

The Stark Effect and Translational Control of Hydrogen Molecules

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Abstract

The Stark effect is studied for the gerade Rydberg states (principal quantum number $n \geq 16$) of molecular hydrogen by using vacuum ultraviolet/ultraviolet two-photon excitation and detecting ions produced by delayed field ionization. Experiment and theory show that the nd Rydberg states with $N^+ = 2$, $J = 1$, $M_J = 0$ are long-lived, and have predominant contributions to the intensities of the Stark manifolds (the quantum numbers are defined as N^+ : rotational angular momentum of the ion core, J : total angular momentum, M_J : quantization-axis projection of J). The deflection of a supersonic beam of Rydberg H_2 molecules is demonstrated by using the inhomogeneous dipole electric field. With the dipole rods mounted parallel to the beam direction, the high-field-seeking and low-field-seeking Stark states are deflected towards and away from the dipole, respectively.

Keywords:

Rydberg state, Stark effect, vacuum ultraviolet photoexcitation, cold molecule

1. Introduction

This paper reports on the demonstration of the deflection of Rydberg H_2 molecules in a supersonic beam and high-resolution spectroscopy of the Stark effect in the Rydberg states of H_2 . Controlling the translational motion of atoms and molecules in the gas phase is of interest for experimental methods in studies on cold collisions and Doppler-reduced spectroscopy in the gas phase. It is connected with the research area of cold molecules, following the successful development of laser cooling methods for atoms. However the optical-cycling methodology used in the laser cooling cannot be extended to molecules due to complicated internal energy levels in molecules.

One of the alternative approaches for cooling molecules is the use of the Stark effect which takes place in a molecule with a significant electric dipole moment in the ground state. An electric-field gradient opposing a molecular beam direction can create decelerating (or accelerating) forces $F = -\nabla E$ on molecules in so-called low-field-seeking states (high-field-seeking states). For ND_3 molecules translational temperatures of ~ 25 mK have been achieved with respect to the laboratory frame [1].

The method presented in this paper can be regarded as an extension of this approach. Since the Rydberg states are highly susceptible to electric fields, the Stark effect in Rydberg states leads to a significant force on

Rydberg atoms [2,3] and molecules [4]. The advantages of the Rydberg-Stark control method include that it can be applied to any non-polar, non-magnetic molecule in principle and that it does not need a large electric field of order 100 kV/cm. However the disadvantages to be overcome include the complicated energy-level structures of the Rydberg series converging to different ro-vibrational levels of the ion, and the short lifetimes due to autoionization, predissociation and radiative processes. In this paper we report on the spectroscopic results for the Stark effect in Rydberg states of H_2 and discuss the behavior in electric fields such as field ionization properties, state mixing, and decay processes. Spectral comparisons between experiment and theory allow us to understand the Rydberg-Stark control experiment quantitatively.

2. Method

The experimental apparatus has been described in detail elsewhere [5,6]. Briefly the Rydberg states are excited by two-photon, two-color (110.81 nm and ~ 295 nm) excitation via a selected rotational level of the $B^1\Sigma_u^+$ intermediate state by using nano-second pulsed dye lasers (~ 6 ns). The vacuum ultraviolet (VUV) radiation is generated by non-resonant frequency tripling in a cell filled with rare gases (Kr/Ar=1100/200 mbar). Both laser beams are focused into a vacuum chamber

perpendicularly to each other and also to a supersonic molecular beam.

In the measurement of the Stark effect, a homogeneous electric field is applied across a pair of grids V_1 and V_2 (15 mm separation), as shown in Fig. 4 (a) (i). The Rydberg states are excited between V_1 and V_2 , and then field ionized by a pulsed field of magnitude ~ 5000 V/cm when they enter the region between grids V_2 and V_3 (10 mm separation). Laser polarizations are set perpendicular to the electric field, defining the final state to be $M_J = 0, \pm 2$ for excitation from an initial state with $J = 0, M_J = 0$. Deflection experiments are performed with a pair of rods mounted parallel to the molecular beam (diameter 0.9 mm, length 20 mm, center-to-center distance 4 mm). The Rydberg states are field ionized, and detected as ions with a position sensitive detector after travelling through a ~ 30 cm field-free region.

Theoretical calculations are performed by diagonalization of the effective Hamiltonian $\widehat{H} = \widehat{H}_0 + eFz$ with a basis set of the form $\{v^+N^+nlJM_J\}$ [7-9]. The previously reported values for the quantum defects [7-9], and the ionization thresholds $I(0) = 124417.507(10)$ cm^{-1} [10] and $I(2) = 124591.743$ cm^{-1} are used in the calculations.

3. Results and Discussion

At zero field, the Rydberg states accessible are the ns and nd series converging to the $N^+ = 0$ and 2 vibrational level ($v^+ = 0$) of the H_2^+ ion since the electronic wavefunction of $\text{H}_2^+(X^2\Sigma_g^+)$ has a gerade symmetry. The selection rule $\Delta J = 0, \pm 1$ restricts the final states of the present two-photon excitation to the $(ns0)_0$, $(ns2)_2$, $(nd0)_2$, $(nd2)_0$, $(nd2)_1$, $(nd2)_2$, and $(nd4)_2$ states [notated $(nN^+)_J$].

Fig. 1 (bottom) shows the Rydberg excitation spectrum of H_2 recorded at 0 V/cm. Most of the observed peaks are assignable to the nd series converging to the $N^+ = 0$ and 2 thresholds as shown in the figure. It is noted that the $N^+ = 2$ series are observed as strongly as the $N^+ = 0$ series although autoionization is energetically possible for the $N^+ = 2$ series. Since the ions produced by rapid autoionization or direct ionization are eliminated by a small delayed discrimination field $V_2 \approx 20$ V/cm, the observed peaks are undoubtedly ascribed to the Rydberg states which survive a delay time of 3.7 μs . Applying the Stark field makes all the $N^+ = 0$ Rydberg states disappear very easily (see Fig. 1); even at 100 V/cm the $N^+ = 0$ Rydberg states are hardly noticeable except for a weak broad band around 124350 cm^{-1} . If we examine the appearance onsets for the Stark manifolds, they seem to be correlated with the

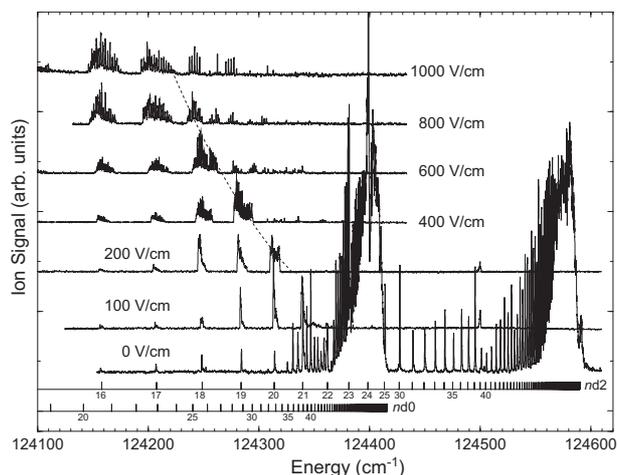


Fig. 1 Pulsed field ionization spectra of H_2 obtained in the presence of various homogeneous electric fields in the range 0–1000 V/cm shown as a function of the sum of the VUV and UV excitation energies. The ionizing pulsed field is applied after a delay of 3.7 μs . The dotted line represents the classical saddle point energy of the $N^+ = 0$ threshold.

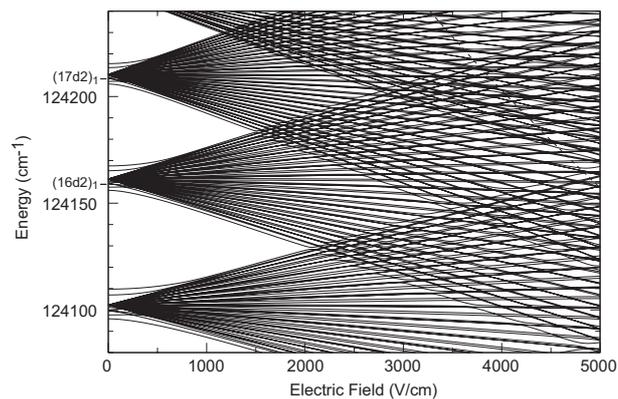


Fig. 2 Stark map including $N^+ = 0$ ($n=15-17$) $M_J = 0$ states. The dotted line indicates the position of the classical saddle point energy.

classical saddle point energy associated with the $N^+ = 0$ threshold at $IE(0) = 124417.507(10)$ cm^{-1} (dotted line in Fig. 1). Thus the Stark manifolds of the $N^+ = 2$ threshold are likely to be field ionized in the presence of the static electric fields through interaction with the continuum associated with the $N^+ = 0$ threshold.

Fig. 2 shows the Stark map calculated for the $N^+ = 2, M_J = 0$ states. The Stark map showing how the energy levels vary with electric field is used to predict the force exerted on the molecule in an inhomogeneous field (see below). Fig. 3 represents simulated Stark spectra. Although the selection rule $\Delta M_J = \pm 1$ for the σ -polarization for two photons allows the final states with $M_J = 0, \pm 2$, spectral simulations for the $M_J = \pm 2$ states do not fit the observed spectra at all. The exper-

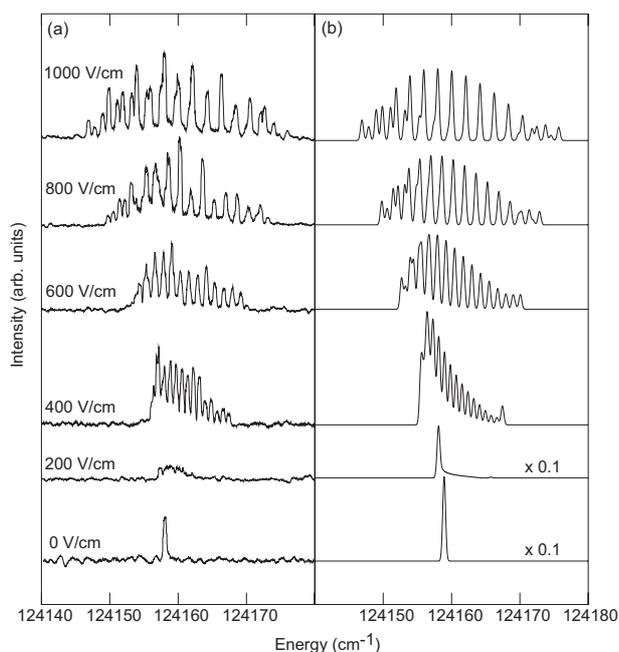


Fig. 3 Comparison between (a) experimental and (b) calculated Stark spectra of the $N^+ = 2$, $n = 16$, $M_J = 0$ Stark manifold. The simulation has been convoluted with a Gaussian laser bandwidth with full width at half maximum of 0.5 cm^{-1} .

perimental spectra are fairly well reproduced only if the transition probability to the $(nd2)_1$, $M_J = 0$ states is assumed to be non-zero and to the other optically-allowed states zero (Fig. 3). From comparisons between experiment and theory the following can be mentioned:

1. At 0 V/cm and 200 V/cm, the calculated $(16d2)_1$ band is more than ten times stronger than the experimental one. The discrepancy may seem to be due to decay by predissociation, but the $(16d2)_1$ states give rise to no peaks in the previous ion-detected Rydberg excitation spectra [8]. Therefore the weak intensities are caused by other reasons. It is noted that intensities become increasingly small on going from high Rydberg states of $n \approx 65$ to lower states, which is in contrast to the general tendency of oscillator strengths in atomic Rydberg states [11].
2. Some of the sub-levels are not observed in the low-wavenumber side of the $n = 16$ Stark manifold in the presence of fields of 400 V/cm and 600 V/cm. A similar behavior is also observed for the $n = 17$ Stark manifold [6]. Thus the absence of these states is unlikely to be caused by an ionization mechanism near the threshold of field ionization.
3. The missing sub-levels regain their intensities at 800 V/cm and 1000 V/cm (Fig. 3), and the intensities of the entire set of sub-levels show a good agreement with calculation. Two fine structure series are noticeable in the low- and high-wavenumber

regions of the manifolds in addition to the main prominent series. Considering the coupling scheme $J = N^+ + I$ (i.e., $M_J = M_N^+ + m_I$) in the present case, it is reasonable to suppose that the three fine structure series in the $N^+ = 2$, $M_J = 0$ manifold are due to unequal contributions from $m_I = 0, 1$, and 2 which result in different quantum defects, intensities and lifetimes. Such a feature was discussed in the previous multichannel quantum defect theory study [12].

4. It might seem contradictory that the classical saddle point energy is located at the middle of the $n = 16$ manifold for a field of 5000 V/cm in comparison to the fact that the entire $n = 16$ manifold is observed at 800 V/cm and 1000 V/cm. However it should be recalled that the excited Stark sub-levels traverse to the zero-field Rydberg states when the Rydberg states

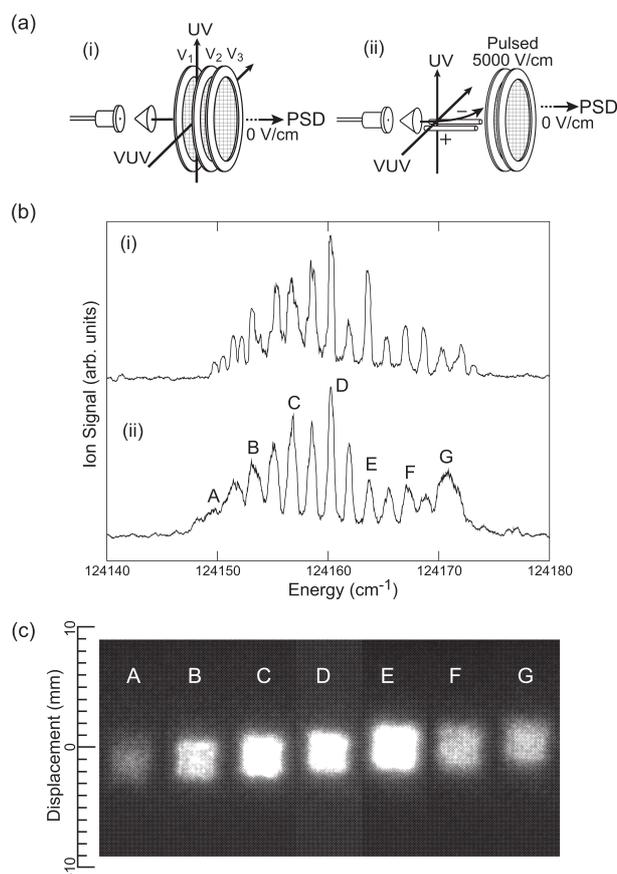


Fig. 4 (a) Schematics of the apparatus, and (b) Rydberg excitation spectra of H_2 recorded in the presence of (i) a homogeneous electric field 800 V/cm and (ii) an inhomogeneous dipole field ~ 800 V/cm. Signals were detected utilizing a position sensitive detector (PSD). (c) Images showing the distributions of the H_2 Rydberg molecules after deflection in the inhomogeneous field (ii) for $7 \mu\text{s}$. The Rydberg levels labeled A-G are excited by scanning wavelength of the UV laser respectively. The Rydberg states are field ionized in a field 5000 V/cm between the grids after 10–11 μs flight time.

enter the field-free region between V_2 and V_3 before an ionizing electric field is applied. Therefore most of the populated sub-levels are at once merged into the field-free eigenstates, presumably diabatically, and then field ionized through zig-zag adiabatic ionization passages shown in Fig. 2.

Figure 4 presents the results of the deflection experiments of Rydberg H_2 . The Rydberg states of $n = 16$ and 17 are excited in the presence of an inhomogeneous dipole field (Fig. 4 (a) (ii)). In the Stark spectrum in Fig. 4 (b) (ii) the extreme Stark sub-levels are broadened by the inhomogeneity of the field and a finite excitation volume compared to that recorded in the homogeneous field (Fig. 3 and Fig. 4 (b) (i)). The images labeled A-G in Fig. 4 (c) correspond to the deflected Rydberg H_2 molecules which are initially populated in Stark states A-G (Fig. 4 (b)), respectively. The supersonic beam interacts with the field along a length of ~ 20 mm (see Fig. 4 (a) (ii)). The dipole field is switched off before being ionized at ~ 28 mm away from the excitation point. The trajectories of the molecules are monitored using ion-imaging and time-of-flight measurements. The off-axis displacement (deflection angle) is estimated to be $+1.3$ mm ($+2.7^\circ$) and -0.6 mm ($+1.2^\circ$) for the low-field-seeking and high-field-seeking states, respectively. The square shapes represent the intersections of VUV and UV lasers which are magnified by non-planar electric fields in the vicinity of the grids and the long flight length for H_2 ions (~ 30 cm). The maximum magnitude of a force in the present experiment is estimated to be 1.0×10^{-19} N from the gradient of the dipole field and the slopes of the Stark map.

4. Conclusion

The experimental spectra contain the details of the decay processes. The long-lived $(nd2)_1$ states are likely to be field ionized into the $N^+ = 0$ continuum. The fine structure is clearly resolved for the $n = 16$ manifold at fields greater than 800 V/cm. Controlling Rydberg molecules can be realized by critically choosing appro-

priate Rydberg states and pulsed electric fields. We believe the present experiment will initiate methodological development for controlling molecular motion in the gas phase.

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