

Dissociation of inner valence states of O_2^+ studied by threshold photoelectron-photoion coincidence spectroscopy

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Introduction

Breakdown of the independent-particle orbital picture is characteristic of inner valence electrons in molecules. Therefore, for molecular photoionization of the inner valence shells, this leads to many final states of configuration interaction satellites. An attractive objective is to obtain detailed information on dissociation processes of the inner valence states, because these processes are closely related to the electronic character and potential energy surface of the final states of the molecular ions. Experimental investigation is still limited, even for diatomic molecules, owing to the small cross sections for photoionization into inner valence states. In contrast, modern configuration-interaction calculations have become capable of accurately describing these inner-valence states.

One of the effective experimental approaches is threshold photoelectron-photoion coincidence spectroscopy, where fragment ions are detected simultaneously with threshold photoelectrons so as to define the binding energy of the initial inner valence states. The experimental setup is that used for Auger electron-threshold electron coincidence measurements [1], except the hemispherical electrostatic analyzer equipped with a position sensitive detector is here used to detect energetic fragment ions.

Experimental results

Measurements were carried out on beamline BL20A at the Photon Factory, equipped with a 3-m normal incidence monochromator. The top panel of Fig. 1 shows a threshold electron spectrum of O_2 in the inner valence region (25 - 45 eV). The spectrum exhibits several broad peaks, which are not always given definite assignments, as well as discrete peaks probably assignable to Rydberg states of O_2^+ converging to O_2^{2+} . We have measured kinetic energy spectra of fragment O^+ in coincidence with threshold electrons at different photon energies, mainly on the broad peaks. The kinetic energy spectra of O^+ , thus obtained, depend on the final molecular states, reflecting potential energy curves of related electronic states and their dissociation dynamics. Typical coincidence spectra are shown in the middle and bottom panels, which are measured for $O_2^+(^2\Sigma_u^-)$ and $O_2^+(4^2\Pi_u)$, respectively. These ion states dissociate mainly to the limits $O^+(^2P) + O(^3P)$ and/or $O^+(^2P) + O(^1D)$, though dissociation to other limits are also recognizable. For the O_2^+ states of higher binding energies, relatively slow O^+ is found to be dominant. This shows that neutral O atoms, dissociation partners of O^+ , are electronically excited.

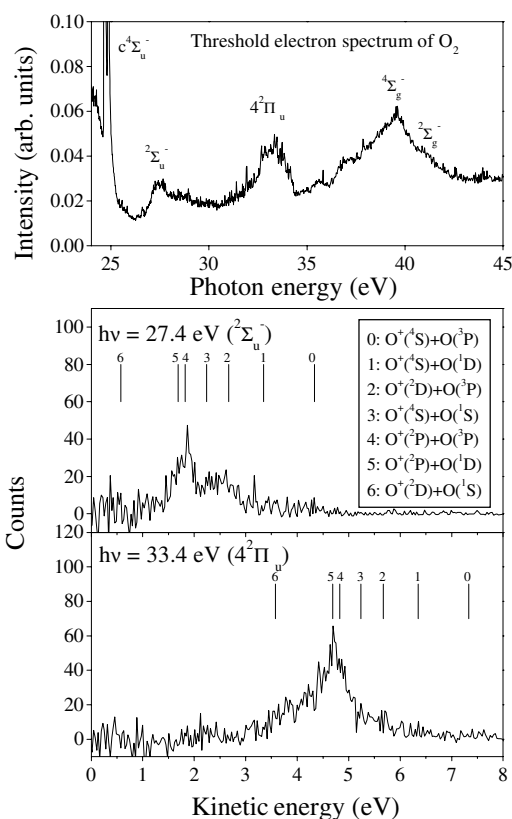


Figure 1. A threshold electron spectrum of O_2 (top), and kinetic energy spectra of fragment O^+ measured in coincidence with threshold electrons (middle and bottom).

References

[1] Y. Hikosaka, F. Penent, P. Lablanquie, R. I. Hall and K. Ito, Meas. Sci. Tech. 11, 1697 (2000).

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