Selective OD-bond Breaking of HOD Molecule: Photodissociation of vibrationally excited HOD in the $5\nu_{\text{OD}}$ state

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Introduction

Recently, selective bond-breaking has been a hot topic in photochemistry. For HOD molecule, selective OH-bond dissociation can be accomplished by using ultraviolet (UV) photolysis of the vibrationally excited state in the OH-stretching mode [1]. After the remarkable success, several groups have investigated UV photodissociation of vibrationally excited HOD [1-3]. The OH-stretching excitation into the $4\nu_{\text{OH}}$ and $5\nu_{\text{OH}}$ vibrational states, followed by the UV photolysis, could lead to the selective OH-bond dissociation with almost complete selectivity [1,2]. On the other hand, the OD-stretching excitation into the $3\nu_{\text{OD}}$ state led to the preferential OD-bond dissociation with the OD/OH branching ratio being $2.6 \pm 0.5$ [3]. However, the selectivity was much smaller than that for the selective OH dissociation induced by the OH-stretching excitation. In the present work, we investigated the photolysis of HOD in the $5\nu_{\text{OD}}$ state, which is higher than that used in the previous study [3].

Experiment

A crossed laser and molecular beams method was used for the present experiment [4]. Sample gas containing HOD was injected into a conventional chamber with time-of-flight mass spectrometer. By a near infrared (NIR) laser light at ca. 850 nm, HOD molecules were excited into the $5\nu_{\text{OD}}$ state, and then photodissociated by a UV laser light at ca. 243.1 nm. The H and D products were detected by utilizing the (2+1) resonance enhanced multiphoton ionization (REMPI) processes.

Results and Discussion

Fig. 1 shows the experimental result. The peak for D atom was clearly observed, whereas the REMPI signal for H atom was too weak to be detected under the present experiment. Base on the signal-to-noise ratio, we determined the lower limit of the OD/OH dissociation ratio to be 12. This result means that the OD-stretching excitation into the $5\nu_{\text{OD}}$ state followed by the UV photolysis at ca. 243.1 nm leads to the OD dissociation with almost complete selectivity. We discuss the selectivity for HOD in comparison with that for NH$_2$D/NHD$_2$, which we previously investigated [4].

References