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Infrared Matrix Spectra of Lithium Fluoride

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Evidence for a linear dimer Li_2F_2 has been obtained by extending the spectral measurements for matrix isolated lithium fluoride into the far infrared region. The vapors from solid ^6LiF, ^7LiF, and $^6LiF/^7LiF$ mixtures were deposited in argon matrices at liquid hydrogen temperatures. Vibrational assignments were made on the basis of the following linear species: $^6Li_2F_2$, $^7Li_2F_2$, $^{6,7}Li_2F_2$ and $^{7,6}Li_2F_2$. Although the specific geometry of the dimer could not be determined, a normal coordinate analysis supported the spectral interpretation of a linear structure ($C_{\infty v}$).

Key Words: Force field; infrared; lithium fluoride dimer; low temperature; matrix; vibrational assignment.

1. Introduction

Infrared spectra of matrix isolated lithium fluoride species indicate the formation of a rhomboid dimer of D_{2h} symmetry in addition to the monomeric form [1–5].[1] Several prominent spectral features, however, are not satisfactorily assigned to a specific LiF system, in particular, the sets of relatively strong bands that occur in argon matrices at 722 and 495 cm^{-1} and at 769 and 522 cm^{-1} for the isolated vapors of ^7LiF and ^6LiF, respectively. Since the matrix absorption bands for the two isotopic forms of the monomer appear at 842 and 888 cm^{-1}, some workers attribute the additional bands to monomeric LiF absorptions arising from supplementary matrix trapping sites [1, 2]. Alternatively, other investigators believe that the unassigned bands may be due to the formation of either a trimer or higher polymeric species [3, 6]. Reddington, however, suggests that the controversial features possibly reflect the two high frequency stretching modes of a matrix stabilized linear dimer [5].

In the present study the infrared measurements on matrix isolated lithium fluoride are extended into the far infrared region. Since the spectrum exhibits absorption features from several species, carefully controlled matrix diffusion experiments in conjunction with double boiler techniques for producing the gaseous molecules allowed the absorption bands of a given molecular type to be grouped together. Spectra from isotopic molecules, as well as mixtures of varying isotopic compositions, aided both the grouping and assignment of the vibrational features. One group of bands which occur in the 700 cm^{-1}, 500 cm^{-1}, and far infrared regions are interpreted as absorptions of a linear dimer with two nonequivalent lithium atoms. Other simple interpretations for these features, such as supplementary trapping sites or a cyclic trimer, are considered and found to be inconsistent with the sum of data observed.

2. Experimental

The methods used to isolate high temperature species in rare gas matrices have been described in detail elsewhere [7]. Depending upon the spectral region studied, the infrared spectra were obtained either with a Perkin-Elmer model 99G monochromator or a Perkin-Elmer model 301 spectrophotometer [8]. An Air Products Cryotip supplied the refrigeration at liquid hydrogen temperatures and provided the

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[1] Figures in brackets indicate the literature references at the end of this paper.

necessary controlled temperature regulation from 20 to 33 K, while an electron bombardment furnace vaporized the LiF samples. ^{6}LiF and ^{7}LiF samples; supplied by the Stable Isotopes Division, Oak Ridge National Laboratory, were evaporated in double oven crucibles and were deposited in an argon matrix on thin CsI windows. These samples, as well as isotopic mixtures, were investigated in the region from 1000 to 150 cm^{-1}.

The narrow absorption bands of the same species will either increase or lose intensity at the same rate upon controlled diffusion at temperatures above 20 K, thus providing a convenient method of identifying groups of bands with a particular molecular species. Mole ratios of the species in the vapor are altered by raising the temperature of the gas effusing from the Knudsen cell; therefore, one can assign bands to the same species by their relative decrease in intensity relative to the LiF monomer. Enriched samples of ^{6}LiF containing 95 percent ^{6}LiF and 5 percent ^{7}LiF were utilized in addition to ^{n}LiF which has about 95 percent ^{7}LiF and 5 percent ^{6}LiF. Additional information was obtained by examining the spectrum of thick deposits of ^{7}LiF in the region of the ^{6}LiF absorptions and vice versa. The difficulties in estimating both the temperature of the effusing gas and the ratio of the matrix diluent to the sample (M/S) have been discussed [1, 2, 5, 7]. M/S ratios of 500 : 1 to 1000 : 1, and temperatures from 850 °C to 1200 °C are representative of the conditions used in these experiments.

Internal and external absorption standards were used to calibrate the observed spectra. Spectral slit widths of about 0.5 cm^{-1} and 1.0 cm^{-1} were employed in the region from 1000 to 400 cm^{-1} and from 400–150 cm^{-1}, respectively.

3. Experimental Results

Classifying the sets of bands of the various species by controlled diffusion experiments and double boiler observations yields the following groups: (1) monomeric bands of LiF at 835 cm^{-1} for ^{7}LiF and 888 cm^{-1} for ^{6}LiF; (2) bands due to the cyclic dimer of $^7Li_2F_2$, $^6Li_2F_2$ and $^6Li^7LiF_2$; (3) bands at 767.8, 518.6, 270.2, 261.0 and 157.1 cm^{-1} for ^{6}LiF and at 720.5, 497.5, 255.2, 245.7, and 152.8 cm^{-1} for ^{7}LiF; (4) all other bands in the spectrum which increased in intensity relative to the monomer during diffusion experiments at temperatures above 20 K (and also are significantly lower in intensity relative to the monomeric species when the temperature of the effusing gas is raised). The behavior of the fourth group of bands indicate that they originate from polymeric species containing more lithium atoms than the species responsible for the other absorption bands in the spectrum.

Upon controlled diffusion at temperatures up to 33 K, the group 2 bands decreased in intensity relative to the monomer at a significantly more rapid rate than the group 3 bands. The group 3 bands decreased in intensity at a somewhat greater rate than the monomeric bands, while the group 4 bands all increased in intensity. At elevated temperatures of effusion both group 2 and 3 bands were reduced in intensity relative to the monomer with the diminution in group 2 greater than that in group 3. As we already indicated, the group 4 bands were decreased in relative intensity to a greater extent than both groups 2 and 3.

The relative intensity of all features compared to the monomeric species was only a function of the temperature of the effusing vapor. Flow rates were varied over the range of 0.05 to 0.20 mmol/min of argon without observing any change in the spectrum. This precludes any explanation of the five bands in group 2 based upon supplementary trapping sites in the matrix for the monomeric species. Also, it is unlikely that an argon matrix could perturb the vibrational frequency of a monomeric lithium fluoride to cause the large observed matrix shifts. The details of the five absorption bands belonging to group 3 which, again, because of their behavior and isotopic splitting patterns, belong to the same molecular species, will now be discussed in detail with particular emphasis directed towards assigning these bands to a linear dimer with two nonequivalent lithium atoms. In a later section a discussion of other possibilities will be included.

3.1. The 400–150 cm^{-1} Region

The observed infrared spectra of matrix isolated ^{7}LiF, ^{6}LiF, and a 1 : 1 mixture of ^{7}LiF/^{6}LiF appear in figure 1a for the 240–300 cm^{-1} region. The strong features at 293.8 and 276.4 cm^{-1} in ^{6}LiF and ^{7}LiF are assigned to the lowest infrared active vibration ν_4 of the planar rhomboid dimer of LiF. Confirmation is given by the triad at 293.8, 284.7, and 276.4 cm^{-1} for the 1 : 1 mixture of ^{7}LiF/^{6}LiF, since the observed relative intensities of 1 : 2 : 1 are those expected for a dimer with equivalent lithium atoms. (A sample containing equal part of ^{6}LiF and ^{7}LiF would be expected to exhibit bands of relative intensity of 1 : 2 : 1 and 1 : 1 : 1 : 1 for the cases of a dimer containing equivalent and nonequivalent lithium atoms.) The observed ratio of 1.0630 for $\nu_4(^6\mathrm{Li})/\nu_4(^7\mathrm{Li})$ agrees quite well with the calculated ratio of 1.0594 from the product rule for this mode. The behavior of this absorption area upon warming the matrix and allowing diffusion to occur is identical to the bands at 626, 646, and 661 cm^{-1} and 537, 550, and 569 cm^{-1} which were previously assigned to the ν_5 and ν_6 species of the rhomboid dimer of $^7Li_2F_2$, $^6Li^7LiF_2$, and $^6Li_2F_2$ [2]. The three sets of features also exhibit the same relative intensity diminution relative to the monomeric species when spectra are observed in samples deposited from higher effusing temperatures.

The other set of bands in this region exhibit a different rate of disappearance on warming the matrix than those demonstrated by the features ascribed to the ring-shaped dimer. Also, the diminution in intensity of these bands, upon deposition from a higher

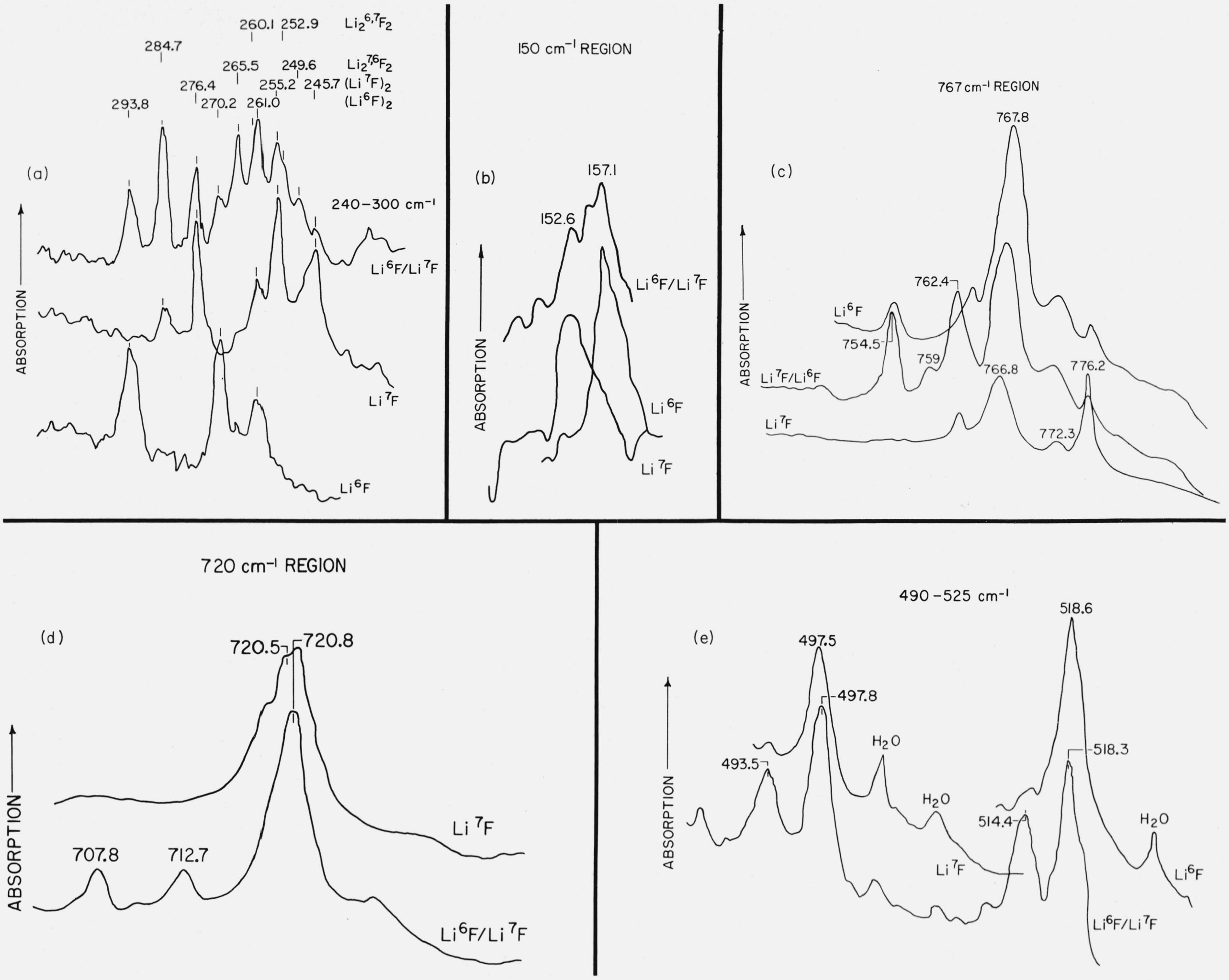

FIGURE 1. *Infrared spectra of matrix isolated* ^{7}LiF, ^{6}LiF, *and a 1:1 mixture of* ^{6}LiF/^{7}LiF.

(a) 240–300 cm^{-1} region
(b) 150 cm^{-1} region
(c) 767 cm^{-1} region
(d) 720 cm^{-1} region
(e) 490–525 cm^{-1} region

effusing temperature relative to the change in intensity of the monomeric species, is distinctly less than that observed for the ring-shaped dimer. These features occur at 270.2 and 261.0 cm^{-1} for ^{6}LiF and at 255.2 and 245.7 cm^{-1} for ^{7}LiF. The spectrum of the isotopic mixture gives additional bands at 265.5, 260.1, 252.9 and 249.6 cm^{-1}. These absorptions are assigned to the linear dimer species. Since the frequencies for the pure isotopic molecules are less than 10 cm^{-1} apart, the vibrations probably correspond to different symmetry representations; namely, the stretching (Σ) and bending (Π) modes of the dimer. Thus, we assign the bands at 255.2, 270.2, 265.5, and 260.1 to the ν_3 vibrations, the lowest stretching mode, of F–^{7}Li–F–^{7}Li, F–^{6}Li–F–^{6}Li, F–^{7}Li–F–^{6}Li, and F–^{6}Li–F–^{7}Li, respectively. The bands at 245.7, 261.0, 252.9, and 249.6 cm^{-1} then correspond to the ν_4 bending modes of F–^{7}Li–F–^{7}Li, F–^{6}Li–F–^{6}Li, F–^{7}Li–F–^{6}Li, F–^{6}Li–F–^{7}Li, respectively. The measurements reported were obtained under higher resolution conditions than those shown. In addition to trapping the species from the isotopic mixtures, thick deposits of the nearly pure isotopic samples, as well as 1:1 to 1:3 mixtures, were observed.

Arguments concerning the assignment based upon intensity considerations in this region are quite difficult. Particularly, there are bands in this region which are due to the polymeric or aggregate species containing more than two lithium atoms. Evidence for these bands is obtained from temperature cycling experiments in which the dimeric bands disappear and the polymeric bands increase in intensity. Also, for the pure ^{6}Li and ^{7}Li spectra, one notices absorptions in the wings of the bands (between 270.2 and 261.0 cm^{-1} in ^{6}LiF and 255.2 and 245.7 in ^{7}LiF) that is due to the polymeric species. Therefore, a detailed intensity match with the expected 1:1:1:1 ratio for the mixed isotope is not possible in this region. Despite these difficulties, however, one observes qualitative agreement for the pairs of lines in the mixed isotope. Consider 265.5, 249.6 cm^{-1} for $^{7,6}Li_2F_2$ and 260.1, 252.9 cm^{-1} for $^{6,7}Li_2F_2$. These lines have roughly the same intensity ratio as the pairs of lines 270.2, 261.0 cm^{-1} and 255.2, 245.7 cm^{-1} for the pure species. (The buildup in intensity of the 261.0 and 260.1 peaks is due to their near coincidence.) Since the natural and enriched samples of the ^{7}LiF and ^{6}LiF contained about 5 percent of the other isotope, the thick deposits of the individual species gave features of the mixed isotope spectra with the appropriate intensity ratios.

Absorption bands at 152.8 and 157.1 cm^{-1} for the ^{7}LiF and ^{6}LiF samples presented the same behavior upon diffusion in the matrix and the same intensity diminution upon deposition from a higher temperature as the previous features assigned to the linear dimer. The spectrum appears in figure 1b. The mixed isotopic sample indicates a superposition of the spectra of the two pure samples. These bands are assigned to ν_5 of the F–^{7}Li–F–^{7}Li and F–^{6}Li–F–^{6}Li species. It was not possible to resolve the spectrum for the mixture into the F–^{6}Li–F–^{7}Li and F–^{7}Li–F–^{6}Li components, although it appears clear from the normal coordinate analysis described below that the frequencies for ν_5 of these mixed species are between about 152 and 157 cm^{-1}.

Several other absorption features, both broad and narrow, were observed in the spectra of the pure and mixed isotopes. Their behavior upon diffusion, however, indicates that these bands arose from systems other than either the dimeric or monomeric species.

3.2. The 900–400 cm^{-1} Region

The absorption bands arising from the two stretching modes of a linear Li_2F_2 molecule are expected in this region. The higher frequency stretching mode of Li_2F_2 occurs at 767.8 and 720.5 cm^{-1} in $^6Li_2F_2$ and $^7Li_2F_2$. Spectra of these regions are given in figures 1c and 1d. In addition to these features, one observes the two stretching modes ν_5 and ν_6 (B_{2u} and B_{3u}) of the rhomboid dimer, as well as the bands for the monomer. Although these features are not presented in the figures, the species occur at substantially the same frequencies as reported previously [1–5].

Features also appear which are attributed to species other than the monomer or either dimer. These bands increase in intensity upon diffusion which indicates that they are possibly due to a polymer of three or more LiF aggregates. No further discussion concerning the species responsible for these absorptions will be given here.

High resolution spectra of 1:1 mixtures of ^{6}LiF/^{7}LiF show the 767.8 cm^{-1} band split into two components of equal intensity. These correspond to ν_1 of F–^{6}Li–F–^{6}Li and F–^{6}Li–F–^{7}Li at 767.8 and 766.8 cm^{-1}. The approximate equality of intensities of these two components (in a 1:1 isotopic mixture) is expected and provides further evidence for a dimer with two nonequivalent lithium atoms. The corresponding absorption in ^{7}LiF is found at 720.5 cm^{-1}. This band is complicated by a shoulder to the low frequency side which is more prominent in a 1:1 mixture of ^{6}LiF/^{7}LiF. Two weaker bands also were found in the mixed isotopic sample. These features, as shown by diffusion experiments, are not due to the linear dimeric form. Careful measurements of ^{7}LiF and various mixtures of ^{6}LiF and ^{7}LiF indicate that ν_1 of F—^{7}Li—F—^{7}Li is at 720.5 cm^{-1} while ν_1 of F–^{7}Li–F–^{6}Li is at 720.8 cm^{-1}. The small isotope shifts for the ν_1 and ν_2 modes, as seen in the normal coordinate calculations, supports the existence of the linear dimer model.

Features attributed to the ν_2 symmetric stretching mode of F–Li–F–Li occur at 497.5 and 518.6 cm^{-1} in $^7Li_2F_2$ and $^6Li_2F_2$. The mixed isotopic spectra, given in figure 1e, show features at 493.5 and 514.4 cm^{-1} that are not due to any dimeric or monomeric species. These bands increase markedly in intensity upon diffusion and may be due to the same species responsible for the unassigned absorptions in the 768 and 721 cm^{-1} regions. Measurements of various mixed isotopic samples of ^{7}LiF and ^{6}LiF show ν_2 of F–^{6}Li–F–^{7}Li to be at 497.8 cm^{-1}, while the corresponding frequency of F–^{7}Li–F–^{6}Li is at 518.3 cm^{-1}. In this region it was again useful to measure the spectrum of ^{7}LiF at 768 and 518 cm^{-1} and ^{6}LiF at 721 and 497 cm^{-1} with thick samples in order to obtain the mixed isotope spectrum in a 5 percent concentration. The sets of observed frequencies for the final assignment of the linear Li_2F_2 molecule appear in tables 3 and 4, along with the calculated frequencies from the normal coordinate analysis.

The absorption spectrum of monomeric ^{7}LiF in the argon matrix is shown in figure 2. The doublets ascribed to the fundamental modes of the diatomic LiF species are the only absorption bands in the spectrum which exhibit reversible temperature dependent behavior. As the temperature is raised from 20–33 K, the doublet is smeared out with an apparent blue shift of about 1 cm^{-1} for the low frequency

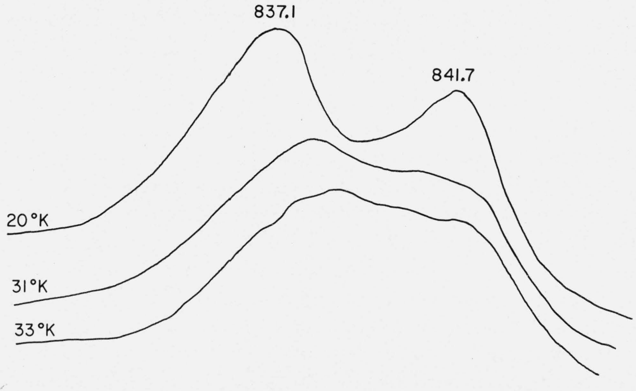

FIGURE 2. *Monomeric* ^{7}LiF *in* Ar *at various temperatures.*

component. No conclusion regarding the cause of this behavior will be given here, except to note that only the absorption bands attributed to monomeric ^{6}LiF and ^{7}LiF at 842 and 888 cm^{-1} exhibit such a phenomenon.

4. Discussion

In order to support the interpretation of a linear Li_2F_2 dimeric species, we performed a normal coordinate analysis for the four isotopic systems. Several models for the linear structure were considered; namely, a F–Li–F–Li dimer in which all bonds were equivalent, a F–Li–F · · · Li dimer with a bifluoride structure, and a species F–Li · · · F–Li containing an elongated central bond. For the normal LiF bonds of the model structures, a length of 1.51 Å from the gas phase was assumed, while a value of 2.01 Å from crystalline LiF was taken for the long bonds [9]. The force field for a chosen model was first refined about the ^{6}Li and ^{7}Li isotopic species. Interaction force constants were systematically varied until close fits to the observed frequencies were attained. This force field was then used to calculate the frequencies for the mixed isotopic species, namely, the F–^{6}Li–F–^{7}Li and F–^{7}Li–F–^{6}Li molecules. In view of the assumptions concerning the bond lengths and interactions in the force constant matrix, the significance of the force field is limited. Consequently, rather than stressing the values of the individual force constants, recognizing that the force field is not unique, we prefer to emphasize the closeness of the frequency fit for the four isotopic molecules as evidence favoring the linear dimeric structure.

For a linear dimer, F–Li–F–Li of $C_{\infty v}$ symmetry, the vibrational representation is $\Gamma_v = 3\Sigma^+ + 2\Pi$, with the stretching vibrations occurring in the Σ^+ species and the bending modes conforming to Π symmetry. The vibrational problem was cast in terms of the internal coordinates and force constant matrix that appear in table 1. Familiar *GF* matrix methods were used in solving the vibrational secular equation.

TABLE 1. *Internal coordinates and force constant matrix for the linear* Li_2F_2 *dimer.*

a) Internal coordinates

F–Li–F–Li
$r \; s \; t$
$\alpha = <$ F Li F
$\beta = <$ Li F Li

b) Force constant matrix

f	r	s	t	α	β
r	f_r	f_{rs}	f_{rt}		
s		f_s	f_{st}		
t			f_t		
α				f_α	$f_{\alpha\beta}$
β					f_β

Since the elements of the *G* matrix for the stretching vibrations are independent of bond length, the frequency fits for the Σ^+ species of the three linear dimers are equivalent. The force constants for the various stretching force constants and the comparison between the observed and calculated frequencies appear in tables 2 and 3, respectively. Again, the force constants were refined about only the $^6Li_2F_2$ and $^7Li_2F_2$ isotopes. The frequencies for the mixed isotopes are determined from this potential function. Since a unique potential function probably cannot be determined from the frequency data alone in this manner, it is not worthwhile to refine the force field over all isotopes. The results of the normal coordinate calculation for the Π species appear in table 4. For these vibrations, the change in geometry affects the calculated frequencies. Table 4 indicates, however, that a distinction in geometry cannot be made decisively for the Π species since the frequency fits are quite reasonable for the three models.

TABLE 2. *Summary of force constants for the linear dimer models of* Li_2F_2. *The stretching force constants are in units of millidynes per angstrom, while the bending force constants are in units of millidynes · angstroms*

Model	Species	Force constant
F–Li–F–Li	Σ^+	$f_r + f_s = 3.71$ $f_{rs} = 0.96$ $f_t = 0.59$ $f_{rt} + f_{st} = 1.41$
	Π	$f_\alpha + f_\beta = 0.26$ $f_{\alpha\beta} = 0.05$
F–Li–F · · · Li [a]	Π	$f_\alpha + f_\beta = 0.36$ $f_{\alpha\beta} = 0.10$
F–Li · · · F–Li [a]	Π	$f_\alpha + f_\beta = 0.46$ $f_{\alpha\beta} = 0.18$

[a] A dotted line represents a longer bond distance.

TABLE 3. *Comparison between the observed and calculated frequencies, in* cm^{-1}, *for the* Σ^+ *symmetry species of the linear* Li_2F_2 *dimer.*

	Obs	Calc	$\Delta\nu$	Obs	Calc	$\Delta\nu$
	F^{6}LiF^{6}Li			F^{7}LiF^{7}Li		
ν_1	767.8	768.0	+0.2	720.5	720.3	−0.2
ν_2	518.6	518.8	+0.2	497.5	498.2	+0.7
ν_3	270.2	266.5	−3.7	255.2	258.7	+3.5
	F^{6}LiF^{7}Li			F^{7}LiF^{6}Li		
ν_1	766.8	767.7	+0.9	720.8	720.8	0
ν_2	497.8	499.5	+1.7	518.3	517.2	−1.1
ν_3	260.1	258.9	−1.2	265.5	266.3	−0.8

Although rather drastic approximations enter the force field calculation, we can make several observations concerning the various possibilities for a linear model. The plausibility of the bifluoride structure suggests that $f_r = f_s$ and $f_{rt} = 0$. The results of this computation yield values of $f_r = 1.8$ mdyn/Å, $f_t = 0.24$ mdyn/Å, and $f_{rr} = 0.91$ mdyn/Å. Although the interaction force constant is rather large, the values are

TABLE 4. *Comparison between the observed and calculated frequencies, in cm^{-1}, for the Π symmetry species of three models for the* Li_2F_2 *linear dimer.*

	Obs	Calc	$\Delta\nu$	Obs	Calc	$\Delta\nu$
a) F–Li–F–Li						
	$^6Li_2F_2$			$^7Li_2F_2$		
ν_4	261.0	261.1	+0.1	245.7	245.5	−0.2
ν_5	157.1	158.5	+0.6	152.8	151.3	−1.5
	$^{6-7}Li_2F_2$			$^{7-6}Li_2F_2$		
ν_4	252.9	260.7	+7.8	249.6	247.6	−2.0
ν_5		152.3			154.6	
b) F–Li–F · · · Li						
	$^6Li_2F_2$			$^7Li_2F_2$		
ν_4	261.0	261.7	+0.7	245.7	244.9	−0.8
ν_5	157.1	157.8	+0.7	152.8	152.0	−0.8
	$^{6-7}Li_2F_2$			$^{7-6}Li_2F_2$		
ν_4	252.9	261.7	+8.8	249.6	245.0	−4.6
ν_5		152.1			157.8	
c) F–Li · · · F–Li						
	$^6Li_2F_2$			$^7Li_2F_2$		
ν_4	261.0	261.0	0	245.7	245.7	0
ν_5	157.1	158.8	+1.7	152.8	151.0	−1.8
	$^{6-7}Li_2F_2$			$^{7-6}Li_2F_2$		
ν_4	252.9	252.0	−0.9	249.6	255.4	+5.8
ν_5		153.9			155.3	

not unreasonable. The frequency fits for the $^6Li_2F_2$ and $^7Li_2F_2$ are approximately 1 cm^{-1}, except for ν_2 which is about 11 cm^{-1}. Including another interaction force constant, however, in the combinational form of $f_{st}+f_{rt}$, we reduce the error in the frequency fit to well within 1 cm^{-1} for the pure 6 and 7 species, except for ν_3, which is about 3.5 cm^{-1} from the observed value. This frequency fit is tabulated in table 3 for all the isotopic species. The values for the diagonal force constants in this case are $f_r=f_s=1.85$ mdyn/Å and $f_t=0.6$ mdyn/Å. Again, the interaction force constants are relatively large; namely, $f_{rs}=0.96$ mdyn/Å and the linear combination of $f_{st}+f_{rt}=1.41$ mdyn/Å. The refinement of the force constants about the observed frequencies depends upon a least squares method; however, the number of known data is not great enough to make a statistical analysis of the force constants profitable. Since additional molecular information, as for example, rotational distortion data or mean-square amplitude data for the gas phase species, is required to further characterize the force field, other sets of force constants may exist which fit the data. Summarizing, we wish to stress that the probable nonuniqueness of the force field precludes a choice of structures on the basis of individual values of the force constants. The close frequency fit determined from the modified potential function, however, strongly indicates the linear nature of the trapped species.

Approximate descriptions of the stretching Σ^+ modes for the ^7LiF and ^6LiF species are defined by the calculated normal coordinate vectors. The highest frequency ν_1 appears to be mainly a F–Li–F out-of-phase stretching mode, while the ν_3 vibration is composed primarily of the Li–F–Li out-of-phase motion. The ν_2 vibration is approximately a F–Li, F–Li symmetric stretching motion. Since it is not clear which linear dimer model is preferred, detailed descriptions of the bending modes are not given.

A further problem arises in the assignment of the ν_3 and ν_4 vibrations to the Σ^+ and Π species, respectively, since the assignment may reasonably be reversed. A choice cannot be made on the basis of the product rule. For example, the assignment presented in table 3 for $^6Li_2F_2$ and $^7Li_2F_2$ gives an isotopic frequency ratio of 1.176 for $\nu_1\nu_2\nu_3/\nu_1'\nu_2'\nu_3'$, which is compared to a calculated value of 1.144 from the product rule. Reversing the assignments for the stretching and bending modes, ν_3 and ν_4, respectively, gives an isotopic frequency value of 1.180. Table 5 presents the frequency fit for the bifluoride model, as an example, for an assignment with the two frequencies reversed. As before, the force field that was refined about the $^6Li_2F_2$ and $^7Li_2F_2$ isotopic frequencies was used to calculate the frequencies for the mixed species. The fit for the reversed frequency assignment is only slightly worse than the fit in tables 3 and 4. Although it is difficult to resolve the choice definitely, we prefer the assignment with the stretching motion at the higher frequency.

TABLE 5. *Comparison between the observed and calculated frequencies, in cm^{-1}, for the bifluoride structure of the* Li_2F_2 *linear dimer. The ν_3 and ν_4 frequencies are reversed from the assignment presented in tables 3 and 4.*

	Obs	Calc	$\Delta\nu$	Obs	Calc	$\Delta\nu$
	$^6Li_2F_2$			$^7Li_2F_2$		
ν_1	767.8	768.0	0.2	720.5	720.3	−0.2
ν_2	518.6	518.1	−.5	497.5	498.5	1.0
ν_3	261.0	257.3	−3.7	245.7	249.3	4.6
ν_4	270.2	271.3	1.1	255.2	254.1	−1.1
ν_5	157.1	157.9	0.8	152.8	151.9	−0.9
	$^{6-7}Li_2F_2$			$^{7-6}Li_2F_2$		
ν_1	766.8	767.7	0.9	720.8	720.7	−0.1
ν_2	497.8	499.8	2.8	518.3	516.6	−1.7
ν_3	252.9	249.5	−3.4	265.5	257.1	−8.5
ν_4	260.1	271.2	11.1	249.6	254.0	4.4
ν_5		152.1			157.7	

The observed product rule for the pure species is also consistent with a D_{3h} cyclic structure for the trimer. If one assigns 767.8, 518.6, and 261.0 cm^{-1} to $^7Li_3F_3$ and 720.8, 497.5, and 245.7 cm^{-1} to $^6Li_3F_3$, the product rule predicts a value of 1.158 for the E' modes as compared to an observed value of 1.180. The infrared active bending modes (A_2'') could then be satisfactorily assigned to 270.2, 265.5, 260.1, and 255.2 for $^6Li_3F_3$, $^6Li_2{}^7LiF_3$, $^6Li^7Li_2F_3$, and $^7Li_3F_3$, respectively. This assignment leaves the far infrared bands at 152–157 cm^{-1} unassigned. It also does not explain the intensity results obtained for the 767.8 and 766.8 cm^{-1} bands nor the intensity ratios obtained by running ^{6}LiF in the region of ^{7}LiF and vice versa. It is, perhaps, interesting to note that any breakdown in symmetry due to site group splitting to D_3 or C_3 symmetry will not affect the number of expected bands, since E' of D_{3h} maps onto E in both D_3 and C_3 groups, while A_2'' maps onto A_2 and A, respectively. Assignment of these features to a cyclic trimer of lithium fluoride is also inconsistent with the vibrational data in the 770 and 500 cm^{-1} regions for the mixed species. In particular, it is hard to envision a molecule of this symmetry experiencing such small isotope shifts for stretching modes; that is, the cyclic model would require an isotope shift for the E' stretching modes of ^{7}Li$_3$F$_3$ and ^{7}Li$_2$^{6}LiF$_3$ to be of the order of one cm^{-1}.

The evidence then for a linear dimer of lithium fluoride can be briefly summarized as follows. Using double boiler and diffusion experiments, five absorption bands are shown to belong to the same molecular species. The expected intensity is found in the 767.8 and 766.8 cm^{-1} bands of ^{6}Li$_2$F$_2$ and the ^{6}Li^{7}LiF$_2$ isotopic variants of the proposed dimers. The Teller-Redlich product rule for the proposed assignment is 1.176 for the Σ modes. If one reverses the assignment for ν_3 and ν_4, the product rule calculation yields 1.180. Both of these product rule values are consistent with the calculated value of 1.144. (While this agreement is a necessary prerequisite for the proposed structure, product rule calculations are not sufficient proofs.) Examining the spectrum of ^{n}LiF and ^{6}LiF (95 percent enriched) in regions of ^{6}LiF and ^{7}LiF, respectively, in rather heavy deposits, one observes the spectrum of the mixed isotope (in a 5 percent concentration) that is consistent with a linear dimer model. Finally, an empirical force field determined from ^{6}Li$_2$F$_2$ and ^{7}Li$_2$F$_2$ predicts quite well the observed vibrational spectrum for the two mixed isotopic linear species.

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5. References

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