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Doubly Excited States of Methane in the Vacuum Ultraviolet Range

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Introduction

Superexcited states play an important role in the photoabsorption of molecules in the vacuum ultraviolet range [1]. One of the hot topics concerning these states is the dynamics and spectroscopy of doubly excited states of molecules[2,3]. As for diatomic molecules such as hydrogen, the doubly excited states have been investigated by means of synchrotron radiation [2] and electron collisions[3]. However, less has been known about the doubly excited states of polyatomic molecules. In this experiment the doubly excited states of methane have been extensively studied by means of UV-Visible fluorescence spectroscopy.

Experimental

Synchrotron radiation dispersed by a 2400 lines/mm grating in the 3m normal incidence monochromator at BL-20A was used as an incident light source. Fluorescences emitted from the neutral fragments produced in the photodissociation of methane were dispersed by a 30cm UV-Visible monochromator equipped with a 300 lines/mm grating and a CCD detector. The liquid nitrogen-cooled CCD detector covers the wavelength-range of 280nm in one frame. Thus, the 2D-fluorescence excitation spectra were recorded by scanning the incident photon energies step by step in the range 10-41eV, where CH(A→X), CH(B→X), and the Balmer-α,β γ and δ fluorescences were observed. The fluorescence intensities were normalized for the incident photon intensity, number density of methane molecules, and accumulation time, and were corrected for the sensitivity of the whole optical system which was determined by measuring the fluorescence spectra of $N_2^+(B\rightarrow X)$. The cross sections for the emission of each fluorescence except for the Balmer-α were placed on the absolute scale by measuring those of $N_2^+(B\rightarrow X)$, of which absolute values were established previously[4].

Results

Figure 1 shows the cross sections of the Balmer-β,γ, and δ fluorescences as a function of incident photon energy. Each curve shows the almost the same shape, and the two peaks are observed around 22 and 29 eV. The peak around 22 eV is attributed to the superexcited states built on the $(2a_1)^{-1}$ ion core, i.e. singly excited states. On the other hand, it could be concluded from an energetical point of view that the peak around 29 eV is attributed to doubly excited states. The peak areas in Fig. 1 give the oscillator strengths for the emission of Balmer series via the singly and doubly excited states separately. Interestingly the oscillator strengths via the doubly excited states amount to approximately twice as large as those via the singly excited states, which seems opposite to the independent particle picture. This extraordinarily large oscillator strengths via the doubly excited states indicate clearly and quantitatively the breakdown of this picture.

References

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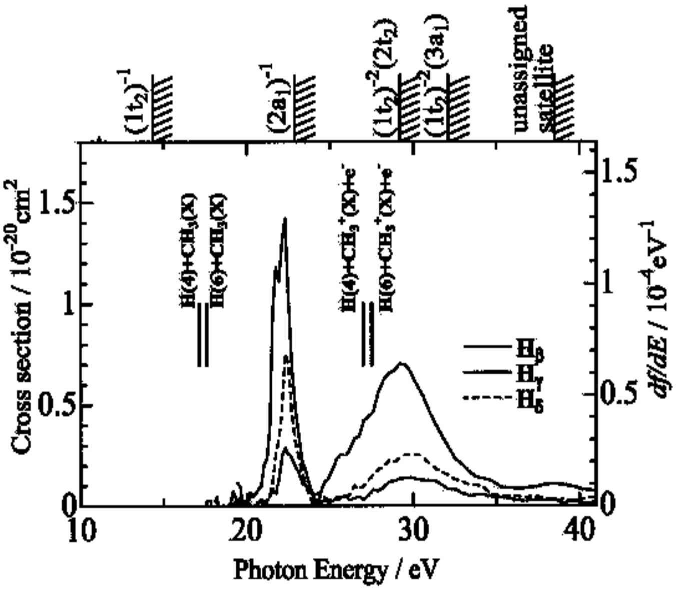

Fig.1 Cross sections and oscillator strength distributions for the emission of Balmer-β, γ, and δ from excited hydrogen atoms produced in the photodissociation of CH_4. The vertical ionization potentials are shown in the upper portion. The dissociation limits are also shown by vertical bars.