

# Theoretical analyses of transition state spectroscopy of chemical reactions: on the relation between transition state structure and quantum resonance

Toshiyuki Takayanagi

*Department of Chemistry, Saitama University*

tako@mail.saitama-u.ac.jp

The concept of “transition state” has been playing an essentially important role in understanding detailed mechanisms, dynamics and rates of chemical reactions. The transition state structure is frequently defined as a saddle point or a specific region around the saddle point on the potential energy surface. Direct spectroscopic detection of the transition-state is called “Transition-State Spectroscopy (TSS)”. The measurement of the photodetachment spectrum of the molecular anion may be one of the most successful TSS methods. It has been shown that the measured photodetachment spectra can provide important information on the transition-state of the neutral system if the stable region of the anionic potential energy surface has good Franck-Condon overlap with the transition-state region of the neutral potential energy surface. However, the analysis of the measured spectra is not straightforward. This is simply because the observed spectral peaks are corresponding to quantum resonance states of chemical reactions. Thus, in order to extract detailed information on transition-state properties, one has to employ reliable theoretical methods that can describe the reaction dynamics at a quantum mechanical level. In this talk I would like to address the transition-state spectra of the  $\text{Br} + \text{HBr}$  and  $\text{I} + \text{HI}$  reactions. We have developed the potential energy surfaces using ab initio electronic structure calculations to study the transition-state spectra of these reactions. It was found that the simulated high-resolution photodetachment spectra show broad anti-symmetric progressions with many sharp resonances associated with van der Waals complex localized around potential energy wells. In addition, it was also found that there is the possibility that the  $\text{BrMuBr}$  and  $\text{IMuI}$  systems have vibrational bonding states, corresponding to true “bound” states whose wavefunctions are localized around the transition state region.