II.
Accurate quantum dynamics on Grid platforms

Some effects of long range interactions on the reactivity of $N + N_2$

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Outline

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The gas-phase nitrogen exchange reaction

$$N\ (^4S) + N_2\ (^1\Sigma_g^+, v, j) \rightarrow N_2\ (^1\Sigma_g^+, v', j') + N\ (^4S)$$

Dynamics and kinetics relevant to

- spacecraft engeneering
- plasma chemistry
- theory of chemical reactions

Available experimental data

- a few estimates of $k(T)$ at 1273 and 3400 K

Available PESs

LEPS

collinear MEP: barrier 1.55 eV

L3

bent (about 120°) MEP: barrier 1.40 eV

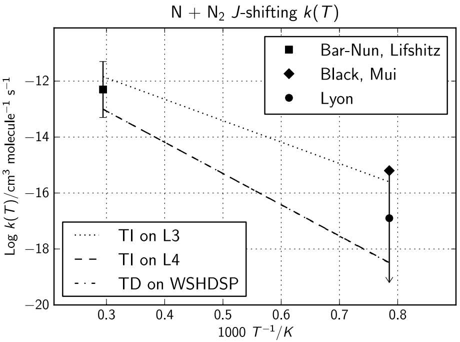
WSHDSP

bent structured MEP: saddle 2.05 eV, well 1.89 eV

L4

bent structured MEP: saddle 2.06 eV, well 1.93 eV

State of the art



J-shifting $k(T)$'s on available PESs

- differ orders of magnitude from experimental data!

Outline

L4, a LAGROBO PES

Weighed sum of "process" potentials

$$V^{\mathrm{LAGROBO}}(r_\tau, r_{\tau+1}, r_{\tau+2}) = \sum_{\tau=1}^{3} w(\Phi_\tau) V_\tau^{\mathrm{ROBO}}(\rho_\tau, \alpha_\tau, \Phi_\tau)$$

Hyperspherical Bond Order coordinates

$$n_\tau = e^{-\beta_\tau (r_\tau - r_{\tau \mathrm{eq}})}$$

$$\rho_\tau = (n_{\tau+2}^2 + n_{\tau+1}^2)^{1/2} \qquad \alpha_\tau = \arctan[n_{\tau+1}/n_{\tau+2}]$$

L4, a LAGROBO PES

$$V^{\mathrm{ROBO}}(\rho,\alpha,\Phi) = a_1(\alpha,\Phi)\left[2\frac{\rho}{a_2(\alpha,\Phi)} - \frac{\rho^2}{a_2^2(\alpha,\Phi)}\right]$$

$a_1(\alpha,\Phi)$

- the depth of the reaction channel as α and ϕ vary

$a_2(\alpha,\Phi)$

- its location on ρ

ML4, lower MEP

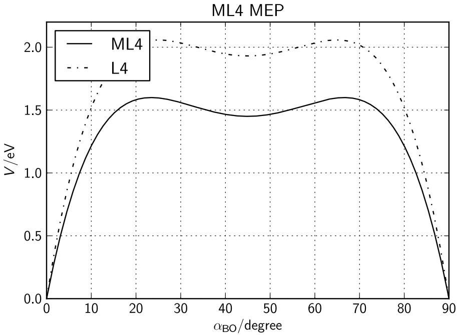
c_{100} controls the MEP height!

$$a_1(\alpha,\Phi) = -D_{N_2} + b_{10}(\Phi) + b_{12}(\Phi)(\alpha - 45^\circ)^2 + \left(\frac{-b_{10}(\Phi) - b_{12}(\Phi)\,(45^\circ)^2}{(45^\circ)^4}\right)(\alpha - 45^\circ)^4$$

$$b_{10}(\Phi) = c_{100} + c_{102}(\Phi - 118.6^\circ)^2 + c_{103}(\Phi - 118.6^\circ)^3$$

$$b_{12}(\Phi) = c_{120} + c_{121}\Phi + c_{122}\Phi^2$$

ML4, lower MEP



ML4 MEP

- saddle 1.60 eV at 116.4°, well 1.45 eV at 118.6°

ML4LJ, accurate LR

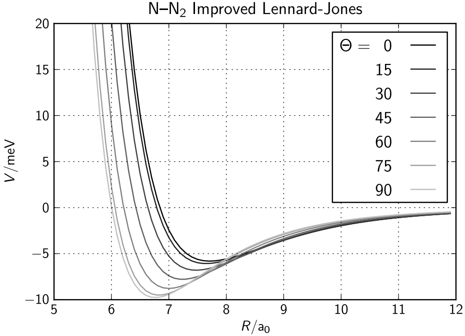
At LR, switch to ILJ

$$V(R,\gamma) = \varepsilon(\gamma)\left[\frac{6}{n(R,\gamma)-6}\left(\frac{R_{\mathrm{m}}(\gamma)}{R}\right)^{n(R,\gamma)} - \frac{n(R,\gamma)}{n(R,\gamma)-6}\left(\frac{R_{\mathrm{m}}(\gamma)}{R}\right)^{6}\right]$$

where

$$n(R,\gamma) = \beta + 4.0\left(\frac{R}{R_{\mathrm{m}}(\gamma)}\right)^2$$

ML4LJ, accurate LR



ILJ profile for $N + N_2$

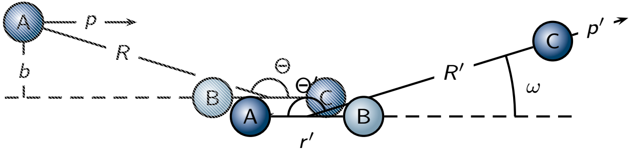
- attractive tail, deeper VdW well for ⊥ approach

Outline

The A + BC reaction

The prototype collision

$$A + BC\ (v, j) \rightarrow AB\ (v', j') + C$$



The B-O "equation of motion"

$$i\hbar \frac{\partial \psi(\mathbf{w}, t)}{\partial t} = \left[\hat{T}_{\mathbf{w}} + V(\mathbf{w}) \right] \psi(\mathbf{w}, t)$$

The A + BC reaction

In TI schemes

$$\left[\hat{T}_{\mathbf{w}} + V(\mathbf{w})\right]\psi(\mathbf{w}) = E_{\mathbf{w}}\psi(\mathbf{w})$$

From an analysis on $\psi(\mathbf{w})$

$$S^{J}_{cv'j'k',avjk}(E) = |P^{J}_{cv'j'k',avjk}|^{2}(E)$$

All observables properties

- can be extracted from the **S** matrix

The J-shifting approximation

Higher-J $P(E)$'s from $P^{J=0}(E)$'s

$$k(T) = \frac{1}{hQ_\mathrm{R}} \sum_{J=0}^{\infty} (2J+1) \sum_{K=-J}^{J} \int_0^\infty \left[e^{-E/k_\mathrm{B}T} \sum_{v,j} \sum_{v',j'} P^{J=0}_{v'j',vj}(E - \Delta E^{JK}) \right] \mathrm{d}E$$

where

$$Q_\mathrm{R} = \left(\frac{2\pi \mu_\mathrm{R} k_\mathrm{B} T}{h^2} \right)^{3/2} \left(\sum_{v,j} (2j+1) e^{-\epsilon_{v,j}/k_B T} \right)$$

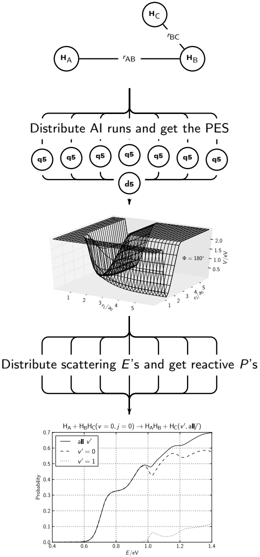
The Grid distribution model

GEMS' Dyn module

- using the TI ABC program
- each fixed-E calculation is independent
- distribute and gather results to get observables

On a grid of 160 E's

- 10 E's per CE's
- speed up of about 16



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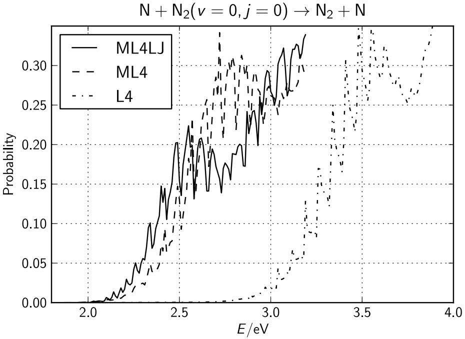
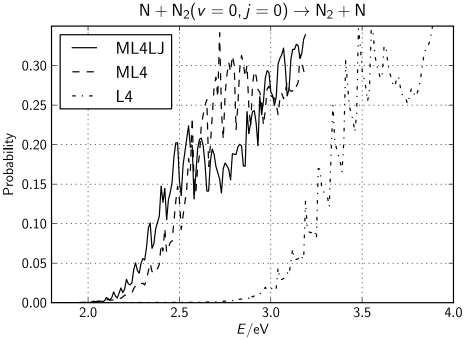
Detailed probabilities



Lowering the MEP

- reduces the threshold, preserves resonances

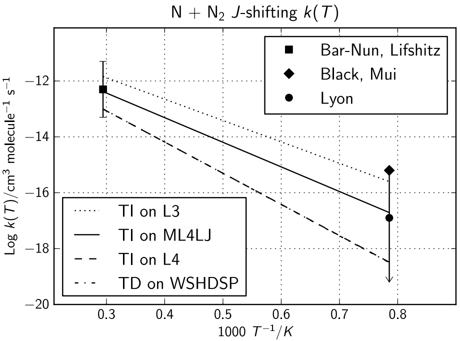
Detailed probabilities



The LR attractive tail

- does not affect the threshold, yet raises low-E P's

Thermal rate coefficients



J-shifting $k(T)$'s

- fairly agree with experimental values

Remarks

The LAGROBO formulation

- offers a flexible and reliable model potential

The ML4LJ PES

- includes accurate LR description
- better agrees with the experiment

However

- similar improvements could be obtained in other ways
- $k(T)$'s relying on the J-shifting approximation

Outline

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References

- D Wang, J R Stallcop, W M Huo, C E Dateo, D W Schwenke, H Partridge
  Quantal study of the exchange reaction for $N + N_2$ using an ab initio potential energy surface
  J Chem Phys 118, 2186-2189 (2003)
- E Garcia, A Saracibar, S Gómez Carrasco, A Laganà
  Modeling the global potential energy surface of the $N + N_2$ reaction from ab initio data
  Phys Chem Chem Phys 10, 2552-2558 (2008)
- F Pirani, S Brizi, L F Roncaratti, P Casavecchia, D Cappelletti, F Vecchiocattivi
  Beyond the Lennard-Jones model: a simple and accurate potential function probed by highly resolution scattering data useful for molecular dynamics simulations
  Phys Chem Chem Phys 10, 5489-5503 (2008)
- D Skouteris, J F Castillo, D E Manolopoulos:
  ABC: a quantum reactive scattering program
  Comp Phys Comm 133, 128-135 (2000)
- J M Bowman
  Reduced dimensionality theory of quantum reactive scattering
  J Phys Chem 95, 4960-4698 (1991)