



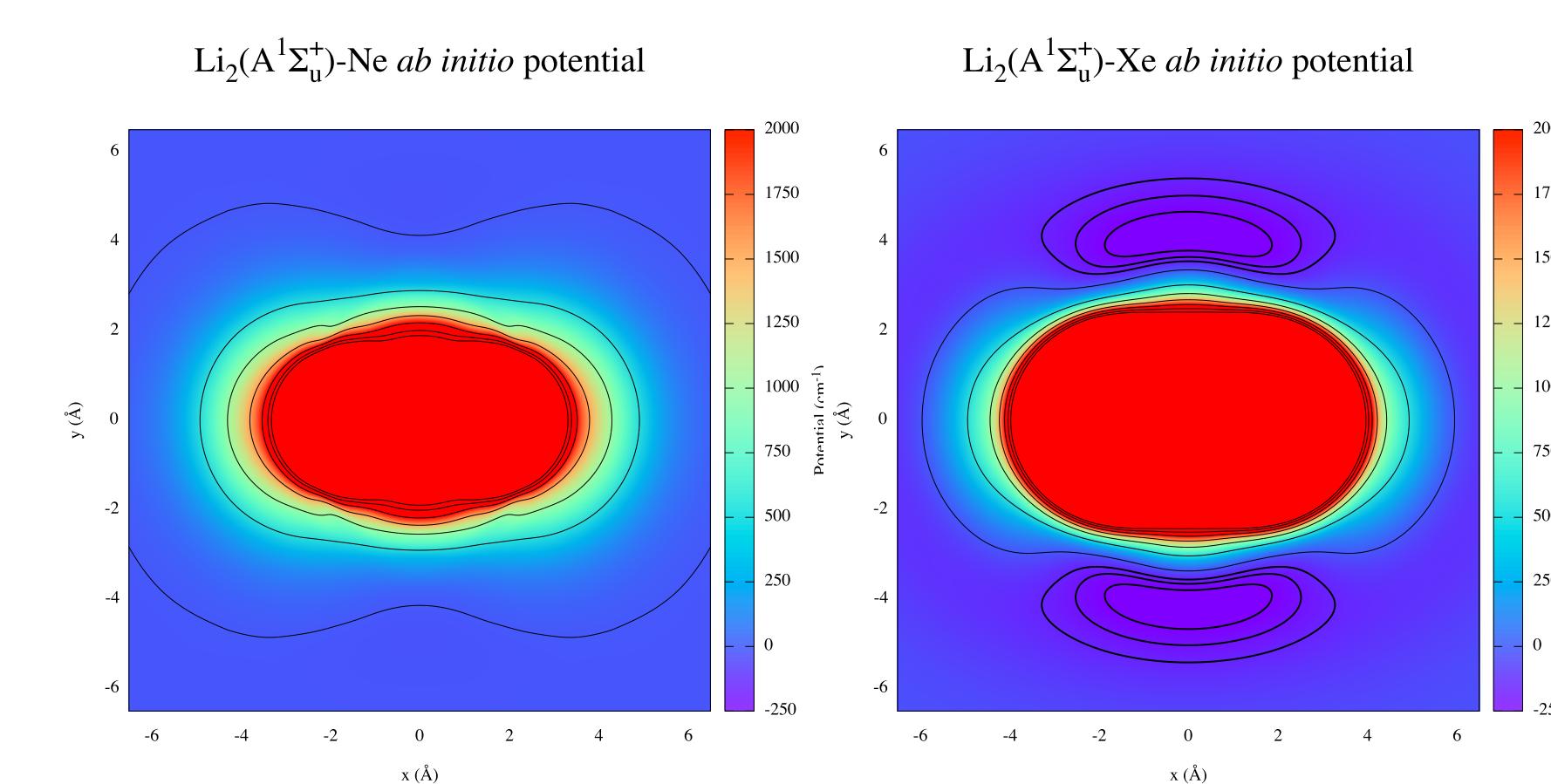
# Equatorial impacts in atom-diatom vibrational energy transfer

## Background

Traditionally, vibrational energy transfer in atom-diatom collision systems is modelled as collinear. In this model, the incoming atom strikes the end of the diatom, inducing a compression that in turn vibrationally excites the diatom. Such collisions are referred to as “end impacts” and are a well-known mechanism of vibrational energy transfer. Alternatively, the atom could collide with the diatom on a trajectory that is nearly perpendicular to the diatomic bond, which would excite molecular vibration via bond expansion. This method of vibrational energy transfer has been coined the “side impact” mechanism and is significantly less well-studied than the end impact. Our group has previously published work on this side impact phenomenon. This work aims to strengthen the previous investigations as well as fully characterize the mechanism and determine the systems in which it is most prominent.

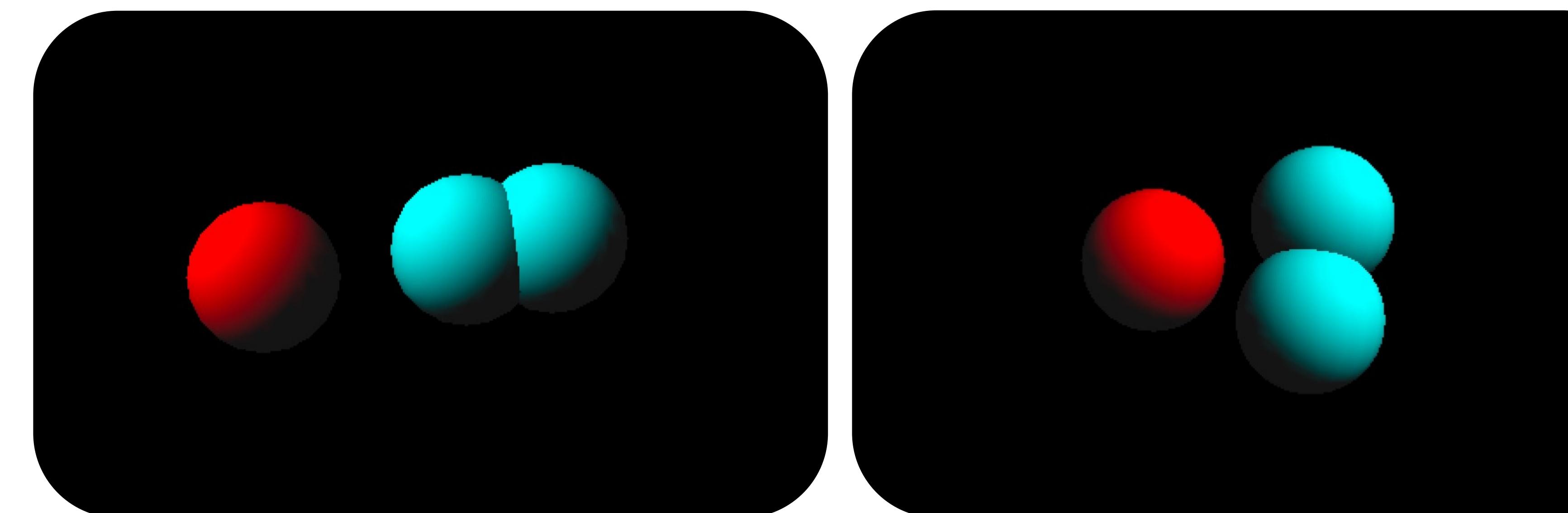
## Methods

We have run Monte Carlo simulations of millions of classical trajectories on both  $\text{Li}_2(\text{A}^1\Sigma_u^+)$ -Ne and  $\text{Li}_2(\text{A}^1\Sigma_u^+)$ -Xe *ab initio* potentials (depicted below). We have analyzed the macroscopic behavior of our simulations to compare with experiments but have also studied individual trajectories to enhance our understanding of the dynamics. Experimentally, the group has previously studied  $\text{Li}_2(\text{A}^1\Sigma_u^+)$ -Ne, and  $\text{Li}_2(\text{A}^1\Sigma_u^+)$ -Xe experiments are ongoing.

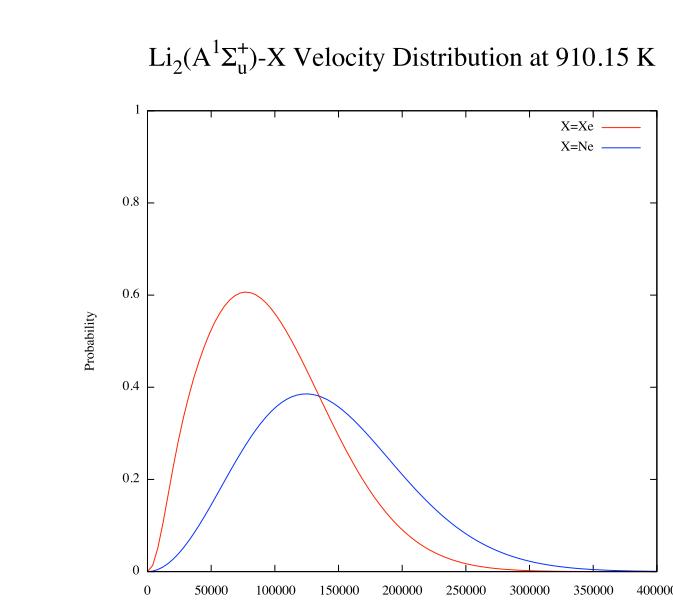


The  $\text{Li}_2$  internuclear separation in both cases is equilibrium ( $3.108 \text{ \AA}$ ). The thin lines correspond to  $500 \text{ cm}^{-1}$  contour intervals. The thick contour lines for the Xe potential are for the attractive well that reaches  $-292.59 \text{ cm}^{-1}$  and correspond to equipotential lines of  $-250 \text{ cm}^{-1}$ ,  $-200 \text{ cm}^{-1}$ , and  $-150 \text{ cm}^{-1}$ .

## Computation

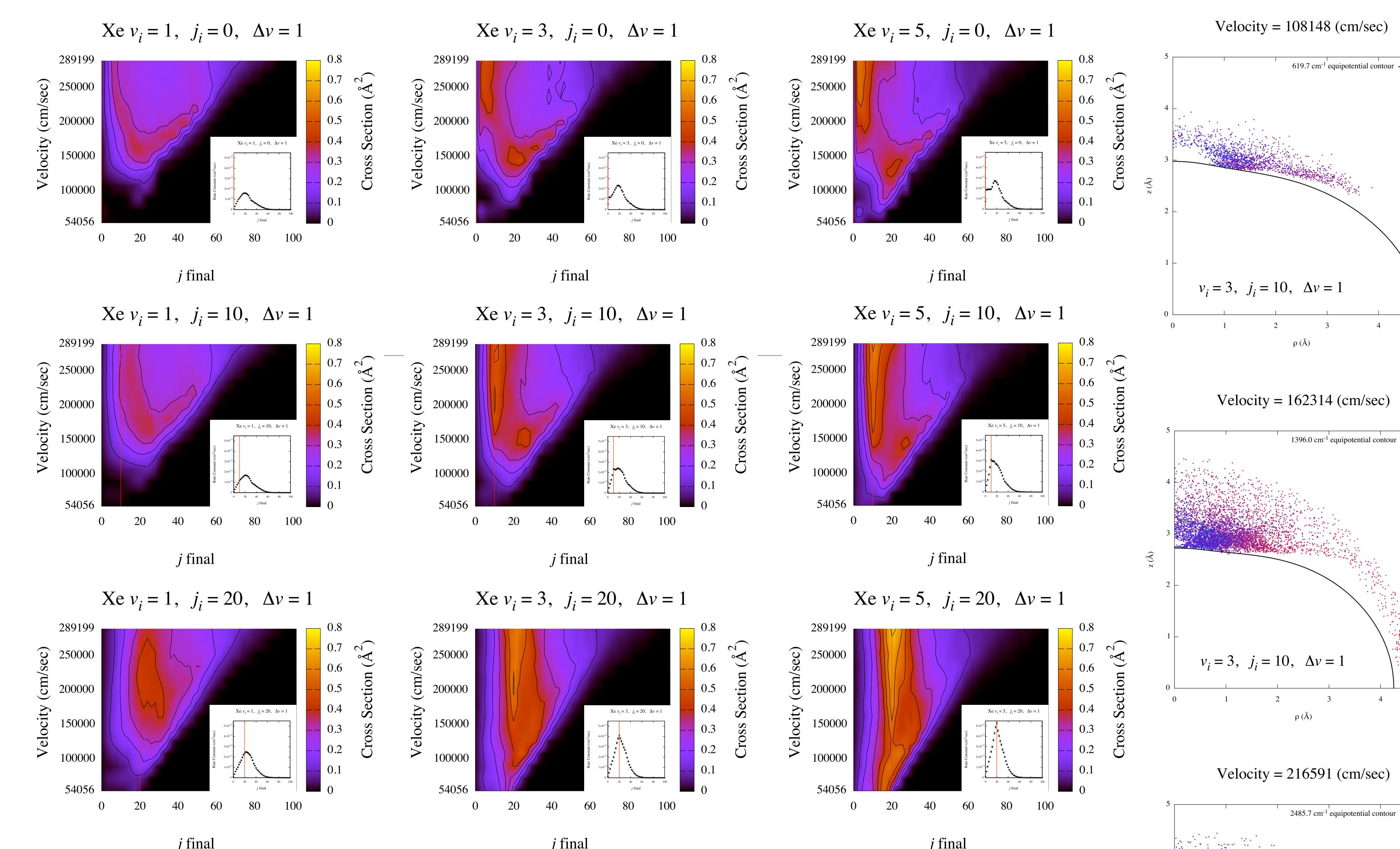


The images above depict end (left) and side (right) impacts. Upon scanning the QR code on the left you will be able to view the collision videos as well as the complete velocity progression of the dot plots below.



Our group experimentally measures rate constants, which are dependent upon cross sections. When we extract rate constants from simulation data, each cross section is weighted by its velocity. Our experimental velocity distributions are included on the left. The structures observed in the rate constants that accompany the following cross section heat maps are due to the weighting by this velocity distribution.

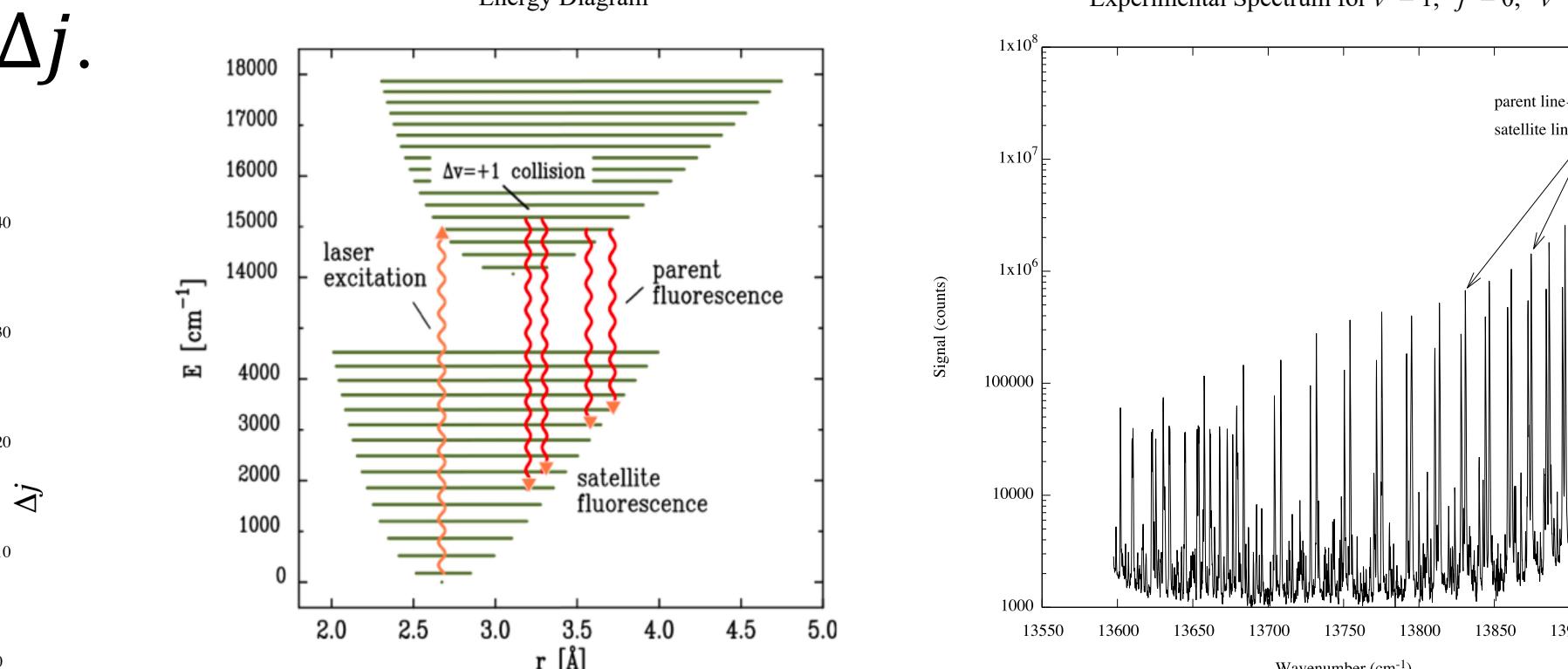
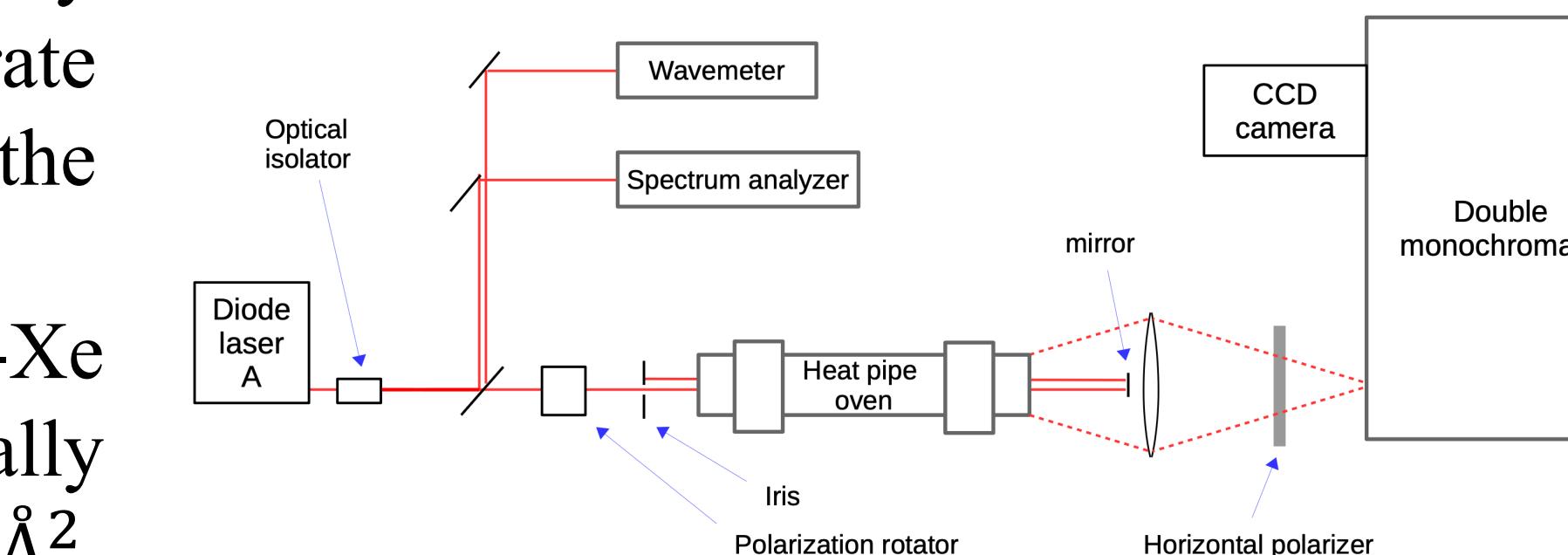
The grid below is composed of heat maps of  $\Delta\nu = 1$  cross sections for various  $\text{Li}_2(\text{A}^1\Sigma_u^+)$ -Xe systems and their accompanying rate constants. The systems increase in  $v_i$  horizontally rightward and increase in  $j_i$  vertically downwards. The interval for the contour lines is  $0.1 \text{ \AA}^2$ . The rightmost panel features “dot plots” of the classical turning points of  $\Delta\nu = 1$  collisions for  $v_i = 3, j_i = 10$  at increasing velocity vertically downward. The plotted points are colored by  $\Delta j$ .



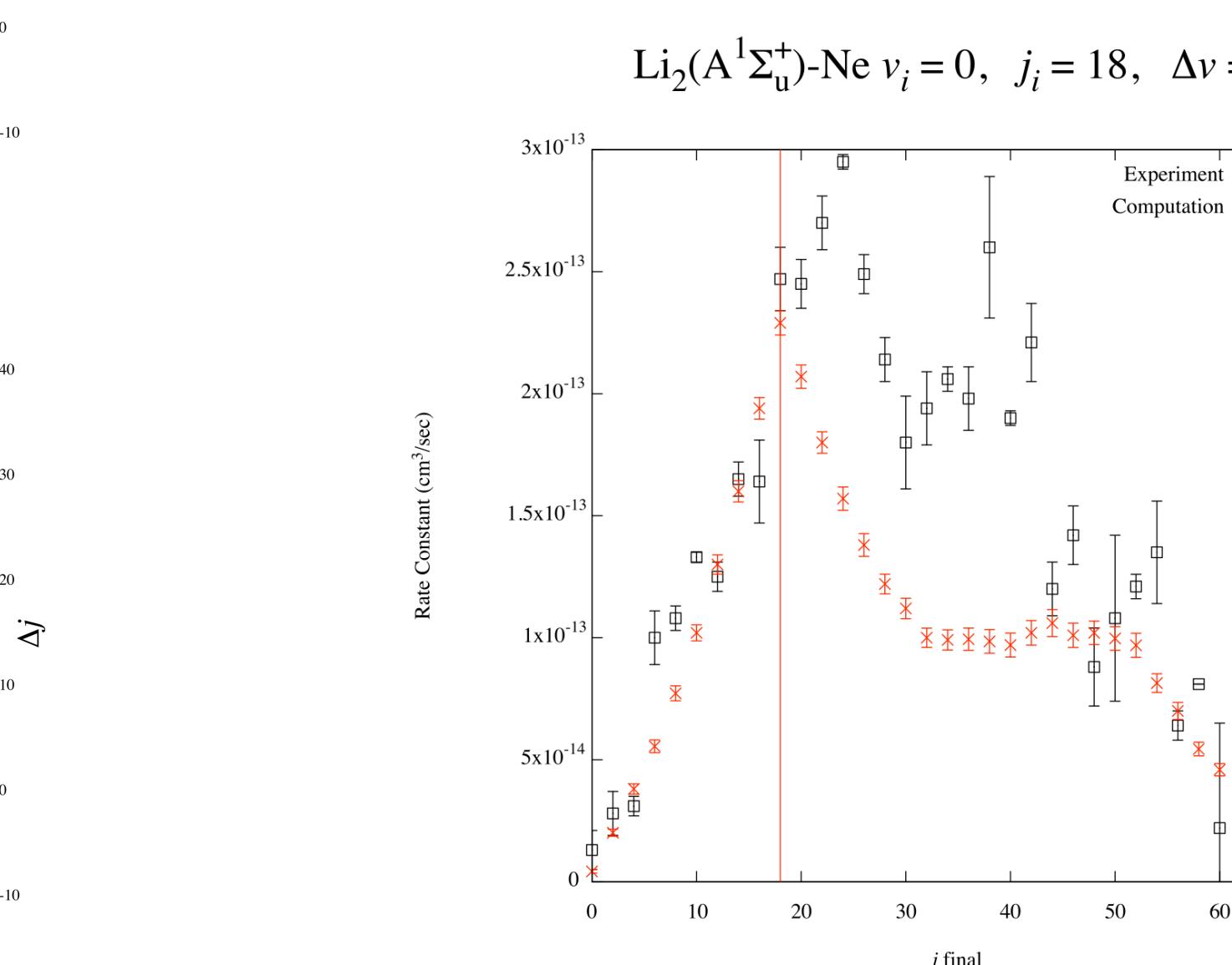
The dot plots only portray one quarter of a two-dimensional cross section of the Lithium diatom. Such a reduction is permissible because of the rotational and reflective symmetries of the  $\text{Li}_2$  molecule. The black line on each plot is an equipotential line on the  $\text{Li}_2(\text{A}^1\Sigma_u^+)$ -Xe potential energy surface, assuming equilibrium internuclear separation.

## Experiment

We use a dispersed laser induced fluorescence procedure to determine absolute level-to-level rate constants. First, a continuous-wave single-frequency laser is used to prepare the molecules into a single electronically excited rovibrational state. Then we examine the resulting spectra, which consist of strong “parent lines” from the fluorescence of molecules from the laser-excited state and weaker “satellite lines” from the fluorescence of molecules that were laser-excited and subsequently collisionally excited within their excited state lifetime ( $\sim 20 \text{ ns}$ ). Our experimental setup, a sample energy diagram, and experimental spectra are shown below.



Below we have a comparison of previous experimental [4] and computational  $\Delta\nu = 1$  rate constants for the  $\text{Li}_2(\text{A}^1\Sigma_u^+)$ -Ne  $v_i = 0, j_i = 18$  system. There is considerable agreement for  $\Delta j \leq 0$  and  $\Delta j \geq 30$  with a region of discrepancy between.



## Analysis

In the low to intermediate  $j_i$  cross section plots we see that as velocity increases a single peak emerges and then bifurcates. The peak centered near  $j_i$  is likely due to the low-torque side impacts. The other peak tends to increase in  $j_f$  as velocity increases and is the result of end impacts. Since they are colliding further from the center of mass of  $\text{Li}_2$ , the end impacts typically exert much greater torques than the side impacts. This shift in  $j_f$  with increasing velocity is also demonstrated in the dot plots. At low velocities, the atoms have much less energy to transfer to the diatom, which is why the lower velocity dot plots are significantly less populated. We observe that the separation of side and end impacts in our simulation data becomes increasingly less clear as our initial quantum numbers increase. Our group has noticed this “washing out” in  $\text{Li}_2(\text{A}^1\Sigma_u^+)$ -Ne systems as well, which bolsters support for a prior claim [3] that side impacts may be more discernable in systems with low to moderate initial excitation. This postulation will continue to be investigated in our future work.

## Future

Following the conclusion of our current  $\text{Li}_2(\text{A}^1\Sigma_u^+)$ -Xe  $v_i = 1, j_i = 0$  experiment, we will explore more Xe systems—possibly Ne and Ar as well—for the prevalence of the side impact mechanism. Computationally, this work will become significantly more comprehensive: we will explore a variety of setups to discover the characteristics of systems in which side impacts are significant. Such characteristics include initial quantum states, atom-diatom mass ratio, potential anisotropy, and more.

## References

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- [4] Stewart, B., et al., *J. Phys. Chem. A* **114**, 9875 (2010).
- [5] Fanthorpe, J. PhD Thesis (2021).