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Dynamical and Kinetic Properties Calculations of the Na+LiH ® NaH+Li

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Introduction

The Potential Energy Surface (PES) play a decisive role to compute the dynamical and kinetic properties of a reactive system. However, the fitting of the *ab initio* electronic energies of polyatomic molecules for different nuclear configurations is a difficult task that involves a significant amount of work and chemical insight. In this work, we have showing the first version of PES built to Na+HLi reaction.

To PES of the Na+HLi reaction, was determined by calculating a gride of the 924 *ab initio* points:

- $2.5a_0 \leq r_{NaH} \leq 14.0a_0$,
- $2.0a_0 \leq r_{HLi} \leq 14.0a_0$,
- $q_{Na\ Li}$ equal 0°, 30°, 60°, 90°, 120°, 150° e 180°

These *ab initio* energies values that cover a relevant portion of the surface at theta, the angle formed by the NaLi and HLi internuclear distances, were obtained using *Gaussian98* program with the 6-311++G(3df,3pd) basis set within a Møller-Plesset perturbation treatment for the correlation energy terms fourth order (MP4).

To better describe the regions of weak interaction towards the asymptotic limits, we used QCISD(T) level of theory and 6-311++G(3df,3pd) basis set.

➢ To fit the *ab initio* calculations for this system, for different nuclear configurations, using a *Bond Order* (BO) polynomial expansion for both two- and three-body terms:

$$V^{(3)}(R_{AB},R_{BC},R_{AC}) = \sum_{\substack{i+j+k\geq 1 \\ i+j+k\leq N}}^{N} c_{ijk}\, n_{AB}^{i} n_{BC}^{j} n_{AC}^{k} \qquad n_{AB} = \exp[-b(R_{AB} - R_{eAB})]$$

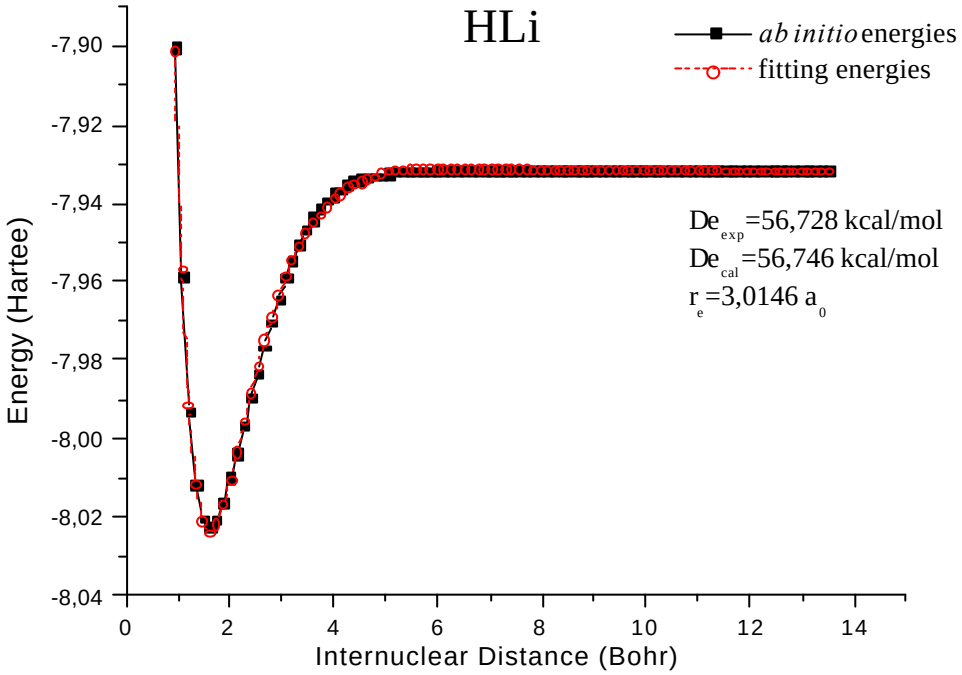
➢ We have used both *Generalized Simulated Annealing* (GSA) and Powell methods.

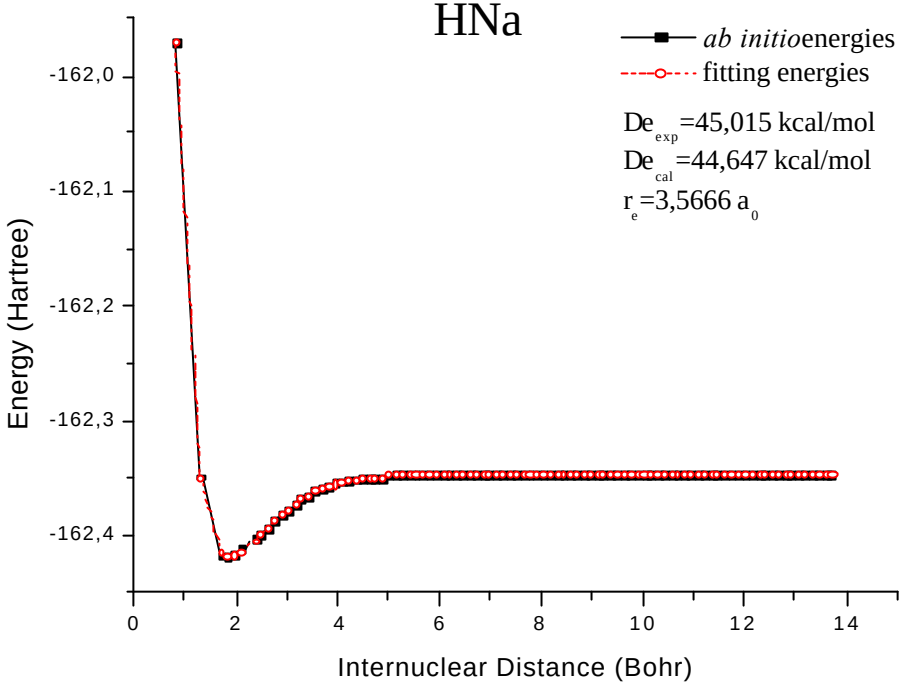
➢ To determine the potential for three-body term, we have used MBE (*Many-Body Expansion*) expansion:

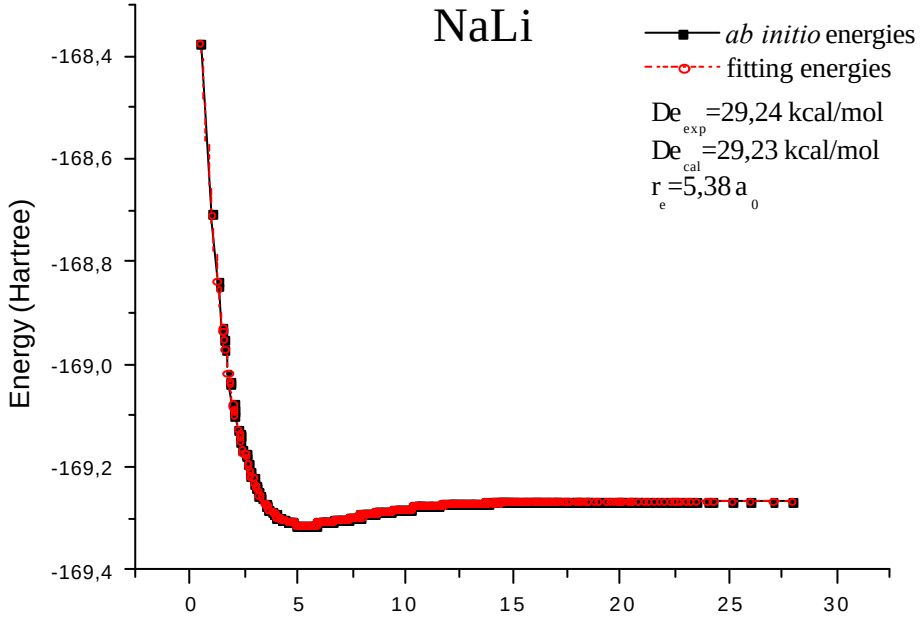
$$V_{ABCD\ldots N}^{MBE} = \sum V_{A}^{(1)} + \sum V_{AB}^{(2)}(R_{AB}) + \sum V_{ABC}^{(3)}(R_{AB},R_{BC},R_{AC}) + \ldots + \sum V_{ABCD\ldots N}^{(N)}(R_i)$$

➢ To complete these studies, we also determine the kinetic properties of this reaction calculating the rate constants using the *POLYRATE* program, which is based on *Transition State Theory* (TST).

Fitting the ab initio Potential of the Two-Body Terms







Rate Constant

$$k_{TST}(T) = \frac{k_B T}{h} \frac{Q_{X^+}}{Q_A Q_{BC}} \exp\left(- \frac{V_a^{G^+}}{RT} \right)$$

$$V_a^{G^+} = V^+ + \varepsilon_{ZPE} \qquad \Rightarrow \text{is the barrier}$$

$$k_{TST}^{W}(T) = \kappa(T) k(T)$$

$$\kappa(T) = 1 + \frac{1}{24} \left| \frac{\hbar \omega^+}{k_B T} \right|^2 \qquad \Rightarrow \text{ is the transmission coefficient}$$

$$\beta = \arccos\left[\frac{m_A m_c}{(m_A + m_B)(m_B + m_C)} \right]^{1/2} \qquad \Rightarrow \text{skew angle}$$

Minimum Energy Path – MEP

➢ Eckart Potential Function

$$V_{MEP}(s) = -\frac{AY}{1+Y} - \frac{BY}{(1+Y)^2}$$

$$Y = e^{\alpha(s-S_0)}$$

$$A = \Delta E_C = V_{MPE}(s = +\infty)$$

$$B = \left(2V^+ - A\right) + 2\left(V^+\left(V^+ - A\right)\right)^{1/2}$$

$$S_0 = -\frac{1}{\alpha}\ln\left(\frac{A+B}{B-A}\right)$$

$$\alpha^2 = -\frac{\mu\left(\omega^+\right)^2 B}{2V^+\left(V^+ - A\right)}$$

➢ Vibrational Adiabatic Ground State Potential

$$V_a{}^{G^+} = -\frac{ay}{1+y} - \frac{by}{(1+y)^2} - c$$

$$y = e^{\alpha(s-s_0)}$$

$$a = \Delta H_0 = V_a{}^{G^+}(s = +\infty) - V_a{}^{G^+}(s = -\infty)$$

$$b = \left(2V_a{}^{G^+} - a\right) + 2\left(V_a{}^{G^+}\left(V_a{}^{G^+} - a\right)\right)^{1/2}$$

$$c = \varepsilon_{int}{}^{G}(s = -\infty)$$

$$s_0 = -\frac{1}{\alpha}\ln\left(\frac{a+b}{b-a}\right)$$

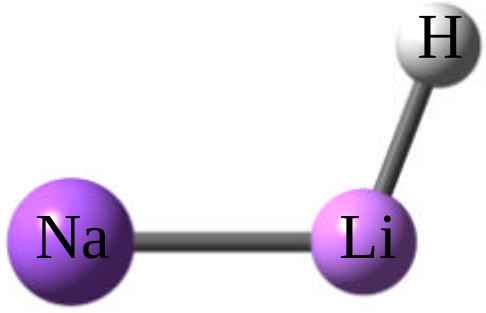
Optimized Geometry

QCISD(T)/Basis	R_{NaLi} (Å)	R_{HLi} (Å)	R_{HNa} (Å)
6-311g(d,p)	3.4501	1.6257	111.12°
6-311g(3df,3pd)	2.96	1.6266	114.89°
6-311+g(3df,3pd)	3.3834	1.6266	114.89°
6-311++g(3df,3pd)	3.4834	1.6266	114.89°
Experiment	2.81	1.5954	1.8874

Transition Structure

HF/Basis	R_{NaLi} (Å)	R_{HLi} (Å)	*q*	ωi (cm^{-1})
6-311g(d,p)	3.4501	1.6257	111.12°	143.264
6-311g(3df,3pd)	3.4834	1.6266	114.89°	133.458
6-311+g(3df,3pd)	3.3834	1.6266	114.89°	133.696
6-311++g(3df,3pd)	3.4834	1.6266	114.89°	133.936

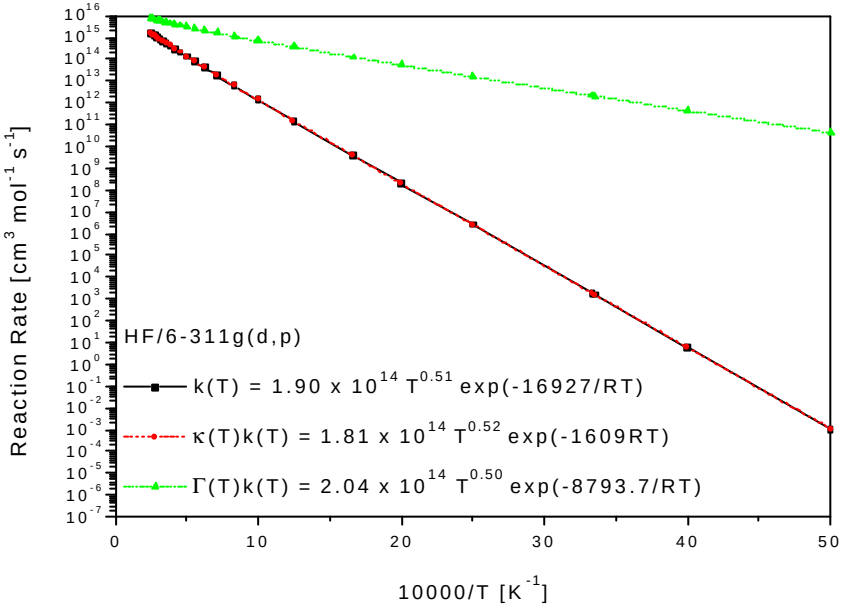
	6-311g(d,p)	6-311g(3df,3pd)	6-311+g(3df,3pd)	6-311++g(3df,3pd)
Na	-161.8459262 (H)	-161.8459262 (H)	-161.8459827 (H)	-161.8459827 (H)
Li	-7.4320264 (H)	-7.4320264 (H)	-7.4320268 (H)	-7.4320269 (H)
H	-0.4998098 (H)	-0.4998098 (H)	-0.4998097 (H)	-0.4998179 (H)
NaLi	-169.3072738 (H)	-169.3087346 (H)	-169.3087987 (H)	-169.3087987 (H)
HNa	-162.4099822 (H)	-162.4167823 (H)	-162.4168271 (H)	-162.4168386 (H)
HLi	-8.0164631 (H)	-8.0219290 (H)	-8.0219274 (H)	-8.0219333 (H)
TS	-169.8353032 (H)	-169.8362039 (H)	-169.8362006 (H)	-169.8362039 (H)
V_{mep}	16.997 (kcal/mol)	19.890 (kcal/mol)	19.898 (kcal/mol)	19.900 (kcal/mol)
V_a^g	17.106 (kcal/mol)	19.994 (kcal/mol)	20.002 (kcal/mol)	20.001 (kcal/mol)
H	8.1276 (kcal/mol)	11.593 (kcal/mol)	11.603 (kcal/mol)	11.599 (kcal/mol)

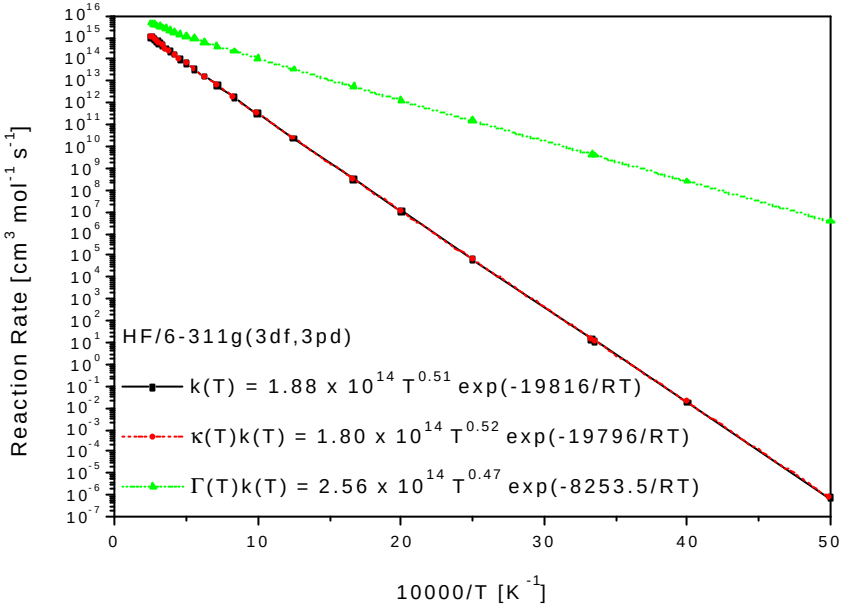


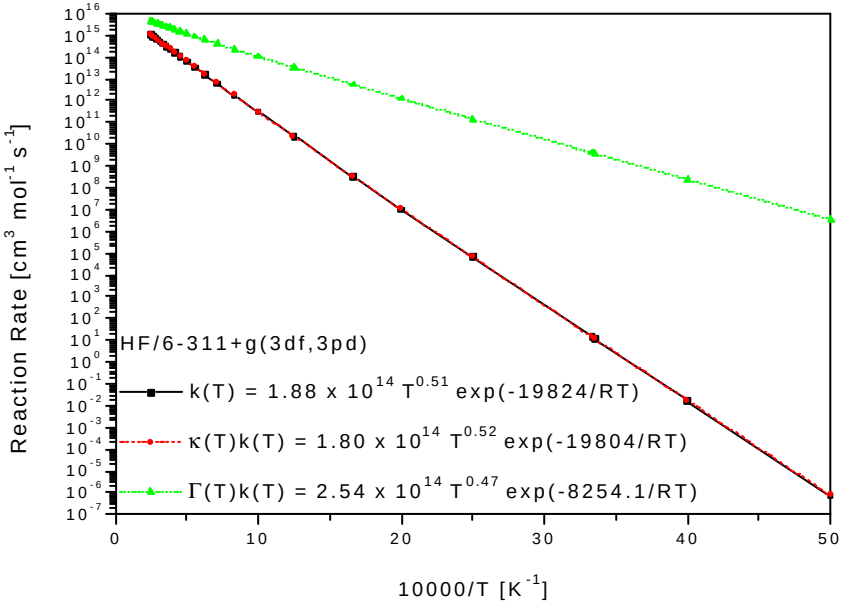
Skew Angle

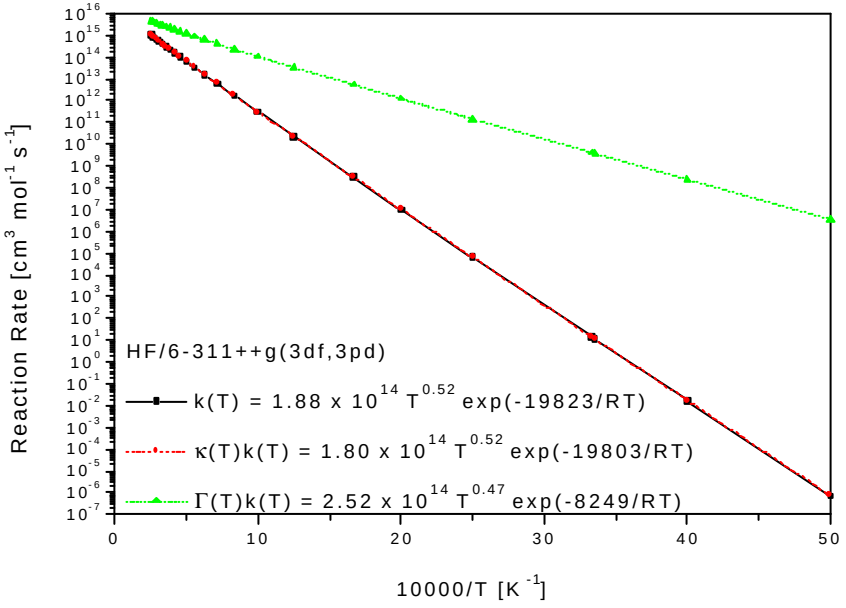
$\beta = 23.76^{o}$

Plot of Rate Constant of the Na+HLi Reaction









Classical (V_{MEP}) and Vibrationally Adiabatic (V^G_a) Potential Energies Curve