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Invited lecture presented at the Conference:
"50 Years Dynamics of Chemical Reactions",
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Y.T. Lee

October 1981

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MOLECULAR BEAM STUDIES OF BIMOLECULAR REACTIONS:
 $F + H_2$ and $Li + HF$

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ABSTRACT

Using reactions of $F + H_2 \rightarrow HF + H$ and $Li + HF \rightarrow LiF + H$ as examples, the application of the crossed molecular beams method in the investigation of dynamics of bimolecular chemical reactions is described. Most of the discussions are centered on the angular distributions of reaction products and their implication to the relation between potential energy surface and reaction dynamics.

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INTRODUCTION

During the fifty year history of the investigation of reaction dynamics, there have been many significant experimental and theoretical advances. One of the most exciting experimental advances perhaps is the development of the crossed molecular beams method which provides detailed information on the dynamics of chemical reactions. Professor Herschbach, whose pioneering research work established much of the foundation and framework for the understanding of reactive scattering during the last two decades has just reviewed the history of the development of crossed molecular beams studies of chemical reactions in the previous lecture entitled "Molecular Beam Reactive Scattering Experiments: Retrospect and Prospect." The charge of my lecture is to take the reactions $F + H_2 \rightarrow HF + H$ and $Li + HF \rightarrow LiF + H$ as examples to show how crossed molecular beams experiments can provide valuable information on the dynamics of simple elementary chemical reactions.

$F + H_2 \rightarrow HF + H$ and $Li + HF \rightarrow LiF + H$ are among the few small triatomic systems which have received extensive attention in the past and will play key roles in bridging the theoretical understanding of reactive scattering from first principles and experimental observations in the future. For systems with heavier atoms, where classical trajectory calculations provide an adequate description of the reaction dynamics, the calculation of an accurate potential energy surface is still not attainable. For $F + H_2 \rightarrow HF + H$ and $Li + HF \rightarrow LiF + H$, however, the potential energy surface can be calculated accurately, and although

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classical trajectory calculations are not expected to be adequate, rigorous quantum mechanical scattering calculations are just around the corner.¹

Reactions of $F + H_2$, D_2 are exothermic by about 32 kcal/mole. HF and DF products can be populated up to $v' = 3$ and 4 respectively. The semiempirical LEPS potential energy surface, derived by Muckerman and denoted as the M5 surface,² is shown in Fig. 1. This reaction has a potential energy barrier in the entrance channel. The collinear configuration has the lowest barrier of ~1 kcal/mole and the height of the barrier increases sharply as the H-H-F bending angle becomes larger. Limited ab initio potential energy surface calculations,³ classical trajectory² and quantum scattering calculations,^{1,4} as well as a vast amount of experimental results from chemical laser,⁵ chemiluminescence⁶ and molecular beam studies⁷ provide a rather good understanding of the general features of the reaction dynamics of this system. In a recent paper by Polanyi and Schreiber⁶ entitled "The Reaction of $F + H_2 \rightarrow HF + F$, A Case Study in the Reaction Dynamics", their results of chemiluminescent studies and classical trajectory calculations for product state distributions in the $F + H_2 \rightarrow HF + H$ have been extensively reviewed. This case study was further examined and extended by Muckerman in "A Case Study Reopened: The $F + H_2$ System" which is a section of his recent article entitled "Application of Classical Trajectory Techniques to Reactive Scattering".² As we will see in this lecture as well as in Professor Wyatt's and Baer's lectures, the classical trajectory calculation is not adequate to bring the case study to completion. Such quantum effects as the dynamic resonance phenomenon in this system,^{1,4} clearly indicate that the

quantum scattering calculation is needed for deriving more definite conclusions.

In contrast to the $F + H_2$ reaction, $Li + HF \rightarrow LiF + H$ is almost thermo-neutral, there is an attractive well of 3-4 kcal/mole and a substantial exit barrier for breaking the HF bond. Figure 2 shows the results of ab initio potential energy surface calculations carried out by Chen and Schaefer.⁸ Their results show that the most stable configuration of the HFLi complex is bent with an HFLi angle of $\theta = 136^\circ$, and the transition state has a very acute angle of $\theta = 78^\circ$. The results of crossed molecular beams experiments⁹ have been substantially reproduced in classical trajectory calculations by Zeiri et al.¹⁰ using a semiempirical surface similar to that used in the ab initio calculation. This system was suggested by Baer and Kouri¹¹ to be the most favorable case for quantum mechanical scattering calculations for several technical reasons involving mass ratio and available quantum states, etc.

CROSSED MOLECULAR BEAMS EXPERIMENTS

A typical crossed molecular beams experimental arrangement is shown schematically in Fig. 3. Beams of atoms and molecules with narrow angular and velocity spread are crossed in a vacuum chamber and the angular and velocity distributions of the products are measured with an ultrahigh vacuum mass spectrometric detector. The advancement of pumping equipment and vacuum technology, both in the areas of high speed pumping and ultrahigh vacuum, the development of intense monoenenergetic atomic and molecular beam sources, especially, using supersonic expansion, and the cross correlation

velocity analysis of product molecules are some of the factors which have made the crossed molecular beams method an extremely powerful tool for the investigation of reaction dynamics. In crossed molecular beams experiments, the dynamics information is derived from the angular and velocity distributions of the product molecules as a function of collision energy. The product velocity distributions reveal how the chemical energy is partitioned among various degrees of freedom. The measurement of the energy distribution of product molecules is not a unique capability of the crossed molecular beams method. From the operational characteristics of chemical lasers,⁵ chemiluminescence measurements,⁶ and laser induced fluorescence studies, detailed state distributions can be derived for some simple favorable systems. But the information on the angular distributions of product molecules are usually only obtainable from the crossed molecular beams experiments. In this lecture, I will focus my attention on the aspects of product angular distributions and their implication to the reaction dynamics.

ANGULAR DISTRIBUTION OF REACTION PRODUCTS

The angular distributions of product molecules reveal much important information on the nature of reaction intermediates. One of the most important aspects of the product angular distributions is whether there exists a forward-backward symmetry in the center-of-mass coordinate system. The symmetric angular distribution is an indication of the formation of a long-lived complex, i.e., a collision complex whose average lifetime is longer than its average rotational period ($\sim 10^{-12}$ sec). The first such

observation was made by Herschbach¹² and coworkers in the exchange reactions between alkali atoms and alkali halides as shown in Fig. 4. Although the observation of forward-backward symmetry alone will not tell us exactly what the average lifetime of a complex is, in many favorable systems, as the excitation energy of the complex is increased, the average lifetime becomes comparable to or shorter than the rotational period as indicated by the appearance of asymmetry in the angular distribution and provides more precise information on the lifetime of the complex for a given excitation energy. The angular distribution of $\text{Li} + \text{HF} \rightarrow \text{LiF} + \text{H}$ shown in Figs. 5 and 6 is one such example.⁹ The rotational period is not the only clock available for measuring the lifetime of a collision complex in crossed molecular beams experiments. In the scattering of $\text{Cs} + \text{O}_2$ by Kleyn, et al.¹³, the collision lifetime in the range of $10^{-14} \sim 10^{-13}$ sec, has been indicated from the oscillations in the angular distributions caused by the vibrational motion of O_2^- ($\sim 3 \times 10^{-14}$ sec).

When the average lifetime of the complex is shorter than the average rotational period, the product angular distribution provides information on the possible geometric constraints on the reaction intermediate. For example, sharply backward peaked HF product⁷ from $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$ at a collision energy of 2 kcal/mole, shown in Fig. 7, clearly indicates that the reaction can only take place for near collinear collisions. Collisions with other types of approach must have higher potential energy barriers to produce reaction products. On the other hand, the observation of pronounced forward peaking angular distributions, with respect to the motion of attacking atoms, probably indicates that either "bend" approach is more

favorable (as in the case of $\text{Cl} + \text{Br}_2 \rightarrow \text{BrCl} + \text{I}^{14}$) or that the reaction has a large cross section and no stringent geometric constraint ($\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$ is such an example¹⁵).

Actually, the geometric constraints imposed on the approach of reactants, reaction intermediates and the critical configuration of departing products are subtly coupled to the correlation between orbital and rotational angular momentum of reactants and products. It has been shown clearly in the statistical complex model of Herschbach and coworkers,¹² that the sharpness of forward backward peaking of product molecules depends on how strongly the final orbital angular momentum, L' , is correlated to the initial orbital angular momentum, L . For example, in the reaction of $\text{K} + \text{RbCl}$ and $\text{Rb} + \text{KCl}^{12}$, shown in Fig. 4, the total angular momentum of the system, J , is mainly from L and is almost entirely carried away as product orbital angular momentum, L' . The fact that $L \approx J \approx L'$ assures an almost perfect correlation between L and L' and a strong forward-backward peaking was observed. The reaction of $\text{Li} + \text{HF}$ is a specially interesting case for the angular momentum disposal. Since two heavier atoms form the LiF product, and the reduced mass of the products, $\text{H} + \text{LiF}$, is very small, the initial orbital angular momentum of the reactants, which is essentially the total angular momentum of the system, is expected to be carried away mainly as rotational motion of LiF , J . Thus, J' should be strongly correlated to L , and L' on the other hand will be determined mainly by geometric relations between departing H and LiF . If a large fraction of the exit potential energy barrier is released as translational energy, it is possible that L' largely comes from this repulsive energy release and could be quite

substantial if the exit impact parameter b' is not small. But the L created by the repulsive energy release will be compensated by antiparallel rotational angular momentum of LiF created simultaneously and is perpendicular to the plane containing LiFH in the critical configuration, or the "transition state". The fact that the angular distribution of LiF has pronounced forward-backward peaking as shown in Fig. 6 means that in spite of the small magnitude of L' compared to L , they are strongly correlated. They are either near parallel or anti-parallel to each other. In other words, the rotational motion of HF and the relative motion between Li and HF as well as the motion of the product molecules will be in the same plane which determines the plane of LiFH in the transition state. This "coplanar" dominated reaction⁹ inferred from the experimental results is not surprising when the features of the potential energy surface are carefully examined. The sharply bent transition state with a sizable exit barrier⁸ requires an effective coupling of the translational and rotational energies of the reagents into the potential and vibrational energies of the complex, and this is most likely to happen in a coplanar approach of the reagents. When the reaction has a potential energy barrier, either in the entrance or exit channel, the product angular distributions are more likely to reveal the geometric constraints of the reaction intermediate for overcoming the barrier. The sideways peaking of the products in $F + C_2H_4 \rightarrow C_2H_3F + H$ has been shown^{16a} and verified^{16b} to be the consequence of the near perpendicular orientation of the C-H bond to the plane containing the planar rotation of C-C-F in the transition state.

The correlation of the angular distribution and the disposal of angular momentum is not restricted to those reactions which go through the formation of long-lived complexes. The same relation as discussed in previous sections should also hold for reactions which are direct and with product angular distributions either peaking forward or backward. The sharpness of forward or backward peaking is also likely to indicate how closely the orientation of L' lies parallel or antiparallel to that of L . The sharp spike in the laboratory angular distribution of DF in $F + D_2 \rightarrow DF + D$ reaction carried out at 4.5 kcal/mole as shown in Fig. 8 is the consequence of a sharp forward peaking of the $DF(v=4)$ angular distribution. This is again a coplanar dominated reaction; the potential energy barrier in the entrance channel is the cause of the transition from collinear to coplanar domination as the kinetic energy is increased.

DYNAMIC RESONANCE PHENOMENA IN $F + H_2 \rightarrow HF + H$

One of the most intriguing aspects of the reaction $F + H_2 \rightarrow HF + H$ is perhaps the quantum mechanical dynamic resonance phenomenon. This phenomenon was first observed by Levine¹⁷, Kuppermann¹⁸ and their coworkers in one-dimensional quantum scattering calculations, and has been extensively studied by several groups during the past five years. In one dimensional calculations, as shown in Fig. 9,⁴ the resonance was seen as a sharp spike in the collision energy dependence of the reaction probability forming $HF(v=2)$. This quantum mechanical resonance phenomenon has been shown to depend very sensitively on the details of the critical region of the potential energy surface, and the experimental observation of the

dynamic resonance phenomenon was suggested to be almost equivalent to obtaining a vibrational spectrum of the "transition state".^{1(c)} Wyatt and coworkers¹⁹ have clearly shown that the resonance, similar to the one dimensional $H + H_2$ system,¹⁷ is related to the well in the vibrational adiabatic potential energy surface and carried out a thorough examination in both one and three dimensional quantum mechanical calculations. More recently, Pollak and Child²⁰ provided a semiclassical explanation of the nature of one-dimensional resonance phenomena and pointed out that the condition for resonance to occur is to have the action integral along periodic orbit dividing surface satisfy the condition, $F = \int_{pod} P d\rho = (n + M + 1)h$. n and m correspond to the vibrational quantum numbers of reagent (H_2) and product (HF). Using hyperspherical coordinates, Launay and LeDourneuf²¹ have shown that the resonance energies in the $F + H_2$ system do in fact correspond to the bound states in the wells in the vibrational adiabatic potential energy curves. The nature of resonance phenomena will be further discussed in great detail by Wyatt and Baer later in the conference.

Schatz and Kuppermann²² have shown that in the $H + H_2 \rightarrow H_2 + H$ reaction, resonances found in one dimensional calculations persist in three dimensional calculations except that the resonance energies are shifted to higher energies, mainly due to the difference in zero point energies. Consequently, in principle, resonances in the $H + H_2$ can be observed experimentally, by carrying out the measurements of the reaction probability as a function of collision energy. However, in $F + H_2 \rightarrow HF + H$, Wyatt et al. have shown that the sharp spike found in the energy dependent reaction

probability of forming HF($v=2$) in one dimensional calculations is absent in three dimensional quantum mechanical calculations using the jz conserving approximation as shown in Fig. 10. The lack of sharp structure in the reaction cross sections as a function of collision energy is mainly due to the upward shifting of the resonance energies when the impact parameter, or the orbital angular momentum, becomes finite. In other words, when the collision energy is increased, the resonance for the formation of HF($v=2$) will first appear at zero orbital angular momentum and then shift outward as shown in Fig. 11. Examination of the results of Wyatt et al.¹ shown in Figs. 10 and 11 clearly indicates that the experimental observation of the resonances will not be possible in the measurements of reaction cross sections as a function of kinetic energy. It will only come from the measurement of reaction probability as a function of impact parameter at a given collision energy. Experimental control of the impact parameter is of course impossible. But, for the $F + H_2 \rightarrow HF + H$ reaction, since the barrier is lowest for the collinear configuration, the product scattering angle is expected to have a pronounced impact parameter dependence. As the impact parameter is increased from the zero value, the scattering angle of the HF product is expected to move from backward to sideways. Consequently, if a high resolution crossed molecular beams experiment were carried out, in which angular distributions of individual product vibrational states of HF were carefully measured, it is likely that the quantum mechanical dynamic resonance phenomena would be observed in the anomalous angular distribution of HF($v=2$) in the center of mass coordinate system at an appropriate collision energy. And it is indeed observed in an experiment carried out at a collision energy of 3 kcal/mole.

Figures 12 and 13 show the laboratory and center of mass angular distributions of the HF products obtained at a collision energy of 3 kcal/mole. In contrast to the angular distribution shown in Fig. 7 for a collision energy of 2 kcal/mole, in which all HF products in $v = 3$, 2 and 1 are peaking sharply backward in agreement with the results of classical trajectory calculations, the product angular distribution shown in Fig. 13 clearly shows that although HF in $v = 3$ and $v = 1$ are peaking backward, HF in $v = 2$ is peaking sideways. These extraordinary angular distributions of the HF products are in qualitative agreement with what would be expected from the opacity functions of Wyatt et al. shown in Fig. 11. The angular distributions of HF($v=2$) obtained by the application of the optical potential analysis to the opacity function of the formation of HF($v=2$) indeed shows the expected sideways peaking.¹ Recent calculations of quantum mechanical infinite order sudden approximation of Jellinek et al.²³ and the distorted wave approximation by Emmon and Suck²⁴ on the M5 potential energy surface, both show the sideways peaking of HF($v=2$). This sideways peaking of HF($v=2$) at 3.0 kcal/mole is unquestionably a quantum effect. Truhlar and Blais²⁵ have shown in their classical trajectory calculations on the same M5 potential energy surface that the angular distribution of HF($v=2$) is peaking backward just the same as those of HF($v=3$) and HF($v=1$).

It is important to note that the first experimental evidence of this dynamic resonance in the reactive scattering is observed in the angular distributions of products, rather than in the energy dependence of reactive cross sections. The decision not to measure reaction cross sections as a

function of collision energy, but to carry out careful measurements of vibrational state resolved product angular distributions at the collision energies of 2 and 3 kcal/mole for the $F + H_2 \rightarrow HF + H$ reaction are largely due to the results of three dimensional quantum scattering calculations of Wyatt et al. The interplay between experiments and theoretical studies will become more and more important in the future.

CONCLUDING REMARKS

In the preceeding discussion, some examples were given to illustrate how crossed molecular beams experiments, especially the measurements of product angular distributions, can provide information on reaction dynamics. There are many other important aspects of crossed molecular beams experiments which have not been included in this lecture, but they will be covered in several lectures in the remainder of the conference.

The detailed experimental information obtained on the reaction dynamics during the last fifty years has not only improved our understanding of many complicated macroscopic phenomena from the atomic and molecular basis, but has also made it possible to calibrate conclusions derived from first principles on elementary chemical reactions. There is no doubt that accurate potential energy surfaces and rigorous quantum scattering calculations on such systems as $Li + HF \rightarrow LiF + H$ and $F + H_2 \rightarrow HF + H$ will become available in the next decade and that these results will be compared along the way with a vast number of additional experimental results which will also be accumulated in years to come. The effect of electronic excitation of Li in $Li + HF \rightarrow LiF + H$ ²⁶ and the resonances in $F + HD$ ²⁷ reactions are under investigation in our laboratory.

At present, although potential energy surface calculations by semiempirical or ab initio methods and scattering calculations by classical, semiclassical and approximate quantum mechanical methods are providing valuable information on the dynamics of many important chemical reactions, we are not yet at the stage where these theoretical calculations can predict quantitative macroscopic properties on a variety of systems. The comparison of experimental and theoretical rate constants for $F + H_2 \rightarrow HF + H$ summarized by Muckerman and shown in Fig. 14 is a good example. Almost all the classical trajectory calculations carried out so far are based on semiempirical potential energy surfaces which are constructed by fitting to the rate constants determined earlier by Mercer and Pritchard²⁹ or to the product vibrational energy distributions determined by Polanyi and coworkers, or to both. It means that in these studies the potential energy surface is "derived" from the experimental results and then additional information on reaction dynamics which is not available from experiment is obtained through classical trajectory calculations. The reliability of these potential energy surfaces is of course dependent on the accuracy of the experimental results and the validity of classical trajectory calculations. Unfortunately, for the $F + H_2 \rightarrow HF + H$ system both these conditions turn out to be negative. Several rate constant measurements carried out recently have given values which are about ten times larger than those of Mercer and Pritchard. Besides, as we have seen in the previous section, quantum effects are indeed very important in this reaction. It is possible to construct an improved potential energy surface using new and more reliable rate constants and product vibrational states and angular

distributions as input, and apply quantum scattering calculations to establish the linkage. Efforts in this direction are already in motion,²⁸ and it is likely that the potential energy surface thus obtained will provide guidance for further development of ab initio potential energy surface calculations. It would certainly be more satisfying if, sometime in the near future, accurate ab initio potential energy surface calculations on such systems as $F + H_2 \rightarrow HF + H$ could be combined with efficient three dimensional quantum scattering calculations to give excellent agreement with experimental results, just as has been accomplished on the exchange reaction of $H + H_2 \rightarrow H_2 + H$. The current experimental and theoretical studies on $F + H_2 \rightarrow HF + H$ and $Li + HF \rightarrow LiF + H$ will undoubtedly push for the early arrival of this new era of reaction dynamics.

The experimental results on $F + H_2$, D_2 shown in this article were obtained by Hayden, Neumark, Sparks and Shobatake. The work on $Li + HF \rightarrow LiF + H$ was carried out by Becker, Casavecchia, Tiedemann and Valentini. Without their "excellent" effort, this lecture would not be possible.

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FIGURE CAPTIONS

Fig. 1. Contour plot of potential energy surface M5 for collinear F-H-H configurations.² Energy spacing between contours is 5 kcal mole⁻¹.

Fig. 2. Contour map of the CI potential energy as a function of Δr_{LiF} and Δr_{HF} with LiFH angle θ fixed at 90° (Chen and Schaefer⁸). The distances are expressed in terms of their differences in a.u. from the calculated diatomic equilibrium values. Thin contours are at 2 kcal/mole intervals, thick ones are at 10 kcal/mole and zero corresponds to the energy of the reactants Li + HF at infinite separation.

Fig. 3. Schematic diagram of the crossed molecular beam apparatus with fixed beam sources and a rotatable detector.

Fig. 4. Reactive and non-reactive scattering of K + RbCl and Rb + KCl (Miller et al.¹²).

Fig. 5. Measured angular distributions of LiF product (solid circles) with error bars representing ± 2 standard deviations of the mean (~95% confidence limit). Nominal Newton diagrams are also shown for the four collision energies, E_c at 2.2 and 3.0 kcal/mole, data are recorded at $m/e = 7$ and elastic contributions subtracted. Solid lines are best fits to the data.

- Fig. 6. Best fit (a) translational energy and (b) angular distributions (solid lines) for $\text{Li} + \text{HF} \rightarrow \text{LiF} + \text{H}$ at $E_c = 3.0$ kcal/mole. Shaded area represents the limit of acceptable fits to the data. The exoergicity (ΔH) is shown in part (a) as is the total energy available (E_{tot}) and the maximum available energy ($E_{\text{tot}}^{\text{max}}$) given by the sum of the upper bound estimate on $-\Delta H$ and maximum E_c obtained from 3% values of the beam velocity spread.
- Fig. 7. Center-of-mass velocity-space contour plot of HF product distribution from $\text{F} + \text{H}_2$ reaction at 2.00 kcal/mole.
- Fig. 8. Experimental LAB angular distribution of the DF product from the $\text{F} + \text{D}_2$ reaction at 4.51 kcal/mole.
- Fig. 9. Twelve channel reactive scattering probability for P_{02} and P_{03} for M5 surface computed by Latham et al.¹⁹
- Fig. 10. Cross sections for forming vibrationally excited HF, for all open HF vibrational manifolds in $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$ reaction (Redmon and Wyatt¹).
- Fig. 11. Reaction probability surfaces for the 3D $\text{F} + \text{H}_2$ reaction (Redmon and Wyatt¹). Total reaction probabilities for the $v = 0 \rightarrow v' = 2$ and $v' = 3$ (in each case, summed over j') reactions are plotted vs. E (total energy) and J (total angular momentum) which is the same as the orbital angular momentum number in the entrance channel.
- Fig. 12. Experimental LAB angular distribution of the HF product from the $\text{F} + \text{H}_2$ reaction at 3.17 kcal/mole.
- Fig. 13. Center-of-mass velocity space contour plot of HF product distribution from $\text{F} + \text{H}_2$ reaction at 3.17 kcal/mole.

Fig. 14. Comparison of theoretical and experimental rate constants for the reaction $F + H_2 \rightarrow HF + H$ (J. T. Muckerman²). Experimental curves are: A, Mercer and Pritchard²⁹; B, Homann et al.³⁰; C, Igoshin et al.³¹; D, Bulatov et al.³²; E, Wurzburg and Houston³³; and F, Heidner et al.³⁴ Curves from quasi-classical trajectory calculations are: JA, Jaffe and Anderson³⁵; WI, Wilkins³⁶; SE1, Polanyi and Schreiber⁶ and M5, Muckerman². Points are from the direct quasi-classical trajectory-rate constant calculations on surface M5 of Muckerman and Faist.³⁷ Curve G and H, Garrett et al.³⁸ also refer to the rate constant on surface M5: G is a transition-state theory results, and H is the result of an "ICVT/MCPSAG" calculation.

Fig. 1

$$\theta (\text{LiFH}) = 90^\circ$$

Fig. 2

XBL 7610-4961 A

Fig. 3

Fig. 4

Fig. 5

$$E_c = 3.0 \text{ kcal/mole}$$

Fig. 6

XBL 7910-4565

XBL 7910-12374

Fig. 7

XBL 7910-12373

Fig. 8

Fig. 9

Fig. 10

Fig. 11

XBL 7910-12372

Fig. 12

Fig. 13

XBL 7910-12376

Fig. 14

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