

# Analytical Potential Energy Surface for the $Na + HF \rightarrow NaF + H$ reaction: Application of Conventional Transition-State Theory

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In this work we present the kinetic properties of the title reaction from calculation of the rate constant using conventional Transition State Theory (TST), for the temperature range of 200-4000K. For that, direct dynamic method was applied, which used information on equilibrium geometries, electronic structure energy, first and second energy derivative calculated *ab initio* along the Minimum Energy Path (MEP). The optimization geometry, for the reactants and products, frequencies and total energies of each stationary point were determined by using the GAUSSIAN98 program. The geometry of the transition state was determined combining data from electronic structure calculation and the best two  $Na + HF$  analytical Potential Energy Surfaces(PES) found in literature: Bond Order 5(BO5) and Generalized Simulating Annealing(GSA) PES.

Two potential energy surfaces (PES) for the gas-phase  $Na + HF \rightarrow NaF + H$  reaction were constructed using both GSA<sup>1</sup> and BO5 method.<sup>2</sup> Several dynamic properties for both PES were calculated using Quasi-Classical Trajectories (QCT)<sup>3</sup> and three dimensional quantum calculation, with total momentum angular equal to zero ( $J = 0$ ).<sup>4</sup> To complete these studies we decided to determine the kinetic properties of this reaction, calculating the rate constant using TST theory, for the temperature range of 200 – 4000 K. For this propose, we determined the geometry of the transition state combining data from both GSA and BO5 PES and from the electronic structure calculation.

The TST theory was developed in the 1930s and has since formed a framework for much of the discussion of rate processes. It is a model to determine the rate constants based in an interaction potential between reactant and products with a statistical representation of the dynamics.<sup>5-8</sup>

Considering a bimolecular reaction, such as:



where  $A$ ,  $B$  or  $C$  are atoms or group of atoms, the thermal rate constants is given by:

$$k_{TST} = \frac{k_B T}{h} \frac{Q_{X^\ddagger}}{Q_A Q_{BC}} \exp\left(-\frac{V_a^{G^\ddagger}}{RT}\right) \quad (2)$$

where  $Q_{X^\ddagger}$ ,  $Q_A$  and  $Q_{BC}$  are the partition functions of the transition state,  $X^\ddagger$  (saddle point), and

the reactant,  $A$  and  $BC$ , respectively,  $k_B$  Boltzmann constant,  $h$  Planck constant,  $T$  temperature and  $R$  universal gas constant,  $V_a^{G^\ddagger}$  is the barrier:

$$V_a^{G^\ddagger} = V^\ddagger + \varepsilon_{ZPE} \quad (3)$$

where  $V^\ddagger$  is the classical potential energy of the saddle point measured from the overall zero of energy and  $\varepsilon_{ZPE}$  is the harmonic zero-point energy (ZPE).

We have also included the transmission coefficient,  $\kappa(T)$ , in equation (2):

$$k_{TST}^W(T) = \kappa(T) k_{TST}(T) \quad (4)$$

where the transmission coefficient is used to account for the tunneling effect along the reaction coordinate. We have decided to estimate the transmission coefficient by using the Wigner correction<sup>5, 8, 9</sup> instead of some semiclassical tunneling approximation.<sup>8</sup> The Wigner correction for tunneling assumes a parabolic potential for the nuclear motion near the transition state and therefore cannot be considered as an accurate correction. The Wigner transmission coefficient is given by:

$$\kappa(T) = 1 + \frac{1}{24} \left| \frac{\hbar \omega^\ddagger}{k_B T} \right|^2 \quad (5)$$

where the imaginary frequency at the saddle point is denoted by  $\omega^\ddagger$ .

For more precise rate constants calculation the variational transition state theory should be used and

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Table 1

Geometrical parameters (bond distance in Angstroms and bond angle in degree) of reaction  $Na + HF \rightarrow NaF + H$ .

Basis	HF	NaF	TS		
			$R_{NaF}$	$R_{HF}$	$\theta_{NaFH}$
6 – 31G(d)	0.9340	1.9192	1.9779	1.6223	74.200
6 – 31G(d, p)	0.9213	1.9197	1.9380	1.9963	74.204
6 – 31 + G(d)	0.9340	1.9197	2.0827	1.4051	72.925
6 – 31 + G(d, p)	0.9265	1.9834	2.0636	1.4803	72.896
6 – 31 + G(2d, 2p)	0.9196	1.9835	2.0765	1.4509	75.247
6 – 31 + +G(d, p)	0.9265	1.9834	2.0519	1.5236	74.234
6 – 31 + +G(2d, 2p)	0.9196	1.9835	2.0600	1.4800	73.419
6 – 31 + +G(2df, 2pd)	0.9166	1.9869	1.9800	3.2000	63.180
6 – 31 + +G(3d, 3p)	0.9204	1.9829	2.0608	1.5042	73.091
6 – 311G(d, p)	0.9129	1.9443	1.9624	2.0123	89.971
6 – 311G(2d, 2p)	0.9146	1.9428	1.9560	2.1387	91.033
6 – 311 + +G(d, p)	0.9166	1.9908	2.0469	1.5879	75.087
6 – 311 + +G(2d, 2p)	0.9178	1.9831	2.0591	1.5134	75.436
6 – 311 + +G(3d, 3p)	0.9180	1.9817	2.0671	1.4820	74.805
Reference	0.917 <sup>11</sup>	1.926 <sup>12</sup>			

also semiclassical methods for the tunneling effect,<sup>8</sup> yet in this case more information about the potential energy surface is required, but it is not employed in the present work. A useful way to verify the importance using the variational transition state instead of conventional transition state is the curvature of the reaction path. A constraint on reaction-path curvature is provided by the skew angle:<sup>8</sup>

$$\beta = \text{ArcCos} \left[ \frac{m_A m_C}{(m_A + m_B)(m_B + m_C)} \right]^{1/2} \quad (6)$$

where  $m_A$ ,  $m_B$  and  $m_C$  are the masses of the  $A$ ,  $B$  and  $C$  moieties, respectively, for the schematic reaction shown by equation (1). Large reaction-path curvature is often encountered in the tunneling region in system with small skew angles, so the tunneling effects should be smaller.

To apply transition state theory to determine the  $Na + HF$  rate constants we must know the geometries, frequencies, and the potential energy for reactants and saddle point. These properties are obtained from accurate electronic structure calculation performed using the GAUSSIAN98 program.<sup>10</sup> In our case, we determined the reactants and saddle point geometry and frequencies of the  $Na + HF$  reaction using fourteen basis set and the same level of calculation (MP2) used to build both GSA and BO5 PES.

The table 1 shows the geometries computed for the  $HF$  reactant,  $NaF$  product and saddle point for all basis set considered in our calculation. The harmonic vibrational frequencies calculated for the  $HF$  reactant,  $NaF$  product and saddle point are

shown in table 2. The experimental data, geometries and frequencies, for the reactant,  $HF$ , and product,  $NaF$ , are also presented in tables 1 and 2, respectively. In table 3 is represented the total energies for reactants, products, saddle point, enthalpy and potential barrier for  $Na + HF$  reaction calculated considering the same basis set and also compares the enthalpy and potential barrier for the GSA and BO5 PES.

The figure 1(a) shows the reaction rate obtained considering conventional transition state theory,  $k(T)$ , calculated by main six different basis set, for the temperature range of 200 – 4000  $K$ . The reaction rate applying the transmission coefficient of Wigner,  $k(T)\kappa(T)$ , maintaining the same six different basis set and temperature range considered in figure 1(a), are shown in figure 1(b). These six different basis set were chosen based in the base size (2 cases) and also through the comparison with the experimental, BO5 and GSA PES reference data. Among these six base the best case is 6 – 31 + G(2d, 2p). The rate constants  $k(T)$  and  $k(T)\kappa(T)$ , considering the best basis set and for the temperature range of 200 – 4000  $K$ , is shown in the figure 1c. The main feature found in these figures was that the  $Na + HF$  rate constants is almost the same, for all temperature range. This fact happen because this reaction has a large skew angle (about 80.44°), so the tunneling effects is minimized.

In a future work, we intent to use the POLYRATE program<sup>13</sup> to determine the rate constant and the MEP of the  $Na + HF$  reaction. The MEP obtained using both GSA and BO5 PES, will be compared with the one from the POLYRATE program, and also the rate constant from our program.

Table 2

Harmonic vibrational frequencies ( $cm^{-1}$ ) for reactant, product and saddle point (transition state) of reaction  $Na + HF \rightarrow NaF + H$

Basis	HF	NaF	TS		
6 - 31G(d)	4039.624	582.3296	472.6025	564.3505	-317.744
6 - 31G(d, p)	4192.401	581.4609	270.0547	562.8661	-128.099
6 - 31 + G(d)	4039.624	581.4609	451.6340	736.3281	-1037.110
6 - 31 + G(d, p)	4118.644	510.5604	465.7802	693.5424	-680.369
6 - 31 + G(2d, 2p)	4115.005	527.2763	492.5818	728.3235	-662.134
6 - 31 + +G(d, p)	4118.687	510.5604	471.7921	596.8234	-495.774
6 - 31 + +G(2d, 2p)	4115.116	527.2763	496.0506	652.1679	-517.480
6 - 31 + +G(2df, 2pd)	4172.329	531.0527	128.9882	528.3954	-36.869
6 - 31 + +G(3d, 3p)	4100.177	524.9793	489.6297	629.3361	-494.362
6 - 311G(d, p)	4250.359	574.5961	226.0533	556.3137	-182.009
6 - 311G(2d, 2p)	4205.293	584.4667	193.2684	567.6268	-134.553
6 - 311 + +G(d, p)	4198.489	521.1158	482.6741	549.1089	-320.500
6 - 311 + +G(2d, 2p)	4165.780	525.5760	490.7662	615.4076	-463.726
6 - 311 + +G(3d, 3p)	4138.719	525.4788	492.8619	640.8783	-525.607
Reference	4138.73 <sup>11</sup>	536 <sup>12</sup>			

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Table 3

Energy of reactant, product and transition state in Hartree, potential barrier and reaction enthalpy in ( $kcal\ mol^{-1}$ ).

Basis	Na	HF	NaF	H	TS	Barrier	Enthalpy
6-31G(d)	-161.84144	-100.18217	-261.49121	-0.49823	-261.98785	18.13	16.47
6-31G(d,p)	-161.84144	-100.19464	-261.49121	-0.49823	-261.99016	23.99	24.07
6-31+G(d)	-161.84144	-100.18217	-261.49121	-0.49823	-262.01309	2.52	16.48
6-31+G(d,p)	-161.84144	-100.21581	-261.52158	-0.49823	-262.01763	20.61	18.31
6-31+G(2d,2p)	-161.84188	-100.25333	-261.55890	-0.49823	-262.05720	19.70	18.74
6-31++G(d,p)	-161.84144	-100.21592	-261.52158	-0.49880	-262.01901	19.68	18.03
6-31++G(2d,2p)	-161.84188	-100.25339	-261.55890	-0.49880	-262.05823	18.98	18.42
6-31++G(2df,2pd)	-161.84188	-100.28011	-261.58043	-0.49927	-262.08003	21.29	21.32
6-31++G(3d,3p)	-161.84204	-100.26379	-261.56897	-0.49880	-262.06882	18.94	18.75
6-311G(d,p)	-161.84593	-100.26722	-261.56321	-0.49981	-262.06331	26.29	26.17
6-311G(2d,2p)	-161.84593	-100.29292	-261.59713	-0.49981	-262.09767	20.89	21.10
6-311++G(d,p)	-161.84598	-100.27889	-261.58249	-0.49982	-262.08160	22.61	21.43
6-311++G(2d,2p)	-161.84598	-100.30306	-261.60922	-0.49982	-262.10981	20.23	18.87
6-311++G(3d,3p)	-161.84598	-100.30743	-261.61608	-0.49982	-262.11652	18.83	18.35
GSA <sup>1</sup>						18.58	17.89
BO5 <sup>2</sup>						18.67	17.55

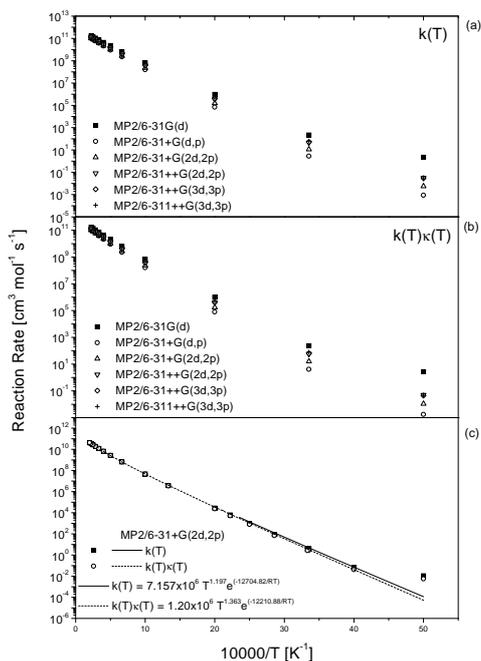


Figure 1. The figures 1(a) and 1(b) show, respectively, the  $k(T)$  and  $k(T)\kappa(T)$  rate constants plotted as a function of reciprocal temperature ( $K$ ) in the range of 200 – 4000K, for reaction  $Na + HF \rightarrow NaF + H$ , obtained using six basis set. The figure 1(c) shows the same plot of figures 1a and 1b, but considering the best basis set 6-31+G(2d,2p).