H^- Formation in Laser-Excited Molecular Hydrogen

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(Received 10 August 1992)

Experimental evidence is reported for the efficient H^- formation in UV laser irradiated H_2.

PACS numbers: 34.80.Qb, 34.50.Rk, 34.60.+z

Only the lowest vibrational level ($v=0$) of the ground electronic state $X\,^1\Sigma_g^+$ of H_2 is populated at room temperature (~ 300 K); for slow electrons, the electron attachment cross section for this state has a peak value of $\sim 1.6\times 10^{-21}$ cm^2 (rate constant $\sim 10^{-14}$ cm^{3}s^{-1}) at 3.75 eV electron energy [1]. However, the electron attachment cross section was shown to increase rapidly with increasing vibrational energy, and an enhancement of more than 4 orders of magnitude was observed for the $v=4$ level [2,3]. Recent extended calculations [4,5] show that the maximum electron attachment rate constant approaches 10^{-8} cm^{3}s^{-1} around $v=8$. As for electron attachment to electronically excited states of H_2, the only available study is a calculation [6] for the metastable $c\,^3\Pi_u$ state which predicts about 3 orders of magnitude enhancement for this state compared to the ground state $X\,^1\Sigma_g^+$ ($v=0$).

In this Letter, we report efficient H^- formation in laser-irradiated H_2. Free electrons produced via laser photoionization convert to H^- ions via attachment to electron attaching species produced by the same laser pulse; however, the identity of these electron attaching species remains unclear and we will discuss several possibilities.

Besides its basic significance, the present observations could be significant for the development of a negative ion source for the generation of neutral beams for magnetic fusion research and other applications [7]. It is possible that the present scheme is more efficient compared to a low-pressure H_2 discharge [8] as a H^- source.

The technique and the experimental apparatus have been described earlier [9,10]. Briefly, the gas under study (in the present case a few Torr of H_2) is irradiated with a UV laser pulse; the attaching electrons are produced via (multiphoton) ionization, some of which are converted to negative ions. The negative ions and the unattached electrons are separated from positive ions resulting from photoionization using a three-electrode configuration [9]: The laser pulse propagates between two of the electrodes and the negative or positive charges produced in the interaction region are extracted to the adjoining detection region through a grid in the middle electrode by applying appropriately oriented electric fields in the two regions. In the "negative mode," the signal components due to the unattached electrons and the negative ions can be distinguished since they travel to the detection region with different (drift) velocities; a "break" in the signal wave form could easily be seen (see Fig. 5 of [10]) when the total pressure in the chamber exceeds ~ 0.1 kPa.

In the present experiments, transitions to energies above the ionization threshold of H_2 were accomplished via three different schemes that have been employed in traditional resonance enhanced multiphoton ionization (REMPI) studies [a $(m+n)$ REMPI process indicates the population of a resonant state with the absorption of m photons and subsequent ionization of the resonant state by the absorption of n more photons from the same laser pulse]. These are the following: (i) a (3+1) REMPI process via the $B\,^1\Sigma_u^+$, $v=7$ state at 307.39 nm [11], (ii) a (3+1) process via the $B'\,^1\Sigma_u^+$, $v=2$ state at 263.50 nm [12], and (iii) a (2+1) process via the $E,F\,^1\Sigma_g^+$, $v=6$ state (this vibrational state is sometimes labeled as $v_E=2$, referring to the level located in the potential well E of the double minimum state) [13–15].

In (i) and (ii) above, a Lumonics EX-500 excimer laser operating at the 308 nm XeCl line pumped a Lambda Physik FL2000 dye laser, the output of which was frequency doubled using an INRAD autotracker II system. The frequency-doubled output energies were ≤ 0.7 mJ and even with focusing with a $f=15$ cm lens, the maximum total signal level (which is proportional to the number of electrons initially produced via photoionization [9]) was ~ 100 mV [16], and was not sufficient to carry out a quantitative study of laser intensity dependence of total and negative ion signals. However, negative ion formation was observed in both cases.

The coincidence of the two-photon energy of the 193 nm ArF excimer laser line with $E,F\,^1\Sigma_g^+$ ($v=6$) level together with the comparatively large pulse energy (~ 100 mJ) at this line helps to induce efficient transitions to the continuum in a (2+1) REMPI process, scheme (iii) above. The signal levels were sufficiently large to carry out quantitative measurements and in the following we restrict the discussion to this process.

A schematic potential energy diagram of H_2 relevant to our discussion is shown in Fig. 1. The cross section for the $X\,^1\Sigma_g^+ \rightarrow E,F\,^1\Sigma_g^+$ two-photon transition has been measured to be $\sim 1\times 10^{-47}$ cm^{4}s^{-1} [14]; the lifetime of the E,F state is ~ 100 ns [13]. Even though the Franck-Condon region for the $X\,^1\Sigma_g^+ \rightarrow E,F\,^1\Sigma_g^+$ two-photon

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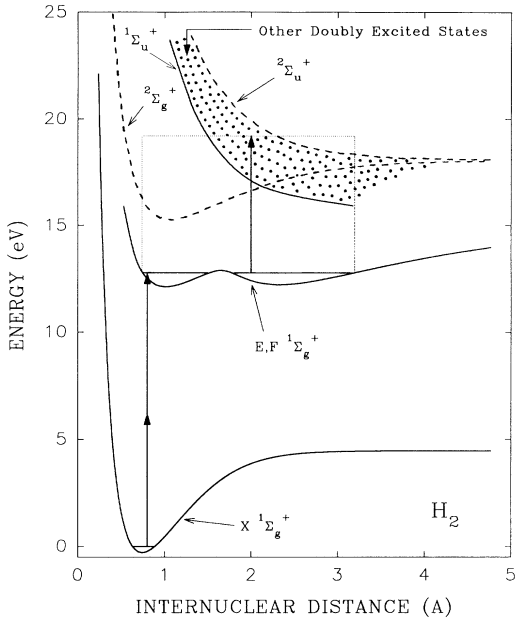

FIG. 1. Schematic energy level diagram of H_2 relevant to the discussion in the text. The solid and dashed curves correspond to the neutral and ionized molecules, respectively. All the potential energy curves were taken from Sharp [17], except for the one for the doubly excited SES $^1\Sigma_u^+$ $(2p\sigma_u 2s\sigma_g)$ which was taken from Guberman [18]. Other optically allowed doubly excited states of H_2, calculated by Guberman [18], that converge the $^2\Sigma_u^+$ state of H_2^+ are located in the dotted region between the $^1\Sigma_u^+$ and $^2\Sigma_u^+$ curves. The rectangular area indicates the approximate range of internuclear distances over which excitations from the E,F state can occur (see the text).

transition is restricted to the inner well of the double minimum state, both wells are populated due to the significant tunneling especially for the $v=6,7$ states lying close to the top of the barrier [19]; therefore, further photoexcitation of molecules from this intermediate state takes place over a large range of internuclear distance; see Fig. 1. It is clear that several outcomes are possible from the photon absorption at the E,F level, viz., (i) direct ionization,

$$H_2^*(E,F)+h\nu \rightarrow H_2^+ + e^- , \tag{1}$$

(ii) population of a Rydberg series composed of doubly excited superexcited states (SES) [18] converging to the $^2\Sigma_u^+$ excited ion state [in the dot-filled region of Fig. 1 lying between the $^1\Sigma_u^+$ $(2p\sigma_u 2s\sigma_g)$ neutral SES and the $^2\Sigma_u^+$ ionic state],

$$H_2^*(E,F)+h\nu \rightarrow H_2^{**} , \tag{2}$$

and (iii) dissociative ionization,

$$H_2^*(E,F)+h\nu \rightarrow H+H^+ + e^- . \tag{3}$$

Furthermore, the SES populated in (2) above may decay via different channels, viz.,

$$H_2^{**} \rightarrow H_2^+ + e^- \quad \text{(autoionization)}, \tag{4a}$$

$$\rightarrow H+H^*(n) \quad \text{(dissociation)}, \tag{4b}$$

$$\rightarrow H^+ + H^- \quad \text{(ion-pair formation)}, \tag{4c}$$

$$\rightarrow H_2^*(\text{HR}) \quad \text{(high-Rydberg formation)}. \tag{4d}$$

Some of these possibilities have been studied [14,15,20, 21] for H_2 for excitation wavelengths at or close to the wavelength of the ArF excimer laser, in connection with photoelectron energies and relative yields of H^+ and H_2^+. The photoabsorption cross section of the E,F state at the ArF laser line has been measured by Buck *et al.* [14] to be $\sim 6\times 10^{-18}$ cm^2; taking into consideration only the contributions due to direct ionization and population of the $^1\Sigma_u^+$ SES, the calculated value for this cross section was $\sim 11\times 10^{-18}$ cm^2 [14]. Once other possible channels—population of other allowed SES and dissociative ionization—are included, this number could be substantially higher, as indicated by our experiments.

In the present experiments, a uniform cross section of 2×0.7 cm^2 of the ArF output (FWHM ~ 10 ns) from the Lumonics EX-500 laser was reduced by a telescope arrangement using two lenses of focal lengths of 46 and 10 cm; the estimated beam cross section in the interaction region (~ 0.07 cm^2) was used to calculate the laser intensity; the interaction region was 9 cm long. The transmitted laser pulse energy was monitored using a Molectron J-25 probe, and was corrected for window loss to evaluate the pulse energy in the interaction region. The signal wave forms were recorded with a Nicolet 450 digitizer. The H_2 gas was purchased from the Aldrich Chemical Company and had a quoted purity of 99.99+%; the experimental chamber had a base pressure of $\sim 5\times 10^{-6}$ Pa.

The laser intensity dependence of the measured total signal, V_T, and the measured negative ion signal, V_I, are shown in Fig. 2 for three values of the applied electric field. It must be noted that V_T is the sum of V_I and V_E, the signal due to (unattached) electrons. At low laser intensities I, $V_T \approx V_E$; with increasing I, the negative ion signal grows rapidly at the expense of the electron signal; see Fig. 2. Thus, it is quite clear that electrons are produced via photoionization and they are converted to negative ions via attachment with increasing efficiency as the laser intensity is increased. Since electron attachment outside the laser irradiated region is negligible [1], the negative ions must be formed via electron attachment in the laser-irradiated region.

From Fig. 2 it is seen that V_T and V_I vary, respectively, as I^2 and I^4 (as the V_I curve approaches the V_T curve, it deviates from the I^4 dependence since $V_I < V_T$). If V_T is proportional to the number density of electrons initially produced via photoionization, then it should display a laser intensity dependence identical to that for laser photoionization. The apparent I^2 dependence we observe for the (2+1)-photon process is due to the efficient photon

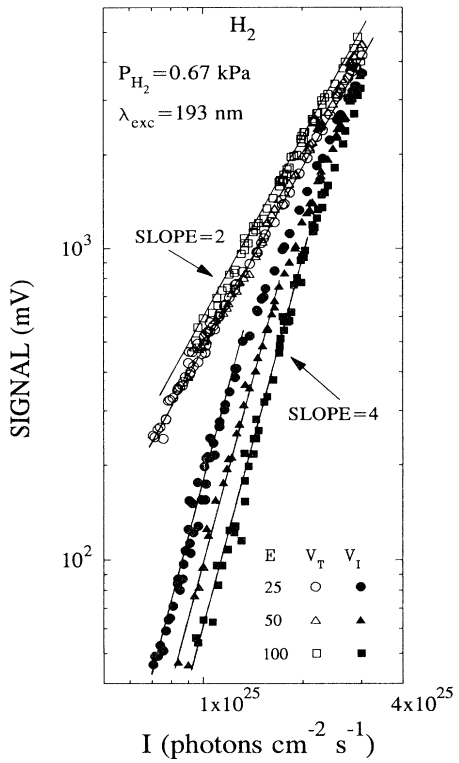

FIG. 2. Laser intensity I, dependence of the measured total V_T, and negative ion V_I signals for the experimental parameters indicated in the figure (see the text).

absorption for the E,F state. A rate equation analysis [9] shows that this should be the case if $\tau_L > \sigma^* I$, where τ_L is the laser pulse duration ($\sim 10^{-8}$ s) and σ^* is the absorption cross section of the E,F state (also see [22]). The number density of molecules excited to the E,F state, in turn, increases linearly with the laser intensity. Since V_T is proportional to the number density of electrons produced via photoionization, one would expect V_T to increase linearly with H_2 pressure, P. However, we observed a less than linear dependence; this was presumably due to the quenching of the intermediate E,F state by collisions with H_2 molecules [13]. The observed dependence of V_I on P together with the above observation indicated that more than two H_2 molecules contributed to the formation of each H^-. This evidence would be consistent with a collisionally enhanced electron attachment process.

Before discussing the possible electron attachment processes, let us first consider two other possibilities for the observed H^- formation. The *first possibility* is the ion-pair formation process, Eq. (4c) above. Even though this is energetically possible (threshold ~ 17.3 eV), it can be ruled out for the following reasons: (i) This mechanism is not consistent with the observed I^4 dependence for V_I. If H^- is produced on a single outward trajectory of the SES, then it should yield at most an I^3 dependence; under our experimental conditions it should yield an I^2 dependence since photoionization is shown to be an apparent two-photon process. (ii) As we mentioned earlier, in experiments with frequency-doubled dye laser radiation we did observe efficient H^- formation at 307.39 nm, which corresponds to a total excitation energy of ~ 16.3 eV which lies below the ion-pair formation threshold. (iii) The ion-pair formation has been shown to be a weak process [23]. Pratt *et al.* [23,24] have recently studied the field dependence of the threshold for ion-pair formation in H_2 in a two-laser experiment where the first laser (wavelength ~ 193 nm) populated the E,F ($v=6$) state. In the two-laser experiments, the H^- signal due to ion-pair formation was much weaker compared to the H_2^+ signal due to photoionization; they also failed to see the H^- signal with only the first laser [24]. It must be noted that their experiments were conducted under low-pressure conditions (pressure $\sim 10^{-3}$ Torr), and with 193-nm laser pulse energies < 100 μJ [24]. The *second possibility* is H^- formation via collisions of electrons with H_2^+ or indirectly populated H_3^+. Formation of H^- via these processes has also been shown [25] to be weak.

Let us then consider the possibility of H^- formation via electron attachment processes. First, the inference we made earlier, i.e., that the number density of molecules excited to the E,F state varies linearly with I, can be used to rule out two possible mechanisms for the observed negative ion formation. These are (i) electron attachment to molecules in the E,F state, and (ii) electron attachment to high vibrational states of the ground electronic state indirectly populated via the $E,F\,^1\Sigma_g^+ \rightarrow B\,^1\Sigma_g^+ \rightarrow X\,^1\Sigma_g^+$ radiative transitions [13]. The observed I^4 dependence for negative ion formation (see Fig. 2) is not consistent with these mechanisms since only three photons would be effectively needed to produce each negative ion, i.e., two to produce the attaching electron and one to produce the excited molecule (also, see [26]).

Three other electron attachment schemes may be possible: (i) Electron attachment to SES themselves. While this may be unlikely because of their estimated short lifetimes of ($\sim 10^{-15}$-10^{-14} s [27]), it cannot be ruled out. (ii) Electron attachment to vibrationally excited high Rydberg (HR) states that may be populated via the decay of SES, 4(d) above. These HR states may be populated at curve crossings at internuclear distances beyond the "stability point" [28,29], i.e., the intersection of the potential curves for SES with that for the $^2\Sigma_g^+$ ground state of the H_2^+ ion (see Fig. 1 of [28]). Depending on the outcome of the curve crossings, formation of HR states or dissociation into neutral fragments will occur, 4(d) and 4(b) above, respectively. The presence of "near-zero-energy electrons" [30] in photoionization of many molecules has been attributed to the rotational or vibrational autoionization or field ionization of such HR states [28-30]. However, in the present case such HR

states that may be populated are likely to dissociate rapidly since the total energy lies above the dissociative threshold; see Fig. 1. The only way to stabilize these HR states is to remove the excess energy via collisions or radiation. While these processes are slow, there is some evidence for a collisionally enhanced electron attachment process as mentioned earlier in the paper. (iii) Radiative attachment to H^* (n) atoms produced via 4(c). To our knowledge no data exist on this process.

To verify the formation of H^- ions in our experiments we have conducted two auxiliary experiments: (i) We repeated the present experiments for using N_2 where it would not be possible to produce negative ions since the electron affinity of N is negative. As in H_2, photoionization of N_2 employing frequency-doubled dye laser radiation yielded the total signal levels ≤ 100 mV even with focusing by a $f=10$ cm lens. It was possible to obtain a large signal using three-photon nonresonant ionization at the ArF excimer laser line; with focusing by a $f=10$ cm lens, total signal levels of ~ 1000 mV were obtained. In all cases negative ion formation (i.e., a slow component of the wave form, see Fig. 5 of [10]) was not observed. (ii) We have initiated a photodetachment study, where the negative ions formed are detached by a second laser pulse. In preliminary experiments, with detachment at 308 nm (XeCl line), we have observed photodetachment signals in qualitative agreement with the known H^- detachment. Refinements on this photodetachment experiment are being carried out and we plan to quantify the detachment data over a range of wavelengths.

In conclusion, we have presented experimental evidence for the efficient [26] formation of H^- in UV laser irradiated H_2. While we do not presently have a clear interpretation for this process, it is likely to be due to an electron attachment process.

This research was sponsored by the Office of Health and Environmental Research, U.S. Department of Energy, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., and by the National Science Foundation under Contract No. CHE-9022903 with the University of Tennessee, Knoxville. We thank Dr. J. N. Bardsley, Dr. R. Johnsen, and Dr. R. Ritchie for useful discussions.

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