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Multiply excited molecular oxygen observed in the production of photon pairs

Takeshi Odagiri*, Haruhide Miyagi, Makoto Murata, Hironobu Fukuzawa,
Manabu Kurokawa, Masashi Kitajima and Noriyuki Kouchi
Department of Chemistry, Tokyo Institute of Technology,
O-okayama 2-12-1-W4-4, Meguro-ku, Tokyo 152-8551, Japan

Introduction

A photon pair from excited fragments in photoexcitaion of molecules:

$AB + h\nu \longrightarrow AB^{**} \longrightarrow A^{*}+B^{*} \longrightarrow A+h\nu'+B+h\nu''$, (1)

is a highly-sensitive probe for the dynamics of the multiply excited states of molecules [1-4] which are embedded in the electronic continuum and hence are hardly observed by conventional photoabsorption or photoionization studies. In the present report, the cross sections for the production of photon pairs in photoexcitation of O_2 have been measured as a function of the incident photon energy to investigate formation and decay of multiply excited states of O_2.

Experimental

The measurements were carried out at BL-20A. The linearly polarized synchrotron radiation from the 3-m normal incidence monochromator was introduced in a gas cell filled with O_2 with the pressure of approximately 0.26 Pa. Two VUV-photons emitted parallel to the electric vector of the incident light and opposite to each other were detected by two photon detectors, each of which is composed of an LiF window and a microchannel plate providing a filter range of 105-150 nm. The pulses from two photon detectors were fed into a standard delayed coincidence circuit. The coincidence counts were normalized for gas pressure, flux of the incident photons and geometrical factor to obtain cross sections for the production of photon pairs (process (1)) in photoexcitation of O_2 differential with respect to solid angles for the emission of photons, $d^2\sigma_2/d\Omega_i d\Omega_j$.

Results

Figure 1(a) shows the doubly differential cross sections for the production of photon pairs in photoexcitation of O_2 as a function of the incident photon energy. Peak structures around 29, 36 and 38 eV and a hump around 44 eV due to intermediate excited states of O_2 are clearly observed in the cross section curve. It is remarkable that such highly excited states of O_2 in the extreme ultraviolet range can never been observed by any other experimental method.

In figure 1(b) displayed is the threshold photoelectron spectra (TPES) of O_2 [5]. The TPES of O_2 reveal the ionic O_2^+ states formed by the removal of an inner valence $2\sigma_g$ electron of O_2 and the correlation states associated with them in this energy range [5]. Hence the excited states observed in figure 1(a) can be attributed to singly or multiply excited states of O_2 built on these ionic states. It is noted that sudden decrease in the cross section for the production of photon pairs around 36 eV (figure 1(a)) coincides well with the double ionization potential of O_2 (36.13 eV [6]). Thus the sudden decrease could be attributed to the spectator Auger decay to Rydberg O_2^+ states conversing to the ground electronic state of O_2^{++} $X\ ^1\Sigma_g^+$.

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* joe@chem.titech.ac.jp

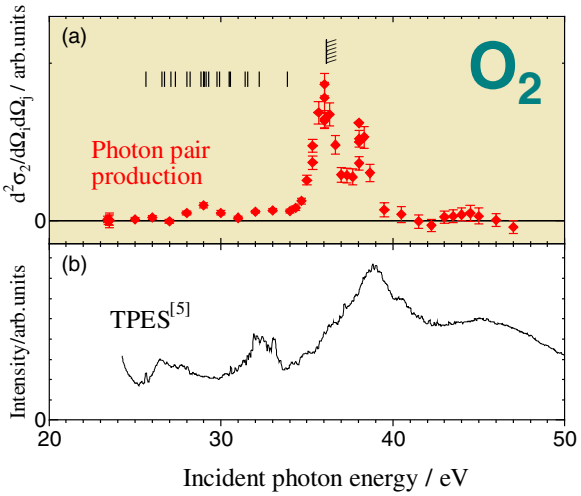

Figure 1. Doubly differential cross sections for the production of photon pairs in photoexcitation of O_2 as a function of the incident photon energy in (a) and the threshold photoelectron spectrum of O_2 in (b). The vertical line with hatch indicates the double ionization potential of O_2 [6]. The short vertical lines indicate the dissociation limits of O*+O*' which give two fluorescence photons detectable by the present photon detectors. The electronic configuration of the ground state of O_2 $X^3\Sigma_g^-$ is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$.