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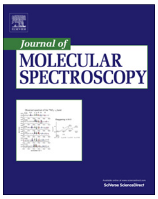

Experimental and theoretical studies of excited states of H_2 observed in the absorption spectrum: II. The $6p\pi$ and $7p\pi$ $^1\Pi_u$ states

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ABSTRACT

A comprehensive study of the absorption transitions leading to the $6p\pi$ and $7p\pi$ Rydberg states of H_2 is presented which includes rovibronic level energies, line intensities and widths up to the 5th dissociation threshold of H_2. The analysis of the experimental data is carried out with the help of multichannel quantum defect theory implemented here purely from first principles. The theory accounts for the strong rovibronic interactions which tie the $6p\pi$ and $7p\pi$ levels to the surrounding *p* Rydberg levels and continua, leading to strong perturbations of the level structure and decay mechanisms, and causing the appearance of numerous 'complex' resonance features.

1. Introduction

This paper continues a series of papers on the absorption spectrum of diatomic hydrogen at room temperature [1–11]. The preceding paper I [12] has been dealing with the $5p\pi D''$ $^1\Pi_u$ state of H_2. Here we discuss the $n = 6$ and $n = 7$ members of the same series of $^1\Pi_u$ states. Our rationale for how to present the wealth of experimental and theoretical results on H_2 absorption has been given in the introduction to the preceding paper I.

Counting from the ground state, the $6p\pi$ and $7p\pi$ states are the ninth and twelvth states of $^1\Pi_u$ symmetry, whereas in absorption they are the fifth and sixth $^1\Pi_u$ states that appear in the spectrum. The reasons for this particular ordering is that the $np\pi$ series of states has a negative quantum defect near equilibrium which places its members above the high-ℓ nf and nh $^1\Pi_u$ series whose first members are $4f$ and $6h$, respectively, and which have near zero quantum defects. These high-ℓ nf and nh states, however, are absent in the absorption spectrum owing to very small dipole transition moments (the transitions are strictly forbidden in the united-atom approximation).

The potential energy curves of the lowest members of the $np\pi$ $^1\Pi_u$ Rydberg series, $n = 2$–4, dissociate adiabatically into $H(1s) + H(n)$, i.e. without a change of the principal quantum number. However, this is not the case for the higher members $n = 5$–7 whose principal quantum number *decreases* by one unit upon dissociation [e.g. $6p\pi \rightarrow H(1s) + H(5f\pi)$ and $7p\pi \rightarrow H(1s) + H(6d\pi)$]. This implies that a configurational change occurs upon dissociation in these states. In terms of quantum defects this means that for $n = 2$–4 the quantum defect function varies only little with the internuclear distance *R*, whereas for $n = 5$–7 a strong variation occurs when *R* increases beyond a certain critical *R* value where the configurational changes set in. These variations are neglected in the present work where we use quantum defect functions that are evaluated from *ab initio* potential energy curves for $n = 2$–4 and subsequently are extrapolated to higher energies. Note incidentally that unlike for $n \leqslant 5$, present-day quantum chemistry is not yet in a position to compute H_2 states with $n = 6$ and 7 with high accuracy. The details of the theoretical approach and the experiment underlying the present study have been described in the preceding paper [12] and in the earlier publications.

2. Results

2.1. Energy levels

2.1.1. Background information

In the 1970s three key papers appeared in which the absorption spectrum of H_2 was studied beyond the Lyman and Werner systems ($n = 2$ upper states). While the first of these [13] was in essence a traditional-style high-resolution spectroscopic study focussing on the energies of observed bound levels with $n \geqslant 3$, the second [14] focussed on dynamical aspects such as the widespread non-adiabatic perturbations and the observation of

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preionization linewidths which were analyzed in terms of an early version of molecular multichannel quantum defect theory. In the third paper [15] the photoionization and absorption spectra were compared and ionization and dissociation yields extracted for the first time for numerous predissociation/preionization Rydberg resonances. In terms of the uncertainties of the frequency determinations, Refs. [13,14] quote the values $1\,\mathrm{cm}^{-1}$ and $0.3\,\mathrm{cm}^{-1}$ respectively, whereas the accuracy achieved in Ref. [15] was somewhat poorer ($5\,\mathrm{cm}^{-1}$).

The number of previously assigned levels belonging to the $6p\pi$ $(7p\pi)\,^1\Pi_u^+$ components is 14 (8), respectively, of which 12 (8) were determined with an accuracy better than $1\,\mathrm{cm}^{-1}$. 23 (12) level positions of $^1\Pi_u^-$ have previously been known for these two states, 20 (12) of them accurate to better than $1\,\mathrm{cm}^{-1}$. In one of our previous papers [1] five additional $N = 1$ levels could be identified albeit with limited accuracy ($9\,\mathrm{cm}^{-1}$).

2.1.2. Comparison of previous data with present calculations

The level positions predicted by our present MQDT calculations are compared in Fig. 1 with the experimental values from the literature. The figure shows that 56 previously published level positions agree with our calculations to within $2\,\mathrm{cm}^{-1}$. The discrepancies for the 8 remaining levels are seen to be far larger, so large that they cannot be due to the uncertainties of the experiments or of the theory, but they must correspond to misassignments. We discuss the different cases in turn.

We find that five transitions leading to $6p\pi$, $v = 1$ disagree with the present calculations, namely $R(2)$, $R(3)$ and $Q(2)$ [13], as well as $R(1)$ and $Q(1)$ [14]. The observed transition energies assigned previously as $R(2)$, $R(3)$ and $Q(2)$ turn out to correspond closely to the predicted positions of the transitions $R(3)$ $5p\sigma$, $v = 2$, $P(2)$ $15p2$, $v = 0$ and $R(2)$ $4p\pi$, $v = 4$, respectively. We calculate the $R(1)$ transition at $123713.7\,\mathrm{cm}^{-1}$ in agreement with the assignment made in Ref. [13]. The same transition was also observed in Ref. [14] but erroneously assigned there as $Q(1)$ $13p\pi$, $v = 0$. Disagreements occur also for the group of transitions leading to $6p\pi$, $v = 2$ rovibronic levels. The misassignment of $R(1)$ made in Ref. [13] has been corrected in Ref. [14]. We find further that the assignment of the $Q(4)$ transition must be incorrect as it corresponds to the calculated values for the blended $R(3)$ $6p\pi$, $v = 2$ and $R(2)$ $9p\pi$, $v = 1$ transitions.

The $Q(2)$ $7p\pi$, $v = 1$ transition had previously [13] been assumed to be blended with $R(2)$ $4p\pi$, $v = 4$. We calculate this transition at $124226.9\,\mathrm{cm}^{-1}$, at a position assigned in Ref. [13] to $R(2)$ $4p\sigma$, $v = 4$. The $Q(1)$ $7p\pi$, $v = 1$ transition was assigned in Ref. [14] to a component of a group including also $R(1)$ $3p\pi$, $v = 6$. Based on our calculations we interchange these assignments. Similarly, the $R(0)$ $7p\pi$, $v = 3$ and $R(0)$ $3p\pi$, $v = 9$ transitions have to be interchanged. This reassignment for $N = 1$ is confirmed by observation of the corresponding $P(2)$ line with an intensity in agreement with the calculation. Further, the $R(1)$ $7p\pi$, $v = 3$ transition was previously [14] assumed to be blended with $R(1)$ $3p\pi$, $v = 9$. Our calculations predict that this transition should be very weak and superimposed on $R(0)$ $3p\pi$, $v = 9$.

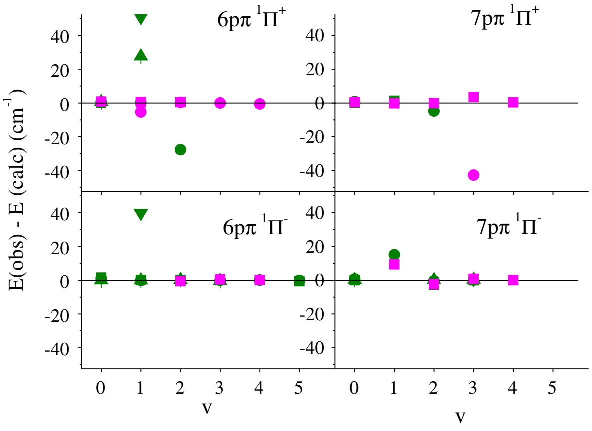

Fig. 1. Residuals $E(\mathrm{obs, previous}) - E(\mathrm{calc, present})$, in cm^{-1}, for the vibration–rotation levels of the $6p\pi$ and $7p\pi$ states of H_2. Symbol colors: green Ref. [13], magenta Ref. [14]. Symbol shapes: squares $N = 1$, dots $N = 2$, up-triangles $N = 3$, down-triangles $N = 4$.

2.1.3. Present measurements

We have measured more than 100 spectral lines belonging to the $n = 6$ and $n = 7$ $np\pi \leftarrow X$, $v'' = 0$ absorption systems. These yield information on 95 distinct upper state rovibronic levels. Out of these 49 are new assignments and 8 have been reassigned, whereas 11 levels have been known previously but are now more accurately determined. These upper state levels correspond to rotational quantum numbers $N = 1$–4, which are all rotational levels that can be populated significantly in absorption by a room temperature sample.

The $6p\pi\,^1\Pi_u^-, v, N = 1^d$ vibrational series could be followed up to $v = 12$ just below the $\mathrm{H}(1s) + \mathrm{H}(n = 5)$ dissociation limit, whereas the $6p\pi\,^1\Pi_u^+, v, N = 1^c$ and $N = 2^c$ could be followed up to $v = 9$, i.e., $3000\,\mathrm{cm}^{-1}$ below the limit. The R transitions leading to the Π^+ levels (c Kronig symmetry) appear with increasingly broad profiles as the energy increases, and therefore are more and more difficult to identify. The $7p\pi\,^1\Pi_u^-, v, N = 1^d$ vibrational series could be followed up to $v = 11$, i.e., to the limit of our recorded spectrum, whereas their $^1\Pi_u^+$ counterparts could be identified up to $v = 7$.

2.1.4. Comparison of the new data with theory

The present knowledge concerning the $n = 6$ and $n = 7$ $np\pi$ $^1\Pi_u$ states of H_2 is collected in Tables 1–4. Fig. 2 displays histograms representing the distributions of the residuals $E(obs)$–$E(calc)$ between the observed and calculated energy levels. Two histograms are actually superimposed in Fig. 2: one, in red, contains all observed levels, whereas the second, in blue, contains only the levels up to $v = 7$. The latter subset includes the 84 rovibronic levels out of 95 whose energies lie lower than the $\mathrm{H}(n = 3) + \mathrm{H}(1s)$ dissociation limit (or just up to $2000\,\mathrm{cm}^{-1}$ above it). The distribution of the subset corresponds approximately to a Gaussian centered at $-0.1\,\mathrm{cm}^{-1}$ with a width of $1.3\,\mathrm{cm}^{-1}$, consistent with the uncertainty of our measurements. The discrepancies are seen to increase up to $\approx 10\,\mathrm{cm}^{-1}$ for higher energies (cf. the red histogram). It is quite probable that they are related to the avoided crossing occurring near $\mathrm{H}(n = 4) + \mathrm{H}(1s)$, discussed in paper I [12], and the shortcomings of our simplified MQDT approach which begin to show up in this range (see [12]).

2.1.5. 'Complex' resonances

The occurrence of ‘complex’ resonances in the H_2 spectrum is a well-known phenomenon [16]; one case, the resonance associated with the $7p\pi$, $v = 1$, $N = 1^c$ and $5p\pi$, $v = 2$, $N = 1^c$ Π^+ structures, has been discussed in some detail in part I [12]. It so happens that the electronic binding energy of the $7p\pi$ state, viz. $\approx -\mathscr{R}/7^2$, corresponds for small v, N values approximately to the vibrational energy quantum of the molecular ion, with the result that the $7p\pi$, v, N levels appear near the $v^+ - 1$ ion limits, in several instances superimposed on the high-n manifold of levels corresponding to $v - 1$. They thus form ‘complex’ resonances via the strong $\Delta v = 1$ vibronic coupling. This situation is depicted by Fig. 3.

Depending on the details of the level structure, the N value and parity, the ‘complex’ resonances may take different forms, corresponding to different ranges of high-n members in the interacting $v - 1$ Rydberg series. In addition the high-n levels may (or may