Spectroscopy on some *g* symmetry states in H_2 and determination of the ionization potential

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Term values of 14 levels of $EF\,^1\Sigma_g^+(v=19)$, $GK\,^1\Sigma_g^+(v=0)$, $I\,^1\Pi_g(v=0)$, and $J\,^1\Delta_g(v=0)$ states in H_2 have been calibrated in a two-step laser excitation experiment with an accuracy of 0.006 cm^{-1}. Combined with literature data on inter-Rydberg transitions these highly accurate values on *g* symmetry levels yield an independent determination of the ionization potential in H_2 at 124 417.476 (12) cm^{-1}, which is consistent with previous experimental values and with *ab initio* calculation.

The hydrogen molecule and its isotopic variants have been a test system for the understanding and calculation of molecular structure since the early days of quantum mechanics. Developments and improvements in theory and experiment have mutually stimulated each other over the years. One issue upon which theory and experiment have focused is a determination of the ionization potential (IP) of the smallest neutral molecule. Herzberg [1] and Herzberg and Jungen [2] were the first to reach sub-cm^{-1} accuracy by analyzing the one-photon absorption spectrum recorded by classical (i.e., spectrograph) methods.

A first attempt to use lasers for determination of the IP focused on the triplet manifold [3], where excitation from the metastable $c\,^3\Pi_u$ can be accomplished with narrow band cw lasers; although the IP for the triplet levels can be determined accurately, the relative energy with respect to the singlet system determines the uncertainty. Later pulsed laser techniques were employed by Glab and Hessler [4] and by Eyler and co-workers [5–8] to perform stepwise excitation from the ground state. Their strategy was based on calibration of the lowest vibrational level in the $EF\,^1\Sigma_g^+(v=0)$ state by two-photon excitation. Glab and Hessler and McCormack *et al.* [6] subsequently laser excited the np Rydberg series to derive the IP. Eyler and co-workers combined their values of improving accuracy over the years on the $EF(v=0)$ levels with the Fourier-transform infrared (FTIR) data on inter-Rydberg transitions of Jungen *et al.* [9], to connect to the ionization limit. In the present study we perform, alternatively, stepwise calibration of term values near 112 000 cm^{-1} pertaining to a number of *g* symmetry states. Combining with the FTIR data of Ref. [9], we determine a value for the IP, which is independent at least for the laser excitation steps.

Double-resonance laser excitation techniques were developed by Tsukiyama *et al.* [10], in which a tunable extreme ultraviolet (XUV) -laser source was employed to prepare single rovibrational quantum levels in the $B\,^1\Sigma_u^+(v=5)$ state, while a second tunable laser in the red range further excited to the $EF\,^1\Sigma_g^+$, $GK\,^1\Sigma_g^+$, $I\,^1\Pi_g$, and $J\,^1\Delta_g$ states. Recently our group has developed similar excitation schemes as in Ref. [10] for the investigation of gerade symmetry states in hydrogen and its isotopomers [11,12]. For the present study the experimental resolution of the laser system and the absolute frequency calibration have been improved by an order of magnitude. In a first step we have calibrated

the energy levels of the $B\,^1\Sigma_u^+(v=5)$ state, employing 1 XUV+1 UV photoionization spectroscopy with a Fourier-transform limited XUV-laser source. A pulsed dye amplifier (PDA), seeded by a cw ring dye laser, generated Fourier-transform limited radiation in the visible wavelength regime, around $\lambda \approx 625$ nm. This radiation was frequency doubled and subsequently frequency tripled in a xenon gas jet, resulting in the production of narrow band XUV radiation. The ratio in frequency of the XUV and the visible radiation is exactly six, and by scanning the cw seed laser, the XUV radiation changes wavelength accordingly. By calibrating the cw radiation against a Doppler-free I_2 saturated absorption spectrum, and comparing with the new I_2 saturated absorption atlas developed in our laboratory [13], the frequency of the XUV beam could be determined.

A typical example of a 1 XUV+1 UV photoionization spectrum of the $R(3)$ line of the B-$X(5,0)$ Lyman band is depicted in Fig. 1. The simultaneously recorded I_2 saturated absorption spectrum and the etalon markers [free spectral range (FSR) = 148.9567 MHz], both taken with the cw output of the ring-dye laser, are shown as well. It is noted that the B-$X(8,3)$ band in I_2 was not specifically calibrated in Ref. [13]; via combination differences the line positions of this band could, however, be derived with high accuracy. To reduce Doppler broadening effects in the supersonic molecular beam, hydrogen gas was mixed with xenon in a 1:5 ratio in the stagnation zone before the molecular beam is produced. In view of the velocity of H_2 in the seeded molecular beam a deviation by 1° from perfect perpendicular alignment would result in a Doppler shift of 30 MHz in the B-X lines. The beam is skimmed and laser excitation takes place at 20 cm from the nozzle under essentially collision-free circumstances. As can be seen from Fig. 1 the linewidth in the H_2 spectrum is ≈ 600 MHz, and transition frequencies of a single recording have been determined with a statistical uncertainty of 60 MHz. However, as described and analyzed in a previous study on the He atom, where the PDA-based XUV laser was used for absolute frequency calibration, chirp effects in the PDA were found to cause systematic uncertainties of up to 100 MHz in the absolute transition frequencies [14], and this uncertainty governs the error budget. The ac-Stark shift is estimated to be <6 MHz for a power density of <2 MW/cm^2, based on the value for the $1\,^1S$-$2\,^1P$ transition in helium [14]. The shift in molecular hydrogen is expected to be lower than in helium, as the oscillator strength
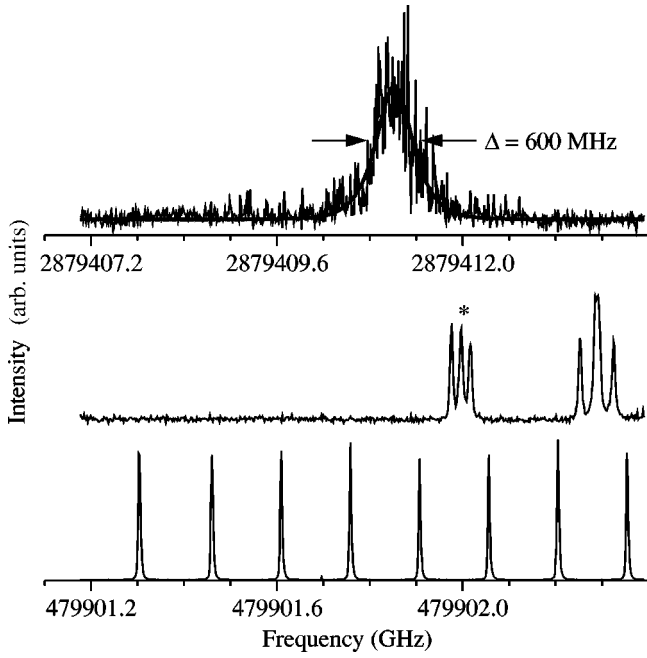
FIG. 1. In the upper trace the spectral recording of the $B\,^1\Sigma_u^+$-$X\,^1\Sigma_g^+(5,0)$ $R(3)$ transition in H_2 is depicted. The lower two traces are, respectively, the simultaneously recorded saturated absorption spectrum of I_2 and the markers of an etalon (FSR $=148.9567$ MHz) taken with the output of the cw ring dye laser, used as the seed laser for the PDA. The I_2 line, marked with an *, is the t component of the $R(59)$ line in the B-$X(8,3)$ band at 479 901 996.3 MHz.

is distributed over the rovibrational states. An overview of the total error budget is given in Table I, resulting in an uncertainty of 105 MHz or 0.004 cm^{-1}.

The transition frequencies of the $B\,^1\Sigma_u^+$-$X\,^1\Sigma_g^+(5,0)$ band are listed in Table II. The level energies of the $B\,^1\Sigma_u^+(v=5)$ states were determined by adding the measured transition frequency to the level energies of the rotational levels of the $X\,^1\Sigma_g^+(v=0)$ ground state, given by Ref. [15]. The values are listed in Table II as well.

In a second experiment a somewhat broader XUV-laser source (10 GHz) was used to prepare these $B\,^1\Sigma_u^+(v=5)$ levels, while the narrow band Fourier transform limited laser source was employed to probe the $EF\,^1\Sigma_g^+$, $GK\,^1\Sigma_g^+$, $I\,^1\Pi_g$

TABLE I. The error budget of the B-X transitions and the transitions from the B state to the states with gerade symmetry. The statistical uncertainty of a single recording is, respectively, 60 and 40 MHz, however, averaging results in 20 and 30 MHz.

	B-X	gerade-B
ac-Stark	<6 MHz	<6 MHz
Doppler	30 MHz	5 MHz
Chirp	100 MHz	80 MHz
Calibration	12 MHz	2 MHz
Statistics	20 MHz	30 MHz
rms	105 MHz	85 MHz

TABLE II. Transition frequencies of the $B\,^1\Sigma_u^+$-$X\,^1\Sigma_g^+(5,0)$ band in H_2 and the level energies in the $B\,^1\Sigma_u^+$ ($v=5$) state. Values in cm^{-1}.

	Frequency	J'	Energy
$P(1)$	96324.532 (4)	0	96443.019 (4)
$R(0)$	96474.270 (4)	1	96474.270 (4)
$R(1)$	96418.076 (4)	2	96536.562 (4)
$R(2)$	96275.091 (4)	3	96629.464 (4)
$R(3)$	96046.817 (4)	4	96752.336 (4)

and $J\,^1\Delta_g$ states. The use of a broader XUV source is advantageous: the molecular resonance acts as a frequency filter in the two-step process, asymmetric excitation is prevented, and the second excitation step is not sensitive to frequency drifting effects in the XUV source. On-resonance signal was produced by ionizing the molecule with a third laser pulse in the UV range. Also in this experiment the wavelength was calibrated by simultaneous recording of a saturated I_2 absorption spectrum. As an example a spectrum of the $EF\,^1\Sigma_g^+$-$B\,^1\Sigma_u^+(19,5)$ $R(1)$ resonance is shown in Fig. 2.

The experimental linewidth of ≈270 MHz on the EF-B transitions is predominantly determined by the short lifetime of the intermediate $B\,^1\Sigma_u^+$ level; the bandwidth of the laser inducing the second excitation step is below 100 MHz. The results of these double-resonance excitation spectra on the $EF\,^1\Sigma_g^+$-$B\,^1\Sigma_u^+(19,5)$, $GK\,^1\Sigma_g^+$-$B\,^1\Sigma_u^+(0,5)$, $I\,^1\Pi_g$-$B\,^1\Sigma_u^+(0,5)$, and $J\,^1\Delta_g$-$B\,^1\Sigma_u^+(0,5)$ bands are listed in Table III. The transition frequencies of in total 16 lines are
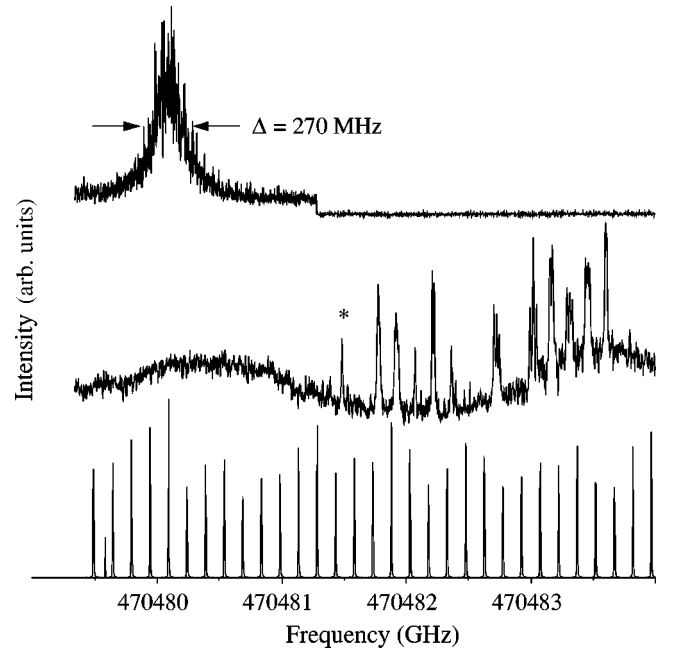

FIG. 2. Spectral recording of the $EF\,^1\Sigma_g^+$-$B\,^1\Sigma_u^+(19,5)$ $R(1)$ line in H_2 at $\lambda=637$ nm; again simultaneous recordings of the I_2 saturated absorption and etalon markers are shown. The I_2 line, marked with an *, is the t component of the $R(66)$ line in the B-$X(9,5)$ band at 470 481 484.3 MHz.

TABLE III. Transition frequencies in the H_2 bands observed. Δ denotes present data minus data from Ref. [10]. The uncertainty is 0.003 cm^{-1}. Values in cm^{-1}.

J	R branch	Δ	Q branch	Δ	P branch	Δ
			$EF\,^1\Sigma_g^+\text{-}B\,^1\Sigma_u^+$ (19,5) band			
1	15693.526	+0.016				
2	15694.300	+0.060			15589.578	+0.038
3	15686.413	+0.003			15538.336	+0.036
4	15669.066				15478.529	
			$GK\,^1\Sigma_g^+\text{-}B\,^1\Sigma_u^+$ (0,5) band			
1	15219.454	+0.004				
2	15223.376	+0.006				
			$I\,^1\Pi_g\text{-}B\,^1\Sigma_u^+$ (0,5) band			
1	15807.998	+0.028	15598.592	+0.042		
2	15934.475	+0.045	15611.056	+0.056	15598.680	+0.070
			$J\,^1\Delta_g\text{-}B\,^1\Sigma_u^+$ (0,5) band			
1	16062.479	−0.011				
2			15989.388	+0.048		

determined with an accuracy of 0.003 cm^{-1}. The error budget is listed in Table I.

In Table III also a comparison is made with the values obtained previously by Tsukiyama *et al.* [10]; in their experiment the bandwidth of the probe laser used was 0.08 cm^{-1}, which is an order of magnitude broader than the linewidth in the present experiment. Moreover, in Ref. [10] the absolute calibration was performed against the less accurate Doppler-broadened I_2 standard. The data sets agree nevertheless with an average difference of 0.03 cm^{-1} albeit that the previous data are systematically lower in energy. In Ref. [10] no uncertainties are specified and the origin of this discrepancy remains unclear.

Results of the calibration of level energies of $B\,^1\Sigma_u^+(v=5)$ are combined with those of the double-resonance spectra to yield level energies of some rotational levels in $EF(v=19)$, $GK(v=0)$, $I(v=0)$, and $J(v=0)$ with an absolute accuracy of 0.006 cm^{-1} (the uncertainties due to chirp effects are added, whereas the root mean square is taken of the remaining effects). The levels denoted as $GK(v=0)$ in fact refer to wave functions confined to the outer well of the third adiabatic state of $^1\Sigma_g^+$ symmetry, which is somewhat lower in energy than the inner well and is referred to as $K(v=0)$ by Yu and Dressler [16]. Results on level energies are listed in Table IV for $^1\Sigma_g^+$ levels and in Table V for $^1\Pi_g$ and $^1\Delta_g$ levels. In Table IV the present values for the $^1\Sigma_g^+$ levels are compared with the most accurate values reported in literature, i.e., Tsukiyama *et al.* [10] for $EF(v=19,J=1$–$4)$ and $GK(v=0)$, and Yu and Dressler [16] for $EF(v=19,J=5)$.

For the $^1\Pi_g$ and $^1\Delta_g$ levels the final values can be compared with the accurate work of Jungen *et al.* [9]. In this comparison the present data are systematically 0.024 cm^{-1} lower in energy than the ones of Ref. [9]. To explain this discrepancy we note the following. Jungen *et al.* state an accuracy of 0.005 cm^{-1} for the frequencies of the inter-

Rydberg transitions observed in the infrared range in their work; but a number of steps in cascading transitions had to be included to connect the $I\,^1\Pi_g$ and $J\,^1\Delta_g$ level energies to the $X\,^1\Sigma_g^+$ ground state in H_2. The values depend on a determination of $EF(v=0)$ levels, presented by Eyler *et al.* [5] with an accuracy of 0.01 cm^{-1}. Since the determination of the lowest $EF(v=0)$ quantum state in 1987 [5] a number of studies have been performed, yielding improved accuracy of its term value. The value of Ref. [8] is 0.017 cm^{-1} lower than the initial 1987 value and for this reason we have lowered the term energies of Ref. [9] by this amount in Table V. With this procedure an average offset of 0.008 cm^{-1} is left between the present data set and the values of Ref. [9]. In view of the estimated uncertainty of 0.006 cm^{-1} we regard this amount as reasonable.

Similar to many of the most recent determinations of the ionization potential in H_2 we connect our findings to the

TABLE IV. Level energies determined for $^1\Sigma_g^+$ states and a comparison with the values listed in the references as indicated in footnotes. Values in cm^{-1}.

J	Experimental	Δ
	$EF\,^1\Sigma_g^+(v=19)$	
1	112126.140 (6)	+0.010 [a, b]
2	112167.798 (6)	+0.008 [a]
3	112230.864 (6)	−0.006 [a]
4	112315.877 (6)	−0.013 [a]
5	112421.402 (6)	−0.088 [c]
	$GK\,^1\Sigma_g^+(v=0)$	
2	111693.724 (6)	−0.006 [a]
3	111759.938 (6)	−0.062 [a]

[a]Comparison with Ref. [10].
[b]Level denoted $V(v=1,J=1)$ in Ref. [16].
[c]Comparison with Ref. [16].

TABLE V. Level energies determined for the $I\,^1\Pi_g$ and $J\,^1\Delta_g$ states and deviations from the values from Ref. [9], which were corrected by -0.017 cm^{-1} following Ref. [8]. Values in cm^{-1}.

J	Experimental	Δ	Experimental	Δ
	(e)		(f)	
	$I\,^1\Pi_g(v=0)$			
1	112135.242 (6)	-0.001	112072.862 (6)	-0.007
2	112282.268 (6)	-0.018	112147.618 (6)	-0.005
3	112471.037 (6)	-0.004		
	$J\,^1\Delta_g(v=0)$			
2	112536.749 (6)	-0.006	112525.950 (6)	-0.012

ionization limit using the results of the FTIR data. Then a value of 124 417.476 cm^{-1} results with an uncertainty of 0.012 cm^{-1}. When compared with the combined results of Refs. [8] and [9] the value is lower by the same 0.008 cm^{-1} as discussed above. In fact, there exists an even more accurate calibration of the intermediate EF levels, performed by the Eyler group, which was published in Ref. [17]. That value would give an IP of 124 417.488 cm^{-1}, which is stated as a private communication with Jungen in Ref. [18]. Although in Ref. [18] an uncertainty of 0.017 cm^{-1} was stated, the actual uncertainty fully relies on the FTIR work and should be lowered to 0.010 cm^{-1}.

In Table VI a list is given of determinations of IP values for H_2 over the years starting with the value of Herzberg in 1969 [1]. The presently determined value for the IP is an independent measurement insofar as laser excitation is concerned. Calibration of $B\,^1\Sigma_u^+$-$X\,^1\Sigma_g^+(5,0)$ Lyman bands is combined with double-resonance calibration of lines in the $I\,^1\Pi_g$-$B\,^1\Sigma_u^+(0,5)$ and $J\,^1\Delta_g$-$B\,^1\Sigma_u^+(0,5)$ bands, and subsequently combined with the FTIR data of Ref. [9] on which all recent values rely. Also the present value is in reasonable agreement with the value obtained in *ab initio* calculations, by Wolniewicz [19] and later by Kołos [20] and again by Wolniewicz [18]; in the latter two studies subtle nonadiabatic

TABLE VI. Values for the ionization potential of H_2 as determined in various studies or combinations thereof (see text). Values in cm^{-1}.

Value	Uncertainty	Ref.	Year
124418.4	0.4	[1]	1969
124417.2	0.4	[2]	1972
124417.42	0.15	[3]	1986
124417.61	0.07	[4]	1987
124417.524	0.015	[6]	1989
124417.507	0.018	[7] [a]	1992
124417.484	0.011	[8] [a]	1993
124417.488	0.010	[17] [a]	1994
124417.476	0.012	Present [a]	2002
	ab initio		
124417.482		[19]	1993
124417.496		[20]	1994
124417.491		[18]	1995

[a]Including the FTIR data of Ref. [9].

effects were included of only 0.01 cm^{-1} magnitude.

In conclusion, the excitation energies of 14 rovibronic levels of g symmetry have been determined with respect to the $X\,^1\Sigma_g^+(v=0,J=0)$ ground state in H_2 with an unprecedented accuracy of 0.006 cm^{-1}. These results establish a partially independent determination of the ionization potential of H_2 at 124 417.476 (12) cm^{-1}, in agreement with previous determination and with *ab initio* calculations. This value is mainly limited by chirp effects in the laser system. Methods of decreasing chirp as followed in Ref. [14] might be applied in future studies to obtain a more accurate value of the IP.

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