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# Doubly excited states of ammonia in the vacuum ultraviolet range as studied by dispersed uv-visible fluorescence spectroscopy

Masahiro KATO, Takeshi ODAGIRI, Kosei KAMETA, Noriyuki KOUCHI*
and Yoshihiko HATANO
Depart. of Chemistry, Tokyo Institute of Tech., Meguro-ku, Tokyo 152-8551, Japan

## Introduction

The dynamics and spectroscopy of doubly excited molecules are subjects of current interest because of the breakdown of the independent electron model and Born-Oppenheimer approximation [1]. However, less has been known about the doubly excited states of polyatomic molecules in comparison with those of diatomic molecules. We investigated the doubly excited states of methane and found that the fluorescence oscillator strengths originating from the doubly excited states are as large as or even larger than those from the single-hole one-electron superexcited states [2]. In the present experiment, we have measured the cross sections for the emission of the fluorescences emitted by excited hydrogen atoms and NH radicals in the photoexcitation of ammonia ($NH_3$) as a function of incident photon energy in the range 13-40 eV and extensively investigate the doubly excited states of $NH_3$ [3].

## Experimental

Synchrotron radiation monochromatized by a 3 m-NIM equipped with a 2400 lines/mm grating at BL-20A was used as an incident light source. The fluorescence due to the photoexcitation of $NH_3$ were dispersed by a 30 cm uv-visible monochromator equipped with a 300 lines/mm grating and then detected by a CCD detector [2]. The Balmer-α, β, β, δ, ε (H($n$=3-7→$n'$=2)), NH($A^3\Pi_i \rightarrow X^3\Sigma^-$), NH($c^1\Pi \rightarrow a^1\Delta$) and NH($c^1\Pi \rightarrow b^1\Sigma^+$) fluorescences were observed.

## Results and Discussion

In figure 1 shown are the absolute cross sections for the emission of Balmer-β as a function of incident photon energy. The peak around 26 eV is attributed to the single-hole one-electron $(2a_1)^{-1}$(mo) state, where mo refers to a molecular orbital. The other two peaks around 22 and 30 eV are attributed to the doubly excited states, which are labeled D1 and D2, respectively. These superexcited states are also seen in the cross section curves for other Balmer fluorescences.

In figure 2 the oscillator strengths for the Balmer fluorescences originating from the $(2a_1)^{-1}$(mo) and doubly excited D2 states are plotted against the principal quantum number of the upper level of the hydrogen atom, $n$. Interestingly the oscillator strengths originating from the doubly excited D2 states are as large as those originating from the $(2a_1)^{-1}$(mo) states. This fact seems not to be amenable to the independent electron model, where double photoexcitation is much weaker than single photoexcitation.

## References

[1] N. Kouchi et al., J. Phys. B, 30, 2319 (1997).
[2] M. Kato et al., J. Phys. B, 35, 4383 (2002).
[3] M. Kato et al, in preparation.

*nkouchi@chem.titech.ac.jp

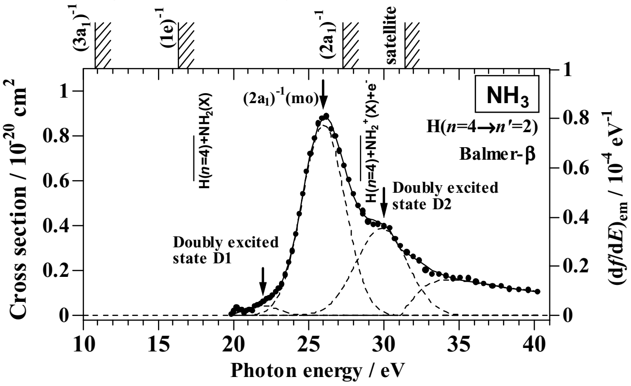

Fig.1 Cross sections (left axis) and oscillator strength distributions (right axis) for the emission of Balmer-β in the photoexcitation of $NH_3$ as a function of incident photon energy. The broken and solid curves show the results of the fits [3]. The dissociation limits and vertical ionization potentials are shown.

$NH_3$: $\tilde{X}^1A_1(1a_1)^2(2a_1)^2(1e)^4(3a_1)^2$

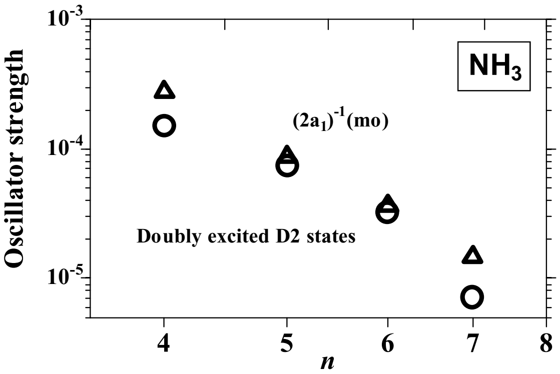

Fig 2. Oscillator strengths for the emission of the Balmer fluorescences (H($n$=4-7→$n'$=2)) originating from the $(2a_1)^{-1}$(mo) and doubly excited D2 states of $NH_3$ against the principal quantum number of the upper level of the hydrogen atom, $n$, on logarithmic scales for both axes.