Comprehensive Understanding of the Decay Dynamics of the Doubly Excited $Q_2\,^1\Pi_u(1)$ State in Photoexcitation of Hydrogen Molecules

The dynamics of doubly excited molecules mediated by the absorption of a single photon are a subject of current interest. The key to observing the doubly excited states is measuring cross sections free of ionization as a function of incident photon energy. In the present investigation, we measured the absolute values of the cross section for the formation of a 2*p* atom pair in the photoexcitation of H_2 and D_2 against the incident photon energy in the range of doubly excited states by means of the coincidence detection of a pair of Lyman-α photons. It turns out that the cross-section curves are attributed only to the contribution of the doubly excited $Q_2\,^1\Pi_u(1)$ state. Using the present results and previous ones obtained by our group [1], the dissociation dynamics of the $Q_2\,^1\Pi_u(1)$ state are comprehensively revealed.

The doubly excited states of molecules are embedded in an ionization continuum. Because of the superposition of the electronically discrete and continuous states, doubly excited states of molecules are not described as a product of the electronic and nuclear wavefunctions unlike the states below the ionization energy. The dynamics of doubly excited molecules have thus attracted much research as one of few-body correlated systems. Even for the simplest neutral molecule, hydrogen, the dynamics of its doubly excited states are not fully understood. Experimentally, the key to observing doubly excited molecules is measuring cross sections free of ionization against the excitation energy since the ionization makes a large contribution that prevents doubly excited states from being observed. Among the doubly excited states of hydrogen molecules, the $Q_2\,^1\Pi_u(1)$ state is known to play an important role in the formation of 2*s* and 2*p* fragment atoms [2, 3, 4, 5]. The photoexcitation process of H_2 via the $Q_2\,^1\Pi_u(1)$ state is shown below.

$$H_2 + \gamma_{ex} \rightarrow H_2(Q_2\,^1\Pi_u(1)) \quad (1)$$
$$\rightarrow H(2s) + H(2p) \quad (2)$$
$$\rightarrow H(2p) + H(2p) \quad (3)$$
$$\rightarrow H_2^+(1s\sigma_g) + e^- \quad (4)$$
$$\rightarrow H_2^+(2p\sigma_u) + e^- \quad (5)$$

In process (1), γ_{ex} stands for the incident photon. The oscillator strengths of process (2) for H_2 and D_2, $f_{2s2p}(Q_2\,^1\Pi_u(1))$, were measured [5] and are shown in Table 1, while those of process (3) are not yet known. In the present study [6], we aimed to measure the cross sections of process (3) for H_2 and D_2 against the incident photon energy and obtain a comprehensive understanding of the decay dynamics of the $Q_2\,^1\Pi_u(1)$ state of H_2 and D_2.

In the present experiment the pair of Lyman-α photons emitted by a pair of H (2*p*) atoms was detected in coincidence. This method was established by Odagiri *et al.* [4], and is referred to as the (γ, 2γ) method. Figure 1 shows the cross section of process (3) for H_2 and D_2 against the incident photon energy together with the theoretical cross sections of neutral dissociation in photoexcitation to the $Q_2\,^1\Pi_u(1)$ state of H_2 and D_2 [7]. It turns out that the pair of 2*p* atoms is produced only through the $Q_2\,^1\Pi_u(1)$ state since the shapes of the experimental and theoretical curves are in agreement with each other. By integrating the experimental curves in Fig. 1, the oscillator strengths of process (3) for H_2 and D_2, $f_{2p2p}(Q_2\,^1\Pi_u(1))$, are obtained and are shown in Table 1. Interestingly, the $Q_2\,^1\Pi_u(1)$ state contributes to the 2*p*+2*p* and 2*s*+2*p* channels, which indicates that the non-adiabatic transition from the $Q_2\,^1\Pi_u(1)$ state to some doubly excited state, probably the $Q_2\,^1\Pi_u(2)$ state, is involved. The schematic potential energy curves of the $Q_2\,^1\Pi_u(1)$ and $Q_2\,^1\Pi_u(2)$ states are shown in Fig. 2 [5, 6]. There is an avoided crossing between these potential energy curves at the internuclear distance of ~5.6 a_0, where a_0 is the Bohr radius [8]. As shown in Table 1, it is remarkable that the isotope effects on the oscillator strengths of 2*p*+2*p* pair formation and 2*s*+2*p* pair formation in photoexcitation to the $Q_2\,^1\Pi_u(1)$ state of H_2 and D_2, f^{D2}/f^{H2}, are almost the same. This channel independence shows that the isotope effects on the oscillator strengths of both channels are dominated by the early dynamics of the $Q_2\,^1\Pi_u(1)$ state before the doubly excited molecule in the $Q_2\,^1\Pi_u(1)$ state reaches the branching point into 2*p*+2*p* formation and 2*s*+2*p* formation around ~5.6 a_0. The dissociation dynamics of the photoexcited $Q_2\,^1\Pi_u(1)$ state of H_2 and D_2 have thus been comprehensively determined.

Table 1: Experimental oscillator strengths of 2*p*+2*p* pair formation, $f_{2p2p}(Q_2\,^1\Pi_u(1))$, and those of 2*s*+2*p* pair formation, $f_{2s2p}(Q_2\,^1\Pi_u(1))$, in the photoexcitation to the $Q_2\,^1\Pi_u(1)$ state of H_2 and D_2. The ratio of the oscillator strengths, f^{D2}/f^{H2}, is also shown for each channel.

	H_2	D_2	f^{D2}/f^{H2}
$f_{2p2p}(Q_2\,^1\Pi_u(1))$ [6]	3.5×10^{-4}	2.4×10^{-4}	0.69
$f_{2s2p}(Q_2\,^1\Pi_u(1))$ [5]	21×10^{-4}	14×10^{-4}	0.67

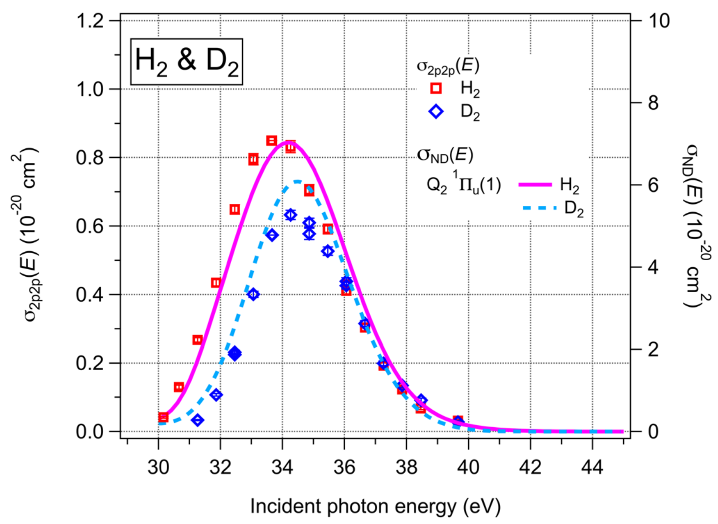

Figure 1: Absolute values of the cross sections of 2*p* atom pair formation in the photoexcitation of H_2 (squares) and D_2 (diamonds) against the incident photon energy [6]. Curves show the theoretical cross sections of neutral dissociation σ_{ND} in photoexcitation to the $Q_2\,^1\Pi_u(1)$ states of H_2 (solid line) and D_2 (dashed line) [7], of which values are shown on the right vertical axis. Reproduced with permission.

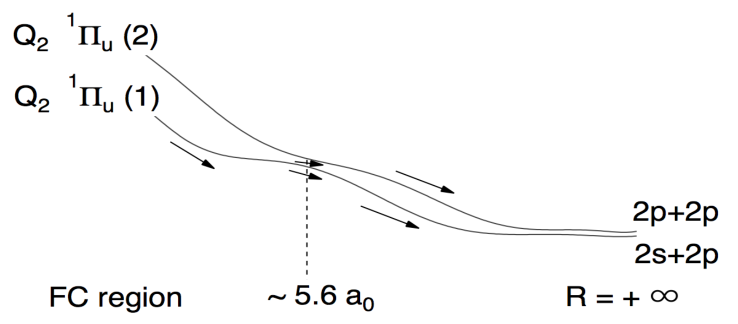

Figure 2: Schematic potential energy curves of the doubly excited $Q_2\,^1\Pi_u(1)$ and $Q_2\,^1\Pi_u(2)$ states of H_2 and D_2 [5, 6]. The arrows show the dissociation pathways of the molecule photoexcited to the $Q_2\,^1\Pi_u(1)$ state in the Franck-Condon region (FC region). Reproduced with permission.

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BEAMLINES

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