

# **Dynamical and Kinetic Properties of the Na+HF Reaction on Two Different Potential Energy Surfaces**

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# Introduction

QuasiClassical Trajectories (QCT) is a well known term on reactive scattering dynamics that is used to show that before the collision process happens, the reactant molecule finds itself in a rovibrational state that corresponds to a quantum state. During the interactions and collisions among the nuclei are used only the Hamilton classical equations. After, when the reactive process is over, the resulting product molecule will also be found in rovibrational quantum state. The canonical variables used were the six internal coordinates and their conjugate momenta, the center of mass having been separated out. In this work, we have utilized a modified version of the Bunker's program.

Two potential energy surface (PES) for the gas-phase  $\text{Na}+\text{HF} \rightarrow \text{NaF}+\text{H}$  reaction were constructed using:

GSA, Generalized Simulating Annealing, and  
BO5, Bond Order 5.

To test this new PES, detailed dynamics properties calculations using two different Potential Energy Surface (PES):

GSA PES and BO5 PES, were obtained using the QCT method.

# QuasiClassical Trajectories Method

$$Q_i = q_{i+6} - q_{i+3}$$

$$Q_{i+3} = q_i - \frac{m_B q_{i+3} + m_C q_{i+6}}{m_B + m_C}$$

$$Q_{i+6} = \frac{m_A q_i + m_B q_{i+3} + m_C q_{i+6}}{m_A + m_B + m_C}$$

Using the Jacobi's coordinates, the Hamiltonian of the triatomic system is given by:

$$H(\{Q\}, \{P\}) = \sum_{i=1}^3 \left( \frac{P_i^2}{2\mathbf{m}_{BC}} + \frac{P_{i+3}^2}{2\mathbf{m}_{A,BC}} + \frac{P_{i+6}^2}{2M} \right) + V(r_1(\{Q\}), r_2(\{Q\}), r_3(\{Q\}))$$

where,

$$\mathbf{m}_{BC} = \frac{m_B m_C}{m_B + m_C} \quad \mathbf{m}_{A,BC} = \frac{m_A (m_B + m_C)}{m_A + m_B + m_C} \quad M = m_A + m_B + m_C$$

The temporal evolution of the system is determined resolving the Hamilton's equations

$$Q_i(t+h) = Q_i(t) + \int_t^{t+h} \dot{Q}_i dt \quad P_i(t+h) = P_i(t) + \int_t^{t+h} \dot{P}_i dt$$

The translational energy of product is given by

$$E'_{tr} = \frac{1}{2m_{C,AB}} \sum_{i=1}^3 (P'_{i+3})^2$$

The product internal energy ( $E'_{int}$ ) is obtained using the conservation of the energy

$$\begin{aligned} E_{tot} &= E_{tr}(A) + E_{int}(BC) + \Delta E \\ &= E'_{tr}(C) + E'_{int}(AB) \end{aligned}$$

- All the dynamic properties were calculated using Quasi-Classical Trajectories (QCT) and three dimensional quantum calculation, with total momentum angular equal to zero ( $J=0$ ).
- The cost function of the GSA fit was  $29.5127 \times 10^{-5}$  kcal/mol and the maximum and minimum difference among the *ab initio* energies  $E_{cal}$  and GSA fitting  $E_{gsa}$  were 0.8159 and 0.0037 kcal/mol, respectively.

# Generalized Simulated Annealing - GSA

1 - Fix the parameters  $q_v$ . Start, at time  $t=1$ , with arbitrary atomic coordinates and high enough value for  $T_{q_v}(1)$  (visiting temperature) and cool as follows:

$$T_{q,t} = T_o \frac{2^{q-1} - 1}{(1+t)^{q-1} - 1} \quad 1 < q < 3 \quad (1)$$

2 - Then randomly generate the new atomic coordinates  $p_{t+1}$  from  $x_t$  as given by the visiting probability distribution  $g_{q_v}(w)$

$$g_{q_v}(w) = \frac{\Gamma\left(\frac{1 - \frac{1}{2}(q_v - 1)}{q_v - 1}\right)}{\Gamma\left(\frac{1}{q_v - 1} - \frac{1}{2}\right)} \frac{[T_{q_v}(t)]^{1/q_v - 3}}{\left\{ 1 + (q_v - 1) \frac{p^2}{[T_{q_v}(t)]^{2/q_v - 3}} \right\}^{\frac{1}{q_v - 1} - \frac{1}{2}}} \quad (2)$$

as following:

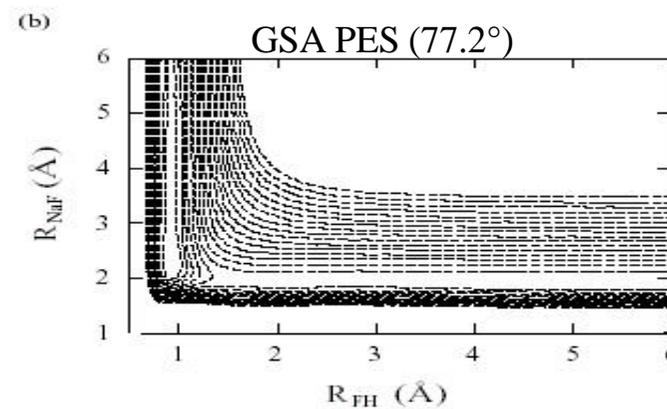
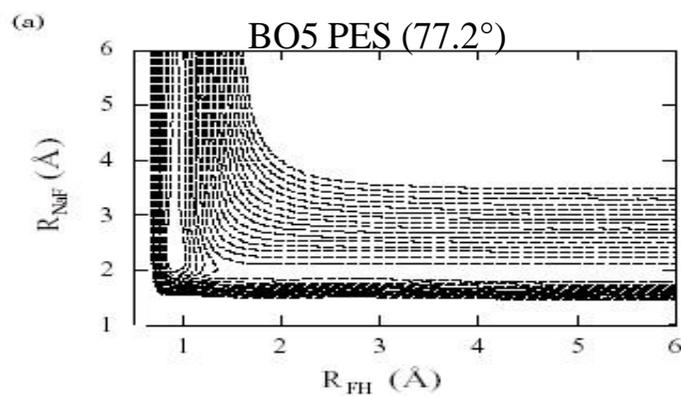
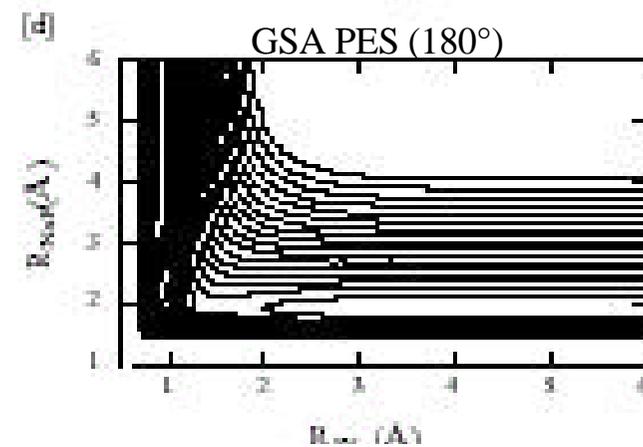
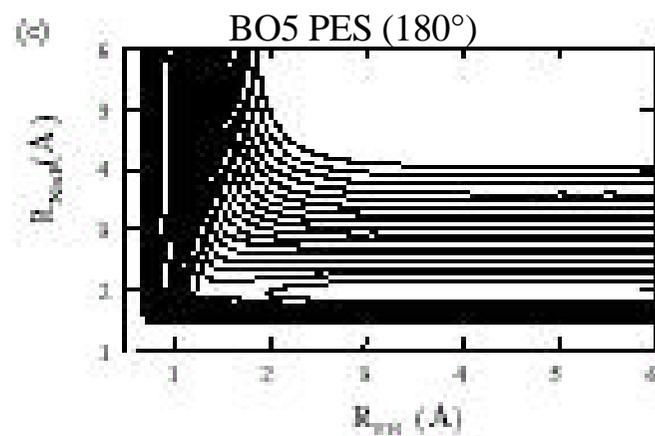
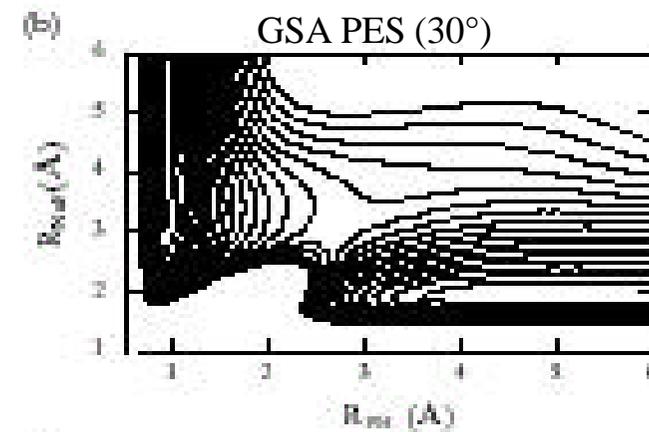
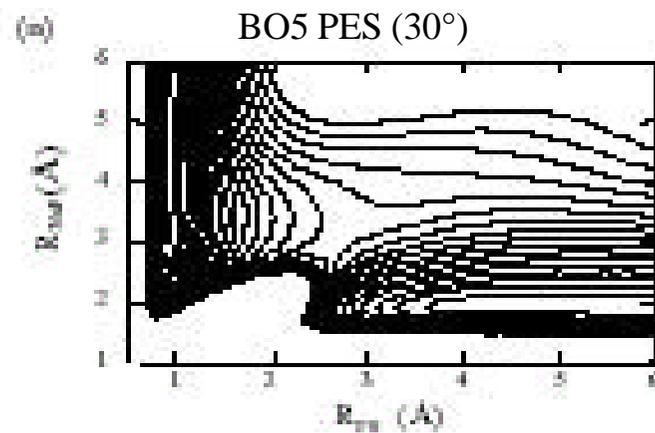
$$p_{t+1} = p_t + \mathbf{D}p_t \quad (3)$$

**3** - Then calculate the conformational energy  $E_{p_{t+1}}$  from the new molecular geometry by using a classical force field (THOR). The new energy value will be accepted or not according to the rule:

- if  $E(p_{t+1}) \leq E(p_t)$ , replace  $p_{t+1}$  by  $p_t$ ;
- if  $E(p_{t+1}) > E(p_t)$ , run a random number  $r \in 0,1$ ;
- if  $r > A_{acc}$  (acceptance probability) retain  $p_t$ ; otherwise, replace  $p_t$  by  $p_{t+1}$ .

**4** - Calculate the new temperature  $T_{qv}(t)$  using eq.(3) and go back to step 1 until the convergence of  $E(p_t)$  is reached within the desired precision.

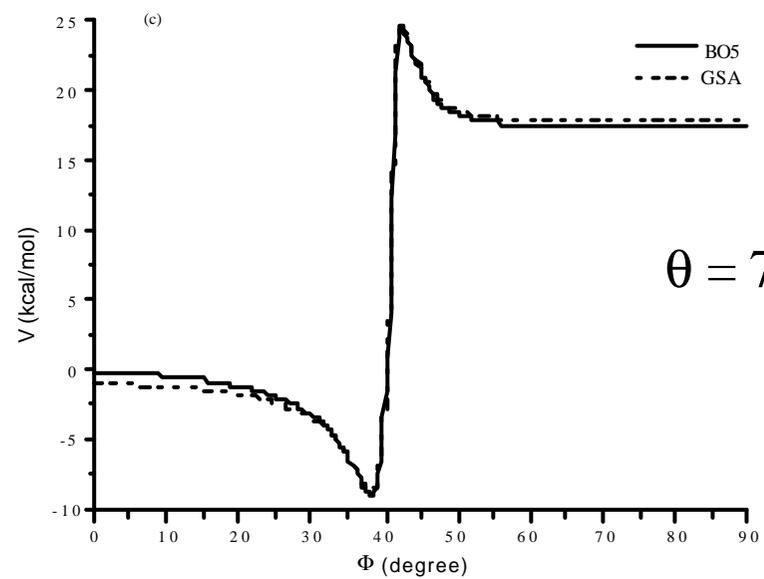
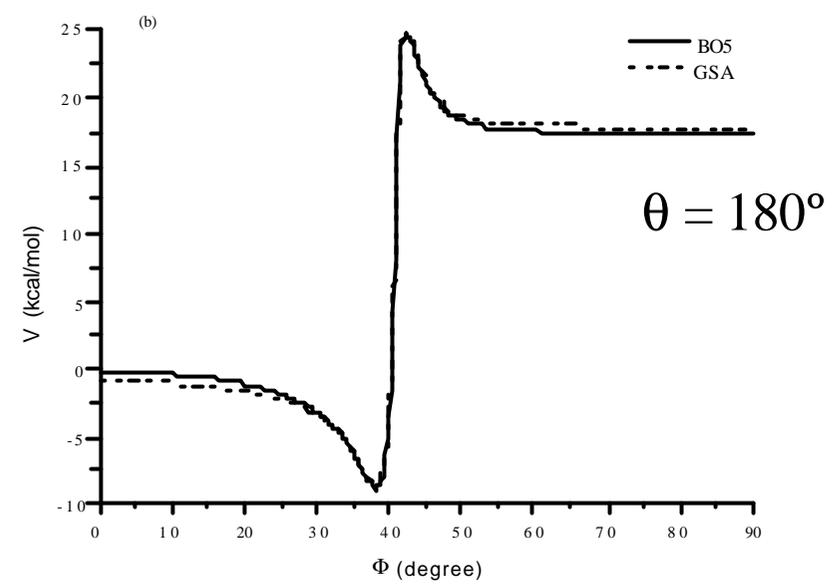
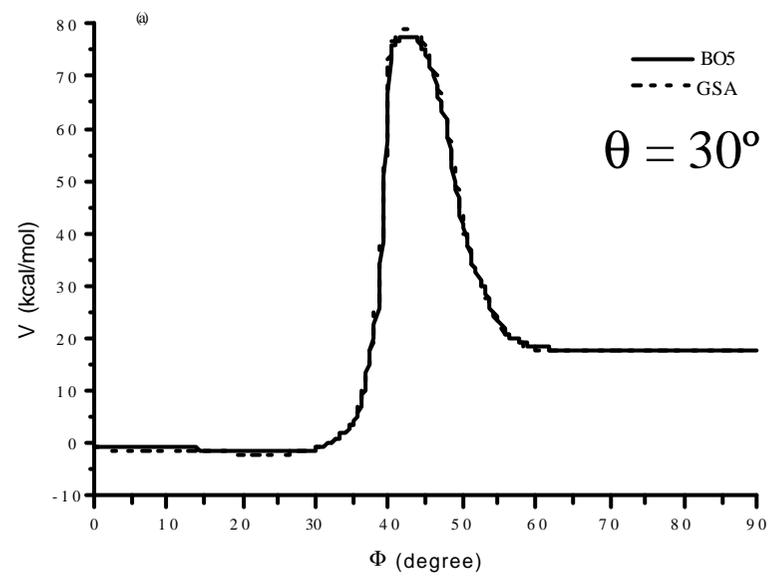
# Isoenergetic Contours of the Reaction



# Minimum Energy Path - MEP

Values of BO5 and GSA MEP for the  $\text{Na}+\text{HF}\rightarrow\text{NaF}+\text{H}$  reactive process at different angle  $\theta$  values

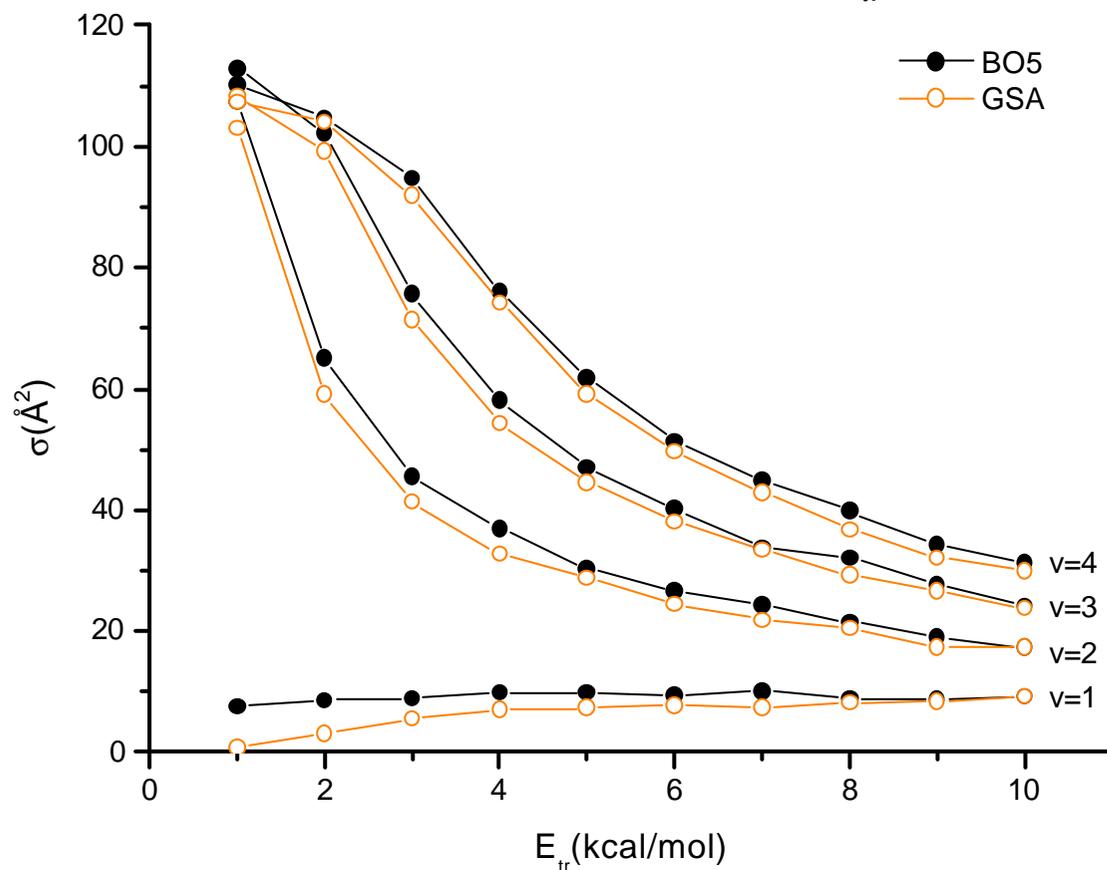
$\theta^\circ$	MEP	Reactant	Product	Barrier	Well
30	BO5	-0.2303	17.6297	77.6465	-1.7699
	GSA	-0.9266	17.9334	78.7675	-2.0017
60	BO5	-0.1978	17.5697	23.2639	-3.1729
	GSA	-0.9001	17.8983	23.3119	-3.0291
77.20	BO5	-0.1817	17.5518	18.6754	-6.1842
	GSA	-0.8869	17.8874	18.5825	-5.9927
90	BO5	-0.1724	17.5444	18.9925	-7.3662
	GSA	-0.8793	17.8829	19.4903	-7.1637
120	BO5	-0.1525	17.5371	22.7954	-8.3329
	GSA	-0.8681	17.8784	22.7551	-8.1231
150	BO5	-0.1525	17.5351	24.3159	-8.7335
	GSA	-0.8631	17.8772	24.3119	-8.4731
180	BO5	-0.1508	17.5347	24.7239	-8.8681
	GSA	-0.8617	17.8769	24.7062	-8.6105



# Cross-Section Reactive

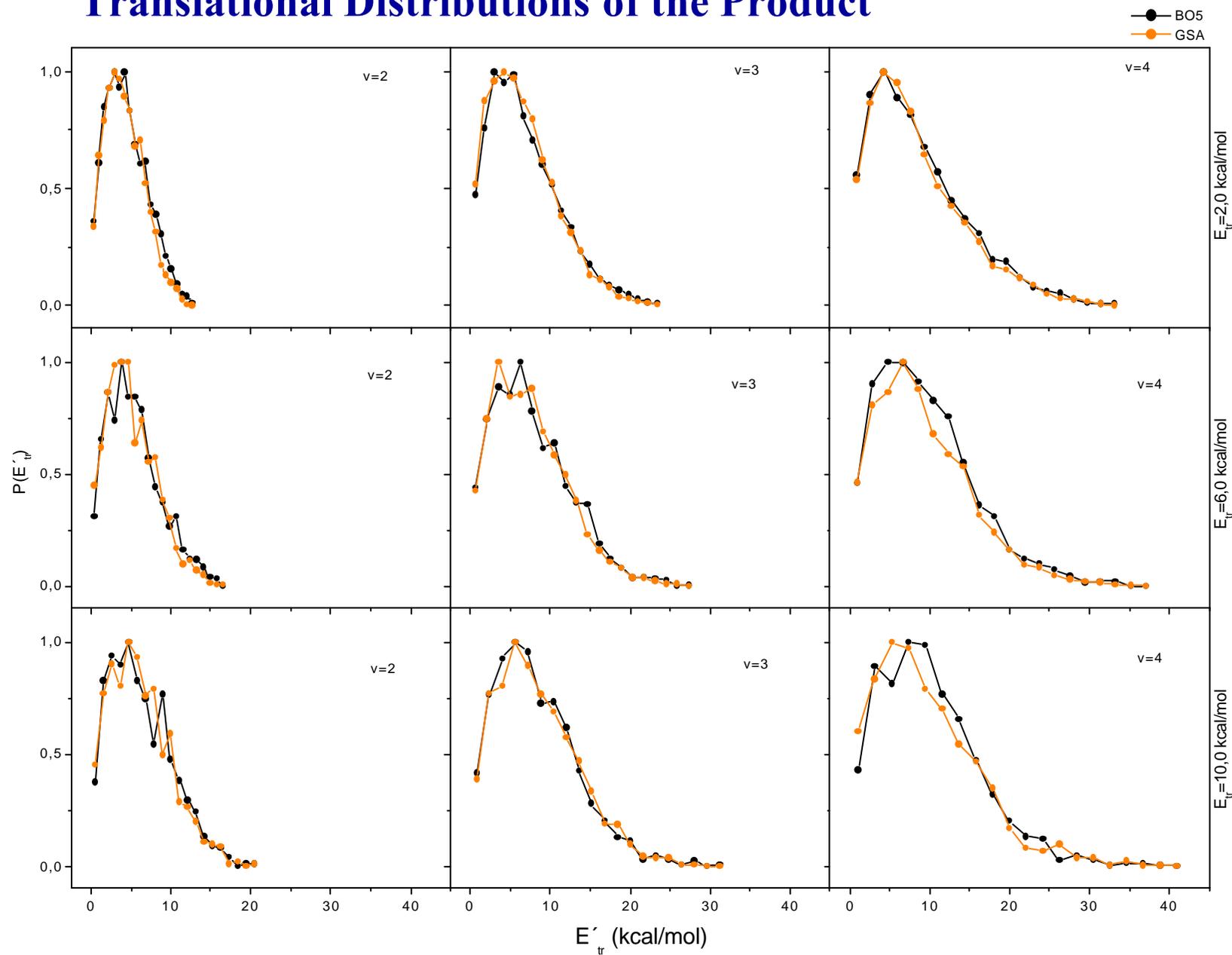
In this methodology the cross-section is given by equation

$$s_r(E_{tr}, \nu, j) \cong pb_{\max}^2 \frac{N_r(E_{tr}, \nu, j)}{N(E_{tr}, \nu, j)}$$

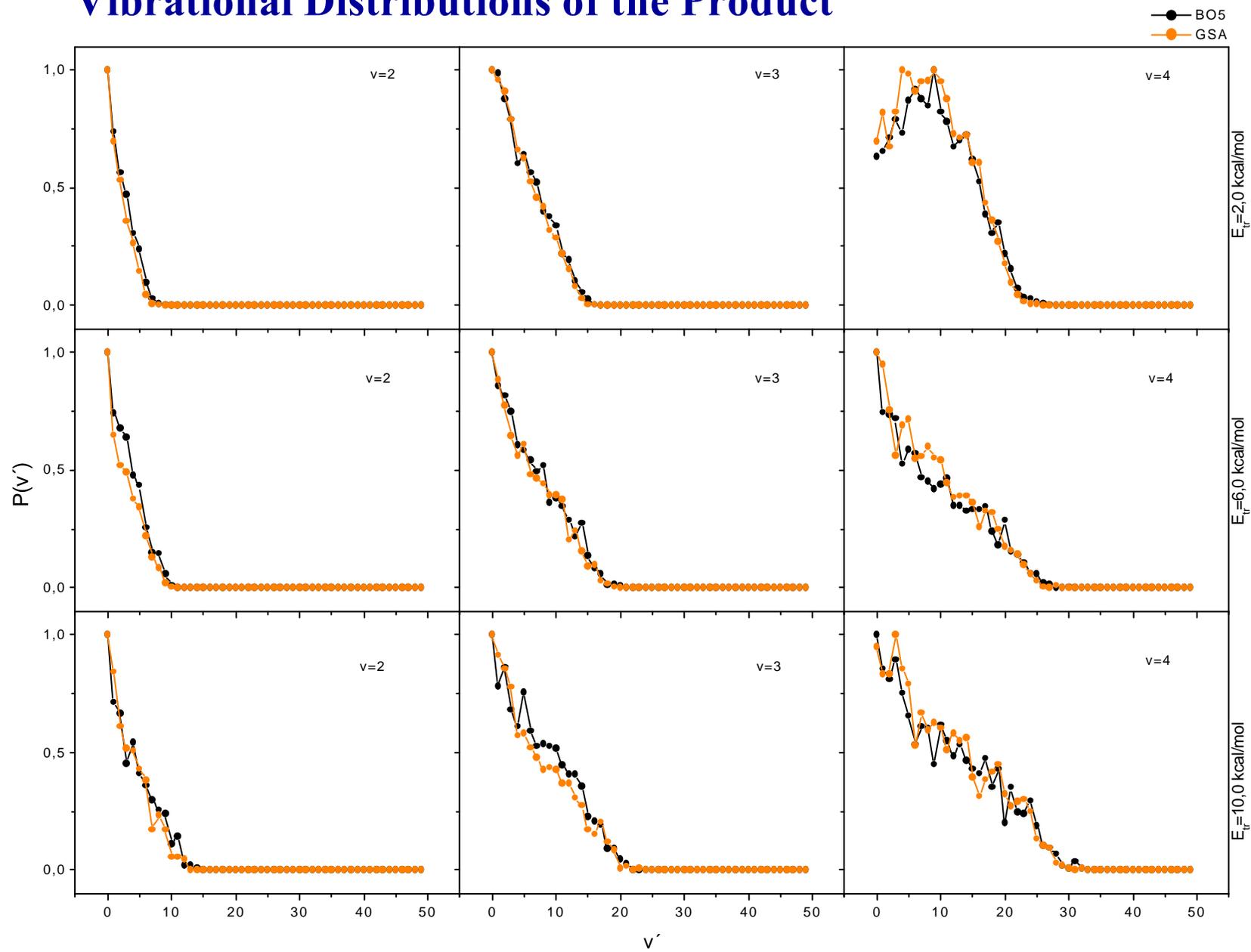


With the following error  $\longrightarrow \Delta s_r(E_{tr}, \nu, j) \cong pb_{\max}^2 \frac{N_r}{N} \sqrt{\frac{N - N_r}{NN_r}}$

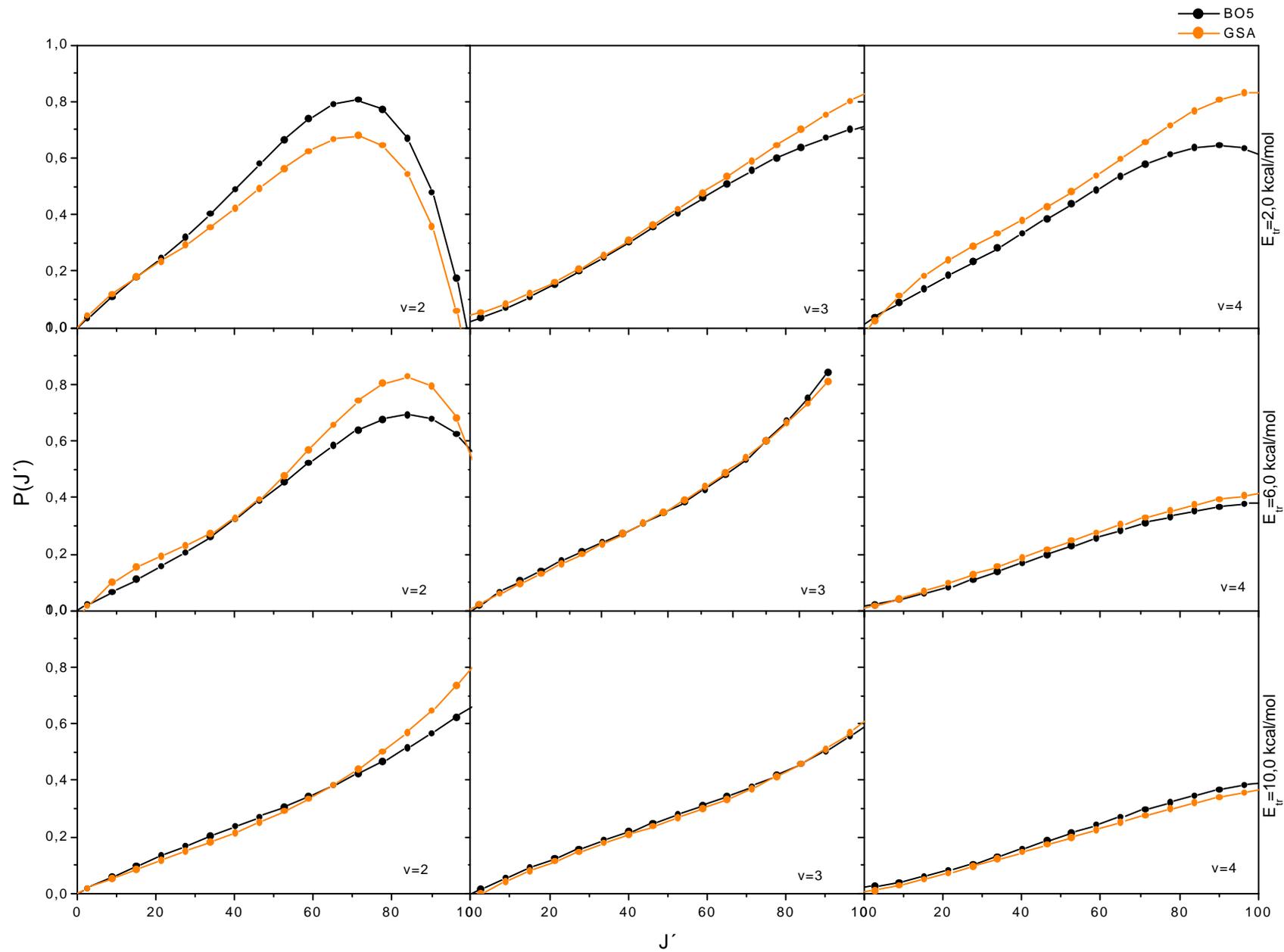
# Translational Distributions of the Product



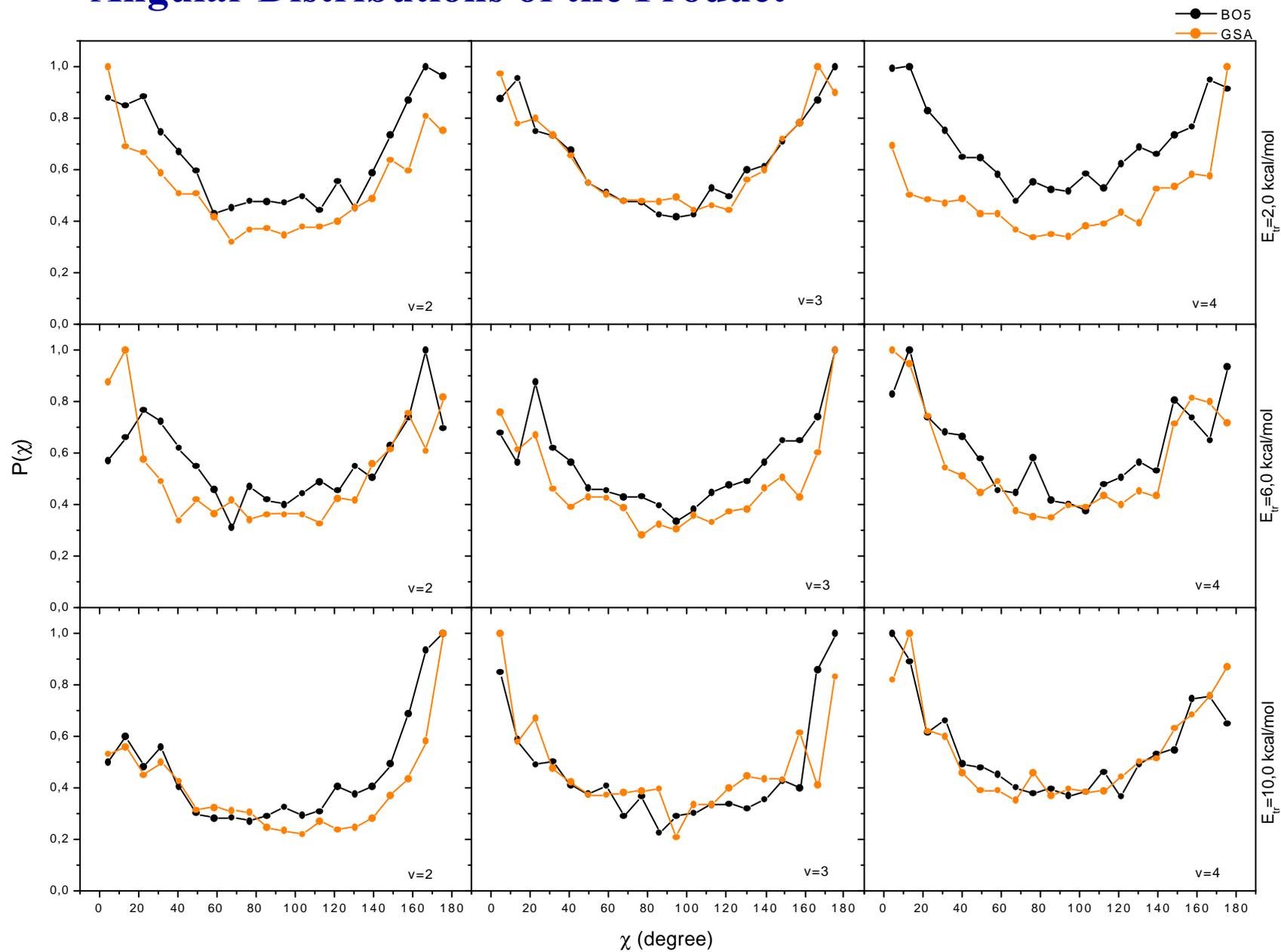
# Vibrational Distributions of the Product



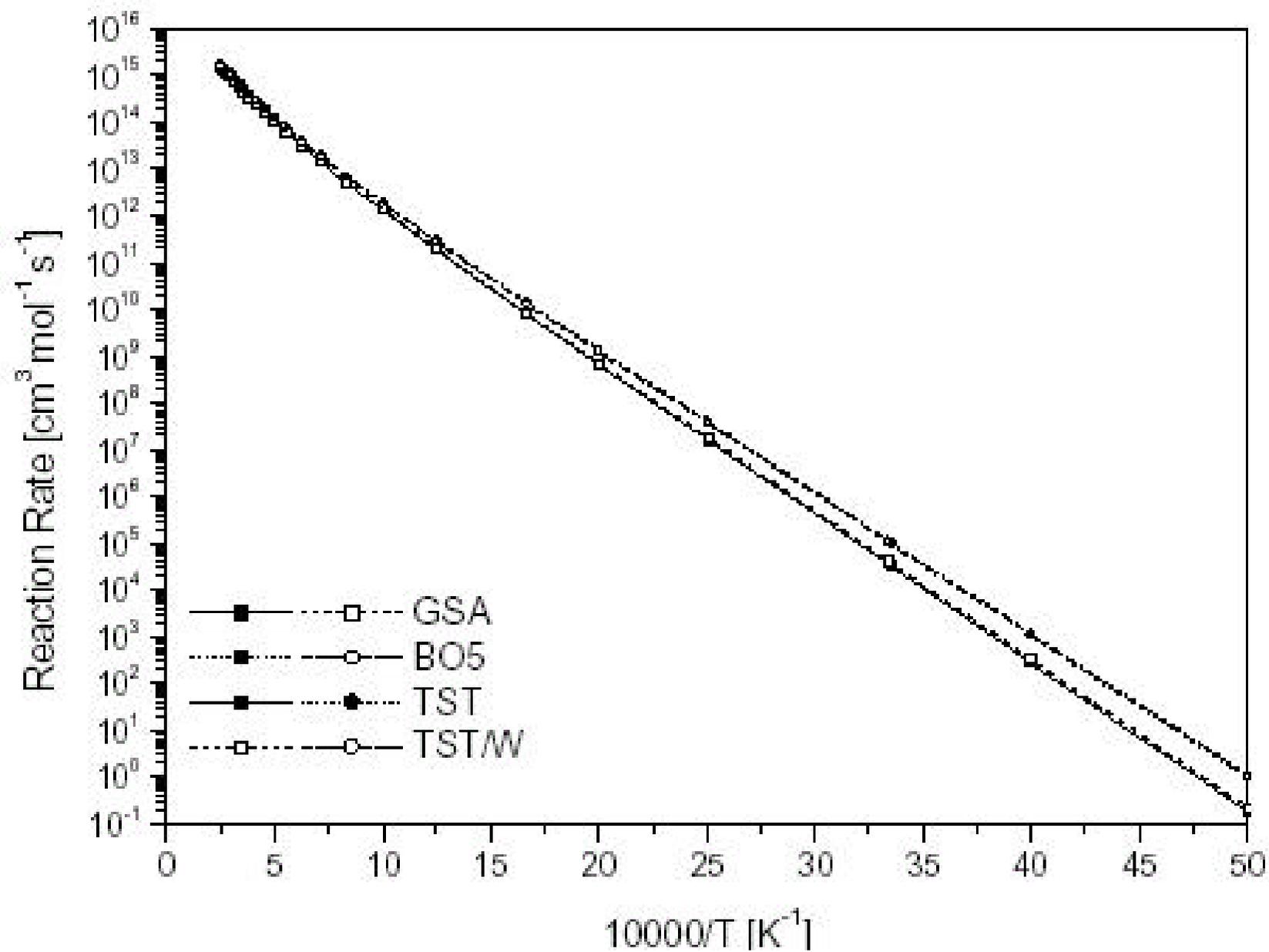
# Rotational Distributions of the Product



# Angular Distributions of the Product



# Reaction Rate of the Na+HF System



# Conclusion

At  $\nu=0$  the GSA PES is not reactive. The GSA cross-section (GSA CS) at  $\nu =1$  is fairly small. However, the reactivity begins only for the reactant vibrational state  $\nu =2$ . The GSA CS is large and it increases when the reactant vibrational energy and decreases with the collision energy increases excepting at  $\nu =1$ .

The GSA translational distributions have a maximum located at the same value of the recoil energy of the products while an increase of the reactant vibrational energy leads only to a widening of the distributions.

The vibrational distributions show a gradual widening of the width and a progressive shift of the maximum when the initial collisional and vibrational energy increases. The vibrational populations show a maximum to  $\nu'=0$  and they decrease while the vibrational states of product increase. This fact shows that these distributions are not inverted.

However, the rotational distributions are inverted showing a great rotational excitation of the products. The angular distributions show an equal probability to forward and backward.

From a comparison between both GSA and BO5 reaction rate one can see that them have the same behavior.

From a comparison among the GSA and BO5 reactivity properties it was possible to concluded that the quality and efficacy of the GSA PES are comparable to the best PES (BO5 PES) found in literature.

