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Trapping translationally cold hydrogen molecules

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Hydrogen molecules in selected core-nonpenetrating Rydberg-Stark states have been decelerated from a mean initial velocity of 500 m/s to zero velocity in the laboratory frame and loaded into a three-dimensional electrostatic trap. Trapping times, measured by pulsed electric field ionization of the trapped molecules, are found to be limited by collisional processes.

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Considerable efforts are being invested in the development of methods to generate translationally cold ($< 1$ K) samples of molecules [1-4]. These efforts are driven by the desires to study molecular collisions at very low energies [5-7], to carry out precision spectroscopic measurements [8, 9], and to explore the properties of molecular gases close to quantum degeneracy [2-4].

Since laser cooling techniques are not in general applicable to molecules, the low temperatures must be reached by alternative means: Photoassociation of ultracold atoms [10], buffer gas cooling [11], multistage Stark [12] and Zeeman [13, 14] deceleration of polar molecules and radicals in supersonic beams, and sympathetic cooling of molecular ions in Coulomb crystals [6, 7] have all been exploited. It has also been possible to load and store the cold samples in electrostatic [15, 16], electrodynamic [17], magneto-electrostatic [18], and magnetic traps [11, 19] and study their physico-chemical properties. Despite these successes, the diversity of species that have been prepared at low temperatures remains limited.

Demonstrated here, with the example of H$_2$, is the single-stage Stark deceleration and electrostatic trapping of translationally cold molecules in Rydberg states initially traveling in supersonic beams. This technique is of particular relevance to species that cannot be laser cooled, and have no permanent electric or magnetic dipole moment in their ground state. The method, first suggested by Breeden and Metcalf [20] and Wing [21], and referred to as Rydberg-Stark deceleration in the following, exploits the large electric dipole moments ($e\alpha_0 n^2$, i.e., $\sim 3000$ Debye at $n = 30$) accessible by photoexcitation of atoms or molecules to Rydberg states in the presence of an external electric field, and the forces that result from the interaction of these dipoles with electric field gradients. Such methods have enabled the deflection of Kr beams [22], the partial deceleration of H$_2$ [23, 24] and Ar [25, 26] beams and the reflection [27] and trapping [16, 28] of H atoms. The ability to control the translational motion of Rydberg atoms and molecules is of interest to a wide range of disciplines, with potential applications in experiments on anti-hydrogen [29], ultracold plasmas [30] and quantum information processing [31].

Although Rydberg-Stark deceleration is in principle applicable to any gas phase species, its application to molecular samples has suffered from two drawbacks: First, the Stark states of non-hydrogenic atoms and molecules undergo avoided crossings for electric field strengths at and beyond the Inglis-Teller limit [32]. At such crossings, low-field-seeking states can be converted to high-field-seeking states limiting the range of useable field strengths to $F < \frac{n}{10}$ (in atomic units). Secondly, whereas the lifetimes of $n > 25$ Rydberg-Stark states of atoms exceed 50 ms the lifetimes of such states in molecules are generally limited by predissociation and usually much shorter [33]. Both of these drawbacks have

![FIG. 1: (color online). (a) Schematic diagram of the experimental setup used to decelerate and trap cold H$_2$ molecules. (b) Avoided crossings between the outermost $n = 22$ blue-shifted and $n = 23$ red-shifted Rydberg states of H$_2$ for $|M_J| = 0$, and (c) $|M_J| = 3$. The Stark states are labeled with the quantum number $k$ which represents the difference between the two parabolic quantum numbers $n_1$ and $n_2$.](image-url)
their origin in core-penetrating, low-\ell components of the Stark wavefunctions and can therefore be overcome simultaneously by eliminating such components using a suitable multiphoton excitation sequence.

In the absence of an external electric field, the excitation sequence chosen for H$_2$

\[
\frac{1}{\sqrt{3}} (1s\sigma_g) (v^+ = 0, N^+ = 0) (nf)^1, (v = 0, J = 3, |M_J| = 3)
\]

raises, at each step, the value of \ell, J, and |M_J| by one. By virtue of the fact that in para-H$_2$ singlet-triplet mixing is negligible below \( n = 100 \) [34], the accessible Rydberg series converging to the \( N^+ = 0 \) ionic ground state are \( \ell = J = |M_J| = 3 \) Rydberg states. In the presence of a dc electric field at excitation, \( \ell \) and \( J \) are no longer good quantum numbers. However, provided the direction of propagation of the laser beams employed is parallel to the electric field vector, the accessible Rydberg states converging to an \( N^+ = 0 \) ion core have \( |M_J| = |m_J| = 3 \) which precludes any \( \ell = 0 - 2 \) components in the Stark wavefunctions and guarantees their nonpenetrating “hydrogenic” character. The sections of the \( |M_J| = 0 \) and \( |M_J| = 3 \) Stark maps displayed in Figs. 1(b) and 1(c) demonstrate the effects of \( |M_J| \) on the size of the avoided crossings between the \( N^+ = 0 \) and \( n = 22 \) and \( n = 23 \) Stark states of H$_2$. These maps were calculated following the matrix diagonalization procedure described in [24] using quantum defect data for the Rydberg states of H$_2$ [34] and take into account the interactions with \( N^+ = 2 \) channels.

A schematic view of the experimental setup is presented in Fig. 1(a). A pulsed supersonic beam of H$_2$ seeded in Kr at a pressure ratio of 2:8, with a mean longitudinal velocity of 500 m/s propagates through a skimmer into a set of six electrodes which constitute the photoexcitation region, the Stark decelerator and the 3D electrostatic trap. At the time of photoexcitation, electrodes 1 and 2 are held at potentials of ±V$_{\text{trap}}$ with electrodes 3 and 4 at \( \mp V_{\text{trap}} \) forming a quadrupole field distribution between these electrodes. Electrodes 5 and 6 are held at 0 V and close off the trap in the third dimension [16]. Photoexcitation takes place in a region between electrodes 1 and 2. To restrict the excitation to \( |M_J| = 3 \) Rydberg-Stark states using three circularly polarized laser beams (see Eq. 1), all three laser beams must propagate parallel to the dc electric field vector at the position of excitation. To achieve this, 1.5 mm diameter holes have been drilled through electrodes 1 and 2 as indicated in Fig. 1(a).

The first step of the excitation sequence requires circularly polarized vacuum-ultraviolet (vuv) radiation at 94093.81 cm$^{-1}$ (~ 106 nm) which was generated by resonance-enhanced four-wave mixing in a pulsed Xe jet \( (\nu_{\text{vuv}} = 2\nu_1 + \nu_2) \). The divergent vuv beam was recollimated, separated from the fundamental laser beams and directed toward the hole in electrode 1 of the decelerator using a toroidal grating. Circular polarization of the vuv radiation was achieved by circularly polarizing the tuneable laser beam \( (\nu_2) \) in the four-wave-mixing process, using a Glan–Taylor polarizer followed by a Berek compensator, while the two-photon resonant laser beam was linearly polarized. The circular polarization of the vuv radiation was checked spectroscopically and optimized to a purity of better than 90% by ensuring the disappearance of the Q(1) line of the 1$^1\Pi_g \rightarrow 3^3\Sigma_g^+$ transition, having independently verified the circular polarization of the 18190.43 cm$^{-1}$ (~ 550 nm) laser beam required for this transition. The third step of the excitation sequence was driven by a laser tuneable in the range 12050-11500 cm$^{-1}$ (~ 830 – 840 nm) which was also circularly polarized.

To decelerate the \( |M_J| = 3 \) Rydberg-Stark states of H$_2$ from their initial longitudinal velocity of 500 m/s to zero velocity in the laboratory frame, pulsed high potentials \( (\mp V_{\text{decel}}) \) are applied to electrodes 3 and 4 following photoexcitation. After a fast rise (30 ns) to their maximal value the potentials decay exponentially with a time constant of 3.65 \( \mu \)s. This guarantees that the decelerating molecules experience a maximal field gradient throughout their trajectories while never being subject to a field of sufficient strength to cause ionization.

At the end of the exponential decay, the potentials on electrodes 3 and 4 return to their initial values and the center of the stationary Rydberg molecule cloud is located at the minimum of the three-dimensional trap (see Ref. [16] for additional details). This single-stage deceleration procedure minimizes transverse losses during deceleration and trap loading.

At any time after photoexcitation \( (t_{\text{ion}}) \), a large positive electric potential of +4 kV can be switched on electrodes 1 and 2 to field ionize the Rydberg molecules and extract the H$_2^+$ ions through a short flight tube toward a microchannel plate (MCP) detector. Analysis of the H$_2^+$ time-of-flight (TOF) profiles allows the particle number in the decelerator and trap to be monitored along with the longitudinal position of the Rydberg molecule cloud [16, 27]. The neutral Rydberg molecules can also be detected directly on the MCP detector if left to propagate through the flight tube without ionization.

A spectrum of the field-free \( |M_J| = 3 \) H$_2$ Rydberg states, measured by pulsed electric field ionization (PFI) at \( t_{\text{ion}} = 3 \) \( \mu \)s, is presented in Fig. 2(a). This spectrum includes states in the range \( n = 21 - 35 \) of the \( N^+ = 0 \) series along with the \( n = 16 - 20 \) states of the \( N^+ = 2 \) series. Fig. 2(b) represents a Stark spectrum, also recorded by PFI, but with \( V_{\text{trap}} = 20 \) V, resulting in an electric field at the excitation position of 56 V/cm. At this field, adjacent Stark manifolds start to overlap in energy at
FIG. 2: (color online). (a) Field-free spectrum of $|\ell, |M_J| = 3$ Rydberg states of H$_2$. (b) $|M_J| = 3$ Stark spectrum recorded in an electric field of 56 V/cm, with PFI at $t_{\text{ion}} = 3 \mu$s. (c) Stark spectrum of long lived $|M_J| = 3$ states recorded by measuring the signal when the neutral molecules impinged on the MCP detector 90 $\mu$s after photoexcitation in a field of 56 V/cm. (d) Low-field seeking $|M_J| = 3$ Rydberg-Stark states recorded by PFI following excitation in the same electric field of 56 V/cm and deceleration and trapping for a time of 50 $\mu$s (see text for details). The field-free states are labeled $(n \ell N^+)_{J=|M_J|}$ and their positions are indicated by vertical dashed lines.

$n = 31$. To assist in the identification of the long-lived states a second spectrum (Fig. 2(c)) was recorded in the same excitation field but by detecting the neutral Rydberg molecules, excited in a pure H$_2$ beam, when they impinge on the (MCP) detector after a TOF of 90 $\mu$s. Unlike the $N^+ = 2$ series, states of the $N^+ = 0$ series are sufficiently long lived to permit detection following deceleration and trapping.

A spectrum containing only the long-lived $|M_J| = 3$ Rydberg–Stark states that are accepted into the trap when $V_{\text{trap}} = 20$ V and $V_{\text{decel}} = 1.7$ kV, and remain trapped until detection by PFI at $t_{\text{ion}} = 50 \mu$s, is presented in Fig. 2(d). As the un-decelerated beam of H$_2$ molecules leaves the PFI region between electrodes 1-4 in less than 8 $\mu$s, all molecules detected by PFI after 50 $\mu$s must have been trapped. Additionally, the TOF distributions of the H$_2^+$ ions to the MCP detector following PFI (not shown) reveal that beyond 25 $\mu$s after excitation, the molecules are ionized from the same narrow spatial region around the trap minimum. The observation that the trapped states lie to the high-energy side of the zero-field resonances (vertical dashed lines) clearly indicates that only low-field seeking states are trapped. The deceleration and the acceptance of the trap depend upon the dipole moment, which scales as the product nk, and states of many different principal quantum numbers can be trapped because a decrease in n (or k) can be compensated by an increase in k (or n). The two shaded regions on the right-hand side of the figure labeled A and B correspond to the energy ranges covered by the Stark manifolds of the n = 34 and n = 35 states of the

FIG. 3: (a) Field-free $n = 22, \ell = 3, |M_J| = 3$ Rydberg state of H$_2$ detected at $t_{\text{ion}} = 3 \mu$s. (b) $n = 22, |M_J| = 3$ Stark manifold recorded in an electric field of 278 V/cm with detection at $t_{\text{ion}} = 3 \mu$s. Electrostatically trapped low-field seeking $k = 10 - 18, n = 22, |M_J| = 3$ Stark states of H$_2$ detected at $t_{\text{ion}} = 50 \mu$s with pulsed potentials of (c) 1.7 kV, and (d) 2.3 kV applied for deceleration.

$N^+ = 0$ series, respectively. The peaks corresponding to the trapped molecules in Fig. 2(d) are located in the region where the two Stark manifolds overlap, i.e. beyond the Inglis-Teller limit. Consequently, all avoided crossings encountered during deceleration and trap loading must have been traversed diabatically.

A demonstration of Stark-state-selective trap loading is presented in Fig. 3. In panel (a), the field-free
$|M_J| = 3$, $n = 22$ line of the $N^+ = 0$ series recorded by PFI at $t_{\text{ion}} = 3$ $\mu$s is presented. In (b) the corresponding Stark manifold, recorded at the same ionization delay, but with $V_{\text{trap}} = 100$ V, such that the electric field at the excitation position was 278 V/cm, is displayed. In this spectrum, the partially resolved Stark states are labeled by their quantum number $k$ which ranges from $k = -(n-|M_J| - 1)$ to $k = +(n-|M_J| - 1)$ in steps of 2. Recording the same spectrum after deceleration with $V_{\text{decel}} = 1.7$ kV and trapping for 50 $\mu$s, only the outer low-field-seeking Stark states with $k = 10 - 18$ are observed (see Fig. 3(c)). This is in agreement with numerical simulations of the Stark state acceptance of the decelerator and trap performed using the procedure described in Ref. [16]. Upon increasing the deceleration potential to $V_{\text{decel}} = 2.3$ kV the acceptance of states with smaller dipoles increases, as is seen in Fig. 3(d) where the intensity of the $k = 10$ and $k = 12$ states is significantly enhanced compared to Fig. 3(c).

The rate of loss of the Rydberg H$_2$ molecules from the trap has been studied by monitoring the ion signal as a function of the time between photoexcitation and PFI and found to be strongly dependent on the stagnation pressure at which the pulsed valve was operated, as illustrated in Fig. 4. The number of H$_2^+$ ions detected by PFI up to 115 $\mu$s after photoexcitation of the $n = 33$, $k = 23$ Stark state of the $N^+ = 0$ series decays exponentially with a time constant of $\tau_{1/e} = 20$ $\mu$s when the pulsed valve is operated at 4.0 bar (dataset A). However, if the stagnation pressure is reduced to 1.75 bar this time increases by a factor of $\approx 2$ to $\tau_{1/e} = 40$ $\mu$s (dataset B), but the magnitude of the signal is also reduced because the lower density of the molecular beam leads to a smaller number of initially trapped molecules. These observations indicate that the measured trap decay times are limited by collisional processes. It is estimated that the trap is loaded at an initial density of $10^7 - 10^6$ cm$^{-3}$ and a temperature of $\approx 150$ mK, corresponding to a loading efficiency of $\approx 60\%$.

Three-dimensional electrostatic trapping of cold molecular hydrogen has been demonstrated for the first time. Essential for the success of these experiments was the excitation of core non-penetrating Rydberg–Stark states in a multiphoton excitation scheme involving circularly polarized laser radiation. As all atoms and molecules possess Rydberg states, the methodologies presented here provide a route to the preparation of cold stationary samples of a wide range of molecules.

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