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Neutral dissociation of hydrogen molecules in a strong laser field through superexcited states

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Abstract
Fragmentation of hydrogen molecules in a strong laser field is studied experimentally and
theoretically. Balmer lines ($n \rightarrow 2$) from hydrogen atoms are observed up to $n = 14$. The
emission intensity of the two strongest Balmer lines versus laser intensity in a log–log plot
gives a slope of more than 11. This indicates that some high-lying states in the continuum are
excited resulting in neutral dissociation. Adapting Rydberg state approximation, the potential
energy curves of superexcited states of hydrogen are plotted. Semi-empirical calculation
confirms dissociation through these superexcited states. The upper limit of the lifetime of the
superexcited states is obtained by an ultrafast pump and probe experiment by monitoring one
of the fluorescence lines.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Hydrogen, the simplest and most abundant molecule in the universe, shows rich and fundamental physical behaviour while interacting with ionizing radiation [1]. Recently the dissociation behaviour of hydrogen molecules in a strong laser field has attracted considerable attention from scientists [2–4]. A neutral hydrogen atom after strong field dissociation has already been observed using biased mass spectroscopy. The interpretation of the dissociation mechanism is based upon a photo ionization channel, where hydrogen molecules undergo ionization to H_2^+ ions, or Coulomb explosion without double ionization [2]. Lyman-α radiation has also been detected after H_2 molecules are irradiated by a strong 800 nm laser pulse. It was attributed to the re-excitation of a neutral fragment, rather than direct dissociation from the excited state [4].

Generally speaking, in an intense laser field, molecules could be highly excited owing to multiphoton absorption. The highly nonlinear laser power dependence of product yield tends to support the multiphoton excitation mechanism. Such highly nonlinear excitation means that molecules can be populated in the superexcited states (SESs). The important features of SESs of a molecule, possessing energy above the ionization potential, were first proposed by Platzman in 1962 [5, 6]. Kouchi *et al* [7] reported the dissociation dynamics of superexcited molecular hydrogen using synchrotron radiation as an excitation source. Recently, Glass-Maujean *et al* measured the absolute cross sections of three competing decay channels from SESs: fluorescence, dissociation and ionization of hydrogen by synchrotron radiation (vacuum ultraviolet photons) [1]. We have used an SES model to study the neutral dissociation process of CH_4, O_2 and NO molecules in a strong laser field [8–11]. Molecules can be stimulated to SESs by
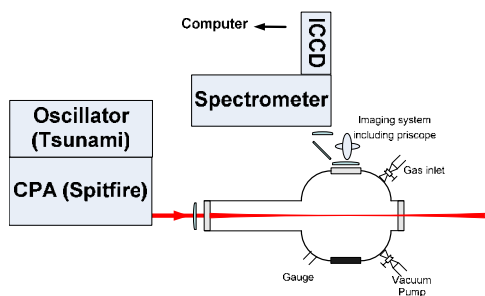
Figure 1. Sketch of the experimental setup which was used to measure fluorescence.

absorbing many laser photons in intense laser fields of 10^{13-14} W cm^{-2}. However, it is still difficult to calculate potential energy curves (PECs) of the SESs by quantum mechanical theory even with approximate methods. Currently, the PEC can be simulated approximately by those of Rydberg states since most observed SESs are assigned to Rydberg states which are vibrationally (or/and rotationally), doubly, or inner core excited and converge to their corresponding ionic states [12]. The neutral dissociation can be considered as taking place from these Rydberg-type PECs.

In this work, an intense femtosecond Ti-sapphire laser is used to excite hydrogen molecules into the SESs. Many spectral lines in the Balmer series are recorded. These series of radiations provide a window to further explore the dissociation mechanism. Using a pump-probe technique and fluorescence spectroscopy, we confirmed multiphoton superexcitation of hydrogen molecules in a strong laser field. We detect the depletion of the fluorescence signals by the probe pulse and determine the lifetime of the SESs. At the same time, coupled to PEC simulation, we found that repulsive PECs could explain the dissociation process.

2. Experimental setup

A schematic diagram of the experimental setup to obtain the fluorescence spectra (Balmer series) is shown in figure 1. The seed pulse from a mode-locked femtosecond Ti-sapphire oscillator (Spectra Physics Tsunami) is sent into a chirp pulse amplification (CPA) module (Spectra Physics Spitfire). In the CPA section, a stretcher is used to stretch the pulses from 30 fs transform limited to around 200 ps positively chirped pulses. These were then amplified by a regenerative amplifier followed by a two-pass amplifier. Finally, a parallel grating compressor is used to give a transform-limited pulse with pulse duration of about 42 fs at FWHM (full width at half-maximum). The pulse duration is measured using a second-order single-shot autocorrelator (SSA, Positive Light). The output beam has a 1 kHz repetition rate, maximum energy of 2 mJ/pulse with a diameter of about 5 mm ($1/e^2$ level of the fluence). A half-wave plate is used before the compressor to change the output energy of the linearly polarized pulses.

The sketch of a pump and probe experimental setup is illustrated in figure 2. The laser beam is separated into two arms by a 50/50 beam splitter. One is used as the pump beam
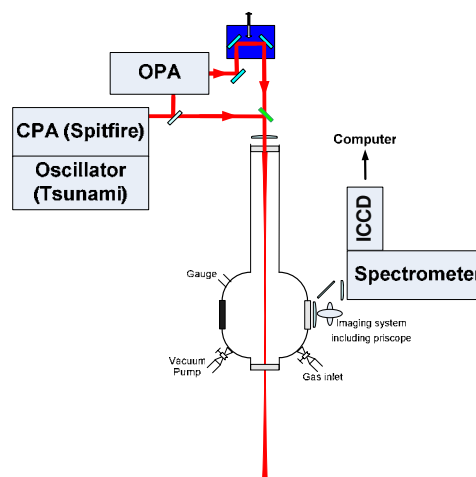

Figure 2. Sketch of the experimental setup which was used to study the dynamics of SESs.

($\sim$900 μJ/pulse). The other is sent to an optical parametric amplifier (OPA800C Spectra Physics) to generate the infrared probe pulses at 1338 nm with pulse duration of about 50 fs (FWHM) and pulse energy of around 65 μJ. In the probe arm, a high-resolution delay line (40 nm) is used. The probe beam has a horizontal polarization parallel to that of the pump beam. Spatial superposition of the two pulses is checked with a far-field measurement, while temporal superposition of these two pulses in air is checked by a four wave mixing (4 WM) process, where two photons of 800 nm are mixed with one infrared photon ($2\omega_{800} - \omega_{ir}$), leading to a yellowish laser emission [13]. Finally, in both experiments, the laser pulses are focused into a vacuum chamber by the same plano-convex lens ($f = 100$ cm). The vacuum chamber is evacuated by a triscroll vacuum pump (Varian Inc.) to the background pressure of 4×10^{-2} Torr. Then pure hydrogen gas was introduced to the interaction chamber at an equilibrium pressure of about 8 Torr.

The collected fluorescence from the interaction zone is delivered to the spectrometer (Acton research Corporation, Spectra Pro 500i) entrance slit with the width of 100 μm. We use an imaging system, including a periscope using metallic mirrors and fused silica lenses, to image the narrow and linear fluorescence column onto the spectrometer's entrance slit. The image and the slit are parallel to each other. The spectrometer is operated with a grating with 1200 groove mm^{-1}. The selected wavelength is detected by an intensified charged coupled devices (ICCD) camera (Princeton Instrument ICCD PIMAX 512). The error in the reading of wavelength is 0.3 nm. We use the gating mode of the ICCD to get rid of the scattered signal coming from the main pulses. The gate delay is chosen to be around 20 ns before the arrival of the main pulse in the interaction zone and the gate width is 400 ns.
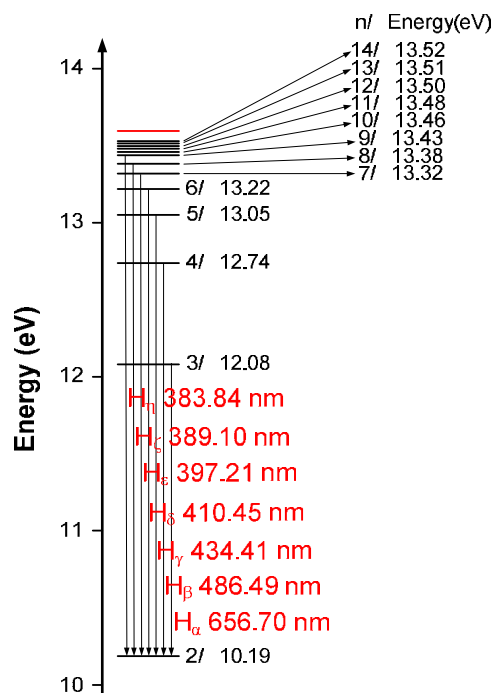
3. Results and discussions

Figure 3 shows the fluorescence spectra obtained in the range of 300–700 nm. The spectral lines are attributed to the Balmer series of the hydrogen atom ($n\rightarrow2$), from $n = 3$ up to $n = 14$. Figure 4 shows the energy levels of fluorescing
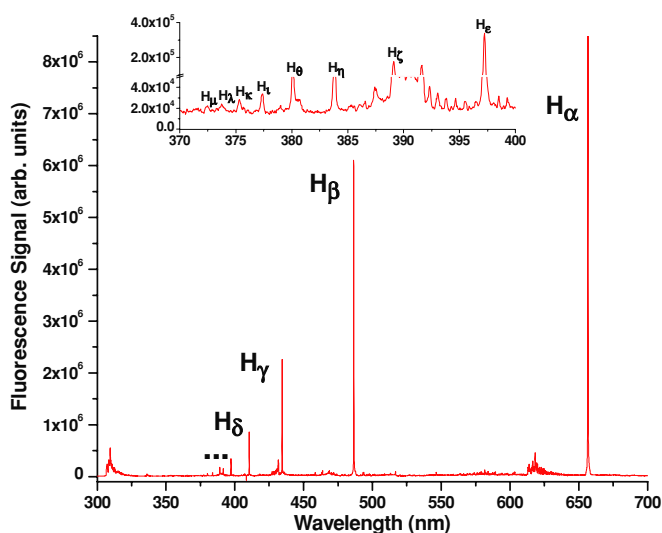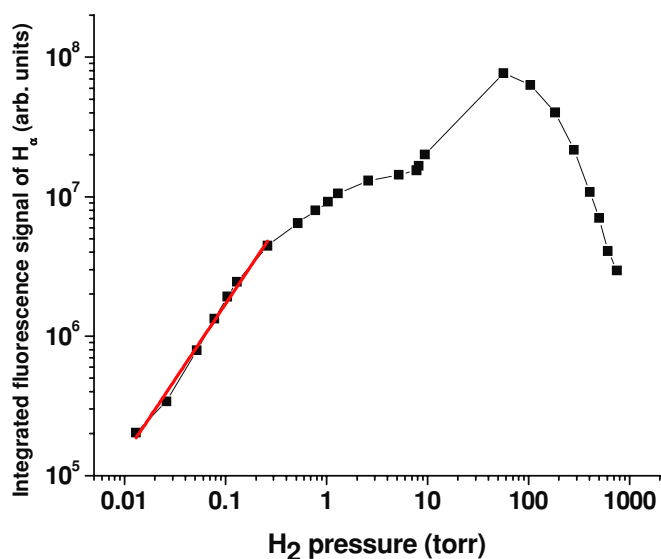
Figure 3. The fluorescence spectra of H$_2$ in a strong laser field at around 8 Torr. The inset shows the lines of H atoms from 370 to 400 nm.

Figure 4. The observed hydrogen atomic lines in figure 3 attributed to excited atomic hydrogen, 12 Ballmer series (ground state energy is zero and the first ionization potential is 13.59 eV) [14].

Figure 5. Integrated fluorescence signal (around 656 nm) versus pressure of hydrogen molecules.

hydrogen atoms according to [14]. The observation of so many excited hydrogen atoms as the dissociation products is indeed significant. On the one hand, the observation of the excited species implies that the parent molecule has been excited to some highly excited states. We note that the dissociation energy of a hydrogen molecule is 4.47 eV, while in the experiment the H(3*l*) state is populated which needs an energy of 12.08 eV (see figure 4). It means that the excitation energy in the dissociation process H$_2$→H(3*l*) + H(1*s*) needs at least 16.55 eV. This is beyond the first ionization potential of the hydrogen molecule (15.42 eV) [15]. In other words, hydrogen molecules are excited to some highly excited states, i.e. SESs, in the intense laser field.

We have investigated the pressure dependence of the fluorescence signal to provide a proof that excited hydrogen fragments are the result of direct laser excitation rather than other processes (see for example [16]). Figure 5 shows the integrated fluorescence signal of the first Balmer line versus pressure in a log–log scale. It is obtained in more than three orders of magnitude in pressure. We have fitted a red line with a slope 1.08 in the low-pressure region. Clearly, in the low-pressure region, the fluorescence signal increases linearly with pressure. At higher pressures, collisional quenching can decrease the fluorescence signal. Therefore, there is no other process that can create neutral excited atomic hydrogen. The abrupt increase starting from around 10 Torrs could be due to self-focusing and filamentation resulting in a sudden increase in intensity in the interaction zone. We have recorded the full spectra for various pressures. The observed Balmer series in all the pressures are identical except that the signal to noise ratio is different at different pressures. Moreover, based on lifetime measurement of SESs in hydrogen molecules we can exclude other processes such as collision as a reason to create atomic excited hydrogen. We will discuss this latter problem in more detail at the end of this paper. In addition, laser excitation to molecular Rydberg states resulting in neutral dissociation to atomic fragments and its competition with ionization was

already shown by recording photoelectron spectra at different wavelengths (310–330 nm) in [17]. However, a full physical interpretation of figure 5 is beyond the scope of this paper.

The highly nonlinear laser power dependence of product yield (fluorescence) provides an experimental evidence in the formation of SESs. Indeed, we measured the fluorescence intensity of two strong Balmer lines as a function of the laser energy. The laser energy is proportional to the intensity of the laser shots. Based on Gaussian beam propagation, one could estimate the intensity from the energy of the pulse (1–2 mJ

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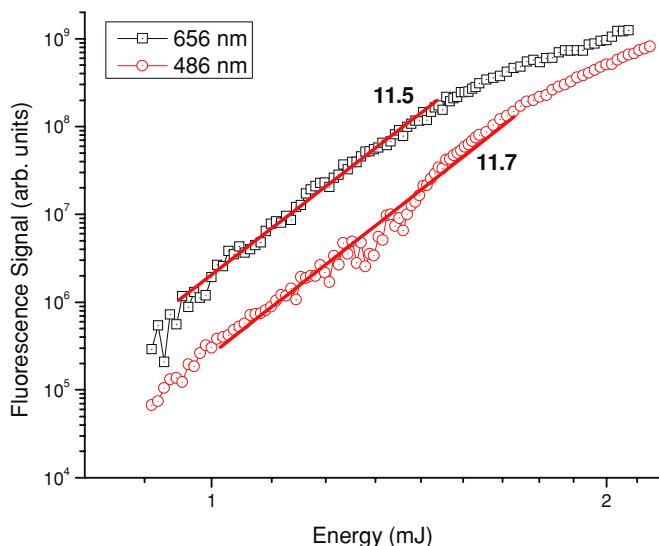
Figure 6. Fluorescence signal versus the laser energy which is proportional to intensity. The fluorescence is collected and integrated around 656 nm, 486 from the first two Balmer series.

Figure 7. Potential energy curves of H_2. H_2 in the ground state (black solid curve), H_2^+ions (blue solid curves), Rydberg states (green dotted curves) and superexcited states (red dotted curves).

corresponding to 1.4×10^{14}–2.9×10^{14} W cm^{-2}). We measured the slope of each line in the energy scale. The slopes are 11.7 and 11.5 in a log–log plot for the wavelengths of around 656 nm and 486 nm, respectively (figure 6). These slopes indicate that the H_2 molecule can be excited to a highly excited state through the absorption of at least about 11 to 12 effective photons (one photon energy ~ 1.55 eV) whose energy (17.05–18.6 eV) is beyond the first ionization potential (15.42 eV). The highly excited states, i.e. SESs, undergo dissociation leading to the product of H atoms which we observed. On the other hand, having observed different products suggests that a variety of dissociation channels exist simultaneously.

For the dissociation of molecules in intense laser fields, there are two classes of pathways. The first considers the dissociation of the molecules under external laser fields. For example, we propose the field assisted dissociation (FAD) model which can successfully treat the dissociation of the molecular ions of acetone, methane, and acetyl aldehyde [18–20]. Other theoretical models such as re-scattering, bond softening, or above threshold dissociation belong to this class of pathways. The second considers that the intense laser field causes an extremely high excitation of the molecule, equivalent to absorbing as many as 12 laser photons and leading to highly excited states with almost 18 eV. A spontaneous dissociation without laser fields thus takes place. Laser field-free PECs can be applied in the subsequent dissociation process. This paper treats the dissociation of a hydrogen molecule through the second pathway. However, there is no quantum mechanically calculated PEC for SESs, since the accurate calculation of the high-lying excited states of molecules is extremely difficult, even for a hydrogen molecule. Recently, we proposed a Rydberg molecule model to estimate the dissociation process. The model successfully explains the neutral dissociation of O_2, NO and CH_4 molecules [8–11]. In the Rydberg model, the SES is considered as the Rydberg state which consists of an excited ion core and a Rydberg electron. The Rydberg
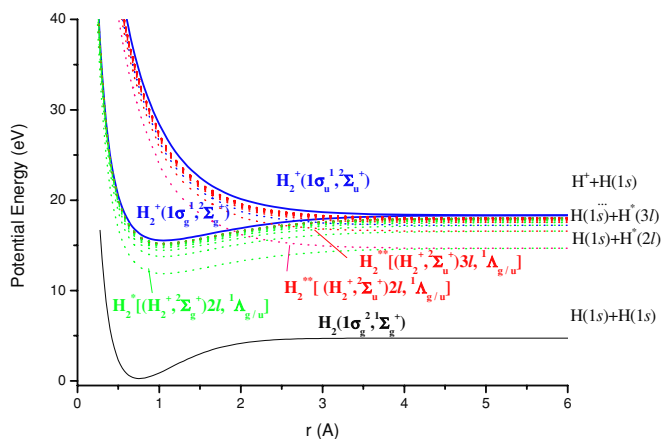
electron can be treated as a spectator, not participating in the dissociation directly. The dissociation products are two neutral fragments. One of them is a Rydberg atom or molecule with the same principle quantum number n and angular momentum quantum number l of the superexcited parent molecule. To obtain the PECs of high-lying Rydberg states, we first calculate the PECs of the corresponding H_2^+ ion cores (figure 7). The calculations are performed with the MOLPRO software package [21] at CASSCF/av5z level. Then, we shift down the curve (PEC) of the state $^2\Sigma_u^+$ until the energy limit on the long-distance side fits the experimental data [14]. In this way, PECs of some superexcited H_2 states are obtained (figure 7). With these Rydberg PECs, we are able to trace the dissociation pathway of the superexcited H_2 molecules. In a strong laser field, the ground state H_2 molecules absorb many photons simultaneously accompanying a vertical excitation in the energy plot. Various SESs of hydrogen molecule, $H_2^{**}[(H_2^+,1^2\Sigma_u^+)nl,1\Lambda_{g/u}]$ and $H_2^*[(H_2^+,1^2\Sigma_g^+)nl,1\Lambda_{g/u}]$, with different quantum numbers are reached, where $(H_2^+,1^2\Sigma_u^+)$ and $(H_2^+,1^2\Sigma_g^+)$ stand for the ion core, nl stands for the spectator electron with a principle quantum number n and an angular quantum number l and $^1\Lambda_{g/u}$ stands for the term of the superexcited H_2^{**}. Rydberg states, $H_2^{**}[(H_2^+,1^2\Sigma_u^+)nl,1\Lambda_{g/u}]$, dissociate spontaneously along the repulsive ion-state-shape PECs or transit to Rydberg states of $H_2^*[(H_2^+,1^2\Sigma_g^+)nl,1\Lambda_{g/u}]$ via avoided crossing, producing a ground state H atom and an excited H atom. The latter species emit lights at wavelengths of 656, 486, 434, 410 nm, . . . which are observed in our experiment. But another Rydberg states series, $H_2^*[(H_2^+,1^2\Sigma_g^+)nl,1\Lambda_{g/u}]$, are not responsible for the observation of H excited atoms, because their vertical excitation energies are smaller than dissociation limits, and corresponding dissociation processes do not occur.

To know the dissociation dynamics and properties of SESs, we measured the fluorescence signals of some of the spectral lines as a function of the delay time between ultra-short pump (800 nm) and probe (1338 nm) pulses. Figure 8 shows the integrated 656 nm fluorescence intensity versus the
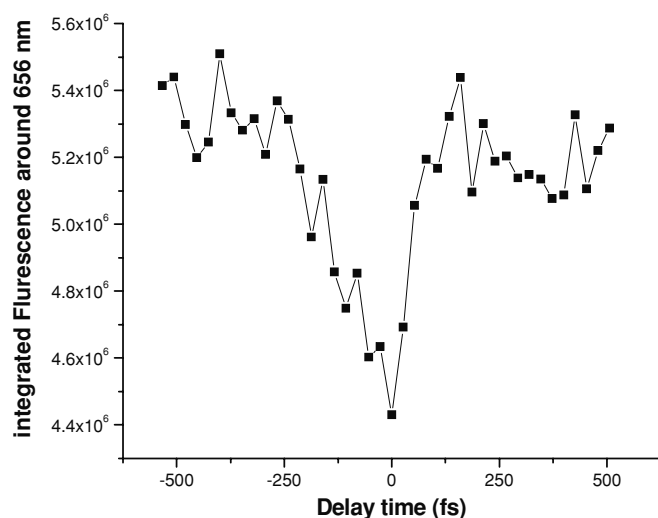
Figure 8. Integrated fluorescence signal at around 656 nm versus the delay time between the pump and probe pulses, a negative delay time means the probe pulses are behind the pump pulses.

delay time between pump and probe pulses. We can clearly see an obvious decrease of the fluorescence signal taking place when the delay time is around zero. The dip width of the fluorescence signal is about 180 fs (FWHM). Coupled to the PEC simulation, we can imagine that SESs will be de-excited by the probe pulse when dissociation is underway. This results in the depletion of the florescence signals. Therefore, the dip width means the lifetime of the SESs. This experiment was performed for the other lines, namely 486 nm. The result is roughly the same with a lifetime of 180 fs. We emphasize here that the fluorescence depletion could not be explained by other reasons. We exclude the simple ionization scheme where the neutral hydrogen atoms are generated by disintegration of the H_2^+ ion or electron–ion recombination since the lifetime of these two processes is very long.

Now we can discuss the fact that SESs are the result of direct laser excitation in more detail. As we showed above, the 42 fs laser pulse (800 nm) excites the molecule into the SESs. Within this pulse duration, there is no collision between molecules at 8 Torr because the mean collision time is of the order of 50 ns. The dissociation of the molecule from the SESs into the two H neutrals takes about 180 fs according to our current measurement. This is the lifetime of the SES. During this time together with the pumping time of 42 fs, there is still no collision with any neighbouring molecule while H* is already formed and will fluoresce. During the fluorescence time of H*, there is collision. But this will only reduce the fluorescence intensity. It would not contribute to the excitation of H atoms. And this is what the experimental data show: a decrease in the fluorescence signal at 8 Torr. Electron collision can be neglected during the pumping and dissociation time of about 222 fs (pump duration + SES lifetime) because the mean free time of an electron at 8 Torr is about 95 ps. Electron collisional excitation of the neutral ground state H atom could be neglected because the free electron energy through ATI (above threshold ionization) at the intensity level we are using is at best a few eV and the probability is very

small. By the same argument, electron excitation of the SES can be neglected. Finally, we would claim that without any ambiguity, the excited hydrogen fragment is a result of direct laser excitation of a hydrogen molecule.

4. Conclusion

We found that the hydrogen molecule undergoes neutral dissociation in a strong laser field at intermediate intensities. The fluorescence spectra of the dissociation products are attributed to the Balmer series of the hydrogen atom ($n \rightarrow 2$), up to $n = 14$. These excited products imply that parent molecules are excited to highly excited states, i.e. SESs, in intense laser fields. This point is supported by the laser intensity dependence of the fluorescence intensity of the H atom. After multiphoton excitation, superexcited H_2 molecules undergo spontaneous dissociation. To understand the dissociation mechanism of the SESs of H_2 molecules, empirical PECs for different SESs are built. Only repulsive PECs are used to interpret neutral dissociation. Using a pump–probe technique, the lifetime of transient SESs is measured to be around 180 fs.

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