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中文摘要

國科會於 2005 年 6 月 1 日開始以「國科會講座」延聘美國 Emory 大學講座教授林明璋院士自美返台主持交通大學分子科學研究中心以致力發展最先進的研究計劃。除了在互益的基礎上，與台灣物理、化學方面的學者就相關聯的研究主題進行數個合作研究計劃之外，已在再生能源以及奈米粒子輔以超快電子動力學與電子在系統中轉換方面之研究為主題的三個大型研究計劃。這些以理論計算為輔的合作研究實驗，去年所作的研究包括：

(1)與王念夏教授合作研究 CN 與 NCO 反應動力學實驗。
(2)與李遠鵬教授合作研究 S+OCS 的反應機制及氧原子與 C_2H_5OH 在巨烈衝擊波反應的動力學實驗。
(3)由李遠哲院長與原分所同仁進行 C_6H_5OH 的光分裂動力學研究。
(4)建立台灣大型計算在太陽能電池及乙醇變氫催化反應的計算。

截至目前為止，本計劃已有 4 篇論文在科學期刊上發表或即將出刊，除此之外，並 11 篇在交通大學準備或撰寫的論文將會陸續以國科會贊助的名義在國際期刊上發表。

關鑑詞：NCN 及 S 原子反應、$O+C_2H_5OH$ 反應、C_6H_5OH 光分解、InN/TiO_2 太陽能系統研究。

英文摘要

The 2005-06 visit of M. C. Lin from Emory University, supported by National Science Council for the full year, had been devoted to the development of a forefront research program for the Center for Interdisciplinary Molecular Science (CIMS) at National Chiao Tung University, and to studies of several collaborative research projects with chemical physicists in Taiwan on selected topics of mutual interest. For the development of a sustainable research program for CIMS, 3 major proposals have been submitted for the Center with focus on renewable energy research aided by quantum chemical calculations. In the collaborative studies, experiments aided by theoretical simulations have been carried out on (1) the kinetics of NCN and S atom reactions; (2) the kinetics of O-atom reaction with C_2H_5OH in shock waves with Y.-P. Lee, aided by theoretical calculations carried out at Emory University; (3) the photo-fragmentation dynamics of C_6H_5OH with Y. T. Lee and coworkers at IAMS; and (4) fabrication of InN/TiO_2 nanoparticle film systems. Four papers have been published or submitted for publication in SCI journals. In addition, 11 papers which were prepared or edited at NCTU by the PI have been credited to NSC for the support of the effort.

關鑑詞：CIMS's program、NCN and S atom kinetics、$O+ C_2H_5OH$ kinetics、$C_6H_5 OH$ fragmentation dynamics、InN/TiO_2 fabrication

一、前言：

The objectives of this project for the period Jun. 1, 2005 – May 31, 2006 centered on: (1) Establishment of a forefront research program at the Center for Interdisciplinary Molecular Science (CIMS) with emphasis on studies renewable energy research, (2) Collaboration with scientists in Taiwan on kinetics and dynamics of chemical reactions of interest to atmospheric chemistry, combustion and photo fragmentation processes, as well as the management of two collaborative research projects with INER (Institute of Nuclear Energy Research) for fabrication of InN/TiO_2 nanoparticle films for solar energy conversion applications.

CIMS, established officially at NCTU in July 2003, has now over a dozen faculty members with a broad spectrum of research fields. The Center's major focus is placed on the applications of ultra-fast spectroscopy to study energy and electron transfer dynamics over a wide range of the spectrum (covering from the infrared to the UV).   On account of the national need in renewable energy research to alleviate the acute shortage in Taiwan's energy resources, the Center's near-term research objectives will be placed on solar energy conversion and the catalytic studies of ethanol to H_2 conversion for fuel cell applications.

In the proposed collaborative research projects, 4 full papers have been completed and submitted for publications (3 published and 1 submitted for publication), with additional 11 papers credited to NSC for works carried out at Emory University but written or edited by the PI during the past year visiting NCTU.


二、報告內容：

1. Atmospheric chemistry

NCN kinetics: NCN is the key radical involved in the formation of NOx in hydrocarbon combustion reaction. In the past year we investigated with N. S. Wang's group the formation of NCN from the reaction of CN with NCO; both radicals are known to be present in the combustion process. The direct detection of NCN formation by laser-induced fluorescence confirms the mechanism CN + NCO → NCN + CO, and it is a very facile process. The result of our detailed *ab initio* calculation reveals that the reaction can take place via several exothermic product channels:
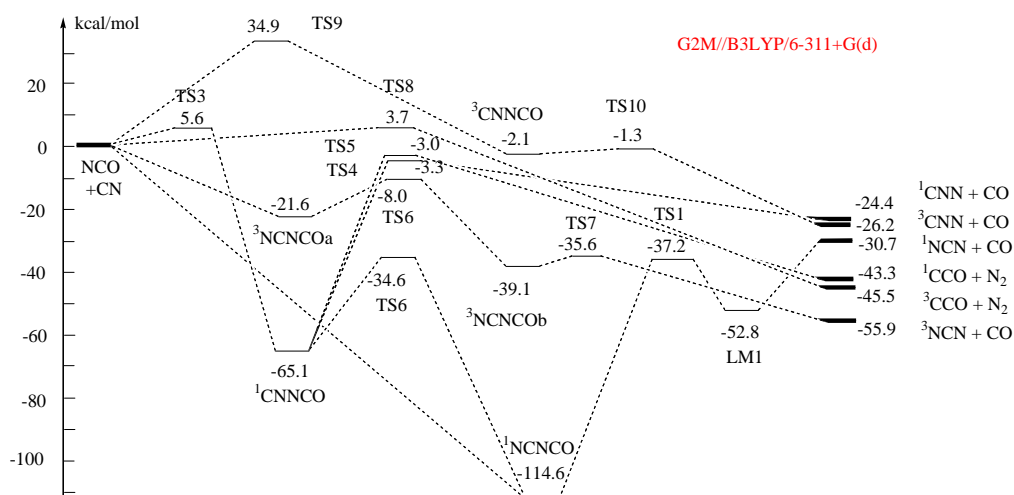
The predicted rate constant by a multi-channel RRKM calculation agrees reasonably with measured experimental data.
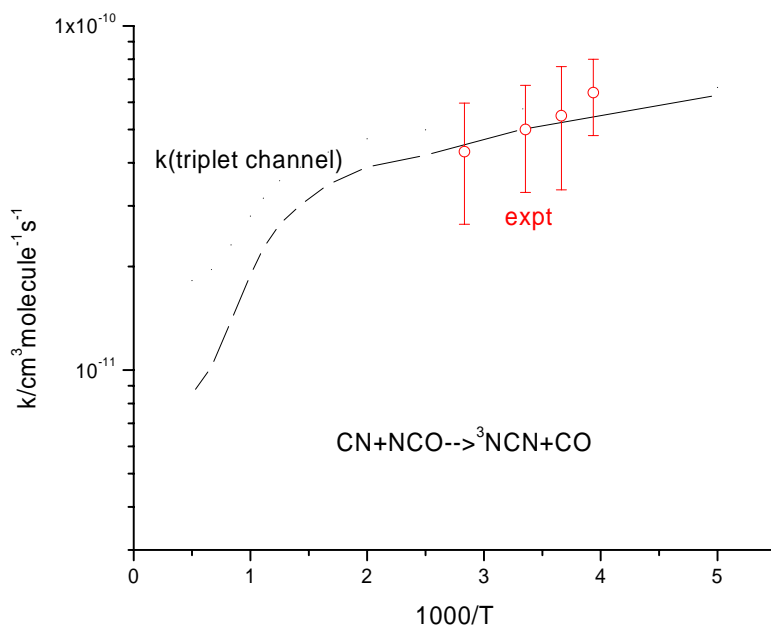

S + OCS kinetics: OCS is a known atmospheric species; it has been employed in many experiments as a convenient source of S atoms. We have investigated collaboratively with Y-P Lee's group the reaction S (^{3}P) + OCS in Ar over the pressure range 50−710 Torr and the temperature range 298−985 K with the laser photolysis technique. S atoms were generated by photolysis of OCS with light at 248 nm from a KrF excimer laser; their concentration was monitored via resonance fluorescence excited by atomic emission of S produced from microwave-discharged SO$_2$. At pressures less than 250 Torr, our measurements give $k(298$ K$) = (2.7 \pm 0.5) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, in satisfactory agreement with a previous report by Klemm and Davies. New data determined for 407−985 K connect rate coefficients reported previously for $T \geq 860$ and $T \leq 478$ K and show a non-Arrhenius behavior. Combining our results with data reported at high temperatures, we derived an expression $k(T) = (6.1 \pm 0.3) \times 10^{-18}$ $T^{1.97 \pm 0.24}$ exp[$-(1560 \pm 170)/T$] cm^3 molecule^{-1} s^{-1} for $298 \leq T/$K ≤ 1680. At 298 K and $P \geq 500$ Torr, the reaction rate was enhanced. Theoretical calculations at the G2M(CC2) level, using geometries optimized with the B3LYP/6-311+G(3df) method, yield energies of transition states and products relative to those of the reactants. Rate coefficients predicted with multichannel RRKM calculations agree satisfactorily with experimental observations. According to our calculations, the singlet channel involving formation of SSCO followed by direct dissociation into S$_2$ (a $^1\Delta_g$) + CO dominates below 2000 K; SSCO is formed via intersystem crossing from the triplet surface. At low temperature and under high pressure the stabilization of OCS$_2$, formed via isomerization of SSCO, becomes important; its formation and further reaction with S atoms partially account for the observed increase in the rate coefficient under such conditions.

The predicted potential energy surface for the S + OCS reaction:

Energy unit: kcal/mol
—— Singlet Surface
------ Triplet Surface
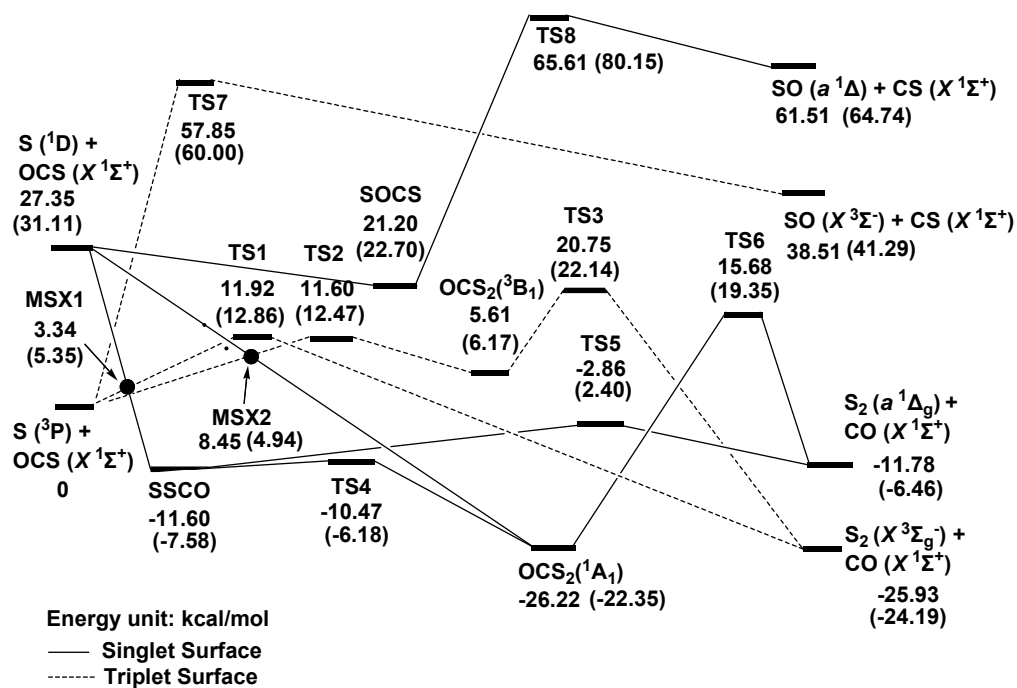
Comparison of the computed rate constant with measured experimental data at NCTU:
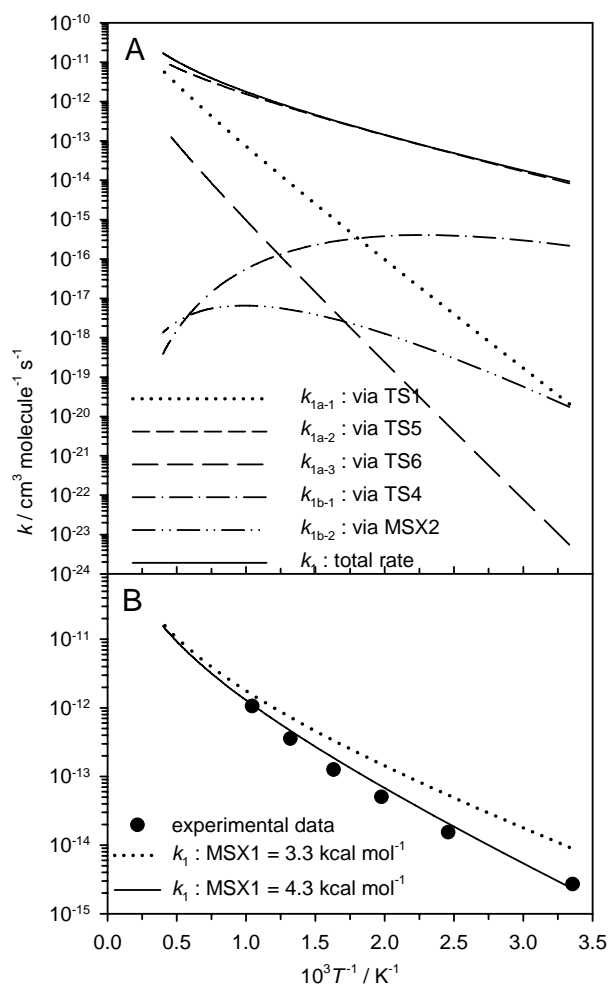
## 2. Combustion chemistry: Kinetics of the O + C_2H_5OH reaction

Ethanol (C_2H_5OH) is a promising alternative fuel. The reaction of ethanol with O(^{3}P) atom is a crucial step in combustion. A higher level theoretical study for the kinetics and mechanism of the reaction of ethanol with O(^{3}P) atom is reported. The geometries of the reactants, intermediates, transition states, and products for this reaction have been optimized at the MP2/6-311+G($3df$, $2p$) level. The potential energy surface of the reaction has been calculated at the CCSD(T)/6-311+G($3df$, $2p$) // MP2/6-311+G($3df$, $2p$) level. The rate constants of the reaction of O + C_2H_5OH in the temperature range of T = 200-3000 K and the branch ratios for the three reaction paths have been predicted by Eckart-tunneling effect correction method. The rate expression of total rate constants is $2.17\times10^{-21}\times T^{3.13}$ exp ($-4/T$) cm^3 molecule^{-1} s^{-1}. The reaction channel for OH+CH_3CHOH is primary channel, whose rate expression is $1.26\times10^{-20}\times T^{2.88}$ exp ($-105/T$) cm^3 molecule^{-1} s^{-1}. The rate expression for the channel of OH+CH_2CH_2OH is $1.49\times10^{-23}\times T^{3.62}$ exp ($-1275/T$) cm^3 molecule^{-1} s^{-1}; and that for the channel of OH+CH_3CH_2O is $4.24\times10^{-26}\times T^{4.24}$ exp ($-1462/T$) cm^3 molecule^{-1} s^{-1}. The predicted total rate constant agrees closely with experimental data obtained by Y-P Lee's research group.

The PES of the O + C_2H_5OH reaction:
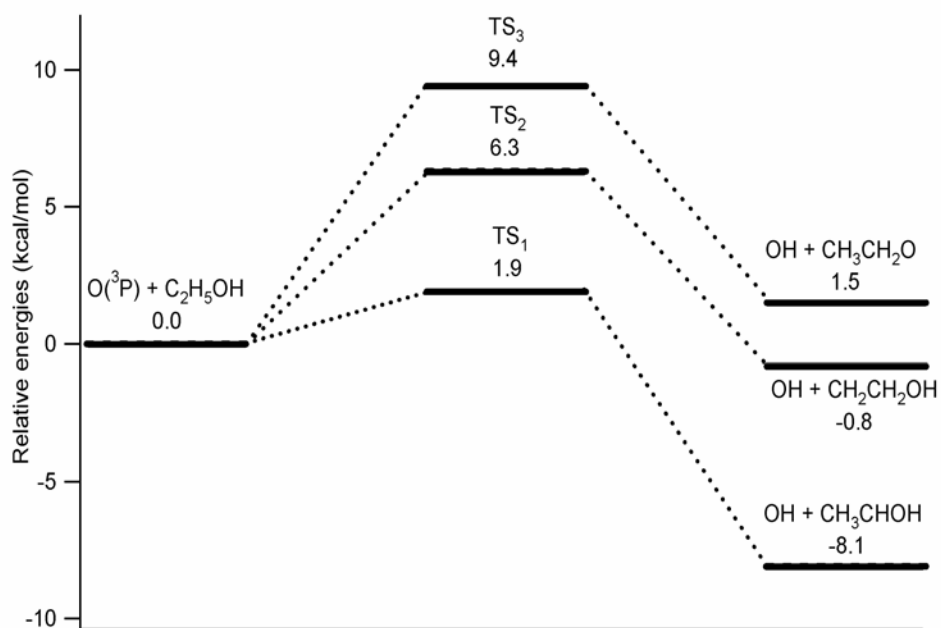
3. Dynamics of the fragmentation of C_6H_5OH

Phenol is a major combustion intermediate in hydrocarbon combustion under sooting conditions. The mechanism for the decomposition of C_6H_5OH, producing CO and cyclopentadiene, is not well established. The kinetics for their formation, however, have been investigated by several research laboratories world-wide. In order to elucidate the mechanism for this fundamentally important process we have performed a high-level ab initio MO calculation to model the kinetics and dynamics of its fragmentation process. The predicted PES is given below:
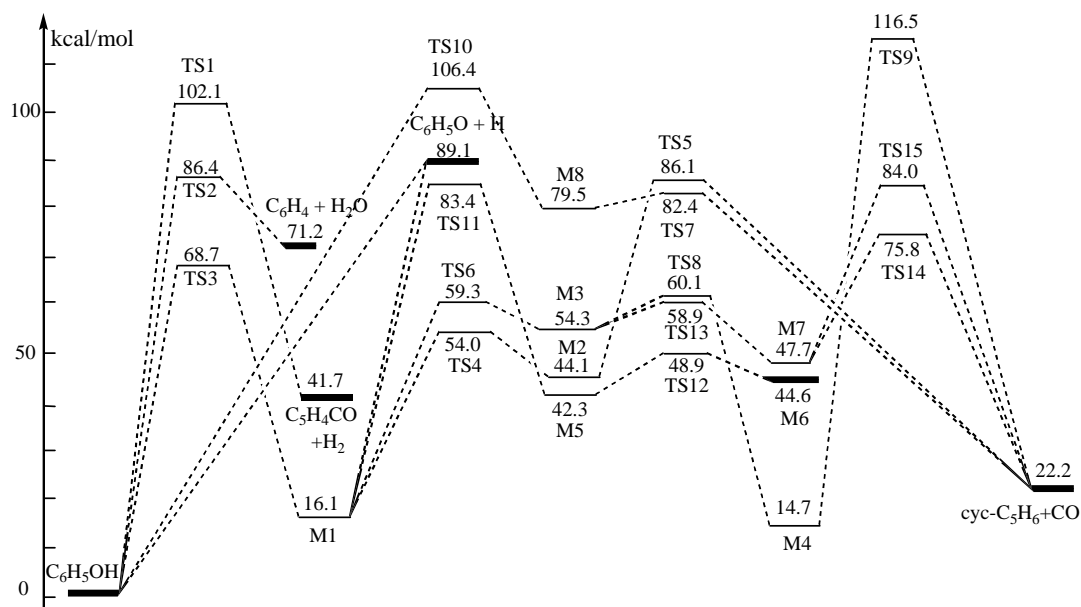
Te result of our multi-channel RRKM calculation for the formation of the major decomposition products agrees quantitatively with available literature data:
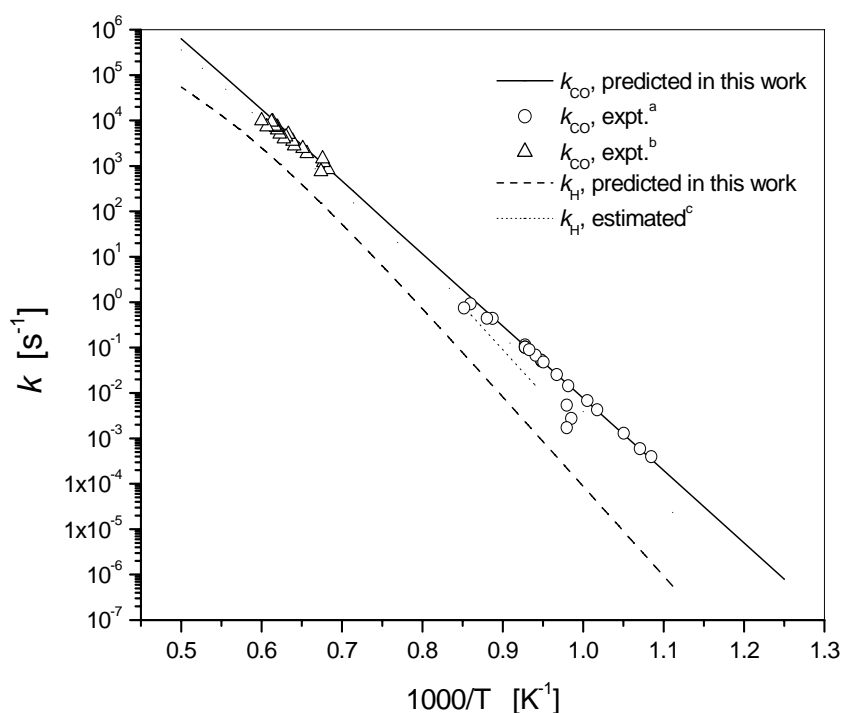
The dynamics of the photo-fragmentation of phenol: We have collaborated with Y.T. Lee, C.-K. Ni et al. at IAMS on the fragmentation dynamics of C_6H_5OH at 193 and 248 nm using multimass ion imaging techniques. Dissociation from both electronic excited state and ground electronic state at these two wavelengths were observed. Major dissociation channels at 193 nm include O-H bond cleavage, CO elimination, and H_2O elimination. Only the first two channels are observed at 248 nm. The translational energy distribution shows that H atom elimination occurs in the electronic excited state, but both the CO and H_2O eliminations occur in the ground
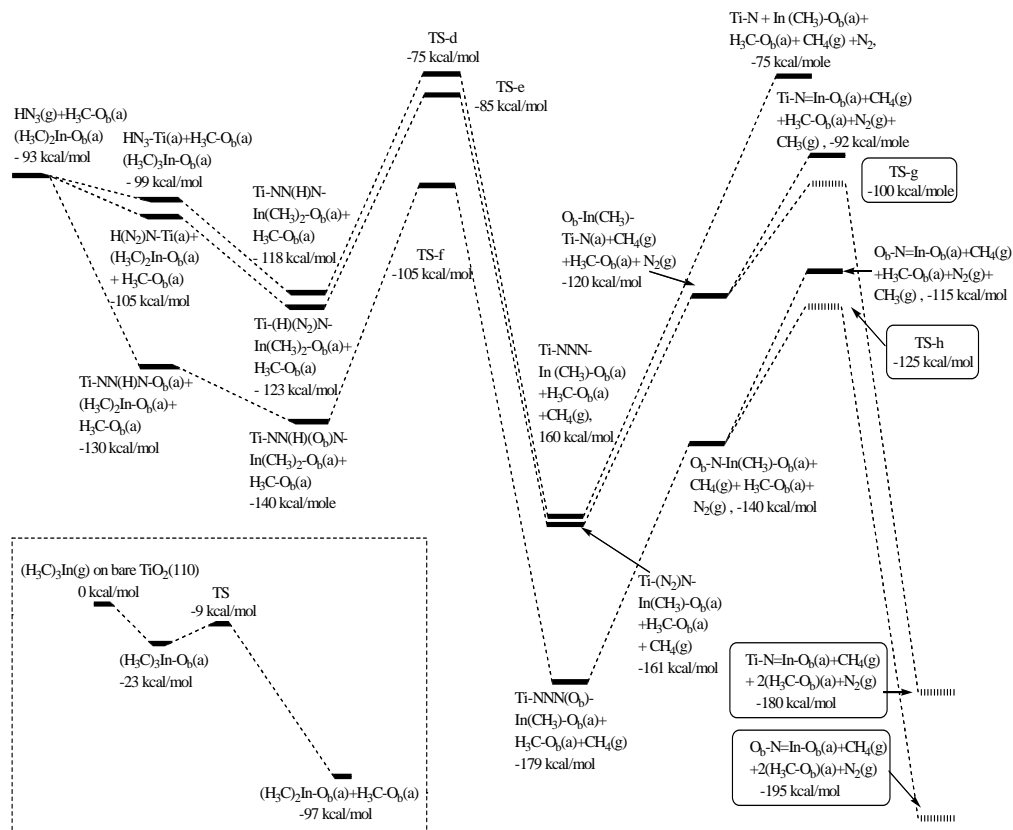
electronic state. Isomerization from phenol to cyclohexadienone were found to play an important role in the dissociation processes. These results can be reasonably accounted for with the PES presented above.

4. Computer simulations of solar cell and fuel cell fabrication processes

In collaboration with INER (Institute of Nuclear Energy Research), the TCCC (Taiwan Computational Chemistry Consortium) team members (B. C. Wang, J. S. Lin, M. Hayashi, J. J. Ho, J. C. Jiang, J. G. Chang and M. C. Lin) have performed large scale simulations of processes relevant to the fabrication of the InN-quantum dot/TiO$_2$ nanoparticle system and the conversion of ethanol to hydrogen for fuel cell applications. In addition, we have also collaborated with Prof. Meilin Liu's group at Georgia Tech on the chemistry of several solid oxide fuel cell systems. Two examples directly involved this author are given below.

InN formation from the reaction of HN$_3$ and trimethyl indium on TiO$_2$: The computational study on the reaction of hydrazoic acid and trimethyl indium (TMIn) begins with co-adsorbed precursors on TiO$_2$ rutile (110) surface. The adsorption geometries and energies of possible adsorbates including HN$_3$-In(CH$_3$)$_3$(a), and its derivatives, HN$_3$-In(CH$_3$)$_2$(a), N$_3$-In(CH$_3$)$_2$(a), N$_3$-In(CH$_3$)(a), and N-In(a) have been predicted by first-principles calculations based on the density functional theory (DFT) and the pseudopotential method. The mechanisms of these surface reactions have also been explicitly elucidated with the computed potential energy surfaces.

Starting from the interaction of three stable HN$_3$ adsorbates, HN$_3$-O$_b$(a), H(N$_2$)N-O$_b$(a) and Ti-NN(H)N-O$_b$(a), where O$_b$ is the bridged O-site on the surface, with two stable intermediates from the adsorption and dissociative adsorption of TMIn, (H$_3$C)$_3$In-O$_b$(a) and (H$_3$C)$_2$In-O$_b$(a) + H$_3$C-O$_b$(a), InN products can be formed exothermically via four reaction paths following the initial barrierless In-atom association with the N atom directly bonded to H, by CH$_4$-elimination (with ~ 40-kcal/mole barriers), the InN-N bond breaking and the final CH$_3$-elimination or migration (with < 20-kcal/mole barriers). These Langmiur-Hinshelwood processes producing the two most stable InN(a) side-on adsorptions and confirms that HN$_3$ and TMIn are indeed very efficient precursors for the deposition of InN films on TiO$_2$ nanoparicles. The result of similar calculations for the reactions occurring by the Rideal-Eley mechanism involving HN$_3$(a) + TMIn(g) and HN$_3$(g) + TMIn(a) indicates that they are energetically less favored and produce the less stable InN(a) with end-on configurations. Part of the complex PES is given below:

Ti-N + In (CH$_3$)-O$_b$(a)+
H$_3$C-O$_b$(a)+ CH$_4$(g) +N$_2$,
-75 kcal/mole

Ti-N=In-O$_b$(a)+CH$_4$(g)
+H$_3$C-O$_b$(a)+N$_2$(g)+
CH$_3$(g) , -92 kcal/mole

TS-d
-75 kcal/mol

TS-e
-85 kcal/mol

TS-g
-100 kcal/mole

HN$_3$(g)+H$_3$C-O$_b$(a)
(H$_3$C)$_2$In-O$_b$(a)
- 93 kcal/mol

HN$_3$-Ti(a)+H$_3$C-O$_b$(a)
(H$_3$C)$_3$In-O$_b$(a)
- 99 kcal/mol

Ti-NN(H)N-
In(CH$_3$)$_2$-O$_b$(a)+
H$_3$C-O$_b$(a)
118 kcal/mol

O$_b$-In(CH$_3$)-
Ti-N(a)+CH$_4$(g)
+H$_3$C-O$_b$(a)+ N$_2$(g)
-120 kcal/mol

O$_b$-N=In-O$_b$(a)+CH$_4$(g)
+H$_3$C-O$_b$(a)+N$_2$(g)+
CH$_3$(g) , -115 kcal/mol

TS-h
-125 kcal/mol

H(N$_2$)N-Ti(a)+
(H$_3$C)$_2$In-O$_b$(a)
+ H$_3$C-O$_b$(a)
-105 kcal/mol

TS-f
-105 kcal/mol

Ti-(H)(N$_2$)N-
In(CH$_3$)$_2$-O$_b$(a)+
H$_3$C-O$_b$(a)
- 123 kcal/mol

Ti-NN(H)N-O$_b$(a)+
(H$_3$C)$_2$In-O$_b$(a)+
H$_3$C-O$_b$(a)
-130 kcal/mol

Ti-NN(H)(O$_b$)N-
In(CH$_3$)$_2$-O$_b$(a)+
H$_3$C-O$_b$(a)
-140 kcal/mole

Ti-NNN-
In (CH$_3$)-O$_b$(a)
+H$_3$C-O$_b$(a)
+CH$_4$(g),
160 kcal/mol

O$_b$-N-In(CH$_3$)-O$_b$(a)+
CH$_4$(g)+ H$_3$C-O$_b$(a)+
N$_2$(g) , -140 kcal/mol

Ti-N=In-O$_b$(a)+CH$_4$(g)
+ 2(H$_3$C-O$_b$)(a)+N$_2$(g)
-180 kcal/mol

Ti-(N$_2$)N-
In(CH$_3$)-O$_b$(a)
+H$_3$C-O$_b$(a)
+ CH$_4$(g)
-161 kcal/mol

O$_b$-N=In-O$_b$(a)+CH$_4$(g)
+2(H$_3$C-O$_b$)(a)+N$_2$(g)
-195 kcal/mol

Ti-NNN(O$_b$)-
In(CH$_3$)-O$_b$(a)+
H$_3$C-O$_b$(a)+CH$_4$(g)
-179 kcal/mol

(H$_3$C)$_3$In(g) on bare TiO$_2$(110)
0 kcal/mol

TS
-9 kcal/mol

(H$_3$C)$_3$In-O$_b$(a)
-23 kcal/mol

(H$_3$C)$_2$In-O$_b$(a)+H$_3$C-O$_b$(a)
-97 kcal/mol

Solid oxide fuel cell chemistry: The mechanisms of interaction between H$_2$S and Ni- or Cu-based anode surfaces in a solid oxide fuel cell (SOFC) were elucidated collaboratively with Meilin Liu's group by density functional slab model calculations. Two reaction pathways via molecular and dissociative adsorption processes were mapped out following minimum energy paths (MEPs). The energy for H$_2$S adsorption at the atop site of Ni(111) lying parallel to the surface is predicted to be –0.55 eV, while that for the dissociative adsorption is –1.75 eV. In contrast, the formation of initial molecular complexes on a Cu surface is energetically unfavorable (E$_{ad}$~0.0 eV), suggesting that Cu is more sulfur-tolerant than Ni. The predicted adsorption energies and molecular configurations are presented below.

Adsorption energies and molecular parameters, i.e., bond length in Å and angle in degree, of adsorbed H$_2$S species on Cu(111) without surface relaxation.

active site	atop		bridge	hcp	fcc
	up	parallel			
E$_{ad}$[a]	–0.04	–0.09	–0.02	0.00	0.01
r(S-H)	1.353	1.352	1.358	1.361	1.360
	1.352	1.351	1.355	1.355	1.353
θ(H-S-H)	92.1	91.7	93.6	92.3	94.2
d(s-S)[b]	3.402	3..408	3.010	2.799	2.698
γ(Ni-H-S-H)	180.0	92.6	151.3[c]	132.8[c]	130.8[c]
			148.1[d]	153.8[e]	161.1[f]

[a] Adsorption energies in eV relative to unrelaxed Cu(111) and a gas-phase H$_2$S molecule.

[b] Vertical distance between surface and sulfur atom.

[c, d, e, f] γ(Cu$_1$-H-S-H), γ(Cu$_4$-H-S-H), γ(Cu$_2$-H-S-H), and γ(Cu$_3$-H-S-H), respectively, are dihedral angles.

Adsorption energies and molecular parameters, i.e., bond length in Å and angle in degree, of adsorbed HS species on Ni(111) via the dissociative adsorption.

active site	atop[b]	bridge	hcp-fcc
species	**datop**	**dabrg**	**dahcp-fcc**
E_{ad}[a]	–1.69 [–1.75]	–1.58	–1.62
r(S-H)	1.412 [1.416]	1.400	1.370
θ(Ni-S-Ni)	68.5 [69.3]	67.3	56.4
d(s-S)[c]	1.747 [1.738]	1.778	1.784
γ(Ni-Ni-S-H)[d]	102.2 [100.6]	105.5	102.7

[a] Adsorption energies in eV relative to unrelaxed or relaxed Ni(111) and a gas-phase H_2S molecule.
[b] The adsorption energy and parameters in brackets were calculated on relaxed Ni(111).
[c] Vertical distance between surface and sulfur atom.
[d] Dihedral angle.

5. Other works credited to NSC supports

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(3) Z. F. Xu and M. C. Lin, "A DFT Computational Study of the C_6H_5 + C_6H_5NO Kinetics and Mechanism", J. Phys. Chem., A, **109**, 9054-60 (2005).

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(8) Jenghan Wang, Meilin Liu and M. C. Lin, "Oxygen Reduction in the SOFC Cathode of Ag/CeO_2", Solid State Ionics, in press.

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(10) Kun Xu, Z. F. Xu and M. C. Lin, "*Ab Initio* Kinetics of the FCO Reaction with NO", J. Phys. Chem., A, in press.

(11) H. T. Chen, Y. M. Choi, Meilin Liu and M. C. Lin, "A Mechanistic Study on the Reduction of CeO_2 (111), (110), and (100) Surfaces by H_2", J. Phys. Chem., B, submitted.