



# Bound energy levels at the $n = 2$ dissociation threshold in HD

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## Abstract

Level energies of g symmetry states lying just below the  $n = 2$  dissociation threshold have been determined in a XUV+IR multi-step laser excitation experiment in HD, with an absolute accuracy of the excitation energy of  $0.015 \text{ cm}^{-1}$ . Intermediate  $B^1\Sigma_u^+$  energy levels have been calibrated by measuring transition frequencies in the  $B^1\Sigma_u^+ - X^1\Sigma_g^+(16, 0)$  Lyman band with an accuracy of  $0.007 \text{ cm}^{-1}$ . It is shown that  $v = 3$  is the highest bound vibrational level in the shallow  $I^1\Pi_g$  outer well potential in HD, and that only two rotational levels exist.

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## 1. Introduction

The HD molecule at its  $n = 2$  dissociation threshold becomes a markedly different system from its homonuclear analogues  $H_2$  and  $D_2$  [1]. The dissociation limit is split into two different limits corresponding to  $H(n = 1) + D^*(n = 2)$  and  $H^*(n = 2) + D(n = 1)$ , where the former is higher in energy by  $22 \text{ cm}^{-1}$ . At large internuclear separations the electronic excitation (2s or 2p) becomes localized on one of the two nuclei and the g/u-inversion symmetry is broken, to an extent of 50/50% mixing when converging to the limit. Because of the symmetry-breaking the so-called resonant-dipole interaction ceases to exist in HD at large internuclear separation. As a consequence potentials asymptotically converging as  $1/R^3$

cannot exist in HD, while they do exist in the homonuclear species. The  $II^1\Pi_g$  double-well state in hydrogen has an outer well, which is separated by a barrier of  $1850 \text{ cm}^{-1}$  from the inner well region. The long-range part of the  $II^1\Pi_g$  potential asymptotically converges towards the  $n = 2$  limit as  $1/R^3$  in  $H_2$  and as  $1/R^6$  in HD [1].

Experimentally sequences of vibrational levels are found in the shallow  $I^1\Pi_g$  outer well ( $200 \text{ cm}^{-1}$  well depth) that accurately follow predictions from a long-range LeRoy–Bernstein extrapolation [2], even including the lowest  $v = 0$  level in the well. For  $H_2$  the highest level observed is  $v = 2$ , while some resonances were observed that were tentatively assigned as  $v = 3$ . The semi-classical model predicts a non-integer vibrational level  $v_D = 6.99$  at the limit, meaning that levels up to  $v = 6$ , and possibly  $v = 7$  should exist. For  $D_2$  the observations were up to  $v = 5$  while predictions go as high as 10 [5]. For the description of the  $I^1\Pi_g$  outer well states the LeRoy–Bernstein extrapolation method

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was found to work well and independently of the exact shape of calculated potentials of the  $II'^1\Pi_g$  state at shorter internuclear separations [3,4].

In the HD isotopomer levels up to  $v = 2$  have been observed previously [6]. In a model where the  $g/u$  symmetry-breaking effect is included in terms of an effective potential describing the transition from  $1/R^3$  to  $1/R^6$  behavior at long range, a prediction was made for level energies of  $I'$ ,  $v = 3$  in HD, which was not observed in the previous study of our group. Here we report observation of the  $I'$ ,  $v = 3$  level using multi-step laser excitation with narrow-band pulsed lasers in conjunction with improved calibration procedures. In this way the excitation energies with respect to  $X^1\Sigma_g^+$ ,  $v = 0$ ,  $J = 0$  could be determined to within  $0.015\text{ cm}^{-1}$ . As will be discussed the  $I'$ ,  $v = 3$  level is the highest bound vibrational level in the  $I'$  outer well in HD.

In our investigations we approach the  $n = 2$  limit through an excitation scheme favoring detection of  $g$  symmetry molecular states, even when in HD the inversion symmetry holds only approximately. There is a long tradition of studies approaching the  $n = 2$  threshold for  $u$ -symmetry states. After the initial study of Herzberg [7] the groups of Stoicheff [8] and Eyler [9] used laser-based sources for an accurate determination of the  $n = 2$  dissociation limit in HD. The Eyler group also investigated the energetic region below and above the  $n = 2$  limit, including broad resonances overlapping with the upper  $H(n = 1) + D^*(n = 2)$  limit in HD [10].

## 2. Experimental setup and results

The experiments for the determination of accurate excitation energies were performed in two steps. First, level energies of  $B^1\Sigma_u^+$ ,  $v = 16$ ,  $J$  rotational levels of HD were determined in a  $1\text{ XUV} + 1\text{ UV}$  two-photon ionization experiment using a narrow-band XUV-laser source with a bandwidth of 300 MHz. The experimental setup as well as its application in molecular spectroscopy have been described previously [11]. The specific methods used here for measurements on the Lyman bands will be described in a separate publi-

cation, where also the error budget for the  $1 + 1'$  experiment and the attained absolute accuracy, estimated at  $0.007\text{ cm}^{-1}$ , will be documented [12]. The results on transition frequencies for the five lowest- $J$  R and P lines in the  $B-X(16, 0)$  Lyman band of HD are presented in Table 1.

Subsequently a second experiment was performed, similar to the previous experiments probing the  $I'$  states in  $H_2$  [5] and HD [6], but with a resolution in the  $I'-B$  transition improved by an order of magnitude. The XUV source was based on a commercial dye laser for these studies, yielding a XUV-bandwidth of  $0.25\text{ cm}^{-1}$ . During the multi-step experiment the XUV laser was kept fixed on either one of the resonances listed in Table 1. The width of the first laser does not affect the width of the resonance probing the  $I'$  states, while the extended bandwidth bears the advantage that the XUV-laser does not drift away from resonance during the measurement procedures. The experimental configuration of the setup for the present studies on the  $I'$  state is shown in Fig. 1. The output of a continuous wave Ti:Sapphire laser running at 778 nm, and pumped by the second harmonic of a cw Nd:VO<sub>4</sub> laser (Millenia), is pulse-amplified in a chain of three dye amplifiers pumped by the second harmonic of a Q-switched Nd:YAG laser. The resulting near-infrared pulses are overlapped spatially and temporally in the interaction zone with the XUV beam and the molecular beam. In fact the IR pulse is timed 2 ns earlier than the XUV pulse, because the XUV pulses have a shorter duration (3 ns vs. 5 ns), to avoid stimulated emission back toward the  $B$ ,  $v = 16$  state. The technique based on non-collinear four-wave mixing and the blocking of the UV-radiation from the laser producing the XUV light, as described in [5], is used. A third pulsed

Table 1  
Transition frequencies (in  $\text{cm}^{-1}$ ) of some rotational lines in the  $B^1\Sigma_u^+ - X^1\Sigma_g^+(16, 0)$  Lyman band in HD

$J$	P( $J$ )	R( $J$ )
0		105 781.679(7)
1	105 727.068(7)	105 675.109(7)
2	105 601.037(7)	105 514.605(7)
3	105 404.639(8)	105 283.989(8)

The accuracy, given in brackets, refers to the last digit.

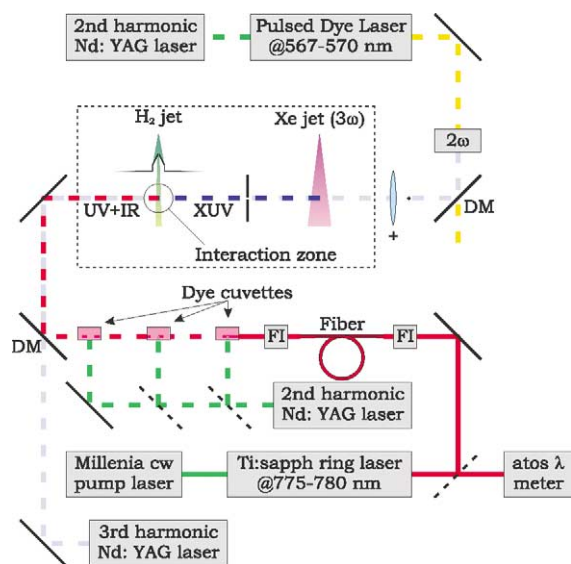


Fig. 1. Schematic layout of the experimental setup. FI: Faraday isolator; DM: dichroic mirror;  $2\omega$ : frequency-doubling crystal.

laser at 355 nm probes the HD molecules excited to the  $I'$  state and generates  $H^+$  ions for signal detection. The excitation scheme is presented in Fig. 2 with the potential energy curves relevant for the present experiment. Wavelengths in the range 775–780 nm were calibrated on-line with the use of a commercial wavelength meter (ATOS-LM007), yielding an absolute accuracy of  $0.003 \text{ cm}^{-1}$ .

An example of a multiple-resonance line, probed while scanning the near-IR laser over the  $I'^1\Pi_g - B^1\Sigma_u^+(3, 16)$  R(1) line is shown in Fig. 3. The three-laser excitation scheme gives rise to rather large signal fluctuations as well as a background from parasitic excitations in the molecule. The trace in the figure shows a spectrum with a typically low signal-to-noise ratio, and a fit of a Gaussian curve through the resonance. Transition frequencies were determined by averaging over several traces. During the experiments the intensity of the second laser was found to affect the width and position of the central resonance frequency of the  $I'$ – $B$  lines. From systematic studies a zero-field extrapolation could be made for the resonances and the overall uncertainty, including all systematic (AC-Stark, laser chirp, Doppler shift, calibration) and statistical effects, is estimated at

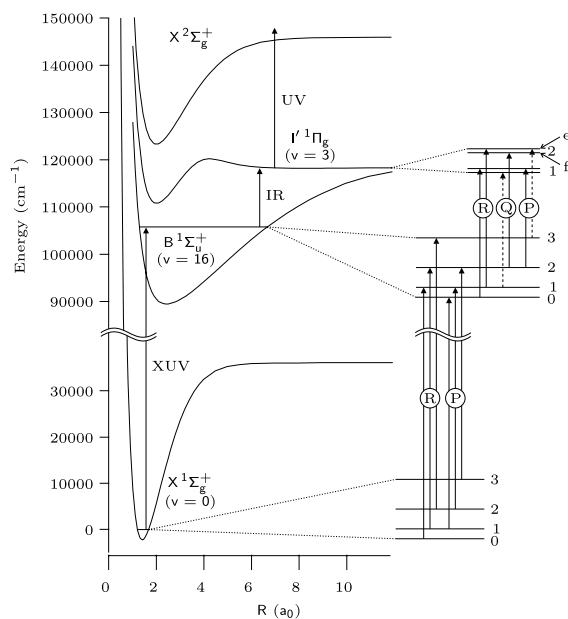


Fig. 2. Level scheme of HD with the relevant potential energy curves. At the right hand side the various branches in the Lyman as well as the  $I'$ – $B$  transitions are indicated.

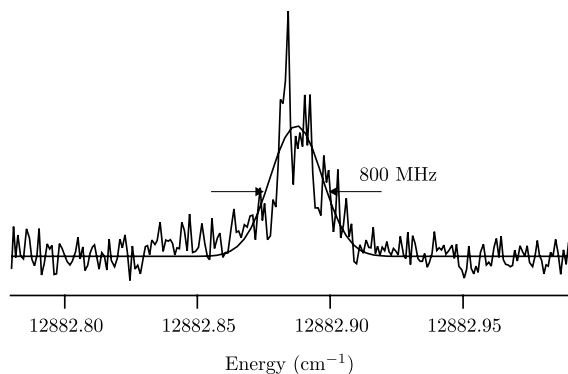


Fig. 3. Spectral recording of the  $I'^1\Pi_g - B^1\Sigma_u^+(3, 16)$  R(1) line in HD.

approximately  $0.010 \text{ cm}^{-1}$ . The resulting transition frequencies are listed in Table 2.

In a preparatory stage of the experiment test measurements on the  $I'$ – $B$  transition were performed in  $H_2$  using the  $B^1\Sigma_u^+$ ,  $v = 14$ ,  $J = 0$  state at an excitation energy of  $105\,657.88(3) \text{ cm}^{-1}$  [14] as an intermediate. The transition frequencies of these measurements are more accurate than

Table 2

Transition frequencies (in  $\text{cm}^{-1}$ ) of some rotational lines in the  $I'^1\Pi_g\text{--}B^1\Sigma_u^+(v', 16)$  bands in HD

$J$	$P(J)$	$Q(J)$	$R(J)$
		(2,16)	
2			12 838.865(10)
		(3,16)	
0			12 899.341(11)
1			12 882.872(15)
2	12 847.345(11)	12 848.182(11)	

The accuracy, given in brackets, refers to the last digit.

Table 3

Accurate frequencies of transitions originating in the  $B^1\Sigma_u^+$ ,  $v = 14$ ,  $J = 0$  level in  $\text{H}_2$

Assignment	Frequency	Level energy	$\Delta$
$I'$ , $v = 2$ , $J = 1$ (e)	12 703.381(7)	118 361.26(3)	0.02
$J = 1$	12 715.348(7)	118 373.23(3)	-0.05
$J = 1$	12 718.797(11)	118 376.68(3)	

The assignment in the left column is that of the two-photon excited state for which level energies are calculated.  $\Delta$  represents the difference with previous observation at lower resolution and accuracy. All values in  $\text{cm}^{-1}$ .

previous data and are listed in Table 3 without further discussion. Even a new hitherto unobserved level close to dissociation threshold is found for which the assignment is not clear, except for the fact that it is a  $J = 1$  level.

### 3. Discussion and conclusion

In the 1 XUV+1 UV two photoionization study of the B–X(16,0) Lyman band of HD

transition frequencies were determined an order of magnitude more accurate than previous results by Hinnen et al. [13] and represent the most accurate measurements performed on the HD Lyman bands. The data may be useful for future comparison with detailed non-adiabatic calculations of energy levels in HD.

The data on the  $I'$ –B system of HD are converted into excitation energies for the  $I'^1\Pi_g$ ,  $v = 3$  state; results are listed in Table 4. Combination differences of multiply measured levels give an extra check on the assignment and result in a somewhat smaller uncertainty; e.g., the  $I'$ ,  $v = 3$ ,  $J = 1$ , e level was measured via  $J = 0$  and  $J = 2$  in the intermediate state. The  $I'$ ,  $v = 2$ ,  $J = 3$ , e level energy was determined previously by de Lange et al. [6] yielding the same value, albeit with a larger uncertainty. The  $I'$ ,  $v = 3$  levels are measured for the first time and they can be compared with predictions made. In [6] the level energies for the  $I'$  outer well of HD were predicted from a LeRoy–Bernstein model invoking an  $R^{-6}$  long-range potential and a lower  $\text{H}^* + \text{D}$  dissociation limit at  $118\,664.80\text{ cm}^{-1}$ , which is the weighted average of the values determined by Balakrishnan et al. [8] and by Eyler and Melikechi [9]. A more sophisticated model for the description of the  $I'$  state in HD was developed, in which the g/u-symmetry breaking interaction between the  $I'^1\Pi_g$  and  $C^1\Pi_u$  states was included at long range, where the two long-range potentials were deduced from the  $\Pi$ -type long-range interaction between H atoms in 1s and 2p states as calculated by Stephens and Dalgarno [16]. De Lange et al. [6] scaled the long-range potentials to hold also for the HD

Table 4

$E_{\text{obs}}$  are energies of  $I'^1\Pi_g$  outer well levels in HD relative to the  $X^1\Sigma_g^+$ ,  $v = 0$ ,  $J = 0$  ground state, which are compared with predicted values  $E_{\text{calc}}$  from de Lange et al. [6] resulting in deviations  $\Delta_{\text{o-c}}$

$J$	$E_{\text{calc}}$	e states		f states	
		$E_{\text{obs}}$	$\Delta_{\text{o-c}}$	$E_{\text{obs}}$	$\Delta_{\text{o-c}}$
$v = 2$					
3	118 655.31	118 655.150(11)	-0.160		
$v = 3$					
1	118 663.42	118 663.650(9)	0.230		
2	118 664.29	118 664.544(16)	0.254	118 664.467(12)	0.177

All values in  $\text{cm}^{-1}$ .

system. At short range ( $R = 12$  a.u.) the ab initio potential of Dressler and Wolniewicz [4] was tied to the long-range part.

With the aid of the thus constructed potential, displaying the transition from a  $R^{-3}$  to  $R^{-6}$  behavior when approaching the dissociation limit, a calculation based on the Schrödinger equation was performed, predicting the energies for  $I'$ ,  $v = 3$ ,  $J = 1$  and  $J = 2$  states; only these two rotational levels exist for  $v = 3$ . The non-adiabatic effect of  $\Lambda$ -doubling was not accounted for. The results of these calculations are listed in Table 4 with the presently obtained values. While for  $I'$ ,  $v = 0$ – $2$  the measured binding energies differed  $\approx 1$ – $2\%$  from the calculated energies [6], the binding energies of  $I'$ ,  $v = 3$  levels differ by  $\approx 20\%$ . Since the experimental levels are closer to the dissociation limit than the predictions from the potential curves, the present data provide further proof that the  $I'$ ,  $v = 3$ ,  $J = 2$  is the highest bound level in the  $I'$  outer well. It lies  $0.25 \text{ cm}^{-1}$  below threshold. The  $\Lambda$ -doubling of this  $I'$ ,  $v = 3$ ,  $J = 2$  level ( $0.08 \text{ cm}^{-1}$ ) is of comparable magnitude as in the lower vibrational levels [6] and in the  $I'$  levels of  $\text{H}_2$  and  $\text{D}_2$  [5].

In the work of the Eyler group particularly in  $\text{H}_2$  [15] strongly perturbed structures were found close to the  $n = 2$  dissociation limit. In  $\text{H}_2$  also a non-adiabatic splitting of the dissociation limit occurs as a result of singlet–triplet interaction and the hyperfine structure, but these splittings are small ( $\leq 0.3 \text{ cm}^{-1}$ ). Singlet–triplet and u/g-symmetry mixing were believed to cause the complicated structure in  $\text{H}_2$  but no quantitative theory could be given to assign the lines observed. In HD in fact no extra lines were observed in the present excitation scheme, and the lines that were found could be assigned unambiguously with a model that explicitly takes into account g/u-symmetry breaking. From such a perspective the HD molecule near the  $n = 2$  limit, with the large ( $22 \text{ cm}^{-1}$ ) splitting, is easier to understand than  $\text{H}_2$  or  $\text{D}_2$  molecules. However, the fact that no extra reso-

nances were found in HD, opposite to the case of  $\text{H}_2$  [15], might also be ascribed to the low signal-to-noise ratio in the present experiment.

It is noted that the strong g/u-symmetry breaking in HD derives from a term in the Hamiltonian that vanishes for homonuclear molecules [1]. The transition to a long-range potential of  $R^{-6}$  asymptotic form in HD presents another simplifying aspect: it causes the number of bound levels to decrease drastically.

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