Thermometry of large molecular anion by laser-induced delayed detachment

M. Goto* [1], **J. Matsumoto*, H. Shiromaru*, Y. Achiba*, T. Majima**[†] [2], **H. Tanuma**[†], **and T. Azuma**[‡]

[*] Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo, 192-0397, Japan
[†] Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo, 192-0397, Japan
[‡] Atomic, Molecular and Optical Physics Laboratory, RIKEN, Wako, Saitama, 351-0198, Japan

Laser-induced delayed detachment of a polyatomic molecule is considered to be a good measure of the internal energy since its rate depends only on the sum of absorbed photon energy and internal energy immediately before the absorption [1]. For example, Sundén *et al*. has determined the cooling rate of C_{60}^- through the *single*-photon detachment at temperatures high enough to induce significant spontaneous decay without photo-absorption [2]. When such a large molecule is not at very high temperature, on the other hand, a *multi*-photon process is necessary to give rise to delayed detachment. This is because raising the single-photon energy is also the way of increasing the energy given to the ion, however, it would be immediately consumed as direct detachment.

In our previous work, we have measured laser-induced delayed detachment of zinc phthalocyanine ($C_{32}H_{16}N_8Zn$) anion stored in an electrostatic ring. The laser fluence dependence of the detachment yield revealed that number of photons needed for delayed signals increased for longer storage time. Assuming that we had detected neutrals yielded from the ions with specific internal energy range, this dependence allowed us to estimate the cooling rate of the ion [3] aside from the absolute values of internal temperature or energy.

In the present study, we evaluated the internal temperature before irradiation, T, by comparing the plot with simulated yield, Y, for various T and the laser fluence. We adopted the equation $Y = \iint k(E)g(E)\exp(-k(E)t)\mathrm{d}E\mathrm{d}t$, where the functions $k(E)$ and $g(E)$ are the rate and the internal energy distribution after the photo-absorption, respectively, and t is time after the irradiation. The $k(E)$ was calculated by following the procedure shown in [4], which is based on detailed balance theory. The estimation of $g(E)$ employed two assumptions. First, the distribution before photo-absorption was described by the Boltzmann distribution with T. Second, the photo-absorption probability of each n-photon process was expressed by the Poisson distribution with the photo-absorption cross section and the number of photons per single laser shot passing through the unit merging area, converted from the fluence.

Considering the $k(E)$ and time window for detection of neutrals, we determined the detectable energy window to be 14 – 18 eV. Furthermore, the calculation reproduces our previous observation well, and thus, we can determine the value of T from the comparison. This result indicates that the ions were cooled from 1300 to 1100 K for the storage time from 25 to 375 ms, which is consistent with the cooling through their infrared emission. In conclusion, the analysis of a multi-photon absorption process works for evaluating moderately high internal temperature.

References

[1] E. E. B. Campbell and R. D. Levine, Annu. Rev. Phys. Chem. **51**, 65 (2000).
[2] A. E. K. Sundén *et al*., Phys. Rev. Lett. **103,** 143001 (2009).
[3] M. Goto *et al*., Chem. Phys. Lett. **460,** 46 (2008).
[4] J. U. Andersen *et al*., J. Phys. B **35,** R1 (2002).

[1] Present address: Department of Physics, University of Gothenburg. E-mail: motoshi.goto@physics.gu.se
[2] Present address: Department of Nuclear Engineering, Kyoto University.