1 Introduction

This paper is outlined as follows: In Sec. 2 we introduce Chesnavich's Hamiltonian model for ion-molecule reaction and discuss the dynamical mechanism underlying roaming in terms of families of unstable periodic orbits and their associated invariant manifolds.

2 Chesnavich's Model and Roaming

2.1 Chesnavich's Model Hamiltonian

The CH_4^+ model due to Chesnavich is a 2 degree of freedom Hamiltonian system comprised of a rigid CH_3^+ molecule (core) and a mobile H atom [1]. The system Hamiltonian is [2]

$$H(r,\theta,p_r,p_\theta) = \frac{1}{2}\frac{p_r^2}{\mu} + \frac{1}{2}p_\theta^2\left(\frac{1}{\mu r^2} + \frac{1}{I_{CH_3}}\right) + U(r,\theta), \tag{1}$$

where (r,θ,ϕ) are polar coordinates describing the position of the H-atom in a body-fixed frame attached to the CH_3^+ core (the coordinate ϕ is ignorable in this model). The reduced mass of the system is given by the expression $\mu = \frac{m_{CH_3}m_H}{m_{CH_3}+m_H}$, where $m_H = 1.007825$ u and $m_{CH_3} = 3m_H + 12.0$ u, and the moment of inertia of the rigid body CH_3^+ has the value $I_{CH_3} = 2.373409$ uÅ^2.

The potential energy function $U(r,\theta)$ is made up of a radial long range potential energy term U_{CH} and a short range potential U_{coup} that models the short range anisotropy of the rigid CH_3^+ core:

$$U(r,\theta) = U_{CH}(r) + U_{coup}(r,\theta). \tag{2}$$

The topography of the potential energy surface is characterised by two deep wells that correspond to the bound CH_4^+, two areas of high potential and a flat area to the outside of these features as shown in Fig. 1.

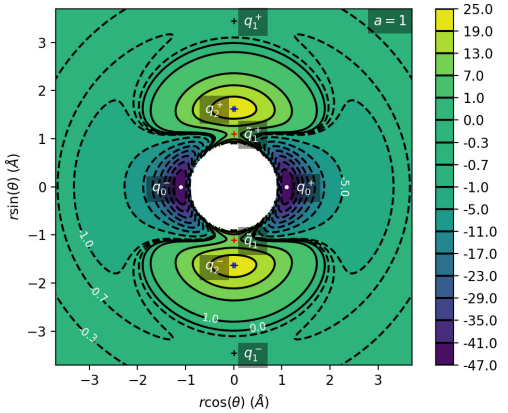

Figure 1: Contour plot of Chesnavich's potential energy surface U for $a = 1$. Dashed lines correspond to $U < 0$, solid lines correspond to $U \geq 0$. Contours correspond to values of potential shown on the colorbar to the right, with some values indicated in the plot. This figure is from [4].

The long range potential has the form:

$$U_{CH}(r) = \frac{D_e}{c_1 - 6}\left(2(3-c_2)e^{c_1(1-x)} - (4c_2 - c_1c_2 + c_1)\,x^{-6} - (c_1-6)c_2x^{-4}\right), \tag{3}$$

where $x = \frac{r}{r_e}$ and we take the parameter values as in the original work [1]. The short range hindered rotor potential U_{coup} has the form:

$$U_{coup}(r,\theta) = \frac{U_e e^{-a(r-r_e)^2}}{2}(1-\cos 2\theta), \tag{4}$$

where U_e is the equilibrium barrier height. The distance at which the transition occurs from rotation to vibration is determined by the parameter a (in Å^{-2}). Various values of a have been considered in previous works. In particular, $a = 1$ [1, 6, 5, 3], $a = 4$ [1, 6] and a range of values $0.7 \leq a \leq 8$. [4]

The CH_3^+ core is a symmetric top in Chesnavich's model. Although the range of the coordinate θ is $0 \leq \theta \leq \pi$, in the planar (zero overall angular momentum) version of the model the range of θ is extended to $0 \leq \theta \leq 2\pi$, and the potential has a four-fold symmetry:

$$U(r,\theta) = U(r,-\theta) = U(r,\pi-\theta) = U(r,\pi+\theta). \tag{5}$$

The potential admits four pairs of equilibrium points pairwise related by symmetry (5), as listed in Tab. 1 and shown in Fig. 1.

Energy (kcal mol^{-1})	r (Å)	θ (radians)	Significance	Label
-47	1.1	0	potential well	q_0^+
-0.63	3.45	$\pi/2$	isomerisation saddle	q_1^+
8	1.1	$\pi/2$	isomerisation saddle	$\widetilde{q}_1^+$
22.27	1.63	$\pi/2$	local maximum	q_2^+

Table 1: Equilibrium points of the potential $U(r,\theta)$.

References

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