Fitting Potential Energy Surfaces For a Range of Internuclear Separations to Account for Vibrational Motion in Scattering Calculations

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Abstract

This SOAR project is a continuation of an ongoing research effort to model changes in quantum rotational energy levels (j) of NaK molecules that undergo collisions with helium (He). Experimental results at Lehigh University showed a propensity for even j transitions. Previous theoretical research on this project completed at Lehigh University, did not account for vibration of the NaK molecule. These calculations demonstrated a need for including the NaK vibrational motion. The next stage included an approximation using weighted averages of multiple Potential Energy Surfaces (PES's) to map the He interaction with an NaK molecule over the range of internuclear separations of Na and K corresponding to the vibrational state. This yielded results that qualitatively matched the experimental observations and made it clear that vibration played a crucial role in the interactions. The goal of this SOAR project was to prepare to include vibrational motion of NaK into scattering calculations by fitting PES's at a range of NaK separations with continuous functions. Each individual PES was fit with a linear combination of functions. The coefficients of these functions for each discrete value of internuclear separation were interpolated. These new fits of the PES's allow for scattering calculations with vibrational effects included.

Introduction

This project focuses on the system of particles depicted in Fig. 1 where Na is bonded with K in a molecule and He is on a collision trajectory with the NaK. This is a Jacobian coordinate system originating from the Center of Mass of the NaK where R_d is the radial distance of He from the origin, r_v is the internuclear separation of the NaK and θ is the angle between R_d and r_v.
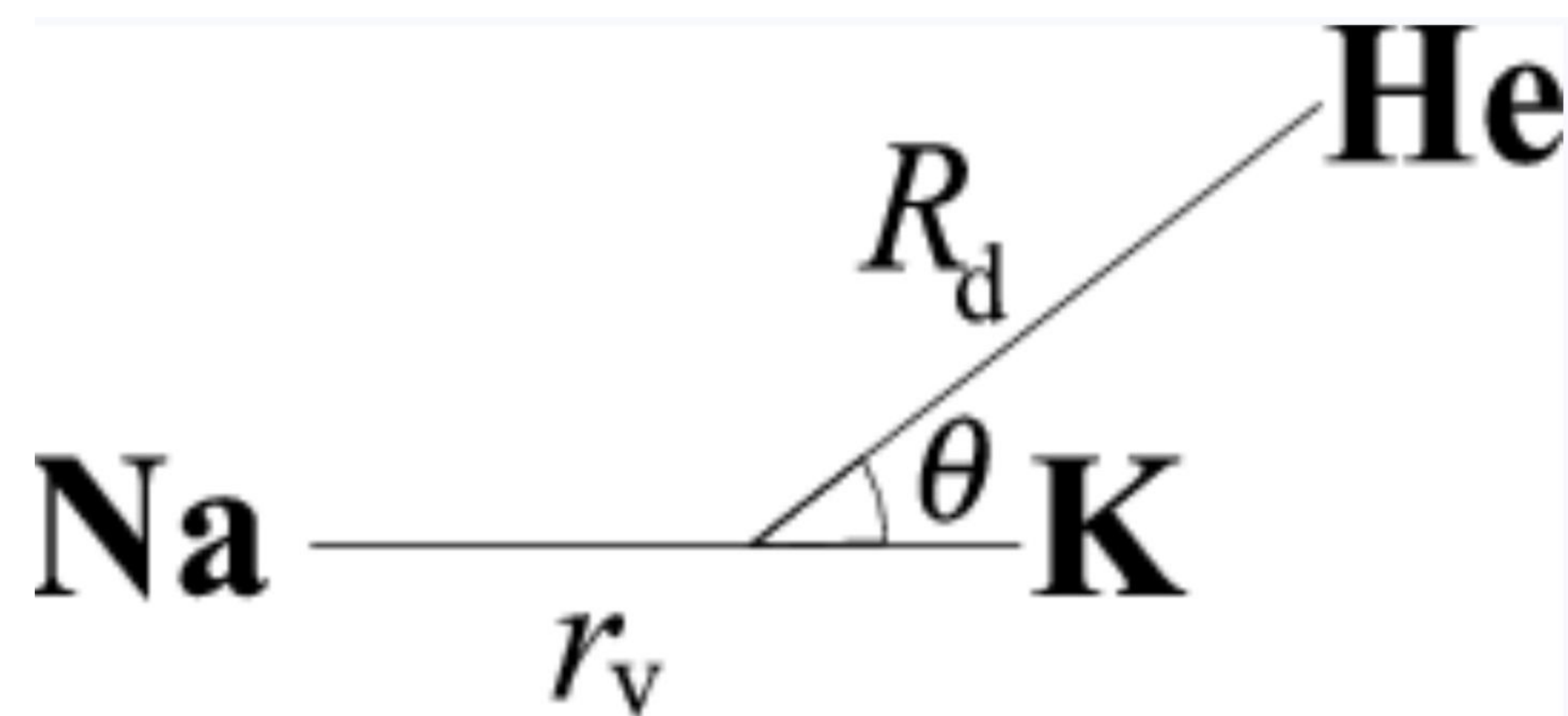
Fig. 1 Jacobian Coordinate System with parameters R_d, r_v and θ.

Objective

Initial research was conducted approximating the NaK as a rigid rotor meaning by fixing the coordinate r_v at the NaK equilibrium distance. Following this method, a weighted average over the molecule's vibrational separation was implemented which supported that vibration was a crucial part of the behavior of these interactions.

The objective for the next phase of this project is to develop a method to incorporate the vibrational motion of the NaK in the MCTDH scattering calculations.

Experimental Background & Motivation

Researchers at Lehigh University were attempting to map rotational quantum energy levels, j, of NaK, using cross laser spectroscopy inside a heat pipe. Helium was used as a buffer gas to prevent the NaK from clouding the windows of the oven. It was expected that NaK molecules starting in j rotational state that collided with He would be most likely to change rotational states to the next nearest j' state followed by transitions to the next j' state, etc. However the data showed an higher probability of $j \rightarrow j'$ being even versus being odd, as seen in Fig. 2.
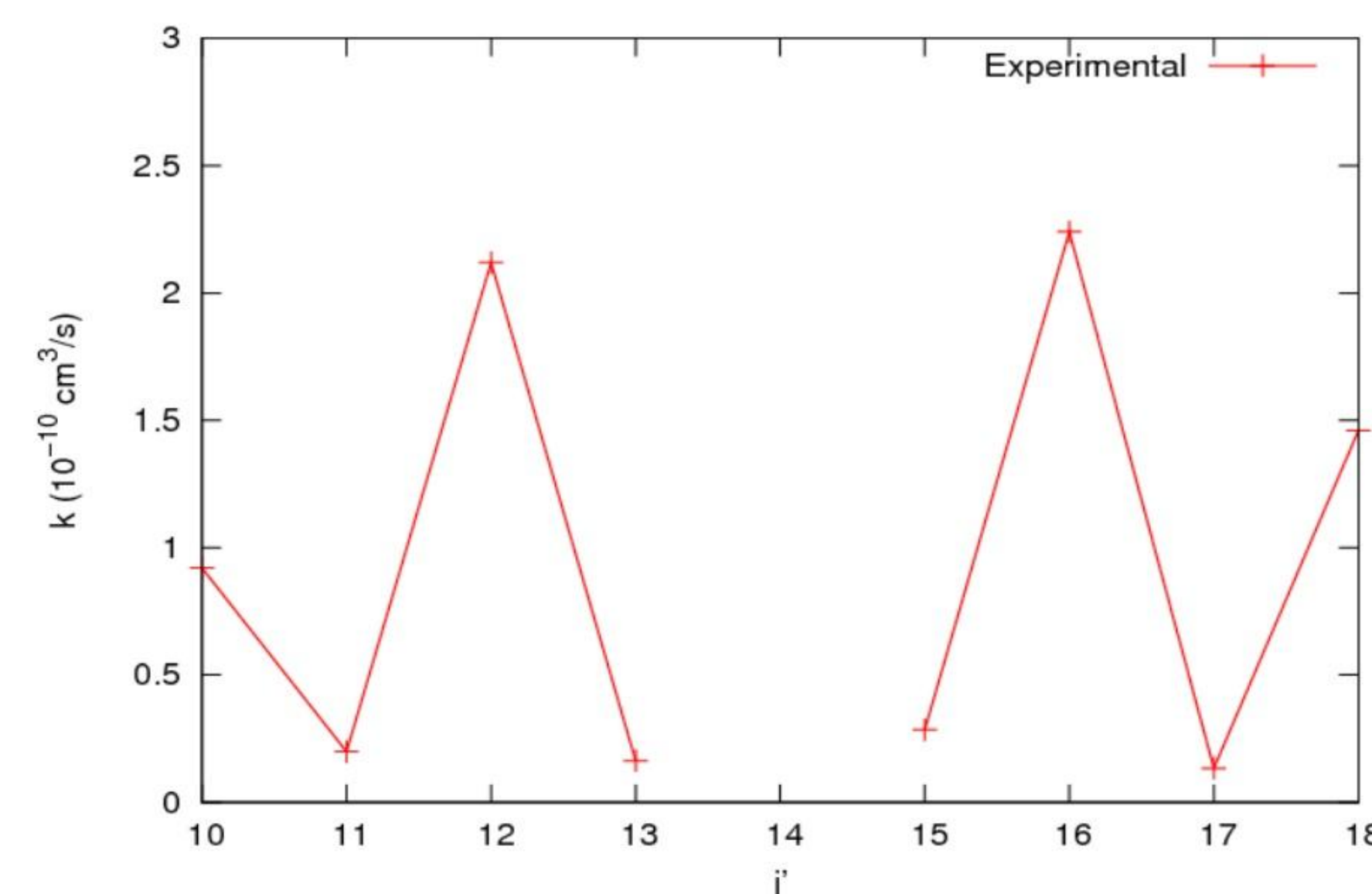
Fig. 2 Rate constant (k) of NaK transitioning from the inital rotational state j=14 to a final state j'. Most NaK remains in the j=14 so this result is omitted from the figure.

Theoretical Background: Wavepacket Method and PES Modeling

Dynamic scattering calculations were performed using the Multi-Channel Time Dependent Hartree MCTDH program. The scattering method involves propagating a wavepacket representing the He atom toward a Potential Energy Surface (PES) which represents the NaK. The General Atomic and Molecular Electronic Structure System program (GAMESS) was used to calculate the potential energy of the He interaction with the NAK over a grid of positions of R_d and theta, similar to that shown in Fig. 3. The original work fixed the R_d value at the NaK equilibrium position. Then to create the final PES, the PES could was represented in MCTDH as the separable function:

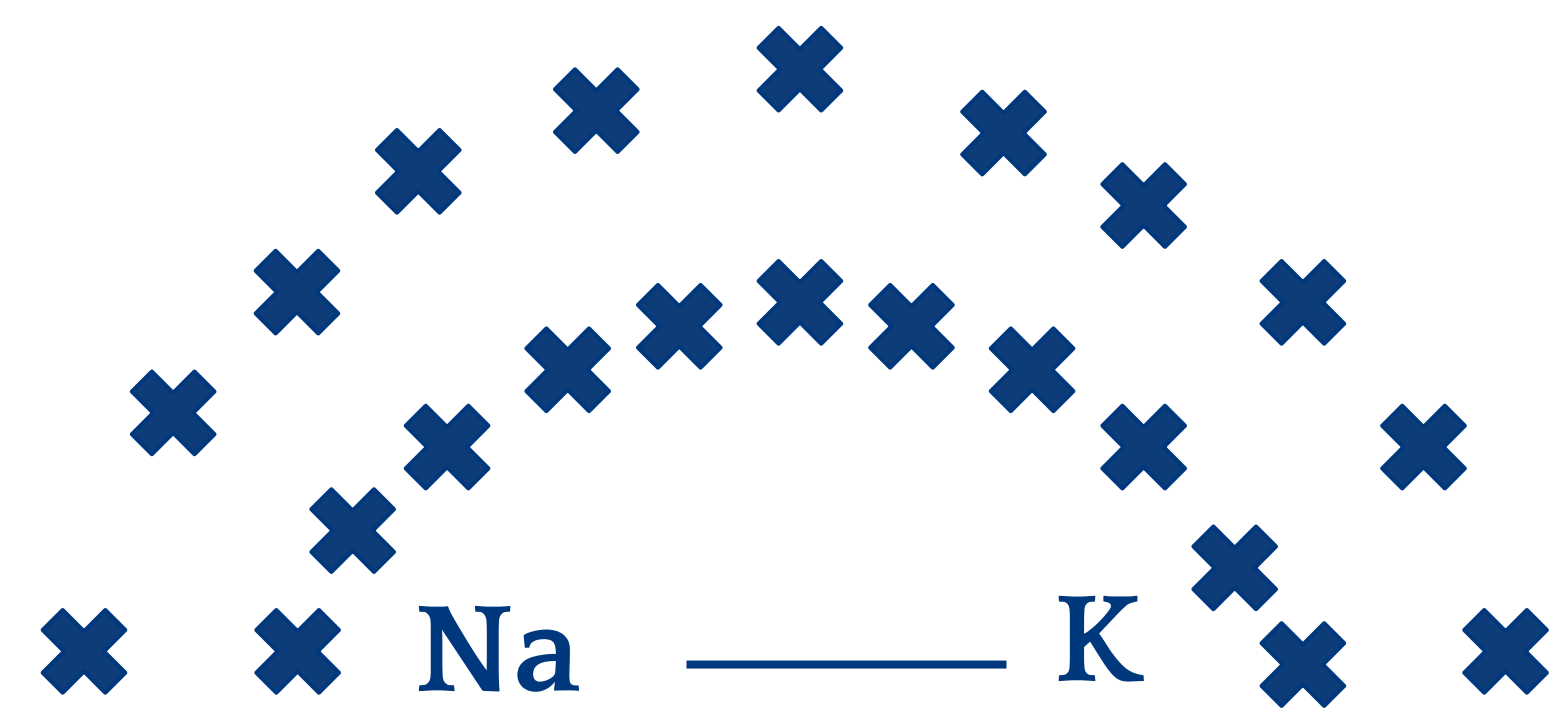$$V(R_d, \theta) = \sum v_\lambda(R_d)P_\lambda(\cos\theta)$$

Fig. 3 Example diagram of GAMESS point calculations.

Rigid Rotor PES & Initial Results
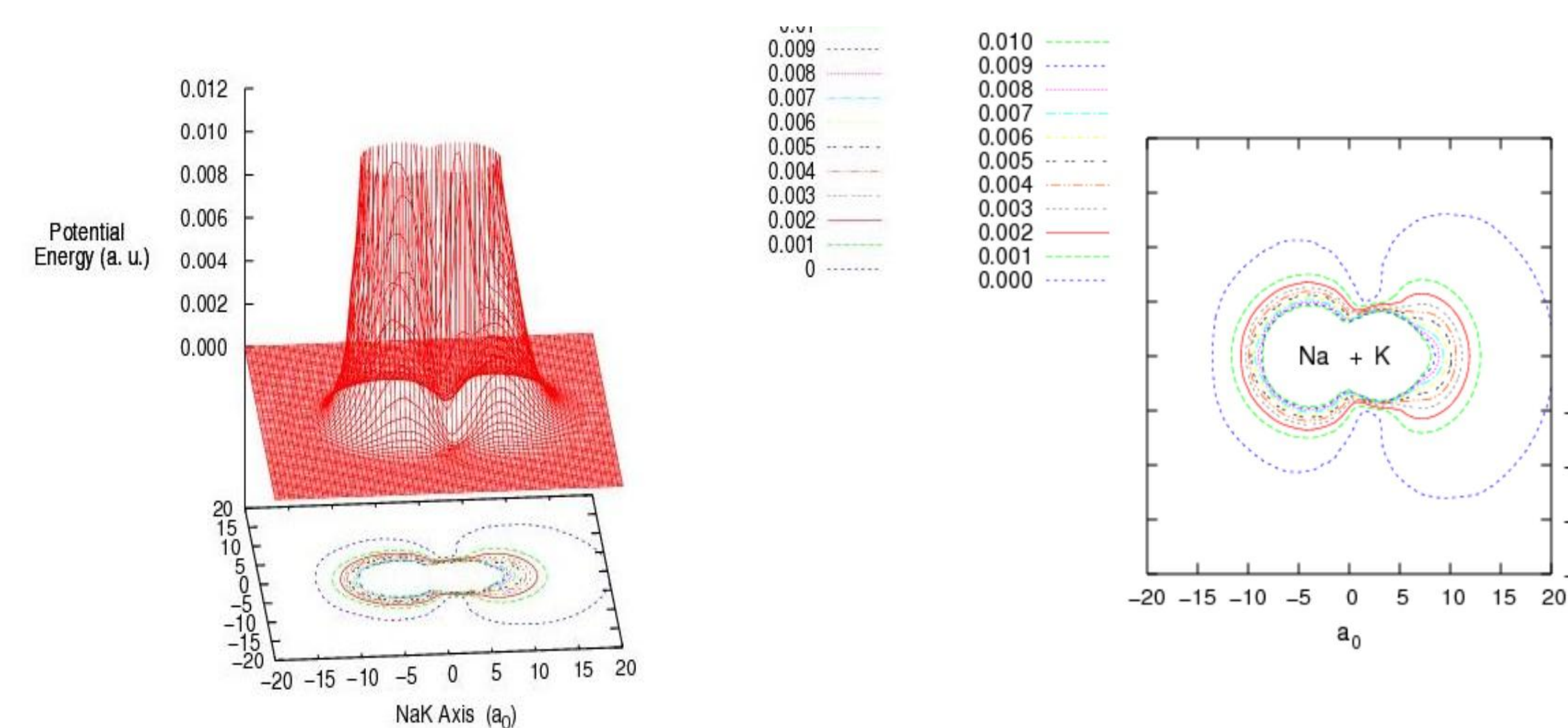
The final interpolated PES is shown in Fig. 4.

Fig. 4 Side by side example of 3D PES and a 2D projection.

This Rigid Rotor PES was used in MCTDH to run scattering calculations. From these, the probability of $j \rightarrow j'$ transitions could be calculation. In Fig. 5 we see the results plotted alongside the experimental data.
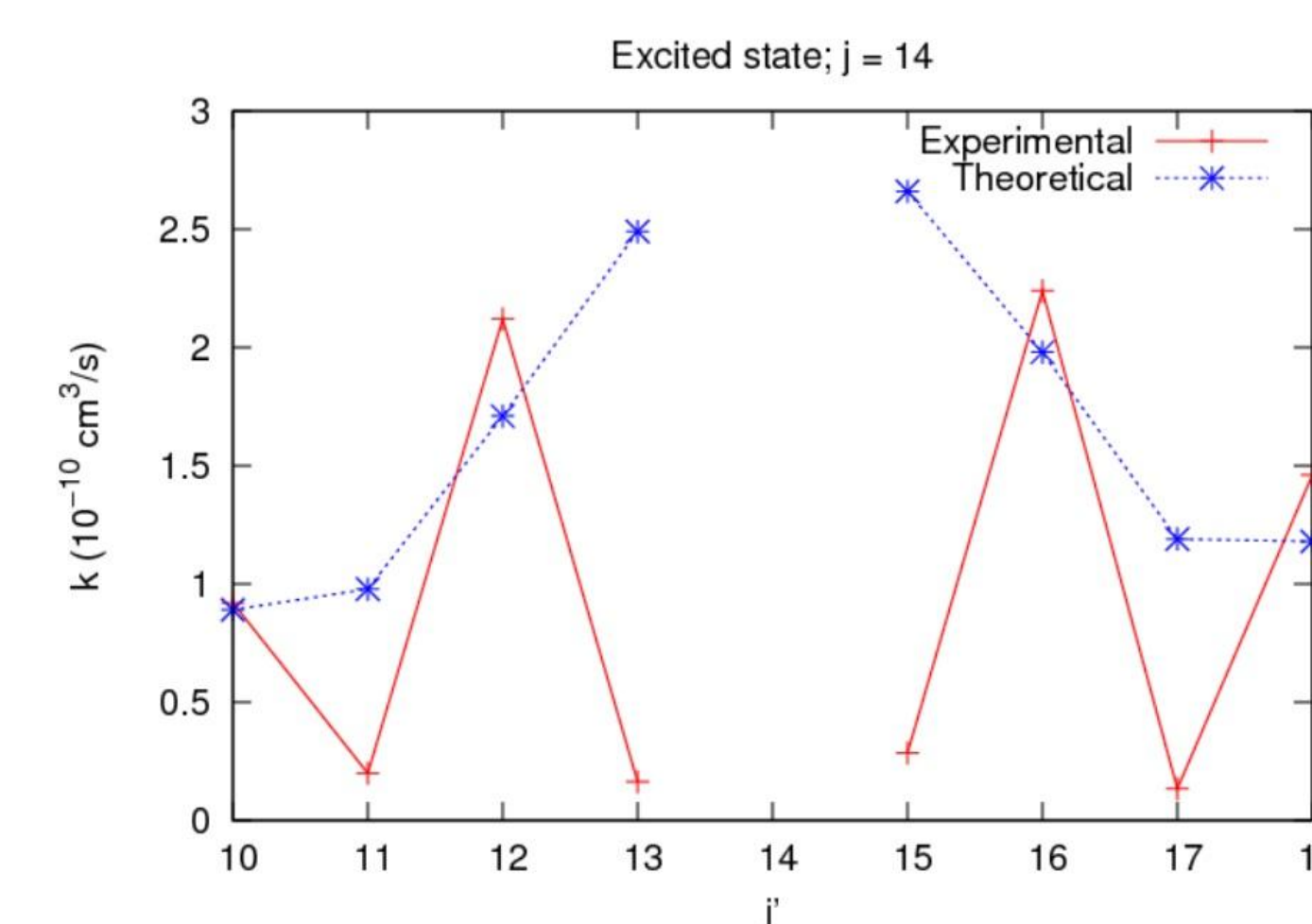
Fig. 5 Results of the rigid rotor model showing the rate constant of j =14 $\rightarrow j'$ transitions vs j' plotted along with experimental results.

Weighted Average Approximation of Vibration Effects

The results of the rigid rotor calculations lead to the conclusion that NaK's vibration has greater significance in the interaction with He than initially hypothesized. As a first step to accounting for the vibration, a weighted average of discrete PES was made over a range of r_v separations. The weighting scheme was determined using the probability density for the NaK separation was determined using the square of the vibrational wavefunction for vibrational level v = 16, which can be seen in Fig 6.
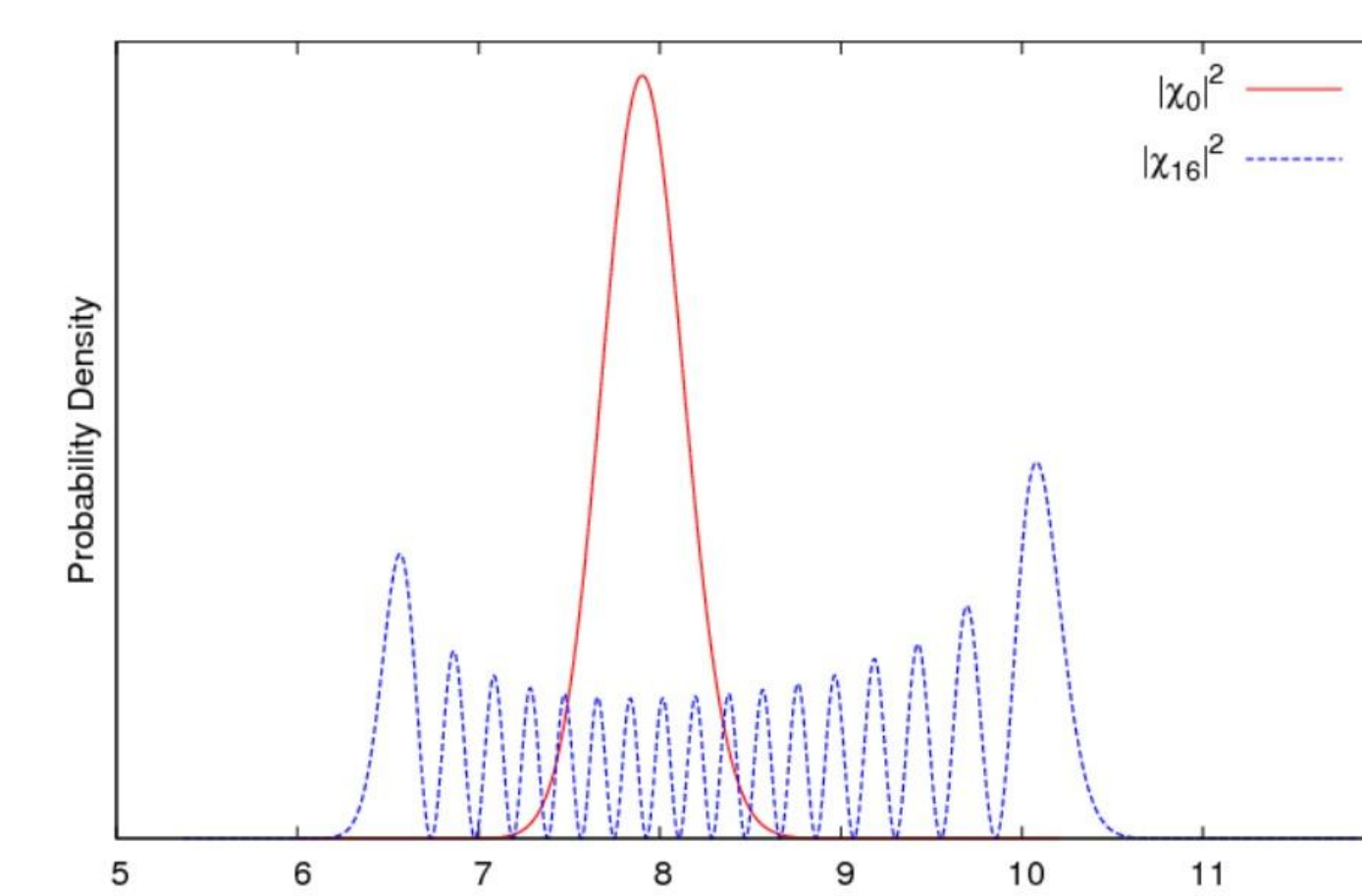
Fig. 6 The probability densities of the vibrational states v = 0 and v = 16 as a function of r_v.

Our Work: Polynomial and tspliner Fitting

The improved qualitative match of the weighted average approximation confirmed that vibration plays a crucial role in the changes of rotational state caused by the collisions. To incorporate the r_v dependence into the scattering calculations, we must interpolate the coefficients $v(R_d)$ over values of vibrational separation r_v. Fig 7 shows initial efforts to fit these coefficients manually with the product of a polynomial and an exponential damping term.
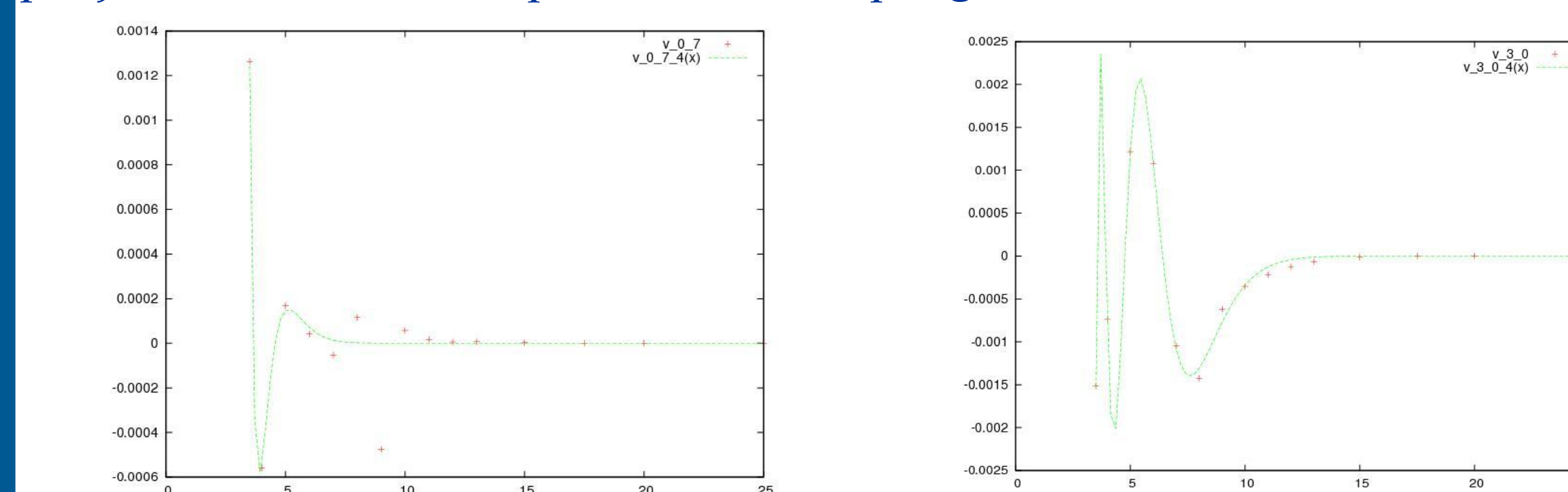
Fig. 7 Examples of manual polynomial fits of Taylor expansion coefficients as a function of R_d

These manual fittings had shortcomings such as not fitting all the data points (left plot) or matching the points by including ringing that did not match the functional behavior (right plot). Other functional forms were tried as well including Legendre Polynomials and Bessel functions.

Manual fitting was a time consuming process and that did not yielding the results we wanted. To improve the efficiency of fitting the coefficients we utilized a program called tspliner provided by Dr. Hickman at Lehigh University. Fig. 8 shows the much improved fits made using the tspliner program.
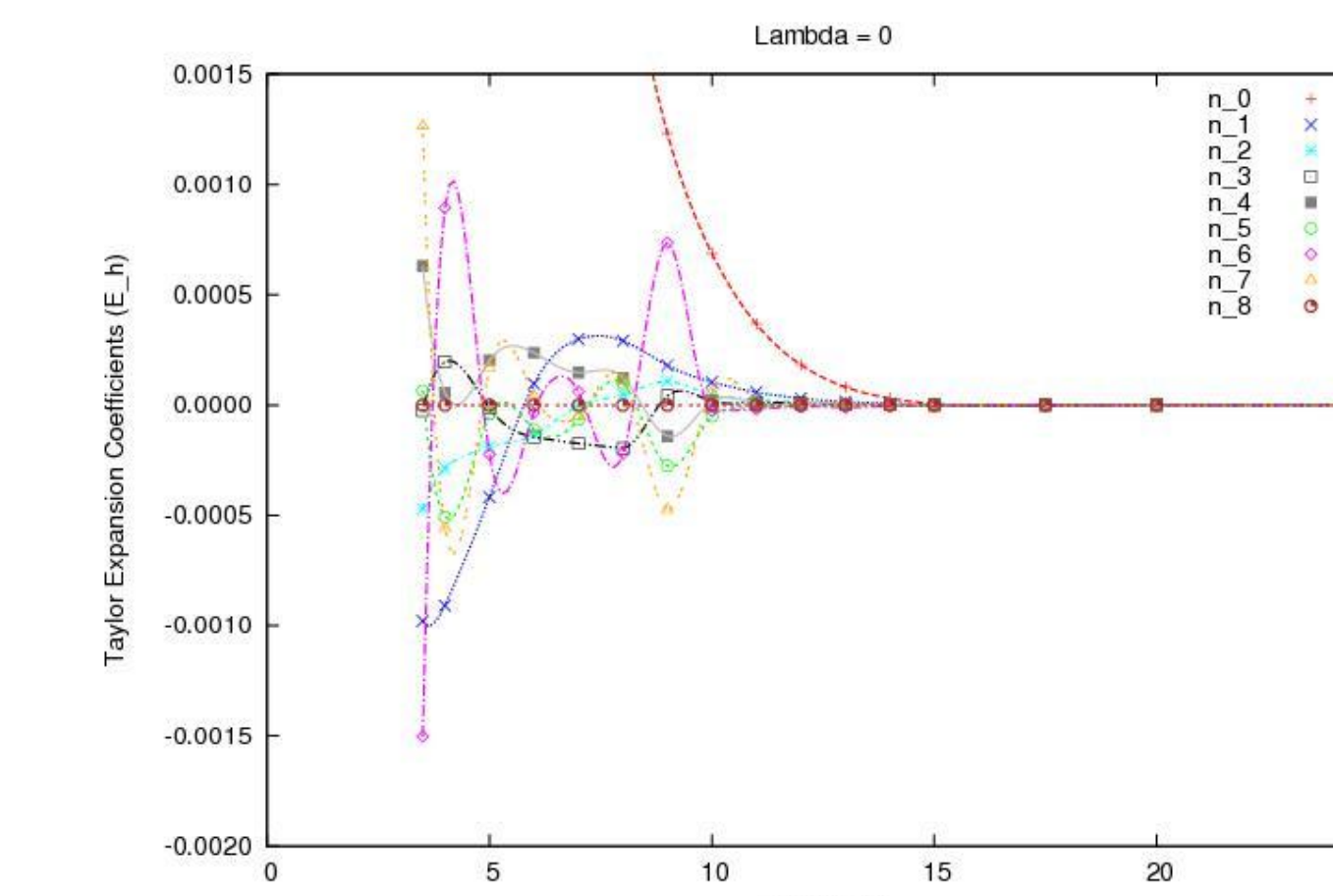
Fig 8 example of tspliner fits for λ=0 and all derivatives of the potential in a single plot

Conclusion & Future Work

The tspliner program will be used to finish fitting the coefficients to obtain a continuous PES that will be used in scattering calculations that include the vibrational effects of NaK on the changes of rotational states.

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