Nuclear-excited Feshbach resonance in Penning ionization reactions

Hiroshi Ohoyama and Toshio Kasai

Department of Chemistry, Graduate School of Science

Osaka University

Combination of oriented molecular beam method with time of flight technique makes us possible to determine orientation-angle and collision-energy specified Penning ionization cross sections for CH_3X (X= Cl, Br, I) reactions. Remarkable oscillation structures in collision-energy dependence of the ionization cross section are observed only if we control molecular orientation. This resonance-type structure can be interpreted as a new type of nuclear-excited Feshbach resonance, where neutral dissociation process competes with the ionization through formation of vibrationally excited CH_3X Rydberg state.

We prepare an oriented halo-methane CH_3X (X=Cl,Br,I) molecular beam by a 70-cm electrostatic hexapole state-selector and the oriented molecular beam crosses Ar* metastable argon beam which is generated by a short-pulse grow discharge. Orientational distribution of the CH_3X oriented beam can be determined from experimental focusing curve. Under three types of molecular orientations experimentally prepared prior to reaction, namely the CH_3-end, the X-end, and random orientations, reaction takes place and produces CH_3X^+. TOF profiles of the product ions were measured. The orientation-angle and collision-energy resolved cross section, called 3D-plot, is then obtained. In the 3D-plot for Ar*+CH_3Br reaction, remarkable oscillation structures can be seen along collision energy axis. The amplitude oscillates with narrow energy widths, so that we will see that this resonance-type structure is caused by branching competition via indirect dissociative recombination during Penning ionization, which leads to neutral dissociation channel. An *ab initio* calculation suggests that there are many CH_3Br Rydberg states near the ionization threshold, and that they are excited in vibration. The energy positions of the oscillation in the experimental cross section are found to be parallel to the energy levels of the Rydberg states calculated. Within the experimental energy region, only three vibrationally excited states, $2\nu_1$, $2\nu_4$ and $2\nu_1+\nu_3$ -vibrational modes of $E_{3/2}$ can be energetically accessible. Therefore, the present result suggests that such new resonance-type structure is closely relevant to vibrationally excited Rydberg states that are coupled with dissociative dissociation exit channels. Similar good correlation between the experimental results and the calculated energies is also recognized for other Penning ionization reactions we have studied so far.