Stability and structure of Li n H molecules (n=3–6): Experimental and density functional study

C. H. Wu and R. O. Jones

Articles you may be interested in

Stability and structure of Li_nH molecules $(n=3-6)$: Experimental and density functional study

C. H. Wu

Max-Planck-Institut für Plasmaphysik, EFDA, Boltzmannstraße 2, D-85748 Garching, Germany

R. O. Jones[a)]

Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

The molecules Li_3H and Li_4H have been identified in mass-spectrometric measurements over solutions of hydrogen in liquid Li, and the gaseous equilibria of the reactions: $Li_3H+Li=Li_2H+Li_2$, $Li_3H+Li_2=Li_2H+Li_3$, $Li_3H+Li=LiH+Li_3$, $Li_3H+LiH=2Li_2H$, and $Li_4H+Li_2=Li_3H+Li_3$ have been measured. Density functional calculations of Li_nH molecules $(n=3-6)$ provide structures, vibrational frequencies, ionization energies, and free energy functions of these molecules, and these are used to estimate the enthalpies of these reactions and the atomization energies of Li_3H (119.4 kcal/mol) and Li_4H (151.8 kcal/mol). © *2004 American Institute of Physics.* [DOI: 10.1063/1.1648305]

I. INTRODUCTION

Clusters containing alkali metals have received much attention from experimentalists and theorists in recent years. They serve as models for "nearly free electron" systems, and they provide means of understanding nucleation and cluster growth, defects, chemisorption, and some problems related to heterogeneous catalysis. Lithium and hydrogenated lithium clusters, in particular, have been studied extensively in recent years, examples being LiH, LiD, LiH^+, LiH_2^+, and Li_n. The role of the highly polar LiH and other lithium molecules in the chemistry of the early universe has been a topic of much recent interest,[1] and open-shell radical cations such as LiH^+ are also important in the upper atmosphere.[2] Lithium is the lightest metallic element and the lightest where there is a distinction between core and valence electrons. Its potential to form multicentered bonds ("hypervalent" clusters with more "bonds" than available valence electrons) has been a focus of attention for many years.

Lithium hydride is, after HeH, the smallest heteronuclear diatomic molecule and has served for years as a benchmark for methods of molecular structure calculation. Lithium hydrides are important as models for simple electron-deficient ionic metal compounds, and the lithium–hydrogen system is important in fusion technology. The first generation power reactors are expected to operate by means of the deuterium–tritium fusion reaction, and tritium can be bred by reaction of neutrons with Li.[3]

Early theoretical work indicated that LiH^+ would be unstable,[4] but later calculations[5] led to a dissociation energy of up to 0.15 eV. Ihle and Wu[6] demonstrated the existence of the stable ion molecules LiH^+ and LiD^+ and measured their binding energies and ionization potentials. Subsequently, Wu and Ihle[7] measured the stability and ionization potential of

LiH, LiD, Li_2H, LiH_2, and Li_2H_2. Vezin and co-workers measured the ionization potential of numerous hydrogenated lithium clusters[8] as well as optical absorption spectra of Li_4H and Li_9H clusters in the visible range.[9] They presented an interpretation of the latter on the basis of *ab initio* calculations. There have been many theoretical studies of hydrogenated lithium clusters, including the work of Kato *et al.*[10] on Li_nH_m $(m\leqslant n\leqslant 4)$. More recent calculations on lithium hydride molecules include *ab initio* work on Li_nH_m clusters $(n\leqslant 4, m\leqslant n)$,[11] Li_nH $(n=1-7)$, Li_nH_2 $(n=2-6)$,[12] and $Li_nH_m^+$.[13]

In the present paper we report the results of experimental measurements on the equilibrium reactions $Li_3H+Li=Li_2H+Li_2$, $Li_3H+Li_2=Li_2H+Li_3$, $Li_3H+Li=LiH+Li_3$, $Li_3H+LiH=2Li_2H$, and $Li_4H+Li_2=Li_3H+Li_3$ and discuss the stabilities of the molecules Li_3H and Li_4H. The measurements have been accompanied by density functional (DF) calculations of the structures, atomization energies, ionization energies, and vibrational frequencies of isomers of Li_nH molecules up to $n=6$, as well as the free energy functions of the above reactions and the reaction enthalpies. Information about the free energy is essential for an analysis of the experimental data. The calculations are described in Sec. II, and the experimental method and the analysis of the data are presented in Secs. III and IV, respectively. Our concluding remarks are in Sec. V.

II. DENSITY FUNCTIONAL CALCULATIONS

The structures and relative energies presented below were determined using all-electron DF calculations with an extended one-electron basis of contracted Gaussian-type orbitals.[14] The results described adopted a double-ζ valence-type basis with a d-type polarization function,[15] with the A1 auxiliary basis[14] to represent the density and exchange-correlation potential. Calculations were performed with the local spin density (LSD) approximation to the exchange-

---
[a)]Author to whom correspondence should be addressed. Electronic mail: r.jones@fz-juelich.de

correlation energy as well as with the gradient-corrected approximation due to Perdew and Wang (PW91).[16] All results given below are for the latter. The tolerance on the energy gradient was chosen to be 2.0×10^{-4} hartree/bohr during structural optimization. The method is the same as used in an earlier study of lithium clusters Li$_n$ and their oxides Li$_n$O.[17] Atomic coordinates, vibrational frequencies, and infrared intensities of the most stable isomers of Li$_n$H ($n=2-6$) are given as supplementary information.[18]

The vibrational frequencies are calculated using linear response theory. Calculations of temperature-dependent contributions to the entropy and enthalpy are based on the rigid rotor for rotational contributions and on the harmonic oscillator for vibrational contributions. The enthalpy correction and entropy can then be used to determine the free energy correction as a function of temperature. Calculations of the free energy functions of Li$_2$ and LiH were in excellent agreement with the data from the JANAF thermochemical tables.[19] The difference contributes less than 0.2 kcal/mol to the uncertainty in enthalpies of reactions involving these molecules. The calculated free energy functions of the most stable isomers of Li$_2$, Li$_3$, and Li$_n$H ($n=1-4$) are given as supplementary information.[18]

A. Results for Li$_2$H, Li$_3$H, Li$_4$H, Li$_5$H, and Li$_6$H

The diatomic molecules H$_2$, Li$_2$, and LiH have been calculated with the present method and basis set to allow its calibration in cases where detailed spectroscopic information is available. The agreement between theory and experiment[20] is consistent with earlier experience with Li$_n$ and Li$_n$O clusters.[17] The LSD values for the dissociation energies D_0^0 are consistently larger than the PW91 values.

Structures of low-lying isomers of Li$_2$H, Li$_3$H, and Li$_4$H are shown in Fig. 1, and isomers of Li$_5$H and Li$_6$H are shown in Fig. 2. The isomers are labeled **mn**, where **m** is the number of Li atoms in the molecule, and **n** orders the energies alphabetically, with **a** the most stable. We study the isomers with the lowest possible spin degeneracy, although calculations were also performed for some structures with higher spin degeneracies. Energy differences are quoted for the PW91 gradient-corrected functional throughout. These molecules are examples of "hypervalent" or "hyperlithiated" systems, and the bond lengths are much longer than the single bonds in LiH or Li$_2$. For the present plots we have adopted a Li "radius" of 1.5 Å.

The most stable structure of Li$_2$H (**2a**) is only slightly (0.4 kcal/mol) more stable than **2b**, with **2c** an additional 16.5 kcal/mol higher in energy. The bond lengths in **2a** are a little longer than those found by Allouche *et al.*,[21] but close to those found in Ref. 12. Li$_3$H is most stable as the distorted rhombus or "kite" **3a**, which is 13.8 kcal/mol more stable than the "T" (C_{2v}) structure **3b**, with the pyramid **3c** an additional 6.6 kcal/mol higher in energy. The most stable configuration of Li$_4$H (**4a**) is 3.2 kcal/mol lower in energy than (**4b**), and this structure is also the most stable found in density functional calculations using the BLYP functional.[9] This work also calculated optically allowed transitions and oscillator strengths and identified **4a** as the isomer responsible for the peaks in the measured Li$_4$H absorption spec-
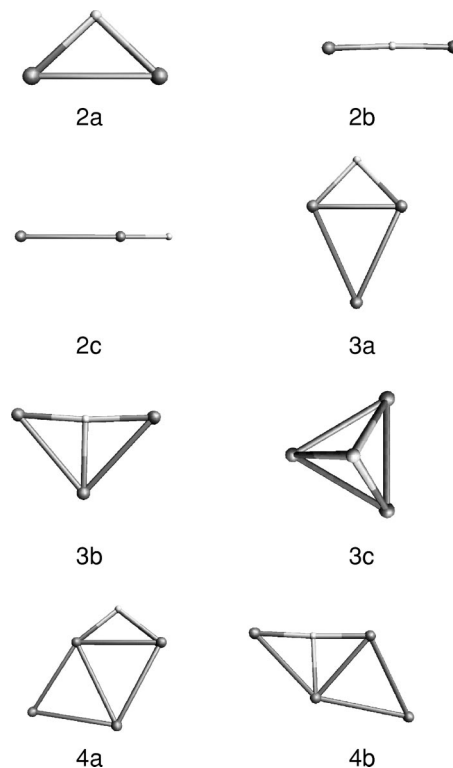

FIG. 1. Structures of isomers of Li$_2$H, Li$_3$H, and Li$_4$H.

trum. The relationship between structures (**4a**, **4b**) and (**3a**, **3b**) is obvious.

The molecules Li$_5$H and Li$_6$H do not form part of the present experimental study, but we have performed calculations on them to study trends as the number of Li atoms
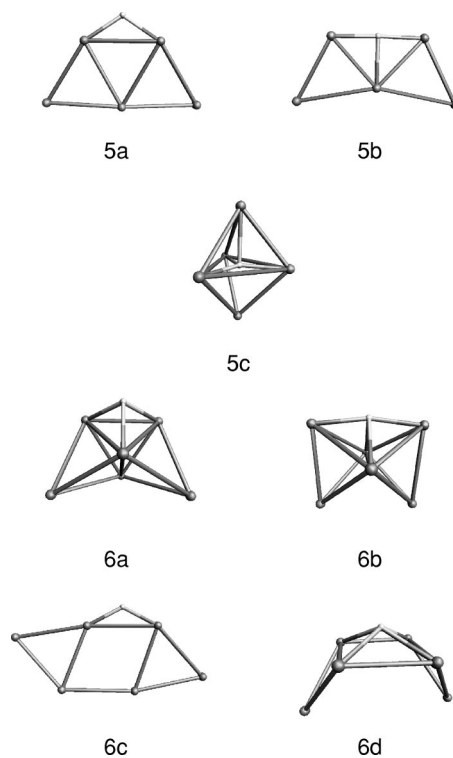

FIG. 2. Structures of isomers of Li$_5$H and Li$_6$H.

TABLE I. Ionization energies of Li_nH (eV), calculated and experimental.

Li_nH n	I_p^{exp} Ref. 8		I_p^v This work	Ref. 12	I_p^{ad} This work	Ref. 12
1	7.7 ± 0.1^a		8.03	7.75	7.67	7.47
2	4.1 ± 0.05	2a	4.85	4.50	4.09	3.80
		2b	4.09		4.09	
3	4.67 ± 0.06		5.32	5.05	5.01	4.42
4	4.10 ± 0.06		4.76	4.47	4.19	3.89
5	4.12 ± 0.06	5a	4.90	4.78	4.82	4.22
		5b	4.79	4.67	4.67	
6	4.08 ± 0.06		4.47	3.96	4.20	3.75

^{a}Reference 6.

increases. The most stable isomer of Li_5H (**5a**, C_{2v}) is the planar structure found in Ref. 12. It is 0.2 kcal/mol more stable than **5b**, but 22 kcal/mol more stable than the bipyramid **5c**. Three-dimensional structures become more stable than planar structures in Li_6H. Structure **6a** is 4.2 kcal/mol more stable than **6b**, with the planar structure **6c** a further 9 kcal/mol higher in energy. Structure **6d** is 18.6 kcal/mol higher in energy than **6a**, and it distorts on long optimization to structure **6b**.

The most stable Li_nH isomers are the same as found in Ref. 12. Trends found in the structures of Li_n and Li_nO clusters are also found here,[17] in particular the transition from planar to three-dimensional structures for molecules with around six atoms. The relationships between the structures of isomers of Li_nH and those of Li_{n+1} are obvious. The hydrogen atoms in the planar structures **3a**, **4a**, and **5a** have two neighbors, and they are quite different from **3b**, **4b**, and **5b** with three Li neighbors to the H atom. The effective charges—atom-centered point charges obtained by fitting to the electrostatic potential of the molecule—show that there is a substantial negative charge on the H in the former. In the latter family, there is a substantial positive charge on the H atom, which has a strongly polar bond at right angles to the almost linear Li–H–Li unit.

The vertical and adiabatic ionization energies are presented in Table I, where they are compared with measured[6,8] and earlier calculated[12] values. In the case of LiH and LiH^+, full CI calculations lead to an adiabatic ionization energy of 7.743 eV,[22] and fourth-order Møller–Plesset (MP4) calculations give a value of I_v of 4.98 eV.[11]
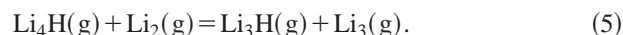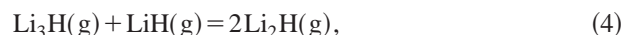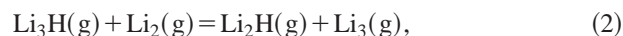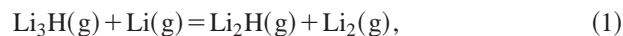
Ionization can result in large changes in the equilibrium geometry, as shown by, for example, the large differences between vertical and adiabatic values of I_p for structures **2a** and **4a**. In the case of Li_2H, ionization of both **2a** and **2b** leads to a structure of the form **2b**. In cases where there are large differences between the I_p values, the present calculations generally agree better with the adiabatic value.

III. EXPERIMENT

The apparatus used in these studies has been described in detail earlier.[6] It consists of a quadrupole mass spectrometer for analyzing the effusate from a heated Mo Knudsen cell containing solutions of hydrogen in lithium. The temperature is measured with an optical pyrometer and a PtRh/Pt thermocouple; calibration is carried out at the triple points of

lithium, silver, and gold. Solutions of hydrogen in lithium have been prepared by reaction of pure lithium contained in a Knudsen cell with known amounts of hydrogen. The hydrogen used in these measurements was purified by formation and decomposition of uranium hydride.

The partial pressures of LiH, Li_2H, and LiH_2 have been measured as functions of T and hydrogen concentration in the liquid lithium. It has been found that $T \sim 900$ K and a concentration of 1000 ppm provide good conditions for measuring the partial pressures of the species involved, and we have measured the following gas equilibrium reactions under these conditions:

$$Li_3H(g) + Li(g) = Li_2H(g) + Li_2(g), \tag{1}$$

$$Li_3H(g) + Li_2(g) = Li_2H(g) + Li_3(g), \tag{2}$$

$$Li_3H(g) + Li(g) = LiH(g) + Li_3(g), \tag{3}$$

$$Li_3H(g) + LiH(g) = 2Li_2H(g), \tag{4}$$

$$Li_4H(g) + Li_2(g) = Li_3H(g) + Li_3(g). \tag{5}$$

A shutter was installed between the Knudsen cell and the ion source of the mass spectrometer in order to distinguish the atoms and molecules effusing from the Knudsen cell from the residual gas. Identification of the ions was achieved from their mass to charge ratio, shutterability, appearance potentials, and isotopic abundances. The relation between partial pressure p_i of species i and the measured ion intensity I_i is given by the equation

$$p_i = k(I_i T / \sigma_i \gamma_i \beta_i), \tag{6}$$

where k is the pressure calibration constant, T is the temperature, σ_i the ionization cross section, γ_i the multiplier gain, and β_i the relative isotopic abundance. For all gaseous isomolecular equilibria performed here, it has been assumed that the ionization cross section and multiplier gains cancel each other when the third law enthalpy changes are evaluated.

IV. RESULTS AND DISCUSSION

A. Equilibrium measurements of Li_3H

The measurements of the gaseous isomolecular exchange reaction equilibria (1)–(4) were carried out for T between 933 and 1100 K, and the third law enthalpies of reactions (1), (2), (3), and (4) were calculated from

$$\Delta H_0^0 = -RT \ln K - T \Delta \left(\frac{G_T^0 - H_0^0}{T} \right), \tag{7}$$

where K, R, and $\Delta((G_T^0 - H_0^0)/T)$ are the equilibrium constant, the gas constant, and the change in the free energy function, respectively, for the corresponding reactions. The effusing gaseous species were ionized by electron impact at 20 eV, and the gas equilibria were evaluated from the measured ion currents I using the relation

$$K_1 = \frac{I(Li_2H)I(Li_2)}{I(Li_3H)I(Li)}, \tag{8}$$

for reaction (1), with corresponding relations for the other reactions.

The threshold appearance potentials evaluated by the vanishing current method for Li$^+$, Li$_2^+$, Li$_3^+$, LiH$^+$, and Li$_2$H$^+$ are 5.5, 5.0, 4.5, 7.9, and 4.5 eV, respectively. The appearance potentials for Li$^+$, Li$_2^+$, Li$_3^+$, LiH$^+$, and Li$_2$H$^+$ agree with the known ionization potentials of corresponding neutral gaseous species, showing that the ions are produced by ionization of the corresponding neutral systems. We expect that the ions Li$_3$H$^+$ and Li$_4$H$^+$ are also produced by ionization of the corresponding neutral molecules, although the signals were too weak to allow us to determine the appearance potentials.

At constant temperature, the ion currents of Li$^+$, Li$_2^+$, and Li$_3^+$ are practically independent of the concentration of hydrogen in the dilute solution of lithium, whereas the ion currents of LiH$^+$ and Li$_2$H$^+$ are directly proportional to the concentration of hydrogen in liquid lithium. To minimize the changes in hydrogen concentration, the measurements were carried out in the following order: Li$^+$, Li$_2^+$, Li$_3^+$, LiH, Li$_2$H, Li$_3$H, and Li$_4$H. The ion intensity of Li$_2$H$^+$ was measured at the beginning and the end of a sequence of measurements of all ions involved in the reactions, and the change was about 3%.

The free energy functions were calculated for all structures as described above, and that for Li(g) was taken from the JANAF tables.[19] We have noted that the comparison between the calculated and tabulated values for Li$_2$(g) and LiH(g) showed extremely good agreement. For the Li$_3$H(g) molecule the free energy function has been calculated for three structures, kite (C_{2v}, **3a**), **3b** (C_{2v}), and pyramid (C_{3v}, **3c**), and the reaction enthalpy was evaluated for the most stable (**3a**). Tables of the third law results of reactions (1), (2), (3), and (4) (equilibrium constants and reaction enthalpies) are given as supplementary information.[18] The mean reaction enthalpies for these reactions are 5.39 ± 0.69, 18.27 ± 0.89, 25.92 ± 1.48, and -3.32 ± 1.18 kcal/mol, respectively, where the errors are given as standard deviations.

B. Equilibrium measurements of Li$_4$H

The measurements of the gaseous isomolecular exchange reaction equilibria (5) were carried out for T between 1190 and 1280 K, and the gas equilibria were evaluated from the ion currents using the relations

$$K_5 = \frac{I(\text{Li}_3\text{H})I(\text{Li}_3)}{I(\text{Li}_4\text{H})I(\text{Li}_2)}. \qquad (9)$$

The third law enthalpy of reaction (5) was calculated using Eq. (7). Free energy functions were calculated for the most stable structure in all cases, as well as in other structures if considered necessary. The third law results of reaction (5) are given in supplementary information.[18] The mean reaction enthalpy is 20.05 ± 0.45 kcal/mol.

C. Atomization energies of Li$_3$H and Li$_4$H

The atomization energies E_{at} of Li$_n$H molecules are defined as

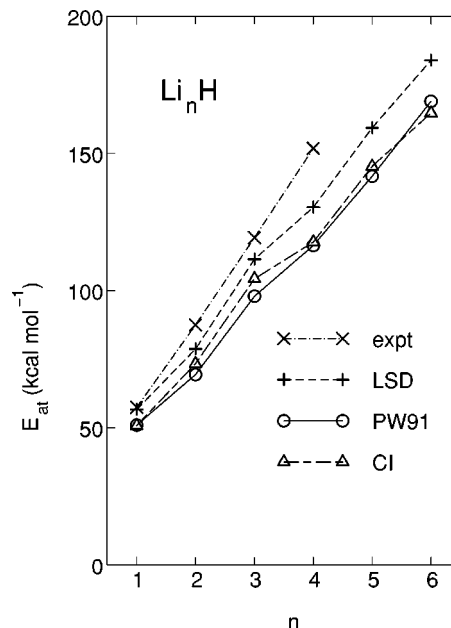$$-E_{at}(\text{Li}_n\text{H}) = E(\text{Li}_n\text{H}) - nE(\text{Li}) - E(\text{H}), \qquad (10)$$

FIG. 3. Atomization energies of Li$_n$H molecules. The CI values (Ref. 12) do not include corrections for zero-point energies.

and the calculated values for the most stable isomers are shown for CI calculations[12] and the present work (LSD and PW91 functionals) in Fig. 3. The agreement between the CI results and the gradient-corrected functional is good, although the former are based on Hartree–Fock geometries and do not include zero-point energies. The LSD values are higher, as found previously for Li$_n$ clusters.[17] $E_{at}(\text{Li}_n\text{H})$ increases with increasing n, but the relative stability of the closed-shell structures with odd values of n is apparent, as also found in Li$_n$ clusters.[17] This is evident in the fragmentation energies $E_{at}(\text{Li}_n\text{H}) - E_{at}(\text{Li}_{n-1}\text{H})$, as noted previously in Ref. 12.

The experimental determination of atomization energies is more complicated. If the atomization energies of some components of the reaction

$$A + B = C + D + \Delta H \qquad (11)$$

are known, the measurement of the reaction enthalpy ΔH can provide information about the atomization energies of the others:

$$E_{at}(A) + E_{at}(B) = E_{at}(C) + E_{at}(D) + \Delta H. \qquad (12)$$

This is obvious in the case of the dissociation of a diatomic molecule, but it assumes that the reactant and product molecules are in their most stable forms.

If we apply this approach to the third law values of reactions (1) and (2) and reactions (3) and (4), we obtain atomization energies for Li$_3$ (38.0 kcal/mol) and Li$_2$H (88.8 kcal/mol) in good agreement with earlier results.[7,23] Using the atomization energies for Li$_2$ (25.5 kcal/mol), Li$_3$ (38.0 kcal/mol), LiH (55.8 kcal/mol), and Li$_2$H (88.8 kcal/mol), the atomization energy of Li$_3$H is 119.6, 119.6, 119.7, and 118.5 kcal/mol (average value 119.4 kcal/mol) for reactions (1), (2), (3), and (4), respectively. Combining the third-law value of the enthalpy of reaction (5) with the atomization

TABLE II. Enthalpies of reactions (kcal/mol), calculated and experimental.

Reaction	Calculated	Experimental
$Li_3H(g)+Li(g)=Li_2H(g)+Li_2(g)$	8.47	5.41
$Li_3H(g)+Li_2(g)=Li_2H(g)+Li_3(g)$	15.73	18.27
$Li_3H(g)+Li(g)=LiH(g)+Li_3(g)$	16.26	25.92
$Li_3H(g)=LiH(g)+Li_2(g)$	28.93	38.5
$Li_4H(g)=Li_2H+Li_2$	26.89	38.0

energies for Li_2 (25.5 kcal/mol), Li_3 (38.0 kcal/mol), LiH (55.8 kcal/mol), and Li_3H (119.4 kcal/mol), this approach leads to 151.8 kcal/mol for the atomization energy of Li_4H. These results are also shown in Fig. 3.

V. CONCLUDING REMARKS

Mass-spectroscopic measurements have been performed over solutions of hydrogen in liquid lithium, and the equilibrium constants of a number of reactions have been measured. Density functional calculations have been performed of the structures, vibrational frequencies, and ionization energies of low-lying isomers of Li_nH molecules. The temperature-dependent contributions to the free energy have been calculated for the temperatures of the measurements, and the resulting free energy functions have been used to analyze the mass-spectroscopic data.

The calculated free energy functions are more reliable than those derived from estimates of the structures and vibrational frequencies, and their use resulted in reaction enthalpies that are both significantly lower and closer to the calculated energies of the components. Nevertheless, Table II shows that significant differences remain. The choice of the gradient-corrected PW91 functional and the basis set affects the structures, vibrational frequencies, free energy functions, and energy differences (see, for example, Fig. 3). We note that the dissociation energies of H_2, Li_2, and LiH using the LSD functional are larger than the PW91 values.

All calculated atomization energies in Fig. 3, as well as all estimates of E_{at} based on reaction enthalpies, assume that each molecule in the reactions is in its most stable form. This need not be the case, as shown by measurements on sulfur cluster anions.[24] Under appropriate experimental conditions, it is possible to generate S_6^- and S_7^- chains, although they are much less stable than the corresponding rings. In spite of these uncertainties, the present work shows that the analysis of mass-spectroscopic data and density functional calculations provide valuable and complementary information about reaction enthalpies, atomization energies, and stabilities of molecules.

[1] See, for example, P. C. Stancil, S. Lepp, and A. Dalgarno, Astrophys. J. **458**, 401 (1996) and references therein. The He–LiH potential energy surface has been studied by B. K. Taylor and R. J. Hinde, J. Chem. Phys. **111**, 973 (1999).
[2] S. Lepp and M. Shull, Astrophys. J. **280**, 465 (1984).
[3] C. H. Wu et al., Fusion Eng. Des. **56–57**, 179 (2001).
[4] O. Plats, R. P. Hurst, and F. A. Matsen, J. Chem. Phys. **31**, 501 (1959).
[5] J. C. Browne, J. Chem. Phys. **41**, 3495 (1964).
[6] H. R. Ihle and C. H. Wu, J. Chem. Phys. **63**, 1605 (1975), and references therein.
[7] C. H. Wu and H. R. Ihle, J. Chem. Phys. **66**, 4356 (1977).
[8] B. Vezin, P. Dugourd, D. Rayane, P. Labastie, J. Chevaleyre, and M. Broyer, Chem. Phys. Lett. **206**, 521 (1993).
[9] B. Vezin, P. Dugourd, C. Bordas, D. Rayane, M. Broyer, V. Bonačić-Koutecký, J. Pittner, C. Fuchs, J. Gaus, and J. Koutecký, J. Chem. Phys. **102**, 2727 (1995).
[10] H. Kato, K. Hirao, I. Nishida, K. Kimoto, and K. Akagi, J. Phys. Chem. **85**, 3391 (1981).
[11] B. K. Rao, S. N. Khanna, and P. Jena, Phys. Rev. B **43**, 1416 (1991). These calculations use a basis of s and p orbitals and estimate correlation effects using fourth-order Møller–Plesset perturbation theory (MP4).
[12] V. Bonačić-Koutecký, J. Gaus, M. F. Guest, L. Češpiva, and J. Koutecký, Chem. Phys. Lett. **206**, 528 (1993).
[13] R. Antoine, P. Dugourd, D. Rayane, E. Benichou, and M. Broyer, J. Chem. Phys. **107**, 2664 (1997).
[14] DGAUSS program, UniChem package of Oxford Molecular Group (double zeta basis with polarization functions DZVP, auxiliary basis A1).
[15] N. Godbout, D. R. Salahub, J. W. Andzelm, and E. Wimmer, Can. J. Chem. **70**, 560 (1992).
[16] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[17] R. O. Jones, A. I. Lichtenstein, and J. Hutter, J. Chem. Phys. **106**, 4566 (1997).
[18] See EPAPS Document E-JCPSA6-120-018411 for (a) atomic coordinates and vibrational frequencies of the most stable isomers of Li_nH (n=2–6), (b) the free energy functions of Li_2, Li_3, Li_nH (n=2–4), and (c) equilibrium constants and reaction enthalpies of all reactions considered here. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.
[19] D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2nd ed., Natl. Stand. Ref. Data Ser. No. **37** (U.S. GPO, Washington, D.C., 1971).
[20] K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure IV: Constants of Diatomic Molecules (Van Nostrand Reinhold, New York, 1979).
[21] A. R. Allouche, M. Aubert-Frecon, and F. Spiegelmann, Can. J. Phys. **74**, 194 (1996).
[22] M. F. V. Lundsgaard and H. Rudolph, J. Chem. Phys. **111**, 6724 (1999).
[23] C. H. Wu, J. Chem. Phys. **65**, 3181 (1976).
[24] S. Hunsicker, R. O. Jones, and G. Ganteför, J. Chem. Phys. **102**, 5917 (1995).