Photoassociation of Spin-Polarized Hydrogen

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Using Lyman-α spectroscopy we observe photoassociation of spin-polarized hydrogen atoms to bound vibrational levels of the triplet $a^3\Sigma_g^+$ potential. At a density of 10^{16} atoms/cm^3 we directly observe light absorption and fluorescence in the photoassociation process. The observed line positions agree with *ab initio* calculations to within the precision of present theory. Magnetic sublevels in the photoassociation spectra indicate an effective internal field which we identify with a nonadiabatic term in the Hamiltonian. We present quantitative models for the magnetic field dependence of the molecular energy and the photoassociation line shape. [S0031-9007(98)08165-4]

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Photoassociation, the process in which a pair of unbound atoms is excited optically into a bound molecular state, is a dramatic form of optical collision. It is also an extremely precise tool for probing the highest energy levels in a molecular potential. Photoassociation (PA) has been observed in laser cooled alkali gases (see, e.g., [1–3]), where it has been used to accurately characterize interatomic interactions and to obtain valuable insights into the physics of these gases. The determination of the ground state scattering lengths of alkali atoms, and the effect of optical and magnetic fields on collision processes are based on PA spectra (see, e.g., [4]).

In this Letter we present the first observation of PA in atomic hydrogen (H). The case of H is particularly interesting for several reasons. First, experimental results can be used to test the *ab initio* calculations of ground state and excited state collision properties which claim very high accuracy for this simplest molecule (see, e.g., [5]). Moreover, in contrast to alkali systems, in H spin-orbit (LS) coupling is very small. In addition, nonadiabatic effects due to the finite mass of the nuclei are most readily investigated in the lightest molecule. In a dense gas of H [6] the PA lines can serve as a sensitive probe of the gas density. PA spectroscopy may also be of use to explore the properties of degenerate samples of H [7], since it probes the two particle correlator.

In contrast to PA experiments in alkali gases, we reach densities that are high enough that we can directly detect the PA process via light absorption and subsequent fluorescence. We obtain these high densities by confining *high field seeking* H (H$\downarrow$) in a cryogenic sample cell [8]. Our measurements take place in a magnetic field that we can vary between 4 and 7 T. The line positions we observe are in agreement with the existing *ab initio* theory. However, the theory needs to be extended to include magnetic field dependence to allow for a full comparison. We find that the excited H_2 molecule displays an internal field of order 1 T, which we identify with a nonadiabatic term in the Hamiltonian.

The apparatus we use to cool and compress H$\downarrow$ is described in the literature [6,9]. It consists of two volumes with liquid helium coated walls: a 0.3 K buffer volume, which we use to precool atoms generated in a cryogenic discharge, and a smaller cold cell, with a wall temperature of 0.1 K. Through preferential recombination almost all atoms in the sample are in the $f = 1$, $m_f = -1$ state. Consequently, the ground state atoms interact via the $b^3\Sigma_u^+$ interatomic potential, which has no bound states. The atoms in the buffer volume can escape over a magnetic field barrier towards the cell. Once thermalized to the cell temperature the atoms lack the thermal energy to return across the barrier to the buffer. By this mechanism the atoms are effectively compressed into the cell. A gas density of 10^{16} atoms/cm^3 at a temperature of 0.15 K is reached routinely in this way. We determine the density and temperature of the gas by spectroscopy on the Lyman-α transition at $\lambda \approx 122$ nm [10]. We measure both transmission and light induced fluorescence (LIF) spectra by scanning the frequency of the Lyman-α light source. The fluorescent light is detected after conversion to visible wavelengths.

PA lines appear in the absorption and LIF spectra at densities higher than $\approx 10^{15}$atoms/cm^3. An example is given in Fig. 1. The detuning Δ is measured with respect to the centroid ω_{2P} of the $2P$ fine structure multiplet. As discussed below, in the molecules under consideration fine structure plays no role. Therefore, when discussing binding energies of the PA levels we will suppress the effect of fine structure on the dissociation limit by defining the level energies relative to ω_{2P}. The fluorescence peak at detuning $\Delta = -134$ GHz is attributed to PA in the cell. A corresponding dip in the transmission signal is observed. The stronger transmission dip at -141 GHz is due to PA in the buffer; it is Zeeman shifted from the cell line as the field

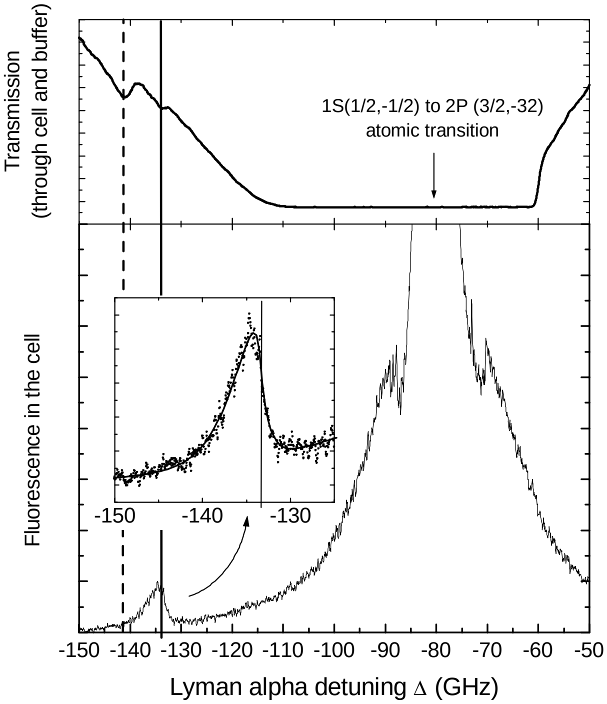

FIG. 1. Transmission and fluorescence spectra of H at $n \simeq 10^{16}$ cm^{-3}. The feature at $\Delta = -134$ GHz is a PA line. The large structure dominating the fluorescence spectrum around $\Delta = -80$ GHz is the atomic transition. Inset: The PA line shape is fit to Eq. (6). The vertical line denotes the inferred position of the unbroadened line. The magnetic field is 6 T in the cell and 1 T higher in the buffer.

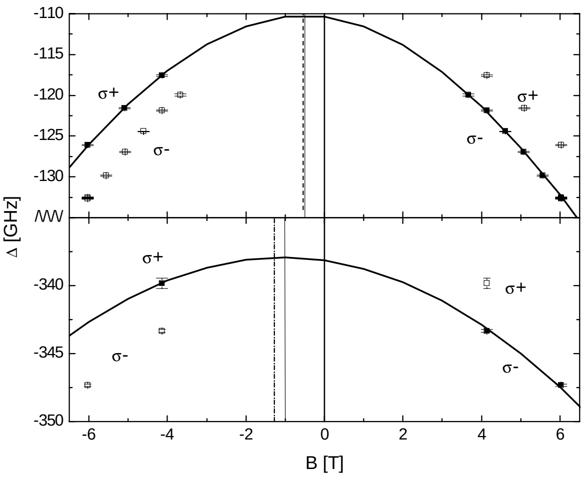

FIG. 2. Magnetic field dependence of $v = 20$ and $v = 19$ PA lines. The data points are shown twice, once reflected in the $B = 0$ axis with the opposite polarization. The error bars indicate the relative precision of the data points, and the absolute frequency accuracy is 1 GHz. The curves are model calculations, with only an overall energy shift as a free parameter. The effective internal field B_i, as estimated from Eq. (3), is indicated (dashed vertical line), as well as the actual symmetry axis of the curve (full line).

in the buffer is 1 T higher. There is no fluorescence signal corresponding to this dip because the fluorescence detector is not visible from the buffer volume. For a given field, we observe three PA peaks separated by a few hundred GHz. The positions of the PA lines are field dependent, as shown in Fig. 2. Apparently, there is a strong second order Zeeman effect and a significant polarization dependence of the Zeeman shifts.

Lyman-α light can excite a pair of atoms from the $b^3\Sigma_u^+$ state to the $a^3\Sigma_g^+$ and $c^3\Pi_g^-$ states [11]. The $c^3\Pi_g^-$ state is repulsive at long range, leaving only the $a^3\Sigma_g^+$ as a candidate upper state for free-bound transitions. Figure 3 shows the positions of the PA lines which we have found. To compare with existing theory, the line positions have been extrapolated to zero field in a way discussed below. Figure 3 also shows the dissociation energies of the calculated $R = 0$ and $R = 1$ bound states as obtained by *ab initio* calculation [5]. (R is used to indicate the angular momentum of nuclear motion.) From Fig. 3, we identify the observed lines as free-bound transitions to the $v = 18, 19, 20$ vibrational levels of the $a^3\Sigma_g^+$ potential. The potential by Kołos and Rychlewski [5] was calculated with the aim to describe tightly bound molecules, and experimental data up to $v = 6$ are discussed in [5]. Apparently it still describes the $v = 20$ molecule well. Quasiclassical theory [12] predicts that in the potential $V(r) = -2C_3/r^3$ the molecular binding energy D scales with v as $D^{1/6} = \hbar\mu^{-1/2}2^{-1/3}C_3^{-1/3}(v_D - v)$. Here, μ is the reduced mass (half the mass of the H atom). This theory does not predict the vibrational quantum number at dissociation v_D. We obtain $v_D = 25.05$ from a fit to the data, as shown in Fig. 3. This quasiclassical theory may break down near the dissociation limit due to LS coupling, as has been observed, e.g., in Ref. [13], in the related $B\,^1\Sigma_u^+$ state.

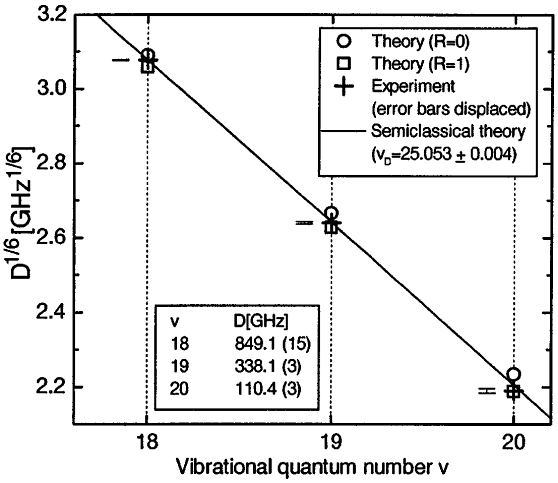

FIG. 3. Molecular binding energy in the $a^3\Sigma_g^+$ potential to the one-sixth power as a function of vibrational quantum number. The theory points shown are the bound states in the adiabatic approximation [5] with nuclear motional angular momentum $R = 0$ and 1, and the line is a fit of quasiclassical theory to our data. The indicated uncertainty is statistical. Inset: Experimental dissociation energies, extrapolated to $B = 0$.

We will now discuss the physics which produces the observed field dependence. For the range of internuclear distances $[(20-35)a_0]$ of interest, the resonant dipole interaction is the dominant term in the Hamiltonian. It is more than an order of magnitude larger than LS terms, (the LS splitting in H is 10.97 GHz) and all first order LS terms cancel in a Σ state [Hund's case (b) [14]]. Therefore, LS coupling can be neglected, and the spins will remain aligned to the magnetic field in the ground state as well as in the excited state. The Zeeman effect must therefore be caused by orbital motion of the electrons. At 0.15 K, s-wave collisions between H atoms are dominant, so the initial $b\,^3\Sigma_u^+$ quasimolecule has total motional angular momentum $N = 0$ [15]. After absorbing a $\sigma_\pm$ polarized photon the molecule has $N = 1, M = \pm 1$. Because the light propagates parallel to the magnetic field, π transitions are not excited. In the absence of LS coupling, reversing the polarization of the light (and therefore the M of the final state molecule) is physically equivalent to reversing the applied magnetic field, while leaving M unchanged. This allows us to treat the σ_+ data points as if they were σ_- points taken at a negative field (see Fig. 2). The polarization dependent Zeeman shift shows that M couples quite strongly to the magnetic field, which indicates that on average a significant fraction of the angular momentum M must be in the electron orbital motion, even in zero field.

When the nuclei are far apart, there are no shared electrons and the molecule consists of two atoms, bound by exchanging virtual photons. Since one of these atoms is in the $2P$ state, the molecule has $L = 1$ and we can express the molecular state in a basis of atomic (m_L) states. Coupling to the nearby $2S$ state is ignored in this long-range approximation, as it does not have resonant dipole interaction. The Schrödinger equation of the molecule acts on three-component vector wave functions $\boldsymbol{\Psi}(r, \theta, \phi)$ where the components of $\boldsymbol{\Psi} = (\Psi_{-1}, \Psi_0, \Psi_{+1})$ represent the different m_L states of the excited atom, r is the internuclear distance, and θ and ϕ are the angles between the internuclear axis and the laboratory frame. The quantization axis for L is taken in the laboratory frame to show more clearly the implications of angular momentum conservation. To transform the vector between the laboratory frame and the molecular frame, where m_L becomes Λ, one must use a three-dimensional representation $D^{(1)}(0, \theta, \phi)$ of the rotation group [14]. The resonant dipole interaction, which is attractive as $-2C_3/r^3$ for the $^3\Sigma_g$, is repulsive as C_3/r^3 for the $^3\Pi_g$ state [16]. The Schrödinger equation in the laboratory frame reads

$$
\begin{aligned}
E\boldsymbol{\Psi} = {} & -\frac{\hbar^2}{2\mu}\nabla^2\boldsymbol{\Psi} \\
& + \frac{C_3}{r^3} D^{(1)}(-\phi, -\theta, 0)\begin{pmatrix} 1 & & \\ & -2 & \\ & & 1 \end{pmatrix} D^{(1)}(0, \theta, \phi)\boldsymbol{\Psi} \\
& + \mu_B B\begin{pmatrix} -1 & & \\ & 0 & \\ & & 1 \end{pmatrix}\boldsymbol{\Psi}\,. \qquad (1)
\end{aligned}
$$

In the molecular states we observe, the interaction term is dominant, and the magnetic field term and commutators of the Laplacian and the $D^{(1)}$ matrices can be treated as perturbations. In good approximation, a Σ wave function with $N = 1, M = \pm 1$ can be written in the lab frame as

$$
\boldsymbol{\Psi}_M(r, \theta, \phi) \approx \Psi(r) Y_{1,M}(\theta, \phi) D^{(1)}(-\phi, -\theta, 0)\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}. \qquad (2)
$$

When substituting Eq. (2) in Eq. (1) the action of the ϕ derivative in the Laplacian on the D matrices gives rise to an extra term, of a tensor form similar to the Zeeman term. This term acts like an effective internal magnetic field B_i. Derivatives of the $D^{(L)}$ transformation matrices are often neglected; in heavy or tightly bound molecules this is a good approximation. However, here we need to keep track of these terms.

We have obtained the curves in Fig. 2 by solving Eq. (1) in a way we briefly sketch here: First, the ϕ dependence is eliminated from Eq. (1). Then we transform the equation to the molecular frame, where the dominant term is diagonal. The r derivatives of the orientation of $\boldsymbol{\Psi}$ can be neglected [cf. Eq. (2)], we also neglect its θ derivatives, which contribute only a small energy shift. The equation now assumes a scalar form, which is easily solved. The resulting curves are in very good agreement with the data. Apart from an overall frequency shift the calculation has no free parameters. We use the zero field values of this calculation to compare with $B = 0$ theory in Fig. 3.

To gain insight we compare the ϕ derivative term in Eq. (1) to the Zeeman term, which leads to an analytical approximation of the internal field B_i,

$$
\mu_B B_i \approx -M\,\frac{3\hbar^2}{4\mu}\,\frac{1}{r_{\text{eff}}^2}\,. \qquad (3)
$$

For the effective radius r_{eff} we take the most probable r (the maximum of the $B = 0$ wave function in the adiabatic approximation). This leads to an estimated $B_i = 0.6$ T for the $v = 20$ state and $B_i = 1.2$ T for the $v = 19$ state. The simple estimate (3) agrees well with both the experiment and the calculated field dependence (see Fig. 2). By combining B_i with the second order Zeeman effect it is possible to define an effective magnetic moment, which is $0.041\mu_B$ for the $v = 20$ state and $0.029\mu_B$ for $v = 19$. This is almost 2 orders of magnitude larger than the nuclear magneton. This internal field is not unique to H_2 molecules. In fact, Eq. (3) holds for any molecule that resembles a S and P pair of (not even necessarily identical) atoms, as long as LS coupling is small. When LS coupling is large a similar effect arises due to the $D^{(S)}$ matrices that transform the spin part of the wave function. In the lightest alkali, Li, for a typical state excited in PA ($1\,^3\Sigma_g^+, v = 59$) the internal field is high ($\approx$0.08 T), but due to the weak second order Zeeman effect the magnetic moment is only of the order of the nuclear magneton.

From the eigenvectors of Eq. (1) we can infer the relative excitation probabilities of the different transitions. For the $v = 20$ state at $B = 6$ T we predict an excitation cross section that is 4.4 times larger for the σ_- transition than for the σ_+ transition. Experimentally we find a ratio of 6 ± 1.5 to 1.

To obtain accurate line positions from the asymmetrically broadened lines (see Fig. 1) it is crucial that we understand the line shape in detail. The lines are broadened due to the kinetic energy distribution of the colliding atoms (to the red) and due to the Zeeman effect (to the blue). The kinetic energy broadening reflects the thermal energy that the atoms have in the initial state. The excitation takes place around the outer turning point r_0, so that the probability to excite the atoms is proportional to the initial ground state wave function $\Psi_0(r_0)$ squared. The initial state is an s wave, $\Psi_0(r) \propto \sin(kr)/r$ (the s-wave scattering length of the ground state is ignored here), and the thermal probability that the system will be found in this state is $\propto \exp(-\hbar^2k^2/2\mu k_BT)$, which leads to the kinetic energy line shape function

$$f_k(\delta\omega) \propto |\delta\omega|^{-1/2}\sin^2[r_0(2\mu|\delta\omega|/\hbar)^{1/2}]e^{-\hbar|\delta\omega|/k_BT} \tag{4}$$

for $\delta\omega < 0$, zero otherwise. The magnetic field gradient in our system is approximately constant, with the highest field ($B_{\max}$) occurring at the cell bottom ($z = 0$). The density profile of $\mathrm{H}\downarrow$ atoms in such a field is exponential, $n(z) = n(0)e^{-\mu_B z|\partial B/\partial z|}/k_BT$, and the PA absorption probability varies as $n(z)^2$. Around $B_{\max}$, the field dependence of the PA line position can be linearized to $\hbar\delta\omega \approx 2g\mu_B(B - B_{\max})$, where $2g\mu_B$ is the field derivative of the line position at $B = B_{\max}$. The Zeeman line shape follows:

$$f_z(\delta\omega) = e^{-\hbar\delta\omega/gk_BT} \tag{5}$$

for $\delta\omega > 0$ and zero otherwise. The line shape is the convolution of f_k and f_z, and can be expressed in error functions,

$$\begin{aligned} F(\delta\omega) &\propto e^{-\hbar\delta\omega/gk_BT}[\mathrm{erfc}(k_0) - e^{-b^2}\mathrm{Re}\,\mathrm{erfc}(k_0 + ib)], \\ b &= \sqrt{\frac{2\mu r_0^2 k_BT}{\hbar^2(1 + 1/g)}}\,; \\ k_0 &= \mathrm{Re}\sqrt{\frac{-\hbar\delta\omega(1 + 1/g)}{k_BT}}\,. \end{aligned} \tag{6}$$

Doppler, lifetime, and instrumental broadening are neglected. This line shape is shown in Fig. 1. The PA line shape for alkali gases in a magneto-optical trap, derived in [17], is different due to the much lower temperature in those experiments.

The fluorescence side peaks in the red and blue wing of the atomic transition (Fig. 1) might be due to PA to very shallow levels. Adiabatic theory predicts that there are bound states up to $v = 25$, but these states may be strongly perturbed by the magnetic field and LS coupling. The peak in the blue wing of the atomic transition suggests that there may be PA to a dissociative level [13].

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