

Comparative studies on the doubly excited states of H₂O and H₂S in the photoexcitation

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1 Introduction

The atomic and molecular doubly excited states are embedded in the ionization continuum. Because of the superposition of discrete and continuous electronic states, the doubly excited states of molecules are not described by the Born-Oppenheimer products. The double photoexcitation dynamics of molecules have thus been attractive subjects of research. One of the means to observe the doubly excited molecules is measuring cross sections for the emission of the fluorescence from neutral fragments as a function of excitation energy [1-3] since the detection of such fluorescence photons remove the superposition of discrete and continuous electronic states. It turned out from our previous investigations on CH₄ [1], NH₃ [2], and H₂O [3] that the superexcited states in the inner valence range are not so amenable to the independent electron model as those in the outer valence range. In other words the electron correlation for the superexcited states in the inner valence range is stronger than the electron correlation for those in the outer valence range. In the present experiment, the superexcited states of H₂S by the absorption of a single photon are investigated with measuring the cross sections for the emission of the Lyman- α fluorescence and the results are compared with the corresponding ones of H₂O [4].

2 Experiment

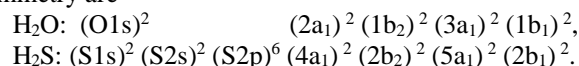
Linearly polarized light was introduced into a gas cell filled with H₂S. The photons emitted at the 54.7° magic angle with respect to the unit polarization vector of the incident light were detected by vacuum ultraviolet photon detectors. Two photon detectors, each of which consists of an MgF₂ window and a microchannel plate (MCP), are fitted to the gas cell and operated simultaneously: one of the detectors incorporates an MCP coated with CsI and the other incorporates an MCP without coating and therefore the detection efficiencies of them are different. The energy of the incident light was scanned in the range between 11 eV and 40 eV with 50 meV steps.

The dispersed fluorescence experiment was carried out at Bessy II. The non-dispersive detection has the advantage that the detection efficiency is much higher than by the dispersive one, but has the disadvantage that

the wavelength resolution is much poorer. Thus we skillfully combine the dispersive and non-dispersive detections to determine the cross sections for Lyman- α fluorescence emission with small contamination of other fluorescences and a small statistical uncertainty, which would not be obtained by the dispersive or non-dispersive detection alone.

3 Results and Discussion

The ground electronic states of H₂O and H₂S in C_{2v} symmetry are



Superexcited states of H₂O and H₂S are compared based on the similarity and difference of the electronic structure. In H₂S, ten superexcited states have been found from the analysis of the fluorescence cross sections against the incident photon energy, two of them are singly excited 2b₂⁻¹(mo) states with a single configuration and the other eight states are doubly excited states with multiple configurations. State-resolved dipole oscillator strengths for H(2p) formation in the photoexcitation of H₂S have been determined. It turns out that the energy-splitting of the doubly excited '4a₁⁻¹(mo)' states of H₂S is enhanced in comparison with that of the doubly excited '2a₁⁻¹(mo)' states of H₂O. This enhancement seems to be caused by the stronger electron correlation in H₂S than in H₂O.

The similarity in shape is seen between the inner valence band and inner shell band in the fluorescence cross sections against the incident photon energy for H₂S and H₂O. This similarity indicates that the electrons are excited to similar orbitals from the valence orbitals or inner shell orbitals.

References

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