Dissociation process of the Kr_2^+ C_2 $^2\Pi_{1/2u}$ state

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Introduction

Studies on the photoionization of rare gas dimers and their ions are important to understand the nature of the van der Waals interaction. In the past two decades, many theoretical and experimental studies on the homonuclear rare gas dimers have been performed. We have already observed threshold photoelectron (TPE) spectra of Kr gas and measured vibrational structures of Kr_2^+[1]. After that, we also observed threshold photoelectron photoion coincidence (TPEPICO) spectra of Kr_2. Unexpectedly, we found that at the peak of the Kr_2^+ C_2 $^2\Pi_{1/2u}$ TPE spectrum, the threshold photoelectrons are detected in coincidence not with Kr_2^+ ions, but with Kr^+[2]. This observation points to a rapid predissociation of the Kr_2^+ C_2 $^2\Pi_{1/2u}$ state to $Kr^+(^2P_{3/2})$+$Kr(^1S_0)$.

Experiment

The measurements were carried out at the beamline 20A of the Photon Factory. The experimental setup and technique were same as our previous study[2]. In brief, photoelectrons extracted by a penetrating field were focused by a lens system and then led to a hemispherical electrostatic analyzer. The Time-of-Flight (TOF) ion mass analyzer enabled us to select mass-identified photoions.

When a dissociation product has a kinetic energy in the ionization region, it is expected that the peak of the TOF spectrum has wide width. Since no competition between dissociation processes is expected and the only final state is $Kr^+(^2P_{3/2})$+$Kr(^1S_0)$, the kinetic energy of the fragment Kr^+ in the ionization region should be dominated by only one energy. Generally, if the kinetic energy of the ion is narrowed, if the ions are released symmetrically, and if all ions are detected, the TOF spectrum would have a rectangular shape, the center of which is the flight time of Kr^+, and its width *W* given by;

$$W = \frac{2\sqrt{2m}}{qE_s}\sqrt{U} \qquad (1)$$

[3], where *m* is the mass of the ion, *q* is the ionic charge, E_s is the electric field in the collision region, and *U* is the kinetic energy of the ion.

We expected it could be observed the rectangular TOF peak, which has the width estimated as ~10 sec from the energy difference between the vibrational level of the Kr_2^+ C_2 $^2\Pi_{1/2u}$ state and the first dissociation limit (~550 meV).

Results

In Fig. 1 is shown the observed TOF spectrum at the photon energy of the Kr_2^+ C_2 $^2\Pi_{1/2u}$ state (v=2). It seems that the spectrum shape is not rectangular and the width is narrower than the estimated width (~10 μsec). This indicated the C_2 $^2\Pi_{1/2u}$ state loses energy before dissociating to Kr^++Kr. We propose that this energy consumption can be ascribed to the radiative transition of the C_2 $^2\Pi_{1/2u}$ state to the intermediate repulsive B_2 $^2\Pi_{1/2g}$ state correlated to the first dissociation limit. We found the shape of the TOF peak could be made up by accumulation of the rectangular spectrum under concerning the effect of the life time. The fitting which designates the potential energy of the B_2 $^2\Pi_{1/2g}$ state and the life time as parameters was performed.

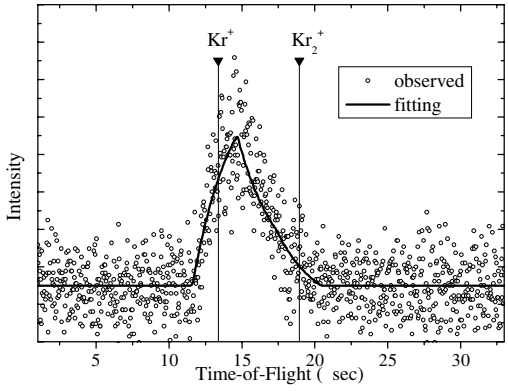

Fig. 1 The TOF spectrum at the photon energy of the Kr_2^+ C_2 $^2\Pi_{1/2u}$ state

The result of the fitting is also shown in Fig. 1. From the fitting, the potential energy of the B_2 $^2\Pi_{1/2g}$ state from the first dissociation limit and the life time of the radiative transition were obtained as ~50 meV and ~2.7 sec. These values were obtained experimentally for the first time and the obtained potential energy of the B_2 $^2\Pi_{1/2g}$ state is comparable with the theoretical prediction[4].

References

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