges had been welded on, in order to minimize corrosion. The soft iron walls provide magnetic shielding for the electron multiplier.

The oven and buffer chambers can be isolated from the vacuum pumping system by closing the Temescal gate valves, which are located directly below the chambers. These valves and one between the main chamber and the buffer chamber eliminate the need to remove liquid nitrogen from the traps or turn off the diffusion pumps when inserting new beam materials. Provision is also made for the installation of a gate valve between the oven and buffer chambers if the need arises.

The gate valve located between the main and electron-multiplier chambers allows maintenance of a vacuum in either chamber when the other is at atmospheric pressure.¹¹ This is an important feature for this apparatus, since prolonged exposure of the electron multiplier to air (more than 3 hours) reduces its gain appreciably.

A list of the vacuum equipment used and some typical pressures

11. The design of both interchamber valves is similar to that shown in N. F. Ramsey, Molecular Beams (Clarendon Press, Oxford, 1956), Fig. XIV.39, p. 414.

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Fig. II-1. The apparatus.
A. High-voltage lines to deflecting fields
B. Collimator mount
C. Detector mount
D. Line voltage regulator
E. Oven chamber
F. Buffer chamber
G. Gate valve
H. Main chamber
I. Electron-multiplier chamber
J. Liquid nitrogen trap
K. Diffusion pump protection panel.

obtained under operating conditions is given in the Appendix. All chambers normally operate at a pressure below 6×10^{-7} mm Hg.

Each diffusion pump (DP) in the system is triply protected against mishap as follows:

1. The Hastings forepump gauges are supplied with interlocks which turn off the DP and ring an alarm bell if the forepressure reaches any preselected value (e. g. , 10^{-2} mm Hg).
2. A relay circuit through a "Shurflo" water regulator (with microswitch) turns off the DP and rings an alarm bell if there is a failure in the flow or pressure of the DP cooling water.
3. A relay circuit through a thermoswitch attached to the DP cooling coil rings an alarm bell and turns off the DP if the temperature rises to any preset value (e. g. , 30°C).

The rack that supports the vacuum chambers is shown in Fig. II-2. It is made from aluminum I beams, channels, and pipes. All joints are welded. The rack is leveled by adjusting 1-in. steel bolts passing through "helicoil" inserts at the bottom corners of the rack. Each bolt head has a 1-in. hemispherical recess milled in it to match a 1-in.-diameter steel ball which is placed between the bolt head and a corresponding partial hemisphere in an aluminum plate on the floor. Provisions are made to mount the power panel and alarm system as well as other electronic equipment on the rack.

A Gaertner model 101-AT depth-focusing telemicroscope is mounted on a traveling microscope stage at the end of the main chamber for optical alignment. Horizontal motion of this system, also shown in Fig. II-2, is monitored by a Starrett dial indicator gauge which can be read to 0.2 mil.

B. Oven

Photographs of the oven and its support are shown in Figs. II-3, II-4, and II-5. The support design allows the oven to be moved in three dimensions. The oven can also be rotated in a plane perpendicular to the beam axis. Horizontal and vertical motion under vacuum are obtained by sliding the Wilson seal mount over a neoprene O ring imbedded

ZN-3361

Fig. II-2. The apparatus, mounting rack, and optical alignment system.

- A. Telemicroscope and stage
- B. Magnet
- C. Gate valve
- D. Detector mount
- E. Deflecting-field supplies.

ZN-3362

Fig. II-3. Oven.

- A. Support tube (15-mil wall)
- B. Radiation shield
- C. Slots in radiation shield for outgassing
- D. Beam slit
- E. Oven lid (hand-lapped for fit)
- F. Thermocouple wires (0.010 in.).

ZN-3370

Fig. II-4. Oven and mount.
A. Clamping screw
B. Positioning screw
C. Wilson seal.

ZN-3363

Fig. II-5. Oven mount.

- A. Oven
- B. Vertical adjustment
- C. Yoke guide for horizontal motion
- D. Horizontal-motion monitor
- E. Oven-rotation adjustment
- F. Shaft clamp
- G. Water cooling coil
- H. Horizontal adjustment
- I. Yoke and vertical guide.

in the port flange. A Starrett dial gauge with 1 in. travel and readable to 0.2 mil indicates motion of the oven in the horizontal direction perpendicular to the beam axis.

The oven heater coil is made of approximately 12 turns of 20-mil tantalum wire about the 1-in.-diameter stainless steel oven body. The coil is electrically insulated by 1/8-in.-long beads made from 2-mm quartz tubing. Power is supplied to the heater coil by a 15-ampere Variac which operates from a 115-volt ac regulated line supply. A current of 7 A at 30 V provides an oven temperature of approximately 800°C as measured with the thermocouple shown at the slits.

Four-mil stainless steel foil was found to be satisfactory as a slit material when LiF, KF, Li, Na, K, or CsCl + Li was used as a source material. Four-mil platinum foil was the only slit material found that would yield stable beams of LiBr without clogging or excessive erosion due to chemical reaction with the beam material. Other slit materials that were tried (unsuccessfully) in LiBr beam production are tungsten, nickel, and tantalum.

Temperatures as high as 900°C have been obtained with temperature drifts of less than 5°C over periods of many hours. The slit width is variable, whereas beam height is fixed at 0.5 cm. The oven can be cooled to room temperature and reheated to 900°C with only a negligible shift in slit position.

C. "A" and "B" Deflecting Fields

End views of the deflecting fields are shown in Figs. II-6 and II-7. The basic field configuration is the conjugate of that due to two parallel line charges of opposite sign separated by a distance $2a$. The field E and the field gradient $\partial E / \partial x$ in the x direction are given by¹²

12. P. Kusch and V. W. Hughes, in Handbuch der Physik (Springer-Verlag, Berlin, 1959), Vol. 37/1, p. 47.

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Fig. II-6. Deflecting-field electrodes (end view).

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Fig. II-7. Deflecting-field assembly (end view).

$$E = 4 aq/r_1 r_2, \quad (II-1)$$

$$\partial E/\partial x = -4aqx(r_1^2 + r_2^2)/r_1^3 r_2^3, \quad (II-2)$$

where q is the magnitude of either line charge per unit length. (See Fig. II-6 for the definition of the geometrical symbols a , r_1 , and r_2 .)

The magnitude of the field is computed by use of Eq. (II-1) and the fact that the potential difference between the electrodes, ΔV , equals the line integral of the electric field between the two electrodes taken along the median plane or x axis. Therefore, since $r_1 = r_2$ along the median plane,

$$r_1 r_2 = a^2 + x^2 \text{ and}$$

$$\Delta V = \int_{x_0}^{x_f} E \, dx = \int_{x_0}^{x_f} 4aq/(a^2 + x^2) \, dx = 4q \tan^{-1} x/a \Big|_{x_0}^{x_f}$$

and, since $x_0 = 1/8$ in., $x_f = 1/4$ in., and $a = 1/8$ in. = 0.318 cm, then

$$4q = \Delta V/(\tan^{-1}(2) - \tan^{-1}(1)) = \Delta V/0.318,$$

and we have $\Delta V = 4aq$ for this somewhat unique case when esu or V/cm are used as the dimensions in calculating E .

From Eq. (II-1) and the above relationship the field at the beam position is given as

$$E_b = \Delta V/r_1 r_2 = \Delta V/(a^2 + x_b^2) = \Delta V/(0.101 + 0.158),$$

$$\text{or } E_b = 3.9 \Delta V \text{ (esu or V/cm).}$$

Since $x_b = 1.25a$, division of Eq. (II-2) by Eq. (II-1) and insertion of the values of r_1 and r_2 at the beam center position results in the ratio

$$\frac{(\partial E / \partial x)_b}{E_b} = 3.1 \text{ (cm}^{-1}\text{)}.$$

Thus, an applied voltage of 1 esu would result in a field of 3.9 esu/cm and a field gradient of 12 esu/cm² at the beam position. The value of x_b was selected as 1.25a, since the gradient of the field is fairly constant along the height of the beam at this position.¹³

The "A" and "B" deflecting fields are each 12 in. long. The stainless steel pieces were accurately machined and hand-polished so that the radii of the curved surfaces were known to within ± 0.2 mil. The surfaces on which the spacers rest are flat and parallel to the curved surfaces to within ± 0.2 mil. The quartz spacers were made after the critical dimensions underlined in Fig. II-8 were known, and are accurate to ± 0.1 mil.

Accurate vertical positioning of the "T-bar" electrode is accomplished through the use of papers that are slid in between the electrodes. Adjustments are made until the amount of drag on insertion and removal of the paper is the same at the top and bottom gaps. This technique was checked by using a micrometer on the same paper, and was found to be reproducible to ± 0.1 mil.

Potentials as high as 30,000 V have been applied across the electrodes with negligible sparking when the quartz insulators were clean.¹⁴ After a beam of KF had been passed through the apparatus, considerable sparking occurred at 18,000 V but diminished to no sparking after a few minutes. This effect could be eliminated by shielding

13. P. Kusch and V. W. Hughes, in Handbuch der Physik (Springer-Verlag, Berlin, 1959), Vol. 37/1, p. 43.

14. The high-voltage supplies used are manufactured by the Condenser Products Co., Highway 41, South, P. O. Box 1046, Brooksville, Florida. They are designed to supply 0 to 30 kV at a current of 5 mA.

MU-28375

Fig. II-8. Isometric view of a C-field electrode.
Note: Shaded areas represent conducting gold film.
The other electrode is identical to the one shown, but with no isolation gap.

the insulators from scattered beam, but, since it has not been necessary to use these high potentials in experiments done to date, the modification has not been made.

D. Homogeneous Electric C Field

An isometric sketch of one of the C-field electrodes is shown in Fig. II-8. The two glass electrode surfaces were made by Mr. Jack A. Borde from a single piece of glass.¹⁵ The glass was ground and polished until one 12×12-in. face was optically flat to approximately 1/8 wavelength of helium light (800 Å; 1 Å = 10⁻⁸ cm). Tests for flatness had to be deferred until many hours after working of the surface, so as to insure thermal equilibrium. The glass was then cut and the top corners were ground and polished as shown in Fig. II-9. Final tests indicate that the surfaces are parallel to within 1/4 wavelength of helium light (1300 Å) along their 10-in. length.

One-mil sheets of silver foil with reinforcing rods and connectors soldered in place were glued to the glass with epoxy resin. Their leading edges are approximately 1/4 in. away from the optical surface. Handy and Harman #781 silver paint was applied over the joints to within 1/16 in. of the optical surface. Approximately 2000 Å of gold was vacuum-deposited on the silver foil and joints up to the optical surface. The conducting gold surface was then vacuum-deposited until transmission of white light through the films was approx 50%. A monitoring foil of known weight and area was used to calculate the thickness of the film, which was found to be 340 ± 35 Å.

A 2×8-in. area on the optical surface was electrically isolated from the rest of the film by making a 5-mil-wide scratch. Gold film was also removed from the 1/2-in.-high areas shown in Fig. II-9 by using "Scotch" tape. Continuity checks were made on the films with a vacuum-tube volt-ohm meter.

15. A 12×12×1-3/4 in. piece of Corning 7740 Fine Annealed pyrex glass was obtained from the Hayward Scientific Co. of Whittier, California.

ZN-3364

Fig. II-9. C-field mounting.

- A. C-field electrodes
- B. B field
- C. 5-in. port
- D. Condensed beam material (light vertical line)
- E. Leveling screw for B-field mount
- F. Locking screw for B-field mount
- G. Clamping screw for C field
- H. Teflon block
- I. Edge of gold film
- J. Gauge block.

The electrodes are mounted by using three 0.50000 ± 0.00001 -cm steel gauge blocks as spacers.¹⁶ Tests with optical flats indicate that all three gauge blocks are comparable to within $500 \text{ \AA}$.

Pressure is applied to the electrodes through Teflon blocks until optical contact with the glass is made at all gauge-block surfaces. A view of one C-field mounting area is shown in Fig. II-9. A helium light source is then placed at one 5-in. main chamber port and Haidinger's fringes are observed through an opposite port, as shown in Fig. II-10. The clamping pressure on the gauge blocks is then varied until very little difference is observed in the fringes as the eye is moved along 5 in. of the field at beam height. The appearance or disappearance of one fringe corresponds to an increase or decrease in gap width of $1/2$ wavelength (approx $2600 \text{ \AA}$). These observations and the quality of spectra obtained lead the author to assume a C-field homogeneity of approximately one part in 50,000. This could be improved upon by widening the gap, but higher applied voltages would then be necessary to obtain a given field strength, and corona effects in the present voltage-measuring circuit might lead to considerable error in the calculated field strength as the applied potential approaches the kilovolt region.

Radio frequency is supplied to the 2×8 -in. isolated portion of the C-field electrode through a 50-ohm line terminated by a 50-ohm resistor to ground. The remaining portion of this C-field electrode is connected to ground. The other electrode, to which dc voltage is applied, is maintained at a radio-frequency ground potential by a $0.01\text{-}\mu\text{F}$ capacitor connected between it and ground. The resistor and the capacitor are outside the vacuum chamber.

A schematic diagram of the C-field voltage-monitoring network is shown in Fig. II-11. The resistances used in calculating the applied

16. The gauge blocks were obtained from the Industrial Tool and Supply Co., 1177 North 15th Street, San Jose, California.

ZN-3384

Fig. II-10. Haidinger's fringes produced by the C-field gap (as viewed through a 5-in. main chamber port). The camera is focused at infinity. A fuzzy reflection of the camera's dark circular lens holder and square frame can be seen. A helium light source is used.

MU-28376

Fig. II-11. Schematic diagram of the C-field voltage-monitoring network.

voltage were measured 18 months ago with a bridge certified at 0.01% by the National Bureau of Standards. Recent measurements indicate changes of less than 0.005% in the resistors and less than 0.01% in the ratios used. A temperature change of 2°C has been found to cause a maximum variation of 0.002% in the resistances.

An Eppley Standard Cell is used as a reference voltage. The cell was originally calibrated against a bank of cells from the National Bureau of Standards. More than a year after installation the cell and potentiometer were rechecked and found to be in agreement with another National Bureau of Standards cell to within 0.0015%.

Although the above calibrations indicate a possible error of one part in 10,000 for the calculated C-field voltage, the author will assume an error of two parts in 10,000 due to certification limitations.

A vernier for fine adjustments has been added to the C-field voltage supply¹⁷ in order to manually hold voltage variations to less than 0.001% while obtaining spectra.

E. Collimator-Buffer Field and Beam Stop-Buffer Field

The combination collimator and buffer field, shown in Fig. I-2, is similar to that originally used by Trischka and Braunstein in their apparatus.⁴ The adjustable gap width usually varies from 1/8 in. to 5 mils to 1/4 in. along the 1.5-in. length of the collimator-buffer field. One side is at ground potential while the voltage applied to the other, which is supported by a 1/8-in. alumina dowel, can be varied. The 1.5-in.-long by 3/4-in.-high by 3/8-in.-wide unit is supported by a brass plate which rests on an O ring on top of the main chamber, thus allowing alignment of the collimator slit while under vacuum. Motion of the unit is monitored by a dial indicator gauge.

Top views of the combination beam stop-buffer field are shown

17. The regulated C-field voltage supply is a model RE 5001 EW, manufactured by the Northeast Scientific Corp. of Cambridge, Mass.

in Figs. I-2 and II-12. This unit can be moved while under vacuum by adjusting a knurled nut on the threaded end of the mounting shaft which passes through a Wilson seal.

F. Detection System

The beam is detected by the conventional hot-wire technique in conjunction with a mass-separating magnet and electron multiplier. The tungsten hot wire, ion accelerator, and mount are shown in Figs. II-13, II-14, and II-15.

The 1×10-mil 3/8-in.-long tungsten hot wire is shown in Fig. II-13. It is heated by a small applied voltage from a filament supply which is at the same potential as electrode A. Most of the beams studied were detected at a hot-wire temperature of approximately 1200°C. This temperature is obtained by passing a current of approximately 0.7 A at 4.5 V through the filament.

An optimum signal is usually obtained when the focusing electrodes, B and C, are at a potential approximately one-seventh below that applied to the hot wire and electrode A. Electrode D is at ground potential. The adjustable slit in electrode D can be narrowed for better isotopic resolution, but this decreases transmission appreciably. A slit width of 70 mils has been found satisfactory for detection of the isotopes of lithium and potassium as well as cesium-133.

Provision has been made for introducing oxygen to the system in the hot-wire region. This is done in order to obtain a higher work function by oxidizing the tungsten surface and thus raising its ionization efficiency for the isotopes of lithium. Dry air at atmospheric pressure is passed through a Veeco type VI variable leak and directed onto the hot wire by means of a hypodermic needle. After high-temperature flash cleaning of the tungsten filament, the lithium signal intensity is greatly increased by introducing enough dry air to raise the main chamber pressure by 1×10^{-7} mm Hg. Continued introduction of oxygen has been found to be unnecessary, because of the relatively poor main chamber vacuum of 5×10^{-7} mm Hg.

An old "C"-type permanent magnet was wound with number 12

ZN-3365

Fig. II-12. Combination beam stop and buffer field (top view).
A. Horizontal adjustment screw
B. Kovar seal for insulated line through vacuum-chamber port.

ZN-3366

Fig. II-13. Hot wire and ion accelerator.
A. Electrode A
B. Alumina stud
C. Tungsten hot wire.

ZN-3367

Fig. II-14. Ion accelerator.

- A. Adjustable defining slit for ion beam
- B. Reflection of hot wire
- C. Alumina spacer (1/4 in.)
- D. Electrode D
- E. Ion-focusing electrodes B and C
- F. Electrode A
- G. Glass spacer (1/8 in.)
- H. Abandoned beam channel.

ZN-3368

Fig. II-15. Hot wire, ion accelerator, and mount.

- A, B, C, D. Electrodes
- E. Ion beam (from hot wire)
- F. Horizontal adjusting screw
- G. Rotation adjusting screw
- H. Vertical adjusting screw
- I. Horizontal motion monitor.

copper wire and remagnetized with the accurately machined 60° pole faces in place. It yields a constant magnetic field of 4,200 gauss in the 1.00-cm gap between the pole faces.

The path length for the detected ions from the hot wire to the first dynode of the electron multiplier is approximately 9 in. Their radius of curvature, R , in the magnet is fixed at 5 cm.

Accelerating potentials for singly charged ions of various masses are calculated by using the relationship

$$R = (144/H\sqrt{E_A M}) = 5 \text{ cm},$$

where H is the magnetic field in gauss, E_A is the potential in volts through which the ion is accelerated prior to entry into the magnetic field, and M is the atomic mass number for the isotope in question. A few accelerating potentials used for various isotopes of interest are as follows.

Isotope	E_A (volts)
Li^6	3,570
Li^7	3,060
K^{39}	549
K^{41}	522
Cs^{133}	161

The electron multiplier, shown in Fig. II-16, is a 14-stage head-on type, complete with ion-beam deflector plates and resistors.¹⁸ Current measurements and pulse counting at the collector of the electron multiplier indicate a gain of 2×10^6 when a potential of -2,500 V is applied to the first dynode.

A block diagram of the electronic system used to monitor the electron multiplier output and the radio frequency is shown in Fig. II-17.

18. The electron multiplier was purchased from the National Radio Co. of Malden, Mass.

ZN-3371

Fig. II-16. Electron multiplier and mount.

Fig. II-17. Block diagram of the electronics of the detection system. (Units are listed in Table II.)

A photograph of some of the equipment is shown in Fig. II-18. Data on the power supplies and electronic equipment are given in Table II of the Appendix.

This system almost automates the procedure for obtaining spectra, and allows a single operator to continuously monitor the C-field voltage during a run.

Normally, the scalers used count for the period selected and then display for a like period or longer if desired. This doubles the minimum time necessary to obtain an electron-multiplier pulse-count reading at one frequency; therefore, a method was sought whereby the pulse scaler would count for a given number of seconds and then display for only one second before starting a new cycle. The 1-second display period would assure restabilization of the signal generator after a small change in frequency, eliminate any errors in the pulse count due to hot-wire response time,¹⁹ and facilitate lock-in with the frequency scaler operating on a 1-sec time base. A modification on the pulse-scaler decade divider network allows the selection of a 3- or 9-sec counting period with a 1-sec display time. The counter can be returned to normal operation by throwing a switch.

The need for a gate-pulse amplifier and complex blocking network to trigger the signal-generator step motor at the proper time was eliminated by installing a microswitch on the activation solenoid of the digital recorder. The microswitch closes the circuit between the step motor and a power supply when the recorder prints.

Thus, the outputs of the signal generator and the electron multiplier are counted and then printed in coincidence with a frequency change. The frequency change takes 0.2 sec, allowing 0.8 sec before the next count starts. The increment of frequency change is selected by means of a gear box²⁰ which couples the signal-generator frequency

19. The reader is referred to Section II-G for a discussion on hot-wire response time.

20. Model No. 00140 Step-function speed reductor, Insco Co., Groton, Mass.

ZN-3385

Fig. II-18. Electronic equipment for detection system.

vernier and the 22.5-degree step motor.²¹ After a frequency change of one part in 10^4 , the signal generator is stable to better than one part in 10^6 during two subsequent 2-sec counting and display periods.

Both counters were checked against the UC Physics Department's atomichron. They were found to be accurate to better than one part in 10^9 . The manufacturer of the counters, who has a tendency to be conservative, specifies a drift of less than one part in 10^8 per week for the internal standard oscillator.

The frequency-scaler reading is printed on the first seven channels of the digital recorder, and the pulse-scaler reading is printed on the remaining four channels. Any row of three channels can be selected for analog output, which converts the numerical reading to a corresponding current (i. e., 1,000 = 0.1000 A). The first three count channels are usually selected and the analog output is fed into a chart recorder for graphical reproduction of the spectra.

G. Operating Procedure

1. Optical Alignment

The traveling microscope stage, shown in Fig. II-2, is aligned by placing a block with parallel surfaces between the stage and the end of the main chamber. The telemicroscope is then placed in an adjustable mounting and aligned with accurately positioned horizontal and vertical wires at each end of the molecular beam apparatus. The oven, the buffer-chamber slits, and the ion accelerator are then aligned with the telemicroscope cross hairs. A small light is placed inside the oven to make the 5-mil beam slit visible.

The A field is assembled and placed in its mount. Accurately machined cross-wire holders are placed at each of its ends. These small removable holders are made to fit the ends of the field so that the horizontal and vertical 1-mil wires cross at the desired beam axis.

21. The step motor is a model BD-5, manufactured by the G. H. Leland Co., Dayton, Ohio.

With the ion accelerator moved to one side, the A-field position is adjusted until the cross wires at both ends are aligned with the telemicroscope cross hairs. The cross-wire holders are removed and the procedure is repeated with the B field.

The C field is aligned by visual sightings through openings on the top of the main chamber, with the A- and B-field electrodes used as reference points.

The collimator-buffer field and the beam-stop-buffer field are then mounted and checked for vertical alignment with the telemicroscope. Horizontal alignment of the collimator is checked by turning on a light at the A-field end of the chamber to make the 5-mil slit easily discernible. No visible difference has been found between the collimator position at atmospheric pressure and under vacuum.

2. Alignment of Mass Spectrometer and Beam

When all chambers have attained a vacuum of less than 10^{-6} mm Hg, the gate valve between the main and electron-multiplier chambers is opened. The ion accelerator is repositioned and checked with the telemicroscope. A potential of -3,000 V is applied to the electron-multiplier resistor network. A potential corresponding to mass number 23 is applied to the ion accelerator. The tungsten hot wire is brought to a temperature of approximately 1500°C in order to obtain a signal through the electrometer that is due to Na^{23} impurities in the tungsten. The signal is maximized by adjusting the focusing-electrode potentials, the magnet position, and the potential applied to the ion-deflecting field in front of the electron multiplier. Lithium and potassium impurities in the hot wire allow a check on the alignment through observation of the signals and relative intensities at mass numbers 6, 7, 39, and 41, which are due to the isotopes of Li and K.

The buffer-chamber gate valve is then opened and the ion-accelerator voltage is adjusted for detection of the isotope of interest in the molecular beam. The oven is slowly moved horizontally while the temperature is increased until a signal is observed. A maximum beam signal is usually obtained within a few mils of the optically determined oven position.

The beam signal is further maximized by lowering the hot-wire temperature to approximately 1200°C . The beam flag is used to check hot-wire response time and noise as the temperature is varied.²²

Figure II-19 shows a rough sketch of the type of behavior observed for a Li^7 signal from a LiF beam as the hot-wire temperature is varied. The temperature measurements were made with an optical pyrometer.

A final check for optimum signal is made by making fine adjustments on all the voltages previously mentioned as well as the oven, collimator, and ion-accelerator positioning screws.

3. Obtaining Spectrum

The oven temperature is adjusted until a current of approximately 10^{-6} A is observed at the electrometer. This corresponds to a detected beam of $\approx 5 \times 10^{-11}$ A or 10^7 molecules per second.

The combination beam-stop-buffer field is then slowly moved into the beam path until the electrometer current reading indicates approximately 100 ions per second leaving the hot wire. If the beam flag is inserted at this time, the hot-wire noise normally amounts to 10 or 20 ions per second.

Voltages are applied to the A and B fields and varied until a maximum signal is obtained. This signal, which will be called the refocused beam, is mainly due to molecules in the $J = 1$ or $J = 2$ rotational states that have made nonadiabatic transitions in the region between the A and B fields. In a LiF beam, potentials of approximately 2000 V are applied to the deflecting fields for a maximum refocused beam of molecules in the $J = 1$ state. A typical refocused beam signal for LiF is 10^4 ions per second.

A voltage is applied to the C field corresponding to the desired radio-frequency region in which a spectrum is to be obtained. Voltages are then applied to the buffer fields and varied until the refocused beam

22. Hot-wire response time is defined here to mean the amount of time taken after insertion of the beam stop for the observed signal to drop by a factor of 100.

MU-28378

Fig. II-19. A sketch of observed Li^7 signal behavior with respect to hot-wire temperature for a LiF beam. (Note: The above graphs are quite arbitrary, since a small change in the surface oxide layer or crystalline configuration of the hot wire may alter its work function appreciably. The observed noise is also critically dependent upon the history of the hot wire used.)

intensity is almost minimized. The application of higher voltages to the buffer fields, beyond the "almost minimal" value, usually results in very little diminution of the refocused beam intensity and a much lower signal-to-noise ratio for the observed spectra. The constant background signal that remains at this point is referred to as the residual beam. The residual-beam intensity varies from 1/5 to 1/2 the intensity of the refocused beam, depending upon the molecule being observed and the temperature of the beam.

An rf voltage of approximately 3 V rms is applied to the C-field transition region. The frequency is varied until an increase in signal is observed. The rf voltage is then lowered until a maximum signal and a minimum spectral line width are observed. Radio-frequency voltages of 0.10 to 0.30 V rms were used for the LiF and KF spectra obtained. This procedure can be revised and the same results obtained by fixing the frequency and varying the C-field voltage.

The electron-multiplier output is then switched to the counting system. The signal-generator stepping mechanism is engaged and the spectrum is taken.

Spectra have been obtained for Li^6F^{19} in which the residual beam intensity (background) is 2,100 counts per three seconds, line heights are 9,000 counts per 3 sec, line widths are approximately 4 kc, and the signal-to-noise ratio is better than 80. (Some spectra are shown in Section III.) Each point in the observed spectra represents a 3-sec count at a fixed frequency.

III. EXPERIMENTAL RESULTS

A. Spectra

The first spectra obtained were of Li^7F^{19} . The transition $(1,\pm 1) \rightarrow (1,0)$ in the $V = 0$ vibrational state was studied in order to check the apparatus with the results previously obtained by Trischka and others.^{23,24} At this time the pulse-counting system had not been added

23. R. Braunstein and J. W. Trischka, Phys. Rev. 98, 1095 (1955).

24. S. O. Kastner, A. M. Russell, and J. W. Trischka, J. Chem. Phys. 23, 1730 (1955).

and spectra were obtained by manually changing the frequency and averaging the output of the electrometer for a period of 5 to 10 seconds at a fixed frequency. The observed line widths were approximately 5 kc at half-maximum intensity, which is in agreement with Eq. (I-4). The relative line positions corresponded fairly well to those given by Trischka and Braunstein; however, the product $\mu^2 A$ calculated for this transition was found to be well outside their stated experimental error.

Therefore, a check on the calculated C-field voltage was made by obtaining a spectrum of $K^{39}F^{19}$ for the transition $(1, \pm 1) \rightarrow (1, 0)$. The results were compared with those previously obtained by L. Grabner and V. Hughes²⁵ for KF and were found to agree well within the expected experimental error. A portion of the observed spectrum is shown in Fig. III-1.

Upon completion of the detection system described in Section II-F, more complete sets of spectra were obtained for Li^7F^{19} and Li^6F^{19} . Figures III-2 and III-3 show a few spectra obtained for the transition $(1, \pm 1) \rightarrow (1, 0)$. Arbitrary names are given to the lines for reference. Tables III through VIII list the relative observed line positions for spectra taken at different field strengths. An average of the frequencies of lines II_A and VI_A is used as a reference for the stated relative line positions in the Li^7F^{19} spectra. Line I_B is used as the frequency reference for the Li^6F^{19} spectra. The errors given are an average of the deviations from the stated mean value.

25. L. Grabner and V. Hughes, Phys. Rev. 79, 819 (1950).

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Fig. III-1. A portion of the spectrum of $K^{39}F^{19}$.

INTENSITY (ONE UNIT = 100 COUNTS PER THREE SECONDS)

← FREQUENCY (MEGACYCLES)

MUB-1301

Fig. III-2. Some spectra of Li^7F^{19} .

INTENSITY (ONE UNIT=100 COUNTERS PER THREE SECONDS)

V = 2

V = 1

V = 0

← FREQUENCY (MEGACYCLES)

MUB-1302

Fig. III-3. Some spectra of Li^6F^{19} .

Table III. Observed line positions for Li^7F^{19} in the $V = 0$ vibrational state (relative line positions, in kc).

Line Name	C-Field voltage (V/cm) and number of spectra		
	459.63	800.00	1,180.00
	3	5	7
I _A	-125.22 ± .14	-124.71 ± .14	-123.55 ± 1.16
I _B	-116.55 ± .21	-116.53 ± .39	-115.20 ± 1.36
I _C	-106.06 ± .21	-105.52 ± .26	-106.06 ± .44
II _A	- 84.88 ± .09	- 84.72 ± .33	- 84.86 ± .83
×II _B	- 75.88 ± .43	- 77.02 ± .76	- 76.96 ± 1.41
III _A	- 48.25 ± .29	- 48.45 ± 1.10	- 47.61 ± .80
III _B	- 40.18 ± .10	- 39.70 ± .29	- 40.00 ± 1.58
III _C	- 32.03 ± .41	- 31.91 ± .16	- 31.83 ± .77
×IV _A		- 23.49 ± 1.18	- 24.01 ± .69
IV _B	- 12.94 ± .13	- 13.00 ± .27	- 12.99 ± .57
×IV _C		- 4.25 ± .37	- 5.21 ± .94
V _A	32.47 ± .16	33.74 ± .23	34.44 ± 1.57
V _B	45.76 ± .06	45.35 ± .29	45.05 ± 1.26
VI _A	84.88 ± .09	84.72 ± .33	84.86 ± .83
×VI _B	(93.8)	92.12 ± .69	93.24 ± .94
VII _A	116.45 ± .25	116.08 ± .18	115.76 ± .75
VII _B	126.31 ± .69	125.68 ± .38	125.14 ± 1.07
×VII _C		134.52 ± .29	133.88 ± 1.04

Table IV. Observed line positions for Li^7F^{19} in the $V = 1$ vibrational state (relative line positions, in kc).

Line Name	C-Field voltage (V/cm) and number of spectra		
	459.63	800.00	1,180.00
	3	3	2
I _A	-122.4 ± .3	-122.5 ± .5	---
I _B	-114.0 ± .2	-113.8 ± .4	-113.8 ± .8
I _C	-103.8 ± .2	-103.4 ± .1	-104.2 ± .7
II _A	- 82.9 ± .1	- 83.1 ₅ ± .0 ₃	- 83.0 ± .5
XII _B		- 74.8 ± .3	- 75.2 ± .6
III _A	- 47.0 ± .2	- 47.2 ± .3	- 46.3 ± .6
III _B	- 39.2 ± .5	- 39.5 ± .3	- 39.0 ± 1.0
III _C	- 32.1 ± .5	- 31.7 ± .6	- 30.9 ± 1.3
XIV _A		- 21.3 ± .1	- 22.4 ± 1.0
IV _B	- 12.6 ± .4	- 13.2 ± .4	- 12.6 ± .4
IV _C		- 5.1 ± .6	- 2.3 ± .1
V _A	30.5 ± 1.0	33.0 ± .4	34.6 ± .4
V _B		44.8 ± .8	45.3 ± .8
VI _A	82.9 ± .1	83.1 ₅ ± .0 ₃	83.0 ± .5
XVI _B		91.5 ± .8	91.5 ± 1.8
VII _A	113.9 ± .1	113.5 ± .3	114.1 ± .9
VII _B	124.1 ± .4	123.4 ± .4	123.7 ± .1
XVII _C		132.4 ± .3	(133.4)

Table V. Observed line positions for Li^7F^{19} in the $V = 2$ vibrational state (relative line positions, in kc).

Line Name	C-Field voltage (V/cm) and number of spectra		
	459.63 2	800.00 1	1,180.00 1
I_A	-119.4	-118.2	-118.6
I_B	-112.2	-109.9	-111.0
I_C	---	-100.0	-100.2
II_A	- 80.6	- 82.1	- 79.5
$\times II_B$		- 71.4	- 69.8
III_A	- 47.8	- 45.2	- 46.6
III_B	- 42.2	---	---
III_C	---	---	- 30.0
$\times IV_A$			- 22.6
IV_B	- 12.2	---	---
$\times IV_C$			- 2.7
V_A	30.6	33.0	29.2
V_B	42.2	45.5	45.0
VI_A	80.7	82.1	79.5
$\times VI_B$		89.4	87.6
VII_A	111.3	112.2	109.5
VII_B	---	121.8	119.6
$\times VII_C$			132.7

Table VI. Observed line positions for Li^6F^{19} in the $V = 0$ vibrational state (relative line positions, in kc).

Line Name	C-Field voltage (V/cm) and number of spectra		
	459.63	800.00	1,180.00
	11	5	6
$\times\text{I}_\text{A}$	- 7.31 $\pm$.28	- 5.9 $\pm$.4	---
I_B	0	0	0
I_C	7.08 $\pm$.20	6.86 $\pm$.32	6.7 $\pm$.7
$\times\text{I}_\text{D}$	14.33 $\pm$.38	13.70 $\pm$.37	13.8 $\pm$ 1.3
II_A	34.10 $\pm$.21	34.03 $\pm$.44	34.0 $\pm$.9
II_B	41.66 $\pm$.22	40.96 $\pm$.54	41.1 $\pm$.9
$\times\text{II}_\text{C}$	48.81 $\pm$.45	47.66 $\pm$.57	48.2 $\pm$ 1.0
$\times\text{II}_\text{D}$	---	54.0 $\pm$.7	54.5 $\pm$ 1.1

Table VII. Observed line positions for Li^6F^{19} in the $V = 1$ vibrational state (relative line positions, in kc).

Line Name	C-Field voltage (V/cm) and number of spectra		
	459.63	800.00	1,180.00
	6	4	4
$\times \text{I}_A$	- 7.8 $\pm$ 1.0		
I_B	0	0	0
I_C	6.91 $\pm$.20	7.0 $\pm$.3	6.8 $\pm$.5
$\times \text{I}_D$	13.91 $\pm$.48	13.9 $\pm$.2	14.0 $\pm$.6
II_A	33.27 $\pm$.21	34.3 $\pm$ 1.0	35.3 $\pm$.9
II_B	40.70 $\pm$.22	41.1 $\pm$.8	40.6 $\pm$.3
$\times \text{II}_C$	47.74 $\pm$.33	47.9 $\pm$.9	48.0 $\pm$.3
$\times \text{II}_D$			54.5 $\pm$.3

Table VIII. Observed line positions for Li^6F^{19} in the $V = 2$ vibrational state (relative line positions, in kc).

Line Name	C-Field voltage (V/cm) and number of spectra		
	459.63	-800.00	1,180.00
	4	6	5
$\times I_A$	-7.4 ± 1.0		
I_B	0	0	0
I_C	$6.8 \pm .4$	$7.2 \pm .8$	$8.0 \pm .4$
$\times I_D$	$12.7 \pm .4$	$14.4 \pm .4$	$16.1 \pm .5$
II_A	$33.1 \pm .2$	$34.2 \pm .5$	$33.3 \pm .2$
II_B	$40.4 \pm .3$	$40.3 \pm .6$	$40.6 \pm .5$
$\times II_C$	$47.4 \pm .4$	47.2 ± 1.1	48.0 ± 1.0

B. Theory and Calculations

The Hamiltonian used to analyze the observed spectra is given as follows:^{26, 27}

$$\begin{aligned} \mathcal{H} = & - \vec{\mu} \cdot \vec{E} - eq_1 Q_1 \left[\frac{3(\vec{I}_1 \cdot \vec{J})^2 + 3/2(\vec{I}_1 \cdot \vec{J}) - \vec{I}_1^2 \vec{J}^2}{2I_1(2I_1 - 1)(2J - 1)(2J + 3)} \right] + \\ & + c_1 \vec{I}_1 \cdot \vec{J} + c_2 \vec{I}_2 \cdot \vec{J} + \\ & + \frac{g_1 g_2 \mu_N^2}{r^3} \left[\frac{3(\vec{I}_1 \cdot \vec{J})(\vec{I}_2 \cdot \vec{J}) + 3(\vec{I}_2 \cdot \vec{J})(\vec{I}_1 \cdot \vec{J}) - 2\vec{I}_1 \cdot \vec{I}_2 \cdot \vec{J}^2}{(2J + 3)(2J - 1)} \right]. \end{aligned} \quad (\text{III-2})$$

The first term in Eq. (III-2) gives the interaction of the external electric field $\vec{E}$ with the electric dipole moment, μ , of the molecule. The second term is the electric quadrupole interaction of nucleus 1, which refers to the lithium nucleus. No quadrupole term is needed for nucleus 2, fluorine, since it has a nuclear spin of $1/2$. The third and fourth terms correspond to the interactions between the nuclear spins and the rotational angular momentum of the molecule, where c_1 and c_2 are constants. The fifth term is the magnetic dipole-dipole interaction between the two nuclei, where g_1 and g_2 are the gyromagnetic ratios for lithium and fluorine respectively, r is the internuclear distance, and μ_N is 1 nuclear magneton. The molecule is assumed to be in a $^1\Sigma$ electronic state.

An approximate solution for the above Hamiltonian has been obtained and the energy levels for various cases are given.²⁷ Attempts to fit the observed spectra with the energy levels given for the "strong

26. P. Kusch and V. W. Hughes, in Handbuch der Physik (Springer-Verlag, Berlin 1959) Vol. 37/1, p. 124.

27. V. Hughes and L. Grabner, Phys. Rev. **79**, 829 (1950).

field" case [i. e., $(eqQ)_1 \ll \mu^2 E^2 / (\hbar^2 / 2A) \ll \hbar^2 / 2A$] were not satisfactory. The parameter $g_1 g_2 \mu_N^2 / r^3$ is calculated from the known values of g_{Li} , g_F ,²⁸ and r for lithium fluoride.²⁹ Discrepancies of several kilocycles persisted and could not be decreased through variations of the parameters $(eqQ)_{Li}$, c_{Li} , and c_F .

A computer program for the solution of the above Hamiltonian using a strong-field approximation was supplied to the author by Professor William Klemperer.³⁰ The basic features of the program have been discussed by L. P. Gold.³¹ In this program the off-diagonal matrix elements of the quadrupole and spin-spin operators that connect states of $m_J = -1$ with states of $m_J = +1$ have not been neglected. The strong-field approximation is used; therefore the matrix elements that connect states with different absolute values of m_J have been neglected. This approximation is valid only when the energy differences between states of different $|m_J|$ is much larger than the nuclear hyperfine energies, i. e., $(eqQ) \ll \mu^2 E^2 / (\hbar^2 / 2A) \ll \hbar^2 / 2A$. Introducing the appropriate values for $Li^7 F^{19}$ into these terms and assuming $E = 600$ V/cm yields $(2.6 \times 10^{-21}) \ll (5 \times 10^{-19}) \ll (3 \times 10^{-16})$. Thus, the use of this approximation in the present calculations on LiF seems valid; further justification is indicated by the invariance of observed relative line positions with changing field strengths (see Tables III through VIII above). The known matrix elements of the quadrupole operator that connect the

28. D. Strominger, J. M. Hollander, and G. T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

29. G. L. Vidale, J. Phys. Chem. 64, 314 (1960).

30. William Klemperer (Harvard University, Cambridge, Mass.), private communication.

31. L. Peter Gold, Thesis, Department of Chemistry, Harvard University, Cambridge, Mass. (November 1961).

states J and $J+2$ and those connecting $J-1$ with $J+1$ have been neglected.^{32, 33} These approximations are not expected to be valid for accurate calculations on alkali halide molecules other than LiF.

The program provides calculations of the eigenvalues, eigenfunctions, transition frequencies, and line displacements relative to the unperturbed Stark frequencies for any given set of the nuclear interaction constants. A series of calculations can be made by varying only one constant in increments while the others are fixed. This process is repeated for each unknown constant until a "mesh" is obtained. The mesh is refined by selecting smaller increments until a best fit is obtained for the observed spectra. The unperturbed Stark line, which is given as zero in the calculated relative line positions, is then easily calculated from one of the observed singlet line frequencies.

The program quickly provided many sets of calculated line positions for different combinations of the molecular constants $(eqQ)_{Li}$, c_{Li} , c_F , and $g_{Li}g_F\mu_N^2/r^3$. Excellent fits to the observed spectra were obtained. Only isolated singlet lines were used to obtain fits to the observed Li^7F^{19} spectra.

Vidale has reported two "most probable" sets of values for the molecular constants B_e , ω_e , a_e , and $\omega_e x_e$ of Li^7F^{19} .²⁹ Two possible sets are given, owing to an uncertainty in the assigned values of the rotational quantum number in the observed infrared spectra. The probable error given for B_e is 0.8%, while establishment of the correct set is expected to reduce this error by approximately one order of magnitude.

In obtaining best fits to the spectra of Li^7F^{19} in the $V=0$ and $V=1$ vibrational states, it was found that use of an average of the two possible calculated internuclear distances in the parameter $g_1g_2\mu_N^2/r^3$ resulted in several significant differences between the calculated and

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32. C. H. Townes and A. L. Schalow, Microwave Spectroscopy, (McGraw Hill Book Company, Inc., New York, 1955), Section VI-4.
 33. U. Fano, J. Research National Bureau of Standards 40, 215 (1948).

observed line positions. These differences were greater than the probable experimental error and could not be eliminated through variations of $(eqQ)_1$, c_1 , and c_2 . Use of the set of constants corresponding to the lower value given for B_e eliminated the differences, while the remaining set led to discrepancies that were two to five times as large as the stated errors. Therefore these data would support a choice of the following set from the pairs of "most probable" values given by Vidale for Li^7F^{19} :

$$\begin{aligned} B_e &= 1.3676 \text{ cm}^{-1}, \\ a_e &= 0.019856 \text{ cm}^{-1}, \\ \omega_e &= 907.64 \text{ cm}^{-1}, \\ \omega_e x_e &= 7.910 \text{ cm}^{-1}. \end{aligned}$$

The above values have been used for all subsequent calculations on LiF in this work.

The observed and calculated line positions for the first three vibrational states of Li^7F^{19} and Li^6F^{19} corresponding to the transition $(1, \pm 1) \rightarrow (1, 0)$ are given in Tables IX through XIV.

The calculated Stark frequencies for the eighteen sets of spectra obtained are listed in Table XV. These values were obtained by matching the observed line positions to those given by the best computer program fit to the observed singlet line positions. All values have been corrected for C-field contact potentials. These corrections were calculated by obtaining spectra with opposite C-field polarities at each of the three voltages used. The corrections amount to approximately one part in 10^4 of the C-field voltage for all sets.

Table IX. Observed and calculated relative singlet line positions (in kc) for Li^7F^{19} in the $V = 0$ vibrational state.

The transition is $(1, \pm 1) \rightarrow (1, 0)$. Line II_A is used as a reference point. The observed values are a weighted average of the eight spectra obtained at $E_C = 459.63$ and 800.00 V/cm.

Line Name	Observed	Calculated	Difference
I_B	-114.7 ± 0.3	-114.6	0.1
I_C	-103.9 ± 0.3	-103.5	0.4
II_A	-83.0 ± 0.2	-83.0	(Automatic agreement)
III_B	-38.1 ± 0.2	-38.2	0.1
III_C	-30.2 ± 0.3	-30.6	0.4
IV_B	-11.2 ± 0.2	-11.2	0.0
V_B	47.3 ± 0.2	47.1	0.2
VI_A	86.6 ± 0.2	86.6	0.0
VII_B	127.7 ± 0.4	127.8	0.1

Table X. Observed and calculated relative singlet line positions
(in kc) for Li^7F^{19} in the $V = 1$ vibrational state.

The transition is $(1, \pm 1) \rightarrow (1, 0)$. Line II_A is used as a reference point.
The observed values are an average of the three spectra obtained at
 $E_C = 800.00 \text{ V/cm}$.

<u>Line Name</u>	<u>Observed</u>	<u>Calculated</u>	<u>Difference</u>
I_B	-112.1 ± 0.4	-112.4	0.3
I_C	-101.6 ± 0.1	-101.5	0.1
II_A	-81.4 ± 0.03	-81.4	(Automatic agreement)
III_B	-37.8 ± 0.6	-37.5	0.3
III_C	-30.0 ± 0.1	-30.0	0.0
IV_B	-11.4 ± 0.4	-11.0	0.4
V_B	46.5 ± 0.8	46.2	0.3
VI_A	84.9 ± 0.03	84.9	0.0
VII_B	125.1 ± 0.4	125.3	0.2

Table XI. Observed and calculated relative singlet line positions
(in kc) for Li^7F^{19} in the $V = 2$ vibrational state.

The transition is $(1, \pm 1) \rightarrow (1, 0)$. Line IV_B is used as a reference point. The observed values are a weighted average of the four spectra obtained at $E_C = 459.63, 800.00, \text{ and } 1,180.00 \text{ V/cm}$. Lines observed in the preceding tables and not listed here were not observed well enough to be reported.

Line Name	Observed	Calculated	Difference
I_B	-109.3 ± 0.8	-109.2	0.1
I_C	98.4 ± 0.1	- 98.4	0.0
II_A	$- 79.0 \pm 0.8$	- 79.3	0.3
IV_B	$- 10.5 \pm 0.1$	- 10.5	(Automatic agreement)
VI_A	82.4 ± 0.8	82.7	0.3
VII_B	122.4 ± 1.1	121.8	0.6

Table XII. Observed and calculated relative line positions
(in kc) for Li^6F^{19} in the $V = 0$ vibrational state.

The transition is $(1, \pm 1) \rightarrow (1, 0)$. Line I_C is used as a reference point.
The observed values are an average of the 11 spectra obtained at
 $E_C = 459.63 \text{ V/cm}$.

Line Name	Observed	Calculated
I_A	-28.2 ± 0.3	— ^a
I_B	-20.9 ± 0.0	-21.0 -20.8 -18.5 -17.7 -16.4
I_C	-13.8 ± 0.2	-13.8 (Automatic agreement)
I_D	-6.6 ± 0.4	— ^a
II_A	13.2 ± 0.2	12.7 13.5 17.2 17.4
II_B	20.8 ± 0.2	20.2 21.0 21.8
II_C	28.0 ± 0.4	24.9 — ^a

a. The unpredicted lines are discussed in Section IV.

Table XIII. Observed and calculated relative line positions
(in kc) for Li^6F^{19} in the $V = 1$ vibrational state.

The transition is $(1, \pm 1) \rightarrow (1, 0)$. Line I_C is used as a reference point.
The observed values are an average of the six spectra obtained at
 $E_C = 459.63 \text{ V/cm}$.

Line Name	Observed	Calculated
I_A	-27.4 ± 1.0	— ^a
I_B	$-20.5_6 \pm 0.0$	-20.7 -20.4 -18.2 -17.4 -16.1
I_C	-13.6 ± 0.2	-13.6 (Automatic agreement)
I_D	-6.6 ± 0.5	— ^a
II_A	12.8 ± 0.2	12.6 13.4 16.9 17.1
II_B	20.3 ± 0.2	19.9 20.6 21.5 24.4
II_C	27.3 ± 0.3	— ^a

a. The unpredicted lines are discussed in Section IV.

Table XIV. Observed and calculated relative line positions
(in kc) for Li^6F^{19} in the $V = 2$ vibrational state.

The transition is $(1, \pm 1) \rightarrow (1, 0)$. Line I_C is used as a reference point. The observed values are an average of the four spectra obtained at $E_C = 459.63 \text{ V/cm}$.

Line Name	Observed	Calculated
I_A	-27.6 ± 1.0	— ^a
		-20.3
I_B	-20.2 ± 0.0	-20.1
		-17.9
		-17.1
		-15.9
I_C	-13.4 ± 0.4	-13.4
		(Automatic agreement)
I_D	-7.5 ± 0.4	— ^a
		12.4
II_A	12.9 ± 0.2	13.1
		16.6
		16.9
		19.5
II_B	20.2 ± 0.3	20.3
		21.1
		24.0
II_C	27.2 ± 0.4	— ^a

a. The unpredicted lines are discussed in Section IV.

Table XV. Calculated Stark frequencies
(in Mc) for Li^6F^{19} and Li^7F^{19} .

Vibrational state, V	C-Field voltage (V/cm)		
	459.63	800.00	1,180.00
<u>Li^7F^{19}</u>			
0	8.0256	24.3103	52.8712
1	8.3613	25.3259	55.0790
2	8.7106	26.3824	57.3745
<u>Li^6F^{19}</u>			
0	7.1659	21.7053	47.2055
1	7.4838	22.6674	49.2968
2	7.8151	23.6709	51.4785

The listed Stark frequencies were used in Eq. (I-3) to calculate values for $\mu^2 A$ by a method of successive approximation. (The fourth-order term in Eq. (I-3) is not large enough to permit an accurate direct calculation of $\mu^4 A^3$ from the data obtained.) The three values of $\mu^2 A$ thus calculated at different field strengths for each vibrational state agree to better than one part in 10^4 for both Li^6F^{19} and Li^7F^{19} . This indicates a relative consistency in C-field measurements of 5 parts in 10^5 , which is well below the assumed error in C-field voltage (i. e., 2 parts in 10^4). The values obtained for $\mu^2 A$ and μ for the first three vibrational states of Li^6F^{19} and Li^7F^{19} are listed in Table XVI. The errors stated for $\mu^2 A$ and μ are mainly due to the uncertainty in C-field voltage. The values used for A were calculated from the rotational and vibrational constants previously listed.

Graphs of two spectra and the calculated line positions for the $V = 0$ vibrational states of Li^6F^{19} and Li^7F^{19} are shown in Figs. III-4 and III-5. The calculated line positions correspond to the best computer program fits to an average of the observed lines as given in Tables IX and XII of this work.

The values obtained for $(eqQ)_{\text{Li}}$, c_{Li} , and c_{F} are given in Table XVII.

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Fig. III-4. Graph of a spectrum for Li^7F^{19} in the $V = 0$ vibrational state and the calculated line positions. The transition is $(1, \pm 1) \rightarrow (1, 0)$. $E_C = 800 \text{ V/cm}$.

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Fig. III-5. Graph of a spectrum for Li^6F^{19} in the $V = 0$ vibrational state and the calculated line positions. The transition is $(1, \pm 1) \rightarrow (1, 0)$. $E_C = 460 \text{ V/cm}$.

Table XVI. Values calculated for the molecular constants μ^2A , and the dipole moments of LiF.

Vibrational state V	μ^2A ($\times 10^{76}$ cgs)	μ (Debye)
<u>Li⁷F¹⁹</u>		
0	838.47 $\pm$ 0.3	6.3783 $\pm$ 0.0013
1	873.54 $\pm$ 0.3	6.4624 $\pm$ 0.0013
2	910.02 $\pm$ 0.3	6.5468 $\pm$ 0.0013
<u>Li⁶F¹⁹</u>		
0	748.62 $\pm$ 0.3	6.3810 $\pm$ 0.0013
1	781.81 $\pm$ 0.3	6.4703 $\pm$ 0.0013
2	816.44 $\pm$ 0.3	6.5597 $\pm$ 0.0013

Table XVII. Values obtained for the molecular constants
(eqQ)_{Li}, c_{Li}, and c_F of LiF (all values in kilocycles).

Vibrational state, V	(eqQ) _{Li} /h	c _{Li} /h	c _F /h
<u>Li⁷F¹⁹</u>			
0	413.0 ± 0.5	1.7 ± 0.1	33.0 ± 0.2
1	405.0 ± 0.8	1.7 ± 0.2	32.5 ± 0.3
2	393 ± 4	1.7 ± 0.4	32.0 ± 0.6
<u>Li⁶F¹⁹</u>			
0	7.3 ± 0.7	0.7 ± 0.2	36.9 ± 0.2
1	7.2 ± 0.7	0.7 ± 0.2	36.4 ± 0.2
2	6.9 ± 0.9	0.7 ± 0.4	35.8 ± 0.4

IV. DISCUSSION AND CONCLUSIONS

A. Dipole Moments

Schlier has given an expression for the dipole moment of a diatomic molecule as a function of vibrational energy.³⁴ It has been shown that this expression may be written for LiF in the form³⁵

$$\mu = \mu_e + K\omega_e(v + 1/2), \quad (\text{IV-1}),$$

where μ_e and K are constants. Thus, a plot of the dipole moment, μ , versus the vibrational energy, $\omega_e(v + 1/2)$, should result in a straight line. A plot of the six dipole moments obtained for Li^6F^{19} and Li^7F^{19} versus vibrational energy is shown in Fig. IV-1. The points are linear well within experimental error (i. e., one part in 6,000 for μ), thus indicating internal consistency for the values obtained.

A comparison of the values presented here for μ^2A (from which μ is calculated), and those previously obtained is given in Table XVIII. This comparison and the results obtained for KF indicate that the reported C-field voltages are correct within the stated error.

B. Quadrupole Interaction Constants

Zeiger and Bolef have shown that the quadrupole interaction constant may be expressed as a linear function of the vibrational quantum number, V , when the rotational quantum number, J , is constant.³⁶ The present results indicate a nonlinear variation for $(eqQ)_{\text{Li}^7}$ with respect to V , although the deviation from linearity is within experimental error.

34. C. Schlier, Z. Physik 154, 460 (1959).

35. L. Peter Gold, Thesis, Department of Chemistry, Harvard University, Cambridge, Mass., November 1961, Section II-12.

36. H. J. Zeiger and D. I. Bolef, Phys. Rev. 85, 788 (1952).

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Fig. IV-1. Dipole moments versus vibrational energy for LiF.

Table XVIII. Values reported for the molecular constants
 μ^2A of LiF.

Vibrational state, V	Present results ($\times 10^{76}$ cgs)	Gold's results ($\times 10^{76}$ cgs) ^a	Trischka's results ($\times 10^{76}$ cgs) ^b
<u>Li⁷F¹⁹</u>			
0	838.47 $\pm$ 0.3	838.63 $\pm$ 0.3	837.1' $\pm$ 0.9
1	873.54 $\pm$ 0.3	873.79 $\pm$ 0.3	872.3 $\pm$ 1.0
2	910.02 $\pm$ 0.3	—	—
<u>Li⁶F¹⁹</u>			
0	748.62 $\pm$ 0.3	748.81 $\pm$ 0.3	747.4 $\pm$ 0.9
1	781.81 $\pm$ 0.3	782.02 $\pm$ 0.3	779.3 $\pm$ 1.1
2	816.44 $\pm$ 0.3	816.37 $\pm$ 0.3	812.0 $\pm$ 1.3
a. Reference 31.			
b. References 23, 24. The values for Li ⁶ F ¹⁹ have been calculated from the relationships given.			

A similar nonlinear variation has been observed by Trischka and Marple for $(eqQ)_{Cl}$ in Li^6Cl ^{35, 37}. They use, to represent their results the equation

$$(eqQ) = eq^0Q + (eq^vQ)_1(v+1/2) + (eq^vQ)_2(v+1/2)^2,$$

where (eqQ) is the observed quadrupole interaction and v is the vibrational quantum number. Use of this expression with the present values for $(eqQ)_{Li^7}$ yields

$$\begin{aligned} eq^0Q &= +415.5 \pm 4, \\ (eq^vQ)_1 &= -4 \pm 7, \\ (eq^vQ)_2 &= -2 \pm 3. \end{aligned}$$

The results for $(eqQ)_{Li}$ in LiF are compared to those previously obtained in Table XIX. A plot of the quadrupole interaction constants of Li^7F^{19} versus vibrational state is shown in Fig. IV-2.

C. Spin-Rotation Interaction Constants

The spin-rotation constant has been shown to be directly proportional to the nuclear g value and inversely proportional to the moment of inertia of the molecule.³⁸ A calculation of the values for c_F/h for Li^6F^{19} from those obtained for Li^7F^{19} , using the above proportionality, results in excellent agreement (± 0.1 kc) with the experimentally determined values. This indicates a high degree of internal consistency in the experimental results.

The Li^7 spin-rotation constant, $c_{Li^7}/h = 1.7 \pm 0.1$ kc, agrees more closely with the magnetic resonance result of 1.4 kc³⁹ than the values reported by Gold³¹ and Trischka.⁴

Comparisons of the values reported for c_{Li^7}/h and $c_{F^{19}}/h$ are

37. D. T. F. Marple and J. W. Trischka, Phys. Rev. 103, 610 (1956).

38. R. L. White, Rev. Mod. Phys. 27, 276 (1955).

39. This value was calculated by Trischka (Reference 4) from the data given by P. Kusch, Phys. Rev. 75, 887 (1949).

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Fig. IV-2. A plot of $(eq Q)_{Li7}$ versus vibrational state.

Table XIX. Values reported for the quadrupole interaction constants, $(eqQ)_{Li}/h$, of LiF.

Vibrational state, V	Present results	Gold's results (Ref. 31)	Trischka's results (Ref. 23)
<u>Li⁷F¹⁹</u>			
0	413.0 ± 0.5	414.0 ± 0.5	412.0 ± 7.0
1	405.0 ± 0.8	402.0 ± 1.0	412.0 ± 7.0
2	393 ± 4	—	—
<u>Li⁶F¹⁹</u>			
0	7.3 ± 0.7	7 ± 1	—
1	7.2 ± 0.7	7 ± 2	—
2	6.9 ± 0.9	7 ± 2	—

given in Tables XX and XXI. The nonlinear variation of c_F with vibrational state reported by Trischka²⁴ is not expected and does not agree with the present results.

D. Unpredicted Lines

The following lines observed in the spectra of LiF are not predicted by theory:

$$\text{Li}^7\text{F}^{19}: \times\text{II}_B, \times\text{IV}_A, \times\text{IV}_C, \times\text{VI}_B, \times\text{VII}_C;$$

$$\text{Li}^6\text{F}^{19}: \times\text{I}_A, \times\text{I}_D, \times\text{II}_C, \times\text{II}_D.$$

The lines lie approximately 8.7 ± 1 kc away from the corresponding predicted lines in Li^7F , and increments of 6.9 ± 0.6 kc away from those predicted in Li^6F . An investigation failed to reveal any 5- to 10-kc frequency components in the signal generator, the rf transmission line, or the apparatus under operating conditions.

The same unexplained lines are evident in the Li^7F spectrum obtained by Gold,⁴⁰ but they have been attributed to experimentally induced effects.⁴¹ Unpredicted line shapes have also been observed for LiF by Trischka.⁴²

Attempts to account for the lines on the basis of forbidden transitions were unsuccessful. No satisfactory theoretical explanation is evident at present.

An explanation of the lines based on C-field inhomogeneity is not valid, since their positions relative to the predicted lines do not vary

40. L. Peter Gold, Thesis, Department of Chemistry, Harvard University, Cambridge, Mass., November 1961, Section II-3.

41. W. Klemperer, L. Wharton, and L. Peter Gold (Harvard University, Cambridge, Mass.), private communication.

42. R. Braunstein and J. W. Trischka, Phys. Rev. 98, 1096 (1955).

Table XX. Values reported for the spin-rotation constant,
 c_F/h , for LiF.

Vibrational state V	Present results	Gold's results (Ref. 31)	Trischka's results (Ref. 4) (Ref. 24)	
<hr/>				
Li ⁷ F ¹⁹				
<hr/>				
0	33.0 ± 0.2	32.5 ± 0.2	32.9 ± 1.0	—
1	32.5 ± 0.3	32.3 ± 0.4	32.4 ± 1.0	—
2	32.0 ± 0.6	—	—	—
<hr/>				
Li ⁶ F ¹⁹				
<hr/>				
0	36.9 ± 0.2	36.6 ± 0.3	37.3 ± 0.7	36.28 ± 0.16
1	36.4 ± 0.2	36.1 ± 0.6	—	36.11 ± 0.27
2	35.8 ± 0.4	35.9 ± 0.8	—	33.89 ± 0.54

Table XXI. Values reported for the spin-rotation constant,
 c_{Li}/h , for LiF.

Vibrational state, V	Present results	Gold's results (Ref. 31)	Trischka's results (Ref. 4)
<u>Li⁷F¹⁹</u>			
0	1.70 ± 0.1	1.9 ± 0.3	2.2 ± 0.6
1	1.7 ± 0.2	2.0 ± 0.6	1.8 ± 0.6
2	1.7 ± 0.4	—	—
<u>Li⁶F¹⁹</u>			
0	0.7 ± 0.2	0.9 ± 0.2	—
1	0.7 ± 0.2	0.9 ± 0.4	—
2	0.7 ± 0.4	0.9 ± 0.5	—

appreciably with large changes in voltage. Also, no changes in relative line positions occurred upon reversing the C-field polarity.

The Millman effect⁴³ has been observed in electric resonance experiments by Hughes and Grabner.⁴⁴ They have shown that a given single line may have satellites. The satellites are produced by circularly polarized components of radio frequency at the ends of the C-field transition region. These components give rise to the two frequencies $\nu + \Delta\nu$ and $\nu - \Delta\nu$, where ν is the frequency of the central line and $\Delta\nu$ corresponds to the separation of a satellite from the central line. The quantity $\Delta\nu$ can be expressed by an equation similar to Eq. (I-4),

$$\Delta\nu \approx v/L \quad (\text{IV-2}),$$

where v is the most probable velocity for molecules in the beam, and L is the length of the region over which the rotation of rf takes place. Hughes and Grabner observed a $\Delta\nu$ of 160 kc for K^{39}F , and thus calculated an L of 0.3 cm. A similar calculation for the present results, using $\Delta\nu = 8$ kc and $v = 8 \times 10^4$ cm/sec, yields an L of 10 cm. Thus, an explanation for the unpredicted lines based on the Millman effect seems untenable.

Explanations based on the Doppler effect⁴⁵ are not applicable, since the observed line widths and relative positions do not vary appreciably with large changes in transition frequency.

A conclusion based on the above arguments does not seem warranted at this time. There is a possibility that the lines may be caused by an undetected radio-frequency effect in the transition region.⁴⁶

43. S. Millman, *Phys. Rev.* 55, 628 (1939).

44. L. Grabner and V. Hughes, *Phys. Rev.* 79, 827 (1950).

45. N. F. Ramsey, *Molecular Beams* (Clarendon Press, Oxford, 1956), p. 140.

46. P. Kusch and V. W. Hughes, in *Handbuch der Physik* (Springer-Verlag, Berlin, 1959), Vol. 37/1, p. 61.

E. Errors in Relative Line Positions

The principal source of error in relative line positions appears to arise from room-temperature variations that influence the C-field voltage. The apparatus has recently been moved to an air-conditioned laboratory in which temperature variations are considerably lower than in the former room. Preliminary studies indicate that the relative line position errors reported in this work may be reduced by an order of magnitude in future experiments.

APPENDIX:

Table A-1 lists the vacuum equipment used and some typical operating pressures obtained. A cross-sectional sketch of a typical liquid nitrogen trap is shown in Fig. A-1.

Table A-II lists data on the power supplies and electronic equipment used.

Table A-I. Vacuum equipment.

	<u>Oven chamber</u>	<u>Buffer chamber</u>	<u>Main chamber</u>	<u>Electron- multiplier chamber</u>
<u>Diffusion pumps^a</u>				
Model	MCF 1400	MCF 300	MCF 720	MCF 300
Maximum rated speed (liters/sec)	1400	300	700	300
Rated base pressure (mm Hg)	10^{-7}	10^{-7}	10^{-7}	10^{-7}
<u>Fore pumps^b</u>				
Model	1397 B	1402 B	1402 B	1403 B
Maximum rated speed (liters/sec)	7	2	2	0.2
Rated base pressure (mm Hg)	10^{-4}	10^{-4}	10^{-4}	10^{-4}
Observed base pressure (mm Hg)	10^{-4}	10^{-4}	10^{-4}	10^{-4}
<u>Observed chamber pressures^c</u>				
(Under operating conditions with a condensable beam) (mm Hg)	2×10^{-7}	2×10^{-7}	5×10^{-7}	5×10^{-8}

- The diffusion pumps are manufactured by the Consolidated Electrodynamics Corp., Palo Alto, California.
- The forepumps are manufactured by the W. M. Welch Scientific Co., Chicago, Illinois.
- VG1/A tubes and standard UCLRL ion-gauge power supplies (#5z1814-9) are used for high-vacuum pressure measurements. Hastings type DV-3M vacuum tubes and power supplies provided with safety interlocks are used for forepressure readings.

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Fig. A-1. Cross-sectional sketch of a typical liquid nitrogen trap.

Table A-II. Detection system power supplies and electronic equipment.

Unit	Model No.	Manufacturer	Modifications
Ion-accelerator voltage supply (0 to 5000 V at 5 mA)	408 A/U	John Fluke Mfg. Co., Seattle, Wash.	None
Hot-wire supply (0 to 10 A at 4.5, 9, or 18 V. Insulated to 10 kV)	None	Designed by George Kilian. Fabricated by LRL ^a Plan No. 3X9783	None
Electron-multiplier voltage supply (0 to 5000 V at 5 mA)	RE 5001EW	Northeast Scientific Corp., Cambridge, Mass.	None
Electrometer	None	E. & H. Mfg. Co., Oakland, Calif.	Resistance box added for selecting 10^7 -, 10^8 -, 10^9 -, 10^{10} -, or 10^{11} -ohm input load
Linear amplifier and pre- amplifier (variable time con- stant 2.5 to 40,000 microsec)	V	LRL ^a Plan No. 1X5334E	None
Pulse scaler (0 to 10^7 counts per second)	524 D	Hewlett-Packard Co., Palo Alto, Calif.	Display time lowered and counting interval changed by throwing switches ^b (see text)
Frequency scaler (0 to 10^8 counts per second)	524 D (with 525A plug-in unit to extend counting range)	Hewlett-Packard Co., Palo Alto, Calif.	None
Digital recorder with analog output	560 A	Hewlett-Packard Co., Palo Alto, Calif.	Microswitch mounted on printer-activation solenoid (see text)
Radio-frequency signal generator (50 kc to 65 Mc)	606 A	Hewlett-Packard Co., Palo Alto, Calif.	None

^a Lawrence Radiation Laboratory, Berkeley, California.

^b This modification was devised and performed by Mr. Charles A Crayne, (UCLRL electronics technician).

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