

# Effects of vibrational excitation on the reactivity of D+MuH

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## Introduction

The use of muonic isotopic variants in studies of the H+H<sub>2</sub> reaction has provided extreme mass combinations for the investigation of kinetic isotope effects and has stimulated a vivid discussion on the role of tunneling, zero point energy (ZPE), and vibrational adiabaticity in the reaction dynamics [1, 2]. The crucial influence of vibrational energy for this system has been recently highlighted by the publication of an accurate experimental value for the rate coefficient for the Mu+H<sub>2</sub>(v=1) reaction [3]. A very interesting aspect of Mu chemistry is the possibility of inducing a fundamental change in the nature of chemical bonding by isotopic substitution. Specifically, rigorous quantum mechanical calculations have shown the heavy-light-heavy (HLH) system BrLBr, where L is an isotope of hydrogen, changes from Van de Waals to vibrational bonding when L=Mu [4]. This type of bonding is a consequence of the decrease in the ZPE of the triatomic system at the saddle point of the potential energy surface (PES). Recently, dynamical resonances, associated also with decreases in the ZPE in the saddle point region, have been experimentally observed for the F+HD [5] and Cl+HD [6] reactions, especially for vibrationally excited states of HD.

In a previous work by our group [7] the reaction dynamics of the asymmetric D+MuH (v=0) reaction was investigated. The reaction path leading to DMu, which corresponds to a HLH mass combination, is characterized by a well of ~ 0.2 eV in the vibrationally adiabatic potential at the saddle point. The dynamics of this channel was found to be more quantum with higher tunneling and more structured reaction probabilities and cross sections. In the present study we investigate the effect of vibrational excitation of MuH on the reactivity of the system.

## Method

QM calculations were carried out on the BKMP2 [3] potential energy surface (PES), using the coupled-channel hyperspherical coordinate method implemented in the ABC code of Skouteris et al. [4]. Reaction probabilities, cross sections and rate coefficients were determined for the two exit channels (DMu+H and DH+Mu) of the reaction. **Thermal cumulative reaction probabilities (CRP)** [6] have also been used for the analysis of the dynamics. They are defined as:

$$C_r(E; T) = \frac{C_r(E) \exp(-E/k_B T)}{h \Phi_{\text{rel}}(T) Q_{v,j}^{BC}(T)}$$

where  $C_r(E)$  is the CRP as a function of total energy and  $\Phi_{\text{rel}}(T)$  and  $Q_{v,j}^{BC}(T)$  are the translational and coupled nuclear-rovibrational partition functions. The integration of the thermal CRP over the total energy  $E$  yields the thermal rate coefficient  $k(T)$ .

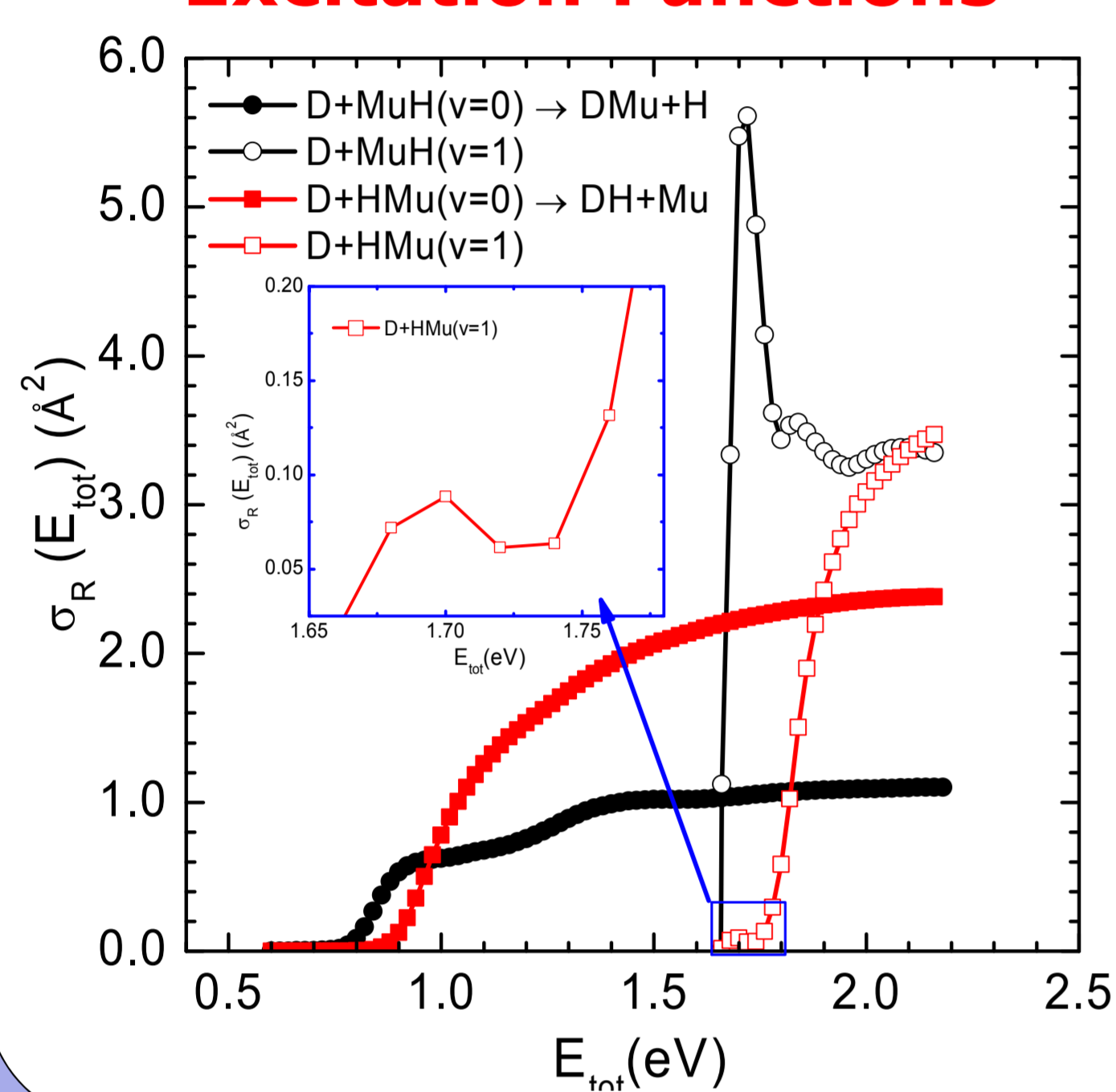
## Conclusions

- The distinct dynamical features of the two exit channels of the D+MuH(v=1) reaction are mostly determined by their respective vibrationally adiabatic potentials (VAP). The VAP of the **D+MuH(v=1)→DMu+H** channel has no threshold and **presents a deep well (~ 1.eV) at the location of the saddle point (vibrational bonding)**, whereas that of the D+MuH(v=1)→DH+Mu channel has a small threshold and no well.
- The  $\sigma_R(E)$  for D+MuH(v=1)→DMu+H has a sharp maximum, due to a **resonance associated with the well in the VAP**, as soon as the channel is energetically open. No resonance peak is observed in the reaction with MuH(v=0). The  $\sigma_R(E)$  for D+MuH(v=1)→DH+Mu has a small tail coincident with the maximum in the other channel and then rises sharply. For the two channels vibrational energy is more efficient than translational energy for promoting the D+MuH reaction.
- The  $k(T)$  for D+MuH(v=1)→DMu+H has a weak temperature dependence typical of barrier-less reactions. The  $k(T)$  for D+MuH(v=1)→DH+Mu has a small curvature suggestive of tunneling through the small threshold in the VAP. The  $k(T)$  for the two channels of D+MuH (v=1) are orders of magnitude larger than those for MuH(v=0).
- The thermal CRPs are bimodal **for the D+MuH(v=1)→DH+M** channel showing that there are **two mechanisms** at play. The first peak corresponds to an initial entrance via D+MuH(v=1)→DMu+H followed by a crossing to D+MuH(v=1)→DH+M within the well. This mechanism explains the tail in  $\sigma_R(E)$  and the curvature in  $k(T)$ . The second peak corresponds to the direct D+MuH(v=1)→DH+M reaction above the VAP barrier.
- The DCSs for D+MuH(v=1)→DH+M are mostly backward and for D+MuH(v=1)→DMu+H mostly forward. At the lowest (total) energy considered (1.72 eV) close to the channel opening, they are more isotropic and correspond to the resonance peak in D+MuH(v=1)→DMu+H and to the small tail in D+MuH(v=1)→DH+M.

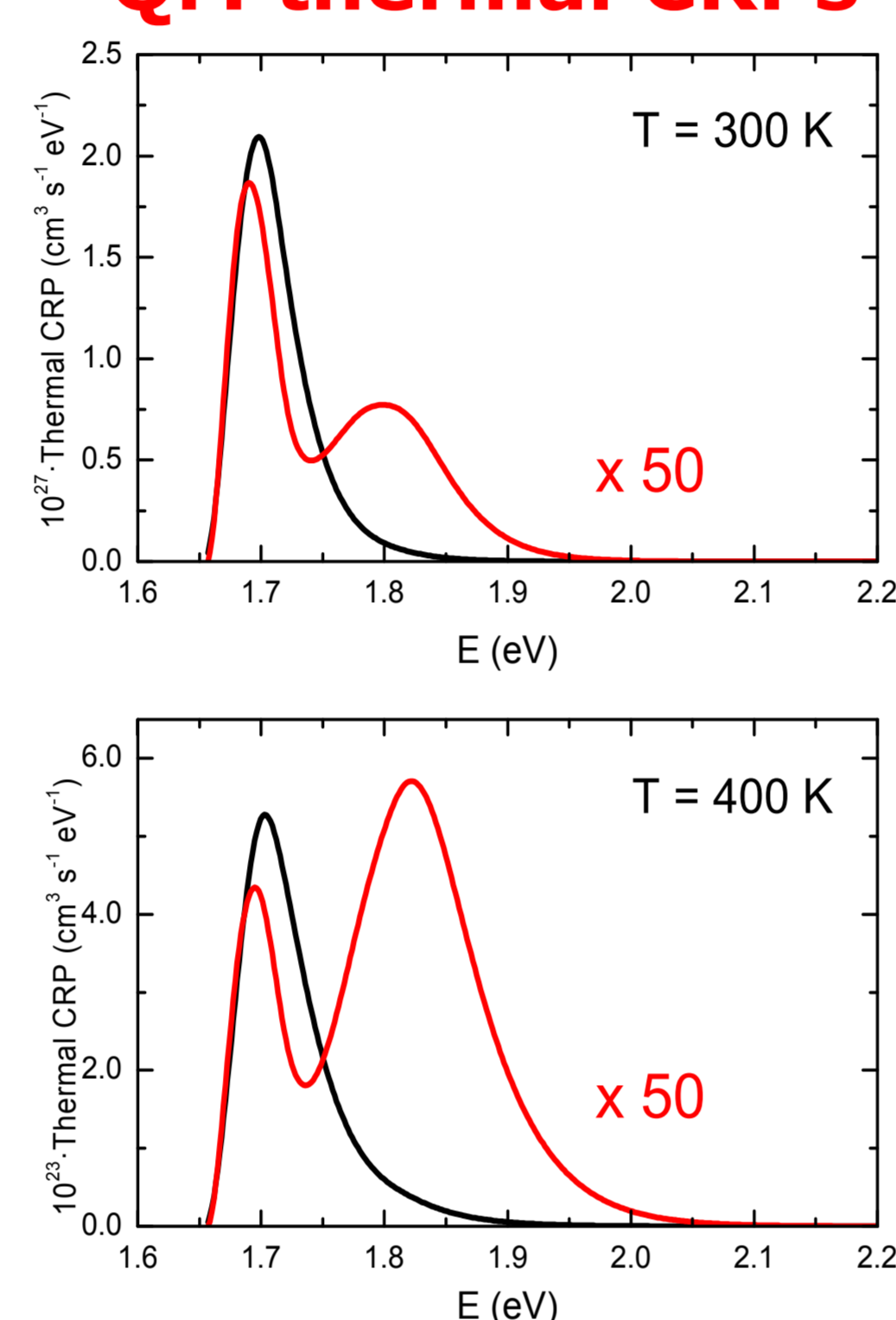
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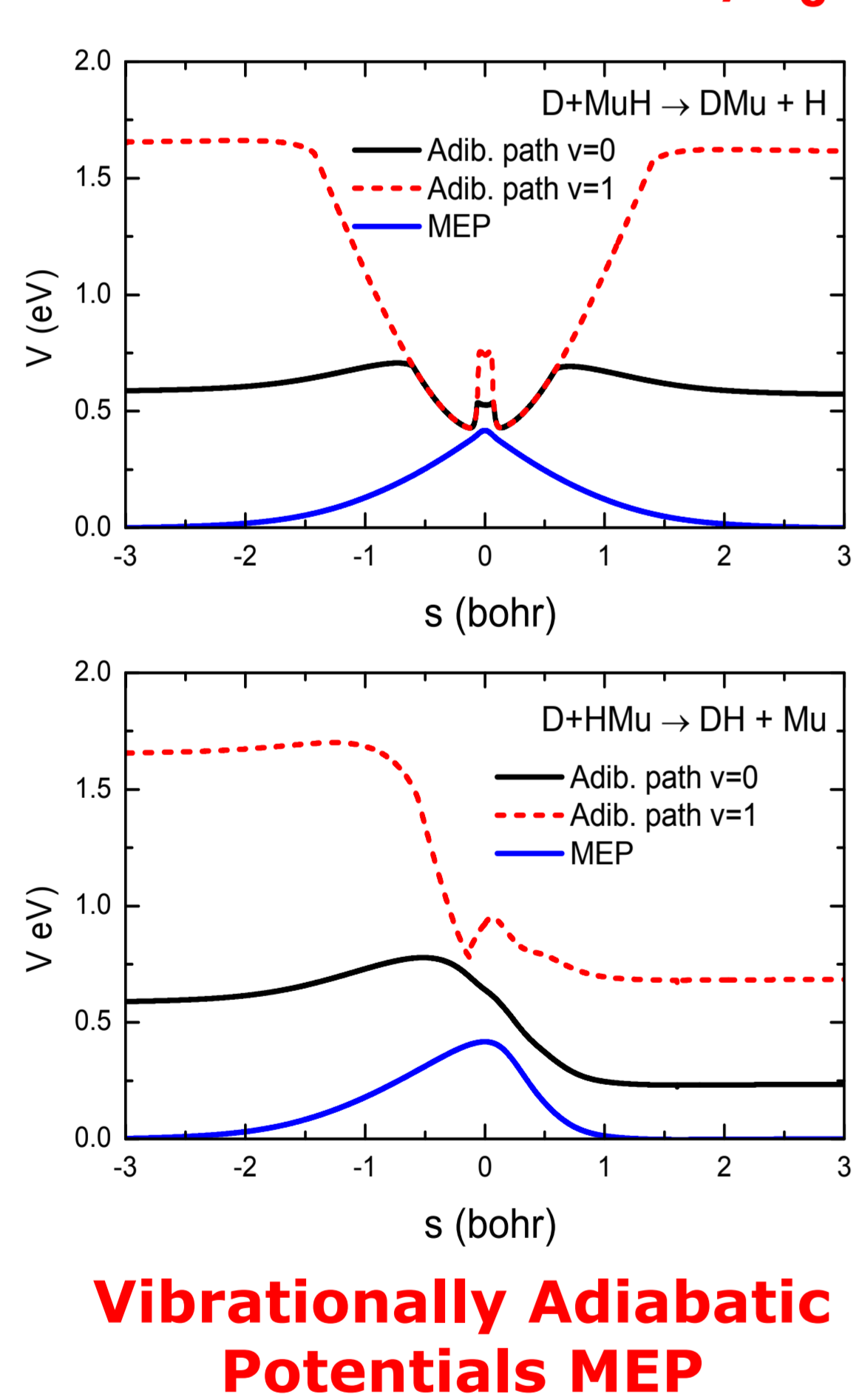
## Excitation Functions



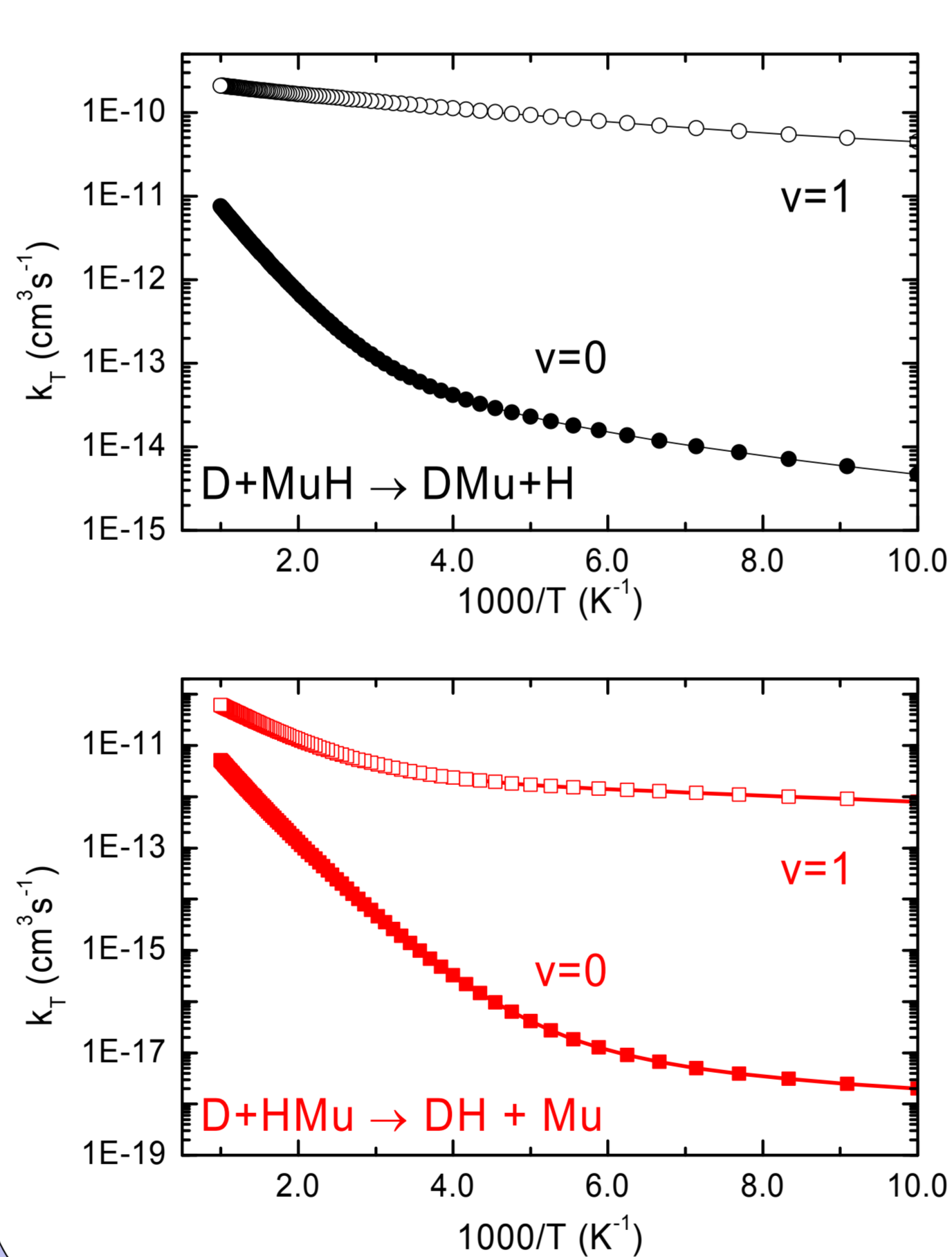
## QM thermal CRPs



## Collinear barriers, epsilon\_0



## Rate constants



## Differential Cross Sections

