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The following article appeared in *Mol. Phys.* **111**, 2100-2107 (2013) and may be found at http://dx.doi.org/10.1080/00268976.2013.788743.
RESEARCH ARTICLE

Precision measurement of the ionization energy of the 3dσ GK state of H₂

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The frequency of the transition between the 3dσ GK¹Σ⁺ (v = 1, N = 1) state of H₂ and the n = 56p (N = 1, S = 0) Rydberg state belonging to a series converging to the X⁺ 2Σ⁺ (v⁺ = 0, N⁺ = 1) ground state of ortho H₂⁺ has been measured with an accuracy of 1.2 MHz using a narrow-band pulsed near-infrared (NIR) laser. Systematic errors originating from ac and dc Stark shifts, from pressure shifts and from the frequency shift and chirp accompanying the generation of the NIR laser pulses were quantified. By combining this frequency with the binding energy of the 56p (N = 1, S = 0) Rydberg state, the ionization energy of the GK¹Σ⁺ (v = 1, N = 1) state of ortho H₂ was determined to be 379855188.3(12) MHz [12670.60522(4) cm⁻¹]. This new result represents the first step towards the determination of the ionization and dissociation energies of molecular hydrogen at a ν/Δν level of accuracy beyond 10⁻¹³. Using the current value of the ionization energy of ortho H₂ [124357.23797(36) cm⁻¹, from Liu et al. (J. Chem. Phys. 130, 174306 (2009))] and the frequency interval between the N = 1 and N = 0 rotational levels of the X (v = 0) ground state of H₂ [118.48684(10) cm⁻¹, from Jennings et al. (J. Mol. Spectrosc. 126, 19 (1987))], the term value of the GK¹Σ⁺ (v = 1, N = 1) state was determined to be 111805.1196(4) cm⁻¹.

Keywords: molecular hydrogen, precision measurement, GK state, Rydberg states, ionization energy, dissociation energy

1. Introduction

Precision measurements of energy intervals in atoms and molecules by high-resolution spectroscopy play an important role in the natural sciences: They help to study the fundamental laws and the fundamental symmetries in nature [1]. They provide rigorous tests of existing theories and, when necessary, they stimulate the development of new theories. For example, the discovery by high-resolution spectroscopy of a splitting between the 2 ²S₁/₂ and 2 ²P₁/₂ states of atomic hydrogen, by Lamb and Retherford [2], led to the development of modern quantum electrodynamics (QED) as an extension of Dirac’s relativistic quantum theory. The measurement of a possible electric dipole moment of the electron by high-resolution spectroscopy of diatomic molecules such as YbF [3] and the study of space inversion symmetry by high-resolution spectroscopy of chiral molecules [4] represent two examples where the study of molecular systems may provide information relevant in the context of the standard model of particle physics and its extensions. The complete interpretation of the corresponding spectroscopic results will necessitate an accurate description of molecular structure, which include effects beyond the...
usual treatment of molecular structure based solely on electromagnetic interactions and the Born-Oppenheimer approximation.

Precision measurements of the ionization and dissociation energies provide rigorous tests of \textit{ab initio} calculations of molecular structure which include adiabatic and nonadiabatic corrections to the Born-Oppenheimer approximation and QED corrections. \( \text{H}_2 \) and its isotopomers HD and D\(_2\) are the simplest molecules displaying all features of a chemical bond, including electron correlation. Because molecular hydrogen has only two electrons, the Born-Oppenheimer electronic potential energy functions of the lowest electronic states, and the adiabatic and nonadiabatic corrections can be calculated with very high accuracy using well-established procedures [5–8], and QED corrections of progressively higher order in the fine-structure constant \( \alpha \) can be evaluated in a perturbative treatment [5, 8, 9].

The current status of the comparison of experimental and theoretical values of the dissociation and ionization energies of \( \text{H}_2 \), HD, and \( \text{D}_2 \) is that they agree within the combined uncertainty of 30 MHz of the theoretical and experimental determinations (see Ref. [10] and references cited therein). To reach this agreement, the leading (one-loop) term of the \( \alpha^4 \) QED correction term had to be evaluated for the first time in a molecular system with more than one electron [5, 9]. Experimental results of a still higher precision are required to test future calculations of the full \( \alpha^4 \) term and terms of higher order in \( \alpha \), and assess the convergence of the expansion in \( \alpha \).

Our approach to measure the dissociation energy \( D_0 \) of \( \text{H}_2 \) is to measure the ionization energy \( E_I \) of \( \text{H}_2 \) and use a thermodynamical cycle to relate \( E_I \) and \( D_0 \) [10, 11]. This approach does not rely on the detection of the onset of dissociation or ionization continua in the spectrum of molecular hydrogen, but on the measurement of the transition frequencies to \( \text{np} \) Rydberg states belonging to series converging on the lowest rotational levels of the \( X^2\Sigma^+ \) \((v^+ = 0) \) ground state of \( \text{H}_2^+ \) and extrapolation to the series limit. The \( \text{np} \ell_1 \) \((0, 0) \) series of \( \pi^- \) electronic character converging on the ground state of ortho \( \text{H}_2^+ \) was found to be the most suitable, because this series is the least perturbed low-\( \ell \) series and the positions of the levels in the range \( n = 54–64 \) with respect to the ionization thresholds are known with an accuracy of better than 100 kHz from millimeter-wave spectroscopic experiments and multichannel quantum defect theory [10, 12]. To label the Rydberg series we use the notation \( n\ell N_N^+ (v^+, S) \). \( N \) and \( N^+ \) are the total angular momentum quantum numbers excluding spins of \( \text{H}_2 \) and \( \text{H}_2^+ \), respectively. \( N \), is the quantum number resulting from the vector addition \( \vec{N}^+ + \vec{\ell} \), \( \vec{\ell} \) being the orbital angular momentum of the Rydberg electron. In the present case, \( v^+ = 0 \) and \( S = 0 \) so that we usually omit these quantum numbers in the labels.

In our previous work [11], we determined the position of the \( \text{np} \ell_1 \) levels with respect to the ground state of ortho \( \text{H}_2 \) as a sum of the interval between the ground state and the \( EF^1\Sigma^+_g (v = 0, N = 1) \) state from Ref. [13] and between the \( EF^1\Sigma^+_g (v = 0, N = 1) \) state and the \( \text{np} \ell_1 \) level (see Fig. 1a). A disadvantage of this method is that the frequency required to pump the \( X \to EF \) two-photon transition is high enough to ionize the \( EF \) state, which leads to the generation of ions in the measurement volume. These ions, in turn, induce inhomogenous line broadenings and line shifts, which eventually limits the accuracy of the measurement of the ionization and dissociation energies to about 10 MHz.

This problem can be overcome by determining the interval between the \( 3d\sigma GK^1\Sigma^+_g (v = 1, N = 1) \) state (designated \( GK (v = 1, N = 1) \) hereafter) and the \( \text{np} \ell_1 \) level after excitation to the \( GK (v = 1, N = 1) \) state in a resonant two-photon excitation via the \( B^2\Sigma^+_u (v = 3, N = 2) \) state (\( \text{see Fig. 1c} \)), and measuring the interval between the \( GK (v = 1, N = 1) \) state and the ground state by...
Doppler-free two-photon spectroscopy in a separate experiment (see Fig. 1b). The lifetime of the $GK \, ^{1}\Sigma_{g}^{+} (v = 1, N = 1)$ state is long enough (25 ns [14–16]) so that the interval can be determined with a precision of $\approx 1$ MHz by near-infrared laser spectroscopy. The disadvantage of this scheme is that the frequency needed to measure the $X$–$GK$ interval by two-photon spectroscopy lies in the vacuum-ultraviolet (VUV), but recent progress in VUV frequency combs [17, 18] suggests that such a measurement should be possible.

In this article we report a measurement of the frequency of the transition from the $GK (v = 1, N = 1)$ state to the $np_{1}$ level following the excitation scheme of Fig. 1c at an accuracy of 1.2 MHz and describe in detail how the systematic errors arising from ac Stark shift and dc Stark shifts were quantified and minimized.

2. Experiment

The measurement of the $GK (v = 1, N = 1) \rightarrow 56p_{1}$ transition of $H_{2}$ relied on the excitation sequence

$$X (v = 0, N = 1) \rightarrow B (v = 3, N = 2) \rightarrow GK (v = 1, N = 1) \rightarrow 56p_{1}. \quad (1)$$

The pulsed vacuum-ultraviolet (VUV) radiation used to drive the $X \rightarrow B$ transition was generated by resonance-enhanced sum-frequency mixing in Xe using two Nd:YAG-pumped dye lasers, as described in detail in Ref. [12]. The visible radiation needed for the $B \rightarrow GK$ transition was produced by a commercial dye laser pumped by the same Nd:YAG laser. The experiment was carried out at a repetition rate of 25 Hz. The durations of the VUV and visible laser pulses were about 2 and 5 ns, respectively.

The narrow-band near-infrared (NIR) radiation employed for the precision measurement of the $GK \rightarrow 56p_{1}$ transition was generated by a home-built laser system described in Ref. [19] which produces near-Fourier-transform-limited pulses with a pulse length that can be adjusted in the range between 10 ns and 1 $\mu$s. The pulses were chopped out of the continuous-wave output of a Ti:Sa ring laser using an acousto-optic modulator (AOM) operated in a pulsed mode at a driving frequency of 1 GHz. The weak pulses of NIR radiation (pulse energy in the range 1-10 nJ) emitted in the first diffraction order of the AOM were amplified to pulse energies of several mJ in Ti:Sa crystals using two successive amplifiers operated in a travelling multipass configuration (see Ref. [19] for details).

The vacuum chamber in which photoexcitation was carried out is depicted schematically in Fig. 2. The $H_{2}$ molecules were introduced into the photoexcitation region by means of a pulsed valve operated at a stagnation pressure of 3 bar. The supersonic beam resulting from the adiabatic expansion in vacuum was collimated using two skimmers before entering the excitation region consisting of a cylindrically symmetric stack of six resistively coupled metallic plates (called electrodes hereafter) designed for the application of homogeneous electric fields. In the middle of this region, the molecular beam was intersected at right angles by the VUV, visible and NIR laser beams. The visible laser beam and the NIR laser beam labeled ”1” in Fig. 2 were recombined using a dichroic mirror before entering the chamber. The VUV laser beam crossed these two beams at right angles and the small volume defined by the interaction of the three laser beams and the molecular beam was located on the axis of the electrode stack. The polarization vectors of the visible and VUV laser radiation were parallel, and the polarization of the NIR radiation was perpendicular, to the molecular-beam propagation axis.

The photoexcitation region was surrounded by two concentric magnetic shields.
made of mumetal to suppress stray magnetic fields in the photoexcitation volume. The cylindrical geometry of the excitation region was chosen to ensure that the stray electric-field components perpendicular to the axis of the electrode stack are negligible (i.e., less than 1 mV/cm) in the region close to the symmetry axis.

The transitions to the $56p_1$ Rydberg states of $\mathrm{H}_2$ were detected by delayed pulsed field ionization followed by the extraction of the $\mathrm{H}_2^+$ ions toward a microchannel-plate detector via a field-free time-of-flight tube. The last plate of the electrode stack on the detector side was earthed and the field-ionization pulses were produced by applying a positive voltage to the plate located on the pulsed-nozzle side (see Fig. 2). The spectra were obtained by monitoring the field-ionization yield as a function of the NIR frequency. To separate the ions produced by photoionization of the $\mathrm{GK}$ state with the visible laser from those produced by delayed pulsed field ionization, a weak electric-field pulse was applied immediately after the (field-free) photoexcitation and was maintained until the application of the larger electric-field pulse used for field ionization. To avoid stray electric fields caused by ions in the photoexcitation volume, the intensity of the visible laser was strongly attenuated (to less than 10 $\mu$J/pulse) when the precision measurements were carried out.

The frequency of the NIR radiation was calibrated by splitting off a fraction of the cw output of the Ti:Sa ring laser to record a Doppler-free spectrum of $\mathrm{I}_2$ for the determination of absolute frequencies and the transmission through an etalon of 149.969(1) MHz free spectral range for the determination of relative frequencies (see Ref. [11] for details). The $a_1$ component of the $X(v'' = 15, J'' = 62) \rightarrow B(v' = 0, J' = 63)$ transition of $\mathrm{I}_2$ at 12635.698110(3) cm$^{-1}$ [20] was used because it is located in the immediate vicinity of the $\mathrm{GK} \rightarrow 56p_1$ transition of $\mathrm{H}_2$ (see Fig. 5 below). The pressure shift of -0.4(0.3) MHz of the iodine transitions in our cell was included in the calibration procedure. The value of this shift was determined as explained in Ref. [11] by comparing the frequencies of seven transitions measured with an iodine cell identical to the one used in the present work and frequencies reported in Ref. [20]. To measure the Doppler shift of the transitions, the pulse-amplified NIR laser beam was split into two beams with a beam splitter and the two beams (labeled 1 and 2 in Fig. 2) were introduced into the chamber from opposite sides. The transition was measured for both beams in the same scan and the Doppler shift was determined as half the separation between the two Doppler components.

The pulse amplification of the chopped NIR beam is accompanied by a frequency chirp resulting from time-dependent changes of the refractive index of the Ti:Sa crystals. To quantify the frequency evolution during a pulse, we followed the procedure described in [19]. The pulse-amplified NIR beam and the cw output of the NIR ring laser were recombined and overlapped on the active area of a fast photodiode. The resulting beat pattern for a 200 ns (full width at half maximum) NIR pulse is depicted in Fig. 3a. The interference signal oscillates with a beat frequency of $\approx 1$ GHz which corresponds to the AOM driving frequency (1 GHz) (see inset). The difference between the observed beat frequency and the AOM driving frequency can be expressed as a time-dependent phase function. The time-dependent frequency chirp was numerically calculated as the time derivative of the phase function following the method described in Ref. [21]. The reconstructed frequency evolution, which was reproducible for all pulses of this length, is displayed in Fig. 3b. The frequency shift evolves from an initial value of $-6$ MHz immediately after the Nd:YAG pulse to about zero in the first 200 ns and then oscillates around zero. To reduce the effects of the frequency chirp on the high-resolution measurements, the laser pulses used for the excitation to the $\mathrm{GK}(v = 1, N = 1)$
state were fired at time 0 in Fig. 3b, when the NIR-frequency shift is negligible. The increasing shift at later times (∼ 50 ns) had no incidence on the measurement because it takes place on a timescale longer than the lifetime of ∼ 25 ns [14–16] of the GK (v = 1, N = 1) state, which is indicated by the area shaded in grey in Fig. 3b. These chirp-free conditions were confirmed for each measurement presented in Section 3 by carrying out the analysis described above. We nevertheless included a systematic uncertainty of 0.5 MHz in the NIR frequency arising from the frequency chirp.

3. Results

One of the major difficulties in the measurement of the frequency of the GK (v = 1, N = 1) → 56p1 (v+ = 0, S = 0) transition lies in the quantification of systematic errors originating from ac and dc Stark shifts caused by the laser fields and by electric stray fields, including those caused by ions generated in the measurement volume. Indeed, the polarizability of Rydberg states scales as the seventh power of the principal quantum number n and even small stray electric fields can shift the frequencies of transitions to high Rydberg states. Moreover, the n−3 scaling of the photoexcitation cross section requires strong laser intensities which inevitably lead to ac Stark shifts.

Because of the cylindrical symmetry of the electrode stack surrounding the excitation volume, the stray-electric-field components perpendicular to the symmetry axis are negligible (see below and also Section 2). The stray field thus points along the axis of propagation of the supersonic beam and of the time-of-flight tube (see Fig. 2). To determine the stray field, we follow the procedure described in detail in Ref. [22], which consists of measuring the shifts of the transition frequency upon application of well-defined electric fields across the electrode stack. At low values of the electric field, the Stark shifts are smaller than the spectral width of about 20 MHz (see Fig. 4a). With increasing field strength, the line shifts and splits into two components corresponding to Rydberg states with M_N values of 0 and ±1. The corresponding Stark shifts are plotted as a function of the applied electric field in Fig. 4c. By minimizing the least-square deviation between the observed Stark shifts (black dots) and Stark shifts calculated with the method described in Ref. [23] (full lines) the compensation field was determined to be 24.6(6) mV/cm, and the uncertainty in the transition frequency resulting from the 0.6 mV/cm uncertainty of the compensation field to be 0.1 MHz. Analysing the data presented in Fig. 4c including the possibility of a stray-field component perpendicular to the molecular beam axis leads to the conclusion that this component must be less than 0.3 mV/cm and thus negligible.

To quantify the ac Stark shifts induced by the NIR laser field, the transition frequency was measured for several NIR pulse energies up to 3.4 mJ/pulse, as depicted in Fig. 4b. A linear regression of these data led to a slope of -11.6(7) MHz/mJ. The final measurements of the transition frequencies were carried out at an average NIR pulse energy of 40 µJ, resulting in a systematic shift of -0.4(6) MHz, the large uncertainty arising from the strong pulse-to-pulse energy fluctuations of the NIR laser.

Initially, we expected that the visible laser used to prepare the initial population in the GK (v = 1, N = 1) level would not cause any shift of the transition frequency because the duration of the visible-laser pulses (5 ns) was much shorter than the lifetime of (25 ns) of the GK (v = 1, N = 1) state and the NIR pulse duration (300 ns). Nevertheless, a dependence (21(20) MHz/mJ) of the GK (v = 1, N = 1) → 56p1 transition frequency on the visible-laser pulse energy was observed.
(see Fig 4d), which we attribute to the stray fields caused by ions generated by photoionization of the $GK (v = 1, N = 1)$ level during the visible-laser pulse. For the final measurements, an average visible-laser pulse energy of 10 $\mu$J was used, which did not result in any systematic shift, but in an uncertainty of 0.5 MHz.

To minimize the Doppler width of the transition, the propagation axes of the molecular and the NIR laser beams were chosen to be perpendicular. A small Doppler shift of the transition frequency may nevertheless result from a remaining deviation from 90°, or from the selection of molecules with a nonzero velocity component in the direction of propagation of the NIR laser by the VUV and visible lasers used to populate the $GK (v = 1, N = 1)$ state. To determine this Doppler shift, the final measurements were performed after dividing the NIR beam into two components using a 50% beam splitter and directing these two beams into the measurement region in a counterpropagating arrangement (see Fig. 2). A typical spectrum measured in this configuration is displayed in Fig. 5a, and consists of two lines, labeled 1 and 2 to designate the NIR beam responsible for the absorption (see inset of Fig. 5). The Doppler shift corresponds to half the separation of the two lines, and the transition frequency can be determined by taking the average of the positions of the two lines.

The NIR laser frequency was determined as described in Section 2 using the $\alpha_1$ component of the $X (v'' = 15, J'' = 62) \rightarrow B (v' = 0, J' = 63)$ transition of $I_2$ at 12635.698110(3) cm$^{-1}$ (378808699.5(1) MHz) [20] for the absolute frequency calibration and the transmission spectrum through an etalon having a free spectral range of 149.969(1) MHz for the determination of relative frequencies. As illustration, the Doppler-free $I_2$ and etalon transmission spectra recorded simultaneously with the spectrum of the $GK (v = 1, N = 1) \rightarrow 56p_1 (v^+ = 0, S = 0)$ transition are displayed in Fig. 5c and b, respectively. The $I_2$ lines measured with our $I_2$ cell are subject to a pressure shift of -0.4(3) MHz, so that the $I_2$ line observed in Fig. 5c has a central frequency of 378808699.1(3) MHz.

To determine the central frequency, each Doppler component was modeled by taking into account the hyperfine structure of the $56p_1 (v^+ = 0, S = 0)$ level as measured in Ref. [12]. The intensities of the (unresolved) transitions to the $F = 0, 1$ and 2 hyperfine-structure components were given weights of 1, 3 and 5, respectively, resulting in the stick spectra depicted in Fig. 5a. The stick spectra were then convoluted using a Gaussian lineshape function. The full width at half maximum of the lines and the central positions were determined in a least-squares fit. We estimate the uncertainty resulting from our lineshape model to be 0.1 MHz.

The pressure shift of the transition was estimated to be negligible at the $H_2$ density in the photoexcitation volume (about $10^{13}$ cm$^{-1}$) using the pressure-shift coefficient of Rydberg states of $H_2$ reported by Herzberg and Jungen [24] $[5.7 \pm 0.5$ cm$^{-1}$/amagat] (see also discussion in Ref. [11]).

The results of 10 measurements carried out on different days after realignment of the lasers are summarized in Fig. 6, which shows the positions of the two Doppler components as filled squares and triangles, and their average as filled circles. The dashed line indicates the position relative to the $I_2$ calibration line of the average of the 10 central frequencies ($-180.8(6)$ MHz). The standard deviation of 0.6 MHz of these measurements was assumed to be representative of the statistical error of our measurement and is limited by the Doppler width of the lines.

Table 1 lists all contributions to our determination of the $GK (v = 1, N = 1) \rightarrow 56p_1 (v^+ = 0, S = 0)$ transition frequency and their estimated uncertainties. The final result is 378809478.7(12) MHz (12635.72410(4) cm$^{-1}$).
4. Discussion and Conclusions

The measurements presented in this article demonstrate that the frequencies of transitions between low and high Rydberg states can be determined by NIR laser spectroscopy with a relative accuracy $\Delta \nu/\nu$ of $3 \times 10^{-9}$ and an absolute accuracy of 1.2 MHz. This accuracy is primarily limited by the uncertainty in the ac Stark shift and by the statistical uncertainty associated with the determination of the centers of the Doppler-broadened lines (full width at half maximum of about 20 MHz).

From the measurement of the $GK(v = 1, N = 1) \rightarrow 56p_1$ transition frequency presented in this article, further intervals can be derived, as summarized in Table 2. The position of the $56p_1(v^+ = 0, S = 0)$ Rydberg state of ortho H$_2$ with respect to the center of gravity of the hyperfine structure of the $X^+(v^+ = 0, N^+ = 1)$ ground state of ortho H$_2^+$ has been determined to be $-1045709.62(10)$ MHz by analysing millimeter-wave spectra with multichannel quantum defect theory [10]. By subtracting this (negative) frequency from the frequency of the $GK(v = 1, N = 1) \rightarrow 56p_1$ transition, one obtains the value of $379855188.3(12)$ MHz for the ionization energy of the $GK(v = 1, N = 1)$ state of ortho H$_2$.

The present measurement of the ionization energy of the $GK(v = 1, N = 1)$ state could be used to derive an improved value of the dissociation and ionization energies of H$_2$ if a precision measurement of the $X(v = 0, N = 1) - GK(v = 1, N = 1)$ interval is carried out. The current uncertainty in the ionization energy of H$_2$ is 11 MHz [28] and the experimental result is in agreement with ab initio calculations which include quantum-electrodynamic corrections up to the leading one-loop member of the $\alpha^4$ term [5] within the combined uncertainties of 30 MHz of the experimental and theoretical determinations. The present results suggest that it should be possible to reduce the experimental uncertainty of the ionization and dissociation energies of H$_2$ by a factor of almost 10 in the near future.

In the meantime, the ionization energy of the $GK(v = 1, N = 1)$ state listed above can be combined with the value of $3728136204(11)$ MHz determined recently for the ionization energy of ortho H$_2$ (i.e., the $X(v = 0, N = 1) - X^+(v^+ = 0, N^+ = 1)$ interval) [11] and the value of $3552146(3)$ MHz known for the $X(v = 0, N = 0) - X(v = 0, N = 1)$ interval to obtain the term value of $3351833162(12)$ MHz ($111805.1196(4)$ cm$^{-1}$) of the $GK(v = 1, N = 1)$ state. This value deviates from the value of $111805.1189(10)$ cm$^{-1}$ reported in Ref. [29] but is in good agreement with, and more precise than, the older result of $111805.139(17)$ cm$^{-1}$ obtained by Jungen et al. [30].

5. Acknowledgements

This article is dedicated to Professor Martin Quack whom we thank for his interest in our work, for his stimulating influence and for fruitful scientific exchanges over many years. We thank Professor Horst Knöckel (University of Hannover) for his advice concerning pressure shifts of the I$_2$ calibration lines and Professor Wim Ubachs (Free University of Amsterdam) for a useful discussion concerning possible origins of the discrepancy between the term value of the $GK(v = 1, N = 1)$ state reported in this article and that reported in Ref. [29]. This work is supported
financially by the Swiss National Science Foundation under project 200020-135342 and by the European Research Council advanced grant program under project 228286.

References

Table 1. Determination of the $GK (v = 1, N = 1) \rightarrow 56p1_{1} (v^+ = 0, S = 0)$ transition frequency and error bud-
get (all values in MHz). The transition frequency corresponds to the center of gravity of the hyperfine structure.
The total uncertainty was determined by summation of the individual uncertainties in quadrature.

<table>
<thead>
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<th>Shift</th>
<th>Uncertainty</th>
</tr>
</thead>
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<tr>
<td>Transition frequency relative to the $I_2$ reference line</td>
<td>$-180.8$</td>
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<td>Position of the $I_2$ reference line [20]</td>
<td>$378808699.5$</td>
</tr>
<tr>
<td>Pressure shift of the $I_2$ reference line</td>
<td>$-0.4$</td>
</tr>
<tr>
<td>Uncertainty of the free spectral range</td>
<td>$&lt;0.1$</td>
</tr>
<tr>
<td>Frequency shift in the Ti:Sa amplifier</td>
<td>$0.0$</td>
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<tr>
<td>ac Stark shift by the NIR laser</td>
<td>$0.4$</td>
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<tr>
<td>dc Stark shift by residual stray electric field</td>
<td>$0.0$</td>
</tr>
<tr>
<td>Frequency shift by VIS laser</td>
<td>$0.0$</td>
</tr>
<tr>
<td>Pressure shift</td>
<td>$&lt;0.1$</td>
</tr>
<tr>
<td>Uncertainty of the line shape model</td>
<td>$0.0$</td>
</tr>
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<td>Shift by AOM used in the iodine spectroscopy</td>
<td>$-40.0$</td>
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<tr>
<td>Shift by AOM used to generate the seed pulse</td>
<td>$1000.0$</td>
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<tr>
<td>Total</td>
<td>$378809478.7$</td>
</tr>
</tbody>
</table>

Table 2. Determination of the ionization energy and the term value of the $GK (v = 1, N = 1)$ state of $H_2$. The frequencies and wave numbers correspond to the center of gravity of the hyperfine structure.

<table>
<thead>
<tr>
<th>Label</th>
<th>Energy interval</th>
<th>Frequency / MHz</th>
<th>Wave number / cm$^{-1}$</th>
<th>Reference</th>
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<tr>
<td>(1)</td>
<td>$GK (v = 1, N = 1) \rightarrow 56p1_{1} (v^+ = 0, S = 0)$</td>
<td>$378809478.7(12)$</td>
<td>$12635.72410(4)$</td>
<td>This work</td>
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<tr>
<td>(2)</td>
<td>$56p1_{1} (v^+ = 0, S = 0) \rightarrow X^+ (v^+ = 0, N^+ = 1)$</td>
<td>$1045709.62(10)$</td>
<td>$34.881118(3)$</td>
<td>[10]</td>
</tr>
<tr>
<td>(3)$^1$</td>
<td>$GK (v = 1, N = 1) \rightarrow X^+ (v^+ = 0, N^+ = 1)$</td>
<td>$379855188.3(12)$</td>
<td>$12670.60522(4)$</td>
<td>This work</td>
</tr>
<tr>
<td>(4)</td>
<td>$X^+ (v^+ = 0, N^+ = 0) \rightarrow X^+ (v^+ = 0, N^+ = 1)$</td>
<td>$1745801.66(3)$</td>
<td>$58.233675(1)$</td>
<td>[25–27]</td>
</tr>
<tr>
<td>(5)$^2$</td>
<td>$GK (v = 1, N = 1) \rightarrow X^+ (v^+ = 0, N^+ = 0)$</td>
<td>$378109386.6(12)$</td>
<td>$12612.37154(4)$</td>
<td>This work</td>
</tr>
<tr>
<td>(6)</td>
<td>$X (v = 0, N = 0) \rightarrow X (v = 0, N = 1)$</td>
<td>$3552146(3)$</td>
<td>$118.48684(10)$</td>
<td>[31]</td>
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<tr>
<td>(7)</td>
<td>$X (v = 0, N = 1) \rightarrow X^+ (v^+ = 0, N^+ = 1)$</td>
<td>$372613620(11)$</td>
<td>$124357.22797(36)$</td>
<td>[14]</td>
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<tr>
<td>(8)$^3$</td>
<td>$X (v = 0, N = 0) \rightarrow GK (v = 1, N = 1)$</td>
<td>$3351833162(12)$</td>
<td>$111805.1196(4)$</td>
<td>This work</td>
</tr>
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</table>

$^1$Ionization energy of the $GK (v = 1, N = 1)$ state, determined as (1) + (2).

$^2$Determined as (3) – (4).

$^3$Term value of the $GK (v = 1, N = 1)$ state, determined as (6) + (7) – (3).
Figures

Figure 1. Schematic energy-level diagram of selected electronically excited states of molecular hydrogen (not to scale) with possible excitation schemes to access the 56p Rydberg state. The values given next to the arrows are the wavelengths necessary to excite the corresponding transition (see text for details).
Figure 2. Schematic diagram of the experimental chamber. At the position where the laser beams intersect the molecular beam the polarizations of the VUV and visible-laser beams are parallel to the propagation axis of the molecular beam, and the polarization of the NIR laser beams is perpendicular to the plane spanned by the propagation axes of the molecular beam and the NIR laser beams (see text for details).
Figure 3. (a) Beat-note signal arising from the superposition of the cw output of the NIR ring laser with an amplified NIR laser pulse. The oscillation frequency of 1 GHz corresponds to the frequency of the accousto-optic modulator used to generate a seed pulse from the cw output of the ring laser. (b) Evolution of the frequency shift caused by the pulse amplification determined from the beat-note signal. The $GK(v = 1, N = 1)$ state is excited at time 0 and the gray area represents its lifetime of $\approx 25$ ns [14, 15]. The horizontal dashed line indicates the nominal frequency (i. e., without chirp) of the NIR laser.
Figure 4. (a) Spectrum of the GK ($v = 1, N = 1$) $\rightarrow$ 56p1_{11} ($v^+ = 0, S = 0$) transition in H$_2$ near 12635.7 cm$^{-1}$ and shifts of the transition frequency as a function of (b) the pulse energy of the NIR laser, (c) the dc electric field applied in the direction parallel to the polarization vector of the VUV laser radiation, and (d) the pulse energy of the visible laser. The straight lines in panels (b) and (d) were obtained by linear regression and have slopes of -11.6(7) MHz/mJ and 21(20) MHz/mJ, respectively. The dashed line in panel (c) indicates the field (24.6(6) mV/cm) which compensates the stray field.
Figure 5. (a) Experimental and simulated (inverted trace) spectrum of the $GK (v = 1, N = 1) \rightarrow 56p_{1/2} (v^+ = 0, S = 0)$ transition in $H_2$. The two lines in the $H_2$ spectrum correspond to the two Doppler components originating from the two counterpropagating NIR laser beams labeled 1 and 2 in the inset. The actual transition frequency is indicated by the vertical arrow. The stick spectrum shows the hyperfine structure of the $56p_{1/2} (v^+ = 0, S = 0)$ level as measured in Ref. [12] and was convoluted by a Gaussian lineshape function with a full width at half maximum of 18 MHz to obtain the simulated spectrum. (b) Transmission spectrum through an etalon for the determination of relative frequencies. (c) Doppler-free spectrum of molecular iodine showing the $a_1$ component of the $X (v'' = 15, J'' = 62) \rightarrow B (v' = 0, J' = 63)$ transition at 12635.698110(3) cm$^{-1}$ [20] used to determine absolute frequencies. Traces (b) and (c) were shifted along the vertical axis for clarity.
Figure 6. Distribution of the measured frequency of the $GK (v = 1, N = 1) \rightarrow 56p_{1}\ (v^+ = 0, S = 0)$ transition. Triangles and squares represent the positions of the lines corresponding to the two Doppler components observed in the spectra and the circles mark their mean values. The final result is indicated by the dashed line. The standard deviation of the measurement is represented by the size of the circles.