Elementary gas-phase chemical reactions have been a treasure trove for learning about chemical transformations. Despite their seeming simplicity, many mysteries remain to be solved in understanding the intricate chemical dance that occurs even in these systems. A simple example is the famous reaction

$$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$$

in which hydrogen and bromine gases combine to form hydrogen bromide gas. This system was among the first to be studied experimentally, and it might be thought that by now we would have a full understanding of this simple system! Thermodynamics sheds some light on this reaction: in particular, thermodynamics tells us that the equilibrium distribution favors the products, due to the relative weakness of the Br-Br bond. Thermodynamics does not tell us, however, enlighten us about the specific manner in which equilibrium is achieved or the time require to obtain equilibrium—for that, we need kinetics and dynamics. The earliest kinetic studies on this system were carried out in the early 20th century by M. Bodenstein. He found that the rate of reaction is given by

$$\frac{1}{2} \frac{d[HBr]}{dt} = \frac{k[H_2][\text{Br}_2]^{1/2}}{1 + k[HBr]/[\text{Br}_2]}$$

In 1919 Christiansen, Herzfeld, and Polanyi put forward the presently accepted multi-step mechanism for this reaction:

Initiation:  \( Br_2 + M \xrightarrow{k_1} 2Br + M \)  (1)

Propagation:  \( Br + H_2 \xrightarrow{k_2} HBr + H \)  (2)
\( H + Br_2 \xrightarrow{k_1} HBr + Br \)  (3)

Inhibition:  \( HBr + H \xrightarrow{k_2} Br + H_2 \)  (4)
\( HBr + Br \xrightarrow{k_1} H + Br_2 \)  (5)

Termination:  \( 2Br + M \xrightarrow{k_1} Br_2 + M \)  (6)

Clearly, a complex chain reaction, consisting of many elementary reactions, accounts for the formation of HBr. Now in the 21st century, chemists have turned their attention to the dynamics of these elementary steps.
One of the most interesting reactions is step (4), the reaction of a hydrogen atom with the HBr molecule – an exoergic step that inhibits product formation. One fascinating question is: what is the distribution of vibration-rotation internal energy states of the H₂ product? Clearly, this internal state distribution will influence the rates of other reactions, such as propagation step (3).

To a first approximation, it might be expected that all the available energy (the exothermicity + the reagent’s translational energy) could be distributed in a fully democratic manner, in which each internal state gets an equal weight (fully statistical outcome). The distribution would then look like:

![Graph showing relative population vs. rotational quantum number for different v' values.]

Another possibility is that the chemical forces that favor a collinear H-H-Br head-on collision constrain the internal state distribution. Valentini and co-workers have suggested that the second alternative is what happens: reactive trajectories must possess at least a minimum amount of translational energy in order to enter the product valley; otherwise, they are returned to the reagent valley. This amount of energy, which is tied up in translation, is therefore unavailable to appear in internal excitation. Consequently, the internal states distribution is kinematically constrained, with the magnitude of the constraint depending on the mass combination (in this case, light + light-heavy). For this reaction, this theory predicts a state distribution that might look like:
My research group has experimentally and theoretically investigated this reaction and compared the measured state distribution to those predicted by these two models. For H$_2$ products with two quanta in vibration, we find a small but significant amount of population in kinematically forbidden rotational states.

Calculations indicate that two different mechanisms are involved for collisions resulting in allowed states versus collisions resulting in excluded states. In most of the reactive collisions, chemical forces allow reaction only if the transition state is collinear; these collisions populate kinematically allowed H$_2$ states. In a small number of collisions, those chemical forces are overcome, resulting in a bent transition state and the formation of H$_2$ with internal energy that can exceed the kinematic limit. This relationship between the geometry at the transition state and the product’s internal energy allows us to consider
a measurement of a reaction product’s internal energy as a primitive spectroscopy of the transition state. The dynamical behavior of even this simple system shows us the richness of detail still to be uncovered about the mechanism of elementary chemical reactions.