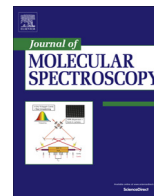




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# Structure and dynamics of $\text{H}_2^+$ near the dissociation threshold: A combined experimental and computational investigation

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## ABSTRACT

The pulsed-field-ionization zero-kinetic-energy photoelectron spectrum of  $\text{H}_2$  has been recorded in the vicinity of the dissociative-ionization threshold following three-photon excitation via selected rotational levels of the  $B\ ^1\Sigma_u^+(v=19)$  and  $\bar{H}\ ^1\Sigma_g^+(v=11)$  intermediate states. The spectra consist of transitions to bound levels of the  $X^+ \ ^2\Sigma_u^+$  state of  $\text{H}_2^+$  with  $v^+$  in the range 14–19 and  $N^+$  in the range 0–9, of the  $A^+ \ ^2\Sigma_u^+$  state with  $v^+ = 0$  and  $N^+ = 0–2$ , and of shape resonances corresponding to the  $X^+(v^+ = 17, N^+ = 7)$  and  $X^+(v^+ = 18, N^+ = 4)$  quasibound levels. Calculations of the level structure of  $\text{H}_2^+$  have been carried out and the influence of adiabatic, nonadiabatic, relativistic and radiative corrections on the positions of these levels, and in the case of the shape resonances also on their widths, has been investigated. Different methods of calculating the widths and profiles of the shape resonances have been tested for comparison with the experimental observations. Slow oscillations of the dissociative-ionization yield have been observed and reflect, in first approximation, the Franck-Condon factors of the  $X^+, A^+ \leftarrow \bar{H}$  bound - free transitions.

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## 1. Introduction

$\text{H}_2^+$  is the simplest molecule and plays in molecular physics the role that the hydrogen atom plays in atomic physics. The level structure of  $\text{H}_2^+$  can be calculated with exquisite precision and accuracy by ab initio quantum-chemical methods, either by solving the eigenvalue problem of the two-proton-one-electron system directly using variational methods [1–4] and artificial-channel-scattering methods [5], or by first making an “exact” electronic-structure calculation for clamped nuclei in the realm of the Born-Oppenheimer approximation, and then calculating adiabatic (i.e., electronically diagonal), nonadiabatic (i.e., electronically off-diagonal) and relativistic corrections by perturbation-theoretical methods [6–12]. Radiative corrections are typically evaluated using the second route [13–15]. From such calculations, an extraordinarily detailed knowledge of the spectrum of  $\text{H}_2^+$  has resulted. The spectral positions of the low-lying rovibrational levels of the  $X^+ \ ^2\Sigma_g^+$  electronic ground state have been calculated at a precision of about 2 kHz [3,4,16,17]. The positions of all 423 bound levels of the  $X^+$  state and the three bound levels of the  $A^+$

$\ ^2\Sigma_u^+$  state ( $v^+ = 0, N^+ = 0, 1$  and 2) are tabulated by Moss [5]. A fourth bound level of the  $A^+$  state, with a calculated nonrelativistic binding energy of only  $E/h = 7.139253$  MHz, was reported later [18,19].

Several energy intervals between fine-structure [20], hyperfine-structure [21,22], rotational [23–25], rovibrational [26] and rovibronic energy levels [27] of  $\text{H}_2^+$  have also been measured (see also Ref. [28]).

Quasibound levels of  $\text{H}_2^+$  above the dissociation limit, often called shape resonances, have also been calculated. 58 such resonances are known to exist from the work of Moss [5] who, however, did not report any data on 19 of them, because they are located too close to the maxima of the centrifugal potential barriers for the calculations to reach the desired accuracy. The ten lowest of these resonances have been calculated by Davis and Thorson within the Born-Oppenheimer approximation [29]. Moss has reported adiabatic corrections for these resonances [30] but did not evaluate nonadiabatic corrections nor did he report resonance widths. Recently, we have observed two such shape resonances by PFI-ZEKE photoelectron spectroscopy, corresponding to the  $X^+(v^+ = 17, N^+ = 7)$  and  $(v^+ = 18, N^+ = 4)$  quasibound levels [31], in spectra in which several of the bound levels of the  $X^+$  and  $A^+$  states located near the dissociation limit of  $\text{H}_2^+$  were also observed. We also calculated the positions and widths of these resonances

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and found overall good agreement, except for the width of the  $X^+$  (17.7) resonance, which the calculations predicted to be narrower than found experimentally. The purpose of the present article is to present new experimental and computational results obtained on a broader range of highly excited levels of  $H_2^+$ .

Shape resonances arising from the nuclear motion in molecules have been discovered before, and correctly interpreted very soon after, the introduction of the quantum theory [32,33], in relation to what Herzberg classified in 1931 as special case III of predissociation [34], i.e., rotational predissociation observed in the spectra of diatomic molecules such as AlH. Since then, rotational predissociation and the corresponding shape resonances have been observed in a multitude of molecular systems. Their quantitative description requires high-quality potential-energy functions and large progress has been made in the development of reliable computational procedures to determine their positions and widths. The shape resonances of  $H_2$  represent an early example for which computations could be performed with spectroscopic accuracy [35]. Today, computer codes such as the program Level [36] are used by experimentalists to calculate resonance widths and positions.

In the case of  $H_2^+$  discussed in this article, achieving spectroscopic accuracy in the computation of shape resonances poses several problems. (i) Adiabatic, nonadiabatic, relativistic and radiative corrections are all large enough that they need to be considered in the theoretical treatment. (ii) To retain the concept of a potential curve and nevertheless include nonadiabatic corrections, which, per definition, mix different electronic states, requires specific measures, such as the introduction of  $R$ -dependent reduced masses ( $R$  is the internuclear distance) for the vibrational and rotational motions of the nuclei (see, e.g., [37–40]). (iii) Protons are light and tunneling resonances can be broad so that Lorentzian line shapes may not always be appropriate to describe them. The approach we followed to calculate the shape resonances was largely inspired by the work of Moss [5], Wolniewicz and coworkers [10,12], and Jaquet and Kutzelnigg [40] and consists of (i) evaluating all corrections to the Born-Oppenheimer energy while retaining a single-potential description, and (ii) going beyond semi-classical WKB methods to compute resonance parameters. Because the positions and widths of the resonances might be sensitive to even small variations of the correction terms, we analyze the effects of the different correction terms separately and use the comparison with the experimental data and earlier calculations to validate the computational procedure. The validation then enables us to predict the positions and widths of the shape resonances of  $H_2^+$  not predicted by Moss in his otherwise complete investigation [5,30].

## 2. Experiment

The bound and quasibound rovibrational levels of  $H_2^+$  located near the  $H^+ + H(1s)$  dissociation limit were studied by pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy. Because these states have a large average internuclear separation, they are not directly accessible from the  $X^1\Sigma_g^+(v=0)$  ground state of  $H_2$ . A resonant three-photon excitation sequence via the  $B^1\Sigma_u^+(v=19, N_B)$  and  $\bar{H}^1\Sigma_g^+(v=11, N)$  intermediate states were used to gradually enlarge the internuclear separation, as explained in Ref. [31]. The same sequence also enabled us to select para or ortho  $H_2$  by carrying out the excitation through rotational levels of the  $\bar{H}$  state with even or odd  $N$  value, respectively.

The vacuum-ultraviolet (VUV) radiation with wave number  $\tilde{\nu}_{VUV} = 2\tilde{\nu}_{UV} + \tilde{\nu}_2$  around  $109750\text{ cm}^{-1}$  used to access the  $B^1\Sigma_u^+(v=19)$  state from the  $X^1\Sigma_g^+(v=0)$  ground state was generated by resonance-enhanced sum-frequency mixing in Kr using two pulsed Nd:YAG-pumped dye lasers (repetition rate 25 Hz,

pulse duration 5 ns). The wave number  $\tilde{\nu}_1$  of the first dye laser was tripled using two successive  $\beta$ -barium-borate crystals and the tripled output ( $\tilde{\nu}_{UV}$ ) was kept fixed at the position of the  $(4p)^5 5p[3/2](J=0) \leftarrow (4p)^6$  two-photon resonance of Kr ( $2\tilde{\nu}_{UV} = 94092.96\text{ cm}^{-1}$ ). The wave number of the second dye laser was then adjusted so as to access the desired rovibrational level of the  $B$  state. A third Nd:YAG-pumped dye laser was used to induce the transition from the selected level of the  $B$  state to the  $\bar{H}(v=11)$  state, from which the region near the  $H_2^+$  dissociation limit was reached with a fourth dye laser, delayed by 10 ns with respect to the other lasers using an optical delay line. This measure helped reducing the intensity of the transitions to Rydberg states of  $H_2$  belonging to series converging on the low-lying vibrational levels of  $H_2^+$  induced by the fourth laser directly from the  $B$  state.

All laser beams intersected a supersonic beam of  $H_2$  at right angles on the axis of a cylindrically symmetric photoexcitation and electron-extraction region consisting of a set of five parallel and equidistant extraction plates designed for the application of homogeneous electric fields [41]. Stray magnetic fields were eliminated by a double layer of magnetic shielding and stray electric fields were maintained at a level below 10 mV/cm. The pulsed solenoid valve used to form the supersonic beam was operated at a stagnation pressure of 2 bar of pure  $H_2$ . The beam was collimated with a skimmer of 1 mm orifice diameter which separated the source chamber from the photoexcitation chamber. The background pressure in the photoexcitation region did not exceed  $10^{-6}$  mbar during operation of the pulsed valve.

The PFI-ZEKE photoelectron spectra of the highest bound levels and the shape resonances of  $H_2^+$  were recorded by monitoring the yield of electrons produced by the delayed pulsed field ionization of high-lying Rydberg states (principal quantum number  $n \gg 100$ ) - either of  $H_2$  for the bound levels of  $H_2^+$  or of H for the shape resonances - as a function of the wave number of the fourth dye laser. This laser had a bandwidth of  $0.03\text{ cm}^{-1}$  and its wave number was calibrated at an accuracy of  $0.02\text{ cm}^{-1}$  with a wavemeter. The pulsed field ionization was achieved with an electric-field pulse sequence consisting of ten pulses of increasing strength [(1) 50 mV/cm, (2) 70 mV/cm, (3) 80 mV/cm, (4) 90 mV/cm, (5) 110 mV/cm, (6) 140 mV/cm, (7) 200 mV/cm, (8) 270 mV/cm, (9) 680 mV/cm, and (10) 1.22 V/cm] to selectively detect Rydberg states of progressively lower principal quantum numbers. The electron signals produced by each of these pulses were recorded separately so that each laser scan led to the recording of ten PFI-ZEKE photoelectron spectra. The spectrum recorded from pulse (1) turned out to be extremely weak, suffered from undesirable contributions from low-energy electrons, and was therefore not used in the analysis. The best resolution (full width at half maximum of  $0.2\text{ cm}^{-1}$ ) was obtained with pulses (2)–(5). The spectrum recorded with pulse (6) had a resolution of  $0.25\text{ cm}^{-1}$ , and those recorded with pulse (7) and (8) a resolution of  $0.35\text{ cm}^{-1}$ . The spectra recorded with pulses (9) and (10) had the best signal-to-noise ratio but the lines in these spectra were too broad to be useful for the determination of line widths and line positions. The relative positions of lines in the photoelectron spectra could be determined at an accuracy of 1 GHz from a statistical analysis of the spectra recorded from the different pulses. The absolute positions of the ionic levels with respect to the selected  $\bar{H}$  intermediate levels were determined with an accuracy of about 2 GHz after correcting for the shifts of the ionization thresholds induced by the pulsed electric fields, as described in Ref. [42].

## 3. Experimental results

Overview PFI-ZEKE photoelectron spectra of para and ortho  $H_2$  in the region of the dissociation limit of  $H_2^+$  (at  $145796.84136$

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