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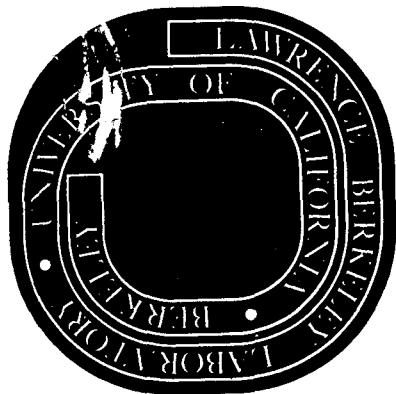
Peter K. Pearson, William J. Hunt,
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December 1972

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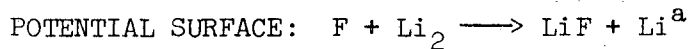


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THE SIMPLEST HALOGEN ATOM PLUS ALKALI DIMER

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December 1972

ABSTRACT

Ab initio electronic structure calculations have been carried out to investigate some features of the potential energy surface for the chemical reaction $F + Li_2 \longrightarrow LiF + Li$. The basis set of contracted gaussian functions was of "double zeta plus polarization" quality, with an additional set of p functions on F added to describe F^- . Single-configuration and two-configuration self-consistent-field calculations are reported here. A minimum energy path was obtained for the collinear reaction, but the most important feature determined was the nature of the potential minimum due to the $F Li_2$ complex. For linear F-Li-Li, this complex is bound by 4 kcal/mole relative to separated $LiF + Li$. The attraction is much stronger, 34 kcal, for C_{2v} geometry, and this species is predicted to have a bond angle of 99° and Li - F bond distance of 1.79 Å. Several excited electronic states of $F Li_2$ are discussed briefly.

INTRODUCTION

In previous papers¹⁻³ we have reported ab initio potential energy surfaces for two simple chemical reactions, $F + H_2 \longrightarrow HF + H$ and $H + F_2 \longrightarrow HF + F$. Both of these exothermic potential surfaces are "repulsive" in the nomenclature of Polanyi.⁴ Perhaps the most obvious feature of a repulsive potential surface is that there is a finite barrier (related⁵ to the activation energy) to reaction. More generally, a repulsive surface is defined to be one on which most of the exothermicity is released as the products separate. The above-mentioned calculations¹⁻³ were indeed encouraging in that they showed that qualitatively correct potential surfaces are now attainable ab initio. In another sense however, the calculations were discouraging: to properly reproduce two known features, the activation energy and exothermicity, rather large basis sets (about three times the size of a minimum basis) and a significant amount of configuration interaction (CI) are required.⁶ Thus the standard model of quantum chemistry, the Hartree-Fock approximation, is not applicable to these repulsive potential surfaces.

For exothermic reactions, the opposite of a repulsive potential surface, sensibly enough, is an "attractive" surface.⁴ An attractive potential surface is one on which the exothermicity is released as the reactants approach each other. An attractive surface has no barrier or activation energy. Thus, one of the two stumbling blocks to the success of the Hartree-Fock or ordinary self-consistent-field (SCF) approximation has been removed. Furthermore, attractive potential surfaces frequently involve ionic species, which are known⁷ to be relatively well-described

within the SCF framework. We conclude that attractive potential surfaces, of which many are chemically important,⁸ might be amenable to qualitative description by ordinary SCF calculations.

One class of reactions for which a good deal of dynamical information is becoming available is the series of halogen atom plus alkali dimer reactions, $X + A_2 \longrightarrow AX + A$. Interestingly, the $X + Na_2 \longrightarrow NaX + X$ ($X = Cl, Br, I$) reactions were the subject of a very important early paper by Evans and Polanyi.⁹ More recently, reactions of the type $A_1 + A_2X \longrightarrow A_1X + A_2$, which also take place on XA_2 potential surfaces, were studied by Miller, Saffron, and Herschbach¹⁰ using crossed molecular beams. Their work was particularly important because it established the importance of a long-lived collision complex XA_2 in interpretations of the dynamics of these simple reactions. Direct molecular beam studies of the $X + A_2$ reaction have only become possible during the last two or three years with the development^{11,12} of suitable sources of alkali dimers. The first such study reported appears to be that of Struve, Kitagawa, and Herschbach,¹³ who observed electronic excitation of alkali atoms following the $Cl + Na_2$ and $Cl + K_2$ reactions. Even more recently Zare and co-workers¹⁴ have performed crossed beam experiments on the $I + K_2$ system. The most important finding of this study is an unidentified chemiluminescence spectrum, which may be due to a bound IK_2 species.

In light of the variety of experiments already carried out on XA_2 systems and the likelihood of further such work, it is clear that reliable ab initio potential surfaces for XA_2 would be of great value. In fact, Herschbach⁸ made this very point two years ago, in questioning whether such

a calculation might not be feasible for the simplest system, FLi_2 . We were led to the present ab initio calculations on $\text{F} + \text{Li}_2$, then, by two considerations a) our intuitive feeling that the Hartree-Fock approximation might be satisfactory for an attractive surface and b) the experimental interest in XA_2 potential surfaces.

DESCRIPTION OF THE CALCULATIONS

Two factors determine the likelihood (or lack of same) that an ab initio calculation will be reliable for the property of interest.⁶ These are the basis set of one-electron functions and the structure of the many-electron wave function.

For the lithium atom our basis set began with Huzinaga's 9s primitive gaussian set,¹⁵ which was contracted to 4s following Dunning.¹⁶ In addition, Williams¹⁷ made available to us his optimized 9s 4p basis for the ^2P ($1s^2 2p$) first excited state of the Li atom. This 4p set was contracted to 2p in the usual¹⁶ manner. The importance of Li 3d functions was tested for LiF and found to be negligible, the total SCF energy being lowered by only 0.0013 hartree = 0.8 kcal/mole.

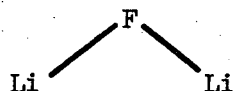
The F atom basis began with Dunning's (9s 5p/4s 2p) set. However, one weakness of this basis, as pointed out by Duke and Bader,¹⁸ is that it provides a far better description of the neutral F atom than the F^- negative ion. Therefore, following Duke and Bader,¹⁸ we added a set (p_x, p_y, p_z) of diffuse p functions ($\alpha = 0.0742$) to the fluorine basis. Finally a set of d-like functions (xx, yy, zz, xy, xz, yz) centered on F was optimized for LiF (yielding a gaussian exponent $\alpha = 0.39$) and added to give the final basis shown in Table I.

Both single-configuration SCF and two-configuration SCF calculations were carried out in the present study. The appropriate SCF equations were solved using the methods developed by Hunt, Hay, and Goddard.¹⁹ The second configuration may be chosen to guarantee, for infinite separation of the nuclei, that $\psi(\text{FLi}_2) = \psi_{\text{SCF}}(\text{F}) \psi_{\text{SCF}}(\text{Li}) \psi_{\text{SCF}}(\text{Li})$, that is, that the total wave function will be the product of wave functions for the three separated atoms. This second configuration was shown³ to be very important for HF_2 at the saddle point. For linear F - Li - Li geometries, the two configurations included are

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 6\sigma$$

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 6\sigma 7\sigma^2$$

For C_{2v} geometries



the two configurations chosen were

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 2b_2^2 4a_1^2 1b_1^2 5a_1$$

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 2b_2^2 1b_1^2 5a_1 6a_1^2$$

Although the second configuration above does not allow proper dissociation to three atoms, this configuration is nevertheless the second most important near the predicted equilibrium geometry. Finally, for general geometry (Cs symmetry) we have

$$1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 1a''^2 7a'$$

$$1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 1a''^2 7a' 8a'^2$$

It may be helpful to point out that in constructing these configurations we have occupied the atomic orbitals in the following order: $1s(F)$, $1s(Li)$, $2s(F)$, $2p\sigma(F)$, $2p\pi(F)$, $2s(Li)$.

RESULTS FOR THE ISOLATED REACTANTS AND PRODUCTS

The exothermicity for the $F + Li_2 \longrightarrow LiF + Li$ reaction can be found by simply carrying out calculations on isolated Li_2 and LiF and subtracting the former dissociation energy from the latter. Our calculated properties of Li_2 and LiF are given in Table II. There it is seen that the SCF exothermicity of 87 kcal is 25.3 ± 7.6 kcal smaller than experiment. Fortunately, the magnitude of the exothermicity is such that the calculated value is nevertheless 77% of experiment. We note from SCF calculations using much larger basis sets that the true Hartree-Fock energy of Li_2 is ~ -14.8719 ($r_e = 5.27$ Bohrs)²⁰ and that of LiF is ~ -106.9918 ($r_e = 2.94$ Bohrs).²¹ Thus, the Hartree-Fock exothermicity of $F + Li_2 \longrightarrow LiF + Li$ is ~ 90.0 kcal, suggesting that only 3 kcal of our 25 kcal exothermicity error is due to the limitations of our basis. The two-configuration SCF calculation represents an improvement of only 1.8 kcal over the single-configuration result. We see then that the correlation energy of LiF is much greater than that of Li_2 and that this correlation error is only slightly decreased by including the most obvious second configuration.

Table II also compares the calculated and experimental bond distances and dissociation energies for Li_2 and LiF . The LiF bond distance is satisfactorily predicted but that for Li_2 is significantly larger than experiment. Das has shown²² that seven-configuration SCF calculations on Li_2 can reduce the bond

distance error to 0.04 bohrs (0.02Å). The fact that the Li_2 molecule is predicted by SCF calculations to lie above the comparable SCF energies of two Li atoms is not as serious a flaw as it might appear. This is due to the well-known²⁰ inability of the Li_2 SCF wave function to dissociate properly to SCF wave functions for the two Li atoms. In reality, the shape of the SCF potential curve near its minimum is very similar to the experimental curve.²⁰

LINEAR F - Li - Li

Our first calculations were carried out for linear approaches of F to Li_2 . After establishing (see below) that the SCF and two-configuration SCF surfaces were very similar, it was decided to compute the SCF minimum energy path for linear $\text{F} + \text{Li}_2 \longrightarrow \text{LiF} + \text{Li}$. This minimum energy path is shown in Table III. A contour map of the collinear surface is seen in Fig. 1.

Starting with separated $\text{F} + \text{Li}_2$, the first interesting feature of Table III is a significant lengthening of the Li - Li separation. After this lengthening occurs, the Li - Li distance remains essentially constant over a considerable range of F - Li distances. This abrupt change in bond distance is undoubtedly due to an electron jump⁸ from the covalent $\text{F} \text{Li}_2$ to the ionic $\text{F}^- \text{Li}_2^+$ potential surface. The Li_2^+ bond distance is known²³ to be longer than that for Li_2 and ab initio calculations by Bardsley²⁴ predict the Li_2^+ internuclear separation to be ~ 5.8 bohrs.

At $R(\text{F} - \text{Li}) \sim 3.2$ bohrs, the Li - Li distance again begins to increase significantly and continues to increase until it reaches the bottom of the potential minimum, where $R(\text{Li} - \text{Li}) = 6.31$ bohrs. The exit channel, leading

to $\text{FLi} + \text{Li}$, may be described very easily, since the $\text{F} - \text{Li}$ distance changes hardly at all (0.03 bohrs). In this region the minimum energy path corresponds simply to removing the end Li atom from a nearly frozen FLi molecule.

POTENTIAL MINIMA

Due to the important experimental work^{9,10,13,14} on XA_2 systems, the most interesting feature of any potential surface for FLi_2 will be the depths and positions of potential minima, in which a collision complex¹⁰ (or even¹⁴ a stable molecule) might be formed. Both SCF and two-configuration SCF calculations were performed to determine these features.

Table IV gives some properties of linear $\text{F} - \text{Li} - \text{Li}$ at its equilibrium geometry. Both calculations are seen to predict a potential well of about 4 kcal with respect to separated $\text{LiF} + \text{Li}$. The analogous results for FLi_2 constrained to be of C_{2v} geometry are shown in Table V. There we see that the isosceles triangle well is much deeper, about 34 kcal/per mole from either of the two calculations. By accepted standards,²⁵ this potential well is quite deep, certainly deep enough to yield a collision complex, although probably not for the highly exothermic $\text{F} + \text{Li}_2 \longrightarrow \text{LiF} + \text{Li}$ reaction. An intriguing experiment,²⁶ in which complex formation would almost certainly influence the dynamics,^{27,28} is the lithium exchange reaction

$${}^6\text{Li} + {}^7\text{LiF} \longrightarrow {}^6\text{LiF} + {}^7\text{Li}.$$

It is of considerable interest to compare the present results with those obtained using much simpler methods. In particular, Struve²⁹ has very recently reported pseudopotential calculations for $\text{F} + \text{Li}_2$ as well as several other halogen atom plus alkali dimer potential surfaces. Struve finds a

collinear well of ~ 9 kcal for F - Li - Li, and an isosceles triangle well of depth ~ 20 kcal/mole. Although one would hope for somewhat closer agreement, the pseudopotential and ab initio results are qualitatively similar. Further, one should not be too quick to conclude that the ab initio results are much more reliable. Although we are cautiously hopeful that the calculated well depths are correct to within, say 20%, the known error in the calculated exothermicity is a reminder that all is by no means perfect. It is clear that a correlated calculation of the type reported² for F + H₂ should be undertaken for F + Li₂.

Tables IV and V also give some information concerning the electronic structure of FLi₂ near the two potential minima. As expected the FLi₂ complex is quite ionic, as may be seen from the Mulliken populations. In each case, between 0.8 and 0.9 electrons have been "transferred" from the lithium atoms to fluorine. The linear FLi₂ is seen to be slightly more ionic. For isosceles FLi₂, this loss of electron density is shared by the two Li atoms. However, as Table IV shows, for F Li Li, the lithium atoms adjacent to fluorine has a much greater "charge", +0.73, than the end lithium, +0.15. The much greater spatial extent of the linear molecule accounts for its much large moment of nearly 11 debyes. Note, of course, that the C_{2v} structure would have no dipole moment for a 180° Li - F - Li bond angle.

EXCITED ELECTRONIC STATES

Thus far we have only mentioned the assumed electronic ground state of FLi₂. The assumed ground state is of ${}^2\Sigma^+$ symmetry for linear configuration, 2A_1 symmetry for the isosceles triangle, and ${}^2A'$ symmetry when only a single

plane of symmetry exists. However, the sixfold degeneracy of the 2P state of the fluorine atom means that the $F + Li_2$ collisions might occur on any of six different potential energy surfaces.^{30,31} Neglecting spin-orbit coupling (the $1.2 \frac{\text{kcal}}{\text{mole}}$ separation between the $^2P_{3/2}$ and $^2P_{1/2}$ states of the F atom) there are three spatially distinct potential surfaces for $F + Li_2$ collisions. A rough idea of the positions of the electronically excited surfaces may be gained from orbital energies, some of which are seen in Table VI. Note that the comparison of Table VI favors (energetically) the lowest surface, since the geometries chosen minimize the total energy of the electronic ground state. To confirm the suggestion of Table VI that the excited surfaces are fairly high-lying, direct SCF calculations were carried out, again for the geometries of the ground state collinear and C_{2v} minima. These results are summarized in Fig. 2, and reinforce the qualitative conclusion that, for the chosen geometries, the excited $F Li_2$ surfaces are relatively high-lying. The qualitative picture also shows that only collisions occurring on the ground state surface will lead to ground state products, $Li + LiF$.

CONCLUDING REMARKS

As mentioned earlier, the next logical step in a theoretical study of the $F + Li_2$ reaction would be an investigation of the dynamics, using either classical trajectories²⁷ or semi-classical procedures.²⁸ One barrier to direct application of these methods is the fact that more than a single potential surface would be required to yield a complete description of $F + Li_2$ collisions. In addition to the fact that we have only briefly mentioned the excited electronic states of $F Li_2$, the question of how to handle the dynamics in a

multi-surface problem^{32,33} is by no means as straightforward as in the single-surface case.^{27,28} Despite these reservations, it appears that a dynamical study of $F + Li_2 \longrightarrow LiF + Li$ and/or $LiF + Li \longrightarrow Li + LiF$, employing only the electronic ground state potential surface, would be useful. Such a study might provide some concrete data concerning the importance of complex formation^{8,10,34} in molecular collisions involving attractive potential surfaces.

We recommend that the dynamical studies be carried out using a potential surface incorporating the following features:

- a) A linear F - Li - Li minimum stable by 4 kcal/mole with respect to separated LiF + Li. The F - Li separation should be 2.99 bohrs and the Li - Li separation 6.06 bohrs. These distances are our calculated SCF values adjusted for the errors in the isolated LiF and Li₂ molecules.
- b) An isosceles minimum stable by 34 kcal with respect to LiF + Li. The LiF bond distance should be 3.16 bohrs and the bond angle 99°.

The remaining features of the FLi₂ potential surface should be dictated by the experimental potential curves for LiF and Li₂ and some standard form, such as that of London, Eyring, Polanyi, and Sato.³⁵

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- ^aWork performed under the auspices of the U. S. Atomic Energy Commission.
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- ^eAlfred P. Sloan Fellow.
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Table I. Basis Set for Calculations on $F + Li_2 \longrightarrow FLi + Li$.The Notation is that of Dunning.¹⁶

Fluorine	<u>Exponents</u>	<u>Coefficients</u>
	9994.79	0.002017
	1506.03	0.015295
s functions	350.269	0.073110
	104.053	0.246420
	34.8432	0.612593
	4.3688	0.242489
	12.2164	1.0
	1.2078	1.0
	0.3634	1.0
p functions	44.3555	0.020868
	10.0820	0.130092
	2.9959	0.396219
	0.9383	0.620368
	0.2733	1.0
	0.0742	1.0
d function	0.39	1.0

Table I (cont.)

Lithium	<u>Exponents</u>	<u>Coefficients</u>
	921.271	0.002240
	138.730	0.017035
	31.9415	0.081481
s functions	9.35329	0.262624
	3.15789	0.563291
	0.44462	0.275931
	1.15685	1.0
	0.076663	1.0
	0.028643	1.0
	1.5343	0.037973
p functions	0.27499	0.231890
	0.073618	0.834779
	0.024026	1.0

Table II. Calculated properties of the isolated diatomic molecules Li_2 and LiF .

	<u>Property</u>	<u>SCF</u>	<u>TCSCF</u>	<u>Experimental</u>
Li_2	r_e (bohrs)	5.305	5.59	5.05 ^a
	D_e (kcal/mole)	3.8	10.0	26.3 \pm 0.7 ^{a,b}
LiF	r_e (bohrs)	3.01	3.04	2.96 ^a
	D_e (kcal/mole)	90.7	98.9	138.5 \pm 7.6 ^{a,b}
Exothermicity for				
	$\text{F} + \text{Li}_2 \longrightarrow \text{LiF} + \text{Li}$	87.0	88.8	112.3 \pm 7.6 ^{a,b}

^aG. Herzberg, Spectra of Diatomic Molecules (Van Nostrand, Princeton, N. J. 1950).

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(Chapman and Hall, London, 1968).

Table III. Self-consistent-field minimum energy path for the collinear $F+Li_2 \longrightarrow LiF+Li$ reaction. Internuclear separations are in bohr radii.

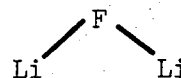
R(F - Li)	R(Li - Li)	E(kcal/mole)
∞	5.31	0.0
5.9	5.77	-26.3
5.0	5.81	-44.0
4.0	5.84	-70.1
3.5	5.86	-83.7
3.2	5.88	-90.8
3.037	6.305	-91.1*
3.02	7.0	-90.6
3.01	8.0	-89.4
3.01	9.0	-88.5
3.01	∞	-87.0

* Potential minimum.

Table IV. Predicted properties of the linear FLi_aLi_b molecule.

<u>Property</u>	<u>SCF</u>	<u>TCSCF</u>
R(F - Li)	3.04 bohrs	3.00 bohrs
R(Li - Li)	6.31 bohrs	6.17 bohrs
$D_e(\text{FLi} - \text{Li})$	4.1 kcal	3.9 kcal
Dipole moment	10.73 debyes	10.68 debyes
Mulliken atomic populations		
F	9.884	9.878
Li _a	2.263	2.277
Li _b	2.852	2.845

Table V. Predicted properties of the bent



molecule.

<u>Property</u>	<u>SCF</u>	<u>TCSCF</u>
R(Li - F)	3.21 bohrs	3.23
θ	99°	101°
$D_e(\text{LiF} - \text{Li})$	34.0 kcal	33.9 kcal
Dipole moment	1.10 debyes	1.20 debyes
Mulliken atomic populations		
F	9.832	9.828
Li _a	2.584	2.586
Li _b	2.584	2.586

Table VI. Orbital energies in hartrees (1 hartree=627.5 kcal/mole)
for linear and C_{2v} equilibrium geometries of FLi_2 .

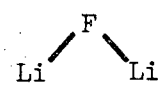
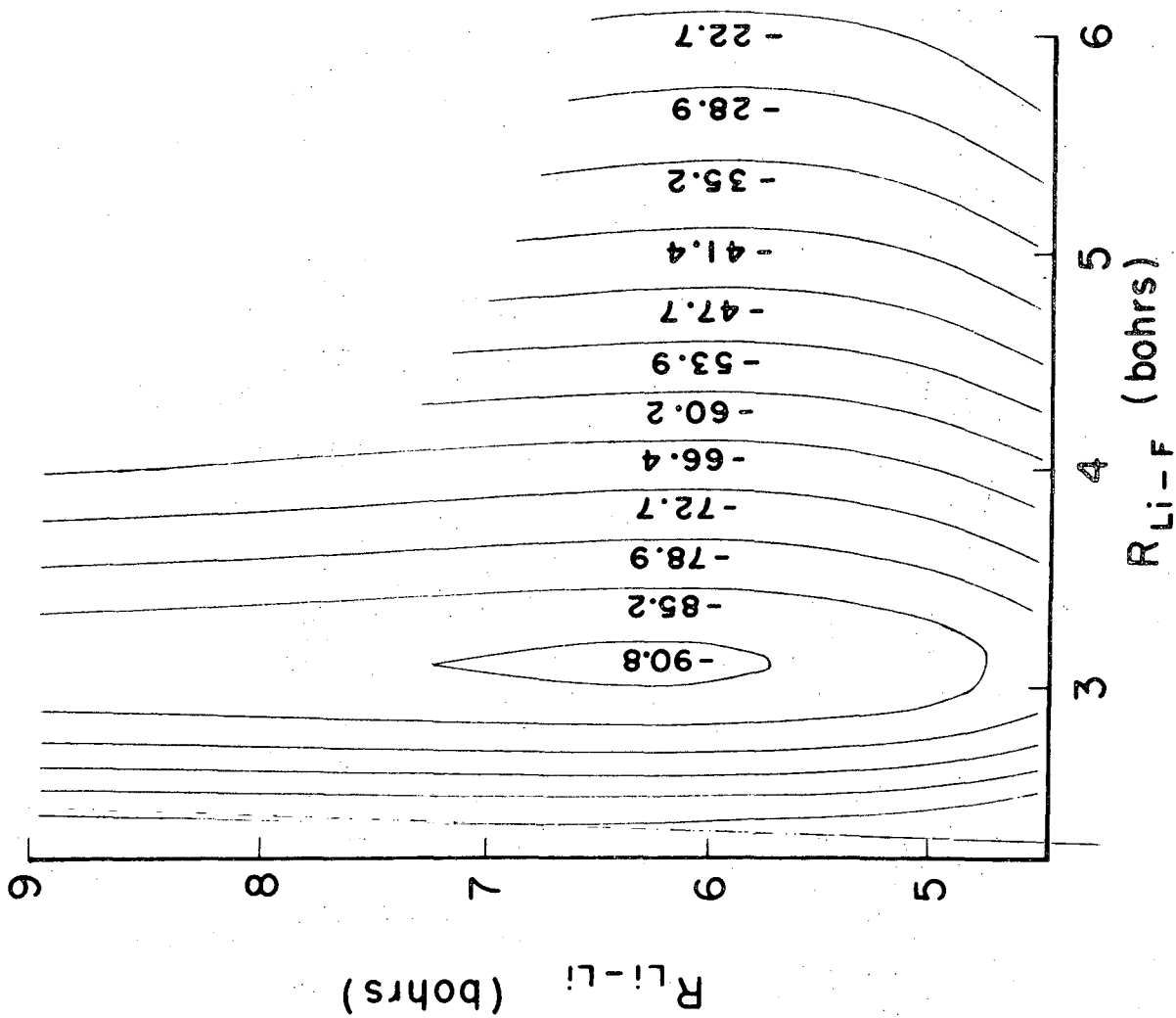
${}^2\Sigma^+$	F - Li - Li	2A_1	
1σ	-26.0909	$1a_1$	-26.1939
2σ	- 2.5191	$2a_1$	- 2.4450
3σ	- 2.4002	$1b_2$	- 2.4440
4σ	- 1.3499	$3a_1$	- 1.4606
5σ	- 0.4720	$2b_2$	- 0.5792
1π	- 0.4484	$4a_1$	- 0.5703
6σ	- 0.2488	$1b_1$	- 0.5547
		$5a_1$	- 0.1721

Figure Captions

Fig. 1. Collinear contour map for the F Li Li potential energy surface.

Fig. 2. Relative positions of the ground and a few excited states of FLi_2 .

The ${}^2\Sigma^+$ and ${}^2\Pi$ calculations were carried out at that geometry which minimized the SCF energy of the ${}^2\Sigma^+$ state. Similarly, the 2A_1 , 2B_1 , and 2B_2 calculations were carried out at the equilibrium geometry of the 2A_1 ground state.



XBL7211-4393

Fig. 1

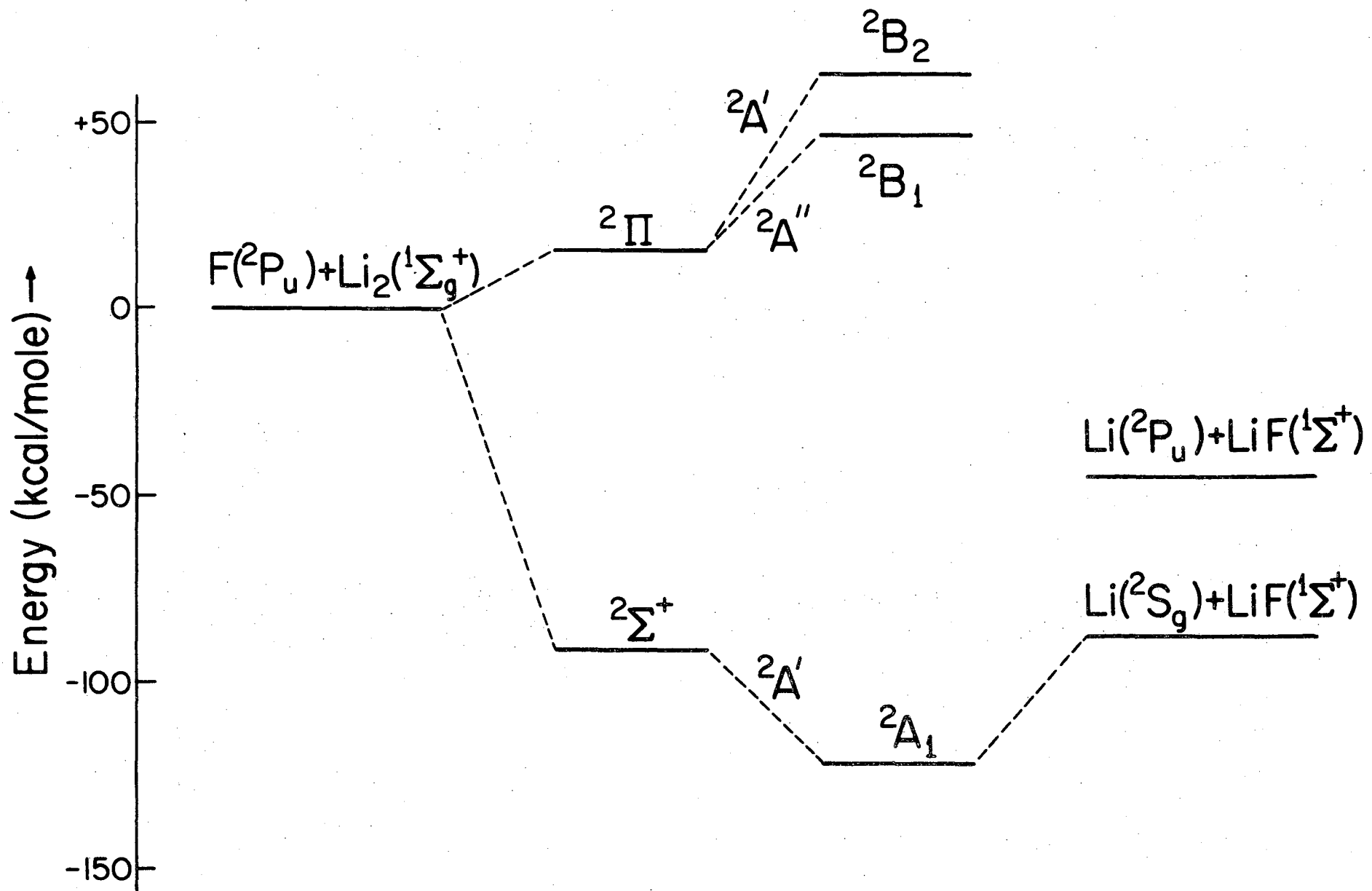


Fig. 2

XBL7212-4984

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