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Research paper

Continuity of heavy Rydberg behaviour in the *ungerade* ion-pair states of H_2

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ABSTRACT

Heavy Rydberg behaviour and absolute quantum defects are reported for resonances in the *ungerade* manifold of H_2 above the $(1s, 3l)$ dissociation limit. The continuity of the vibrational progression of the $B''\bar{B}$ state through the crossing with the $3p$ asymptote is demonstrated and a predominantly diabatic picture of the vibrational motion emerges, indicating that the ion-pair resonances possess little $6\,^1\Sigma_u^+$ state character.

1. Introduction

Asaro and Dalgarno [1] were the first to recognise that Rydberg behaviour characterized by a large negative quantum defect would be found in the high vibrational levels of ionically bound states and illustrated their argument with calculations on Li^+F^-. Pan and Mies [2] later expanded this approach and presented a more detailed discussion of the underlying principles. The long vibrational progressions observed in the ion-pair states of I_2, Br_2, Cl_2 IBr and ICl have all been found to exhibit Rydberg behaviour [3,4]. A short Rydberg series has also been observed in the vibrational levels of Cl_2 by Mollet and Merkt [5,6].

Ion-pair vibronic states in H_2 were first observed in a time-domain experiment and named Heavy Rydberg (HR) states by Reinhold and Ubachs [7]. They were also identified in the frequency domain above the $n = 3$ dissociation threshold by Ubachs and coworkers [8,9] in the *gerade* manifold and later in the *ungerade* manifold by McCormack and co-workers [10,11]. Measured energies of vibrational levels below the $(1s, 2l)$ dissociation threshold belonging to the lowest *ungerade* excited state, the $B\,^1\Sigma_u^+$ state, were recently treated with the HR model, and HR behaviour was found to be continuous from $v' = 0$ up to nearly the $(1s, 2l)$ dissociation limit [12]. HR behaviour was also found in a new analysis of the vibrational levels of the higher energy double-well $B''\bar{B}\,^1\Sigma_u^+$ state up to the $(1s, 3l)$ dissociation limit [12].

Here, we extend the HR analysis to lower vibrational levels of the outer well of the $B''\bar{B}\,^1\Sigma_u^+$ state and to *ungerade* resonances [10,11] observed above the $(1s, 3l)$ dissociation limit (see Fig. 1). The measured energies are consistent with the theoretical results of Kirrander and Jungen [13], who used the *ab initio* potentials of Wolniewicz et al. [14,15], to perform nonadiabatic coupling calculations of the ion-pair levels of H_2 above the $(1s, 3l)$ dissociation limit.

We find that a consecutive numbering from the lower vibrational levels of the $B''\bar{B}\,^1\Sigma_u^+$ state can be continued through the avoided crossing of the diabatic ion-pair potential with the $(1s, 3l)$ dissociation asymptote without interruption to include the ion-pair levels observed above it. The observed resonances are therefore best understood as accessing ion-pair vibrational levels belonging to the diabatic ion-pair potential shown in Fig. 1. This is in contrast to associating the observed above-threshold resonances with the outer-well vibrational levels of the $6\,^1\Sigma_u^+$ state. This is also consistent with the findings of Koelemeij et al. [18], who used a Landau-Zener treatment of the avoided crossing to explain that all of the vibrational levels of the outer well of the $6\,^1\Sigma_u^+$ state, perhaps with the exclusion of the $v' = 0$ level, are expected to rapidly predissociate.

2. Heavy Rydberg analysis

Provided the ion-pair vibrational numbering is known, or can be reliably derived, absolute quantum defects can be calculated. Effective principal quantum numbers n^* are first established using the Rydberg formula [3,4],

$$n^* = \sqrt{\frac{Ry_\mu}{E_b(v)}}, \tag{1}$$

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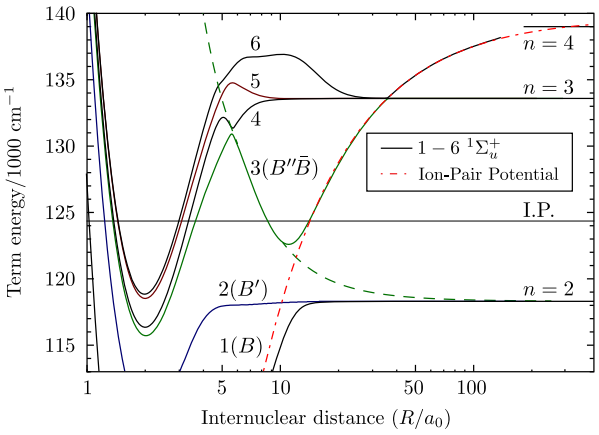

Fig. 1. Ab initio potential energy curves of the six lowest $^1\Sigma_u$ states (Ref. [14]) of H_2 and the ion-pair H^{+-} potential (red dot-dashed curve, Ref. [16]). The dashed green curve shows the diabatic, doubly-excited state that forms the inner wall of the $\bar{B}$ state [17]. Internuclear distance is given in $a_0 \approx 0.529$ Å. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

where Ry_μ is the Rydberg constant scaled for the reduced mass of the H^+H^- system ($Ry_\mu = 1.00802 \times 10^8$ cm^{-1}) and $E_b(v)$ is the positive binding energy of a given vibrational level, v, relative to the ion-pair dissociation limit (139713.84 cm^{-1}). Quantum defects are then given by [9]

$$\delta(E_b) = v + 1 - n^*. \quad (2)$$

The influence of rotation is not addressed here and only $J = 0$ levels are used in our analysis.

We first consider HR behaviour in the $B''\bar{B}^1\Sigma_u^+$ state below the $(1s, 3l)$ threshold and extend the previous quantum defect analysis by Lawley and Donovan [12] to include the lower, below-barrier, outer-well vibrational levels, $v' = 0$–16, predicted by Wolniewicz et al. [15] Note that v' corresponds to outer-well vibrational numbering exclusive of the inner-well vibrational levels. These theoretical predictions agree with experiment, where available [19,20], to within ~ 0.1 cm^{-1}. Fig. 2 includes corresponding quantum defects for the $v' = 0$–16 levels as well as those for the theoretical term energies of the $v' = 43$, 45, 47–49, 54 and 55 vibrational levels

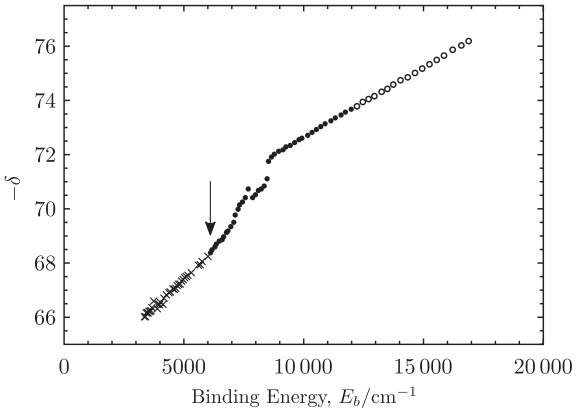

Fig. 2. Plot of quantum defects vs. binding energy for vibrational levels of the $B''\bar{B}^1\Sigma_u^+$ state and the observed resonances above the $(1s, 3l)$ dissociation limit, indicated by the arrow. Open circles indicate the $v' = 0$–16 levels of the outer well of the $B''\bar{B}^1\Sigma_u^+$ state [15] ($E_b = 12,000$–$17,000$ cm^{-1}), closed circles indicate the $v' = 17$–59 levels first reported in Ref. [12], and ×'s indicate the above-threshold ion-pair resonances ($E_b = 3300$–6000 cm^{-1}) as assigned in Table 1.

[15], which were not observed by Chartrand et al. [11]. The quantum defect plot shown in Fig. 2 now includes values for all of the vibrational levels of the outer well of the $B''\bar{B}^1\Sigma_u^+$ state.

The term energies of the resonances observed by Ekey and McCormack [10] above the $(1s, 3l)$ dissociation limit are listed in Table 1 along with ion-pair vibrational assignments, quantum defects calculated from Eq. (2), and term energy differences between the experimental values and predicted theoretical values made by Kirrander and Jungen [13]. Originally, these resonances were identified by n^*, and not all have been observed experimentally [10]. Here we assign those that were observed to vibrational numbers based on a consecutive node counting of calculated vibrational levels of a model diabatic potential constructed from the relevant potential energy curves in Fig. 1. Specifically, the model potential consists of the doubly-excited state at short internuclear spacing to form the inner repulsive wall, the $\bar{B}$ state at mid-range to form the well, and the H^+H^- ion-pair potential at long-range to form the attractive outer wall. The consecutive vibrational counting does not include the $v' = 36$ level, due to its strong inner-well character [12]. The calculated quantum defects of the above-threshold levels using the vibrational assignments made in this way are listed in Table 1 and are plotted in Fig. 2 as ×'s lying in the region $E_b = 3300$–6000 cm^{-1}. They connect smoothly to the quantum defects calculated for the $B''\bar{B}^1\Sigma_u^+$ vibrational levels lying below the threshold, providing direct evidence of the diabatic nature of the crossing of the ion-pair potential with the $(1s, 3l)$ dissociation asymptote.

For comparison we also apply the HR model to vibrational levels of the $6\,^1\Sigma_u^+$ state. Since no observations of the vibrational levels of

Table 1
Measured $J = 0$ term energies, assigned ion-pair vibrational quantum number, and calculated quantum defects (Eq. (2)) for resonances observed above the $(1s, 3l)$ threshold. Δ denotes the difference between observed values and theoretical values from Kirrander and Jungen [13].

Term energy (cm^{-1})	v'	$-\delta$	Δ (cm^{-1})
133773.0	61	68.26	−1.65
134021.9	64	68.07	0.59
134096.0	65	67.95	−0.63
134178.0	66	67.94	3.52
134471.0	70	67.66	0.44
134612.3	72	67.56	1.97
134681.0	73	67.52	3.80
134748.5	74	67.48	5.01
134812.4	75	67.40	3.00
134876.2	76	67.35	1.87
134935.5	77	67.24	−1.98
135000.0	78	67.23	0.99
135060.7	79	67.18	1.56
135117.0	80	67.08	−1.26
135176.3	81	67.04	−0.4
135237.6	82	67.06	3.01
135348.0	84	66.95	0.48
135403.3	85	66.92	1.21
135509.6	87	66.84	1.73
135609.7	89	66.71	−0.13
135649.8	90	66.49	−9.84
135754.4	92	66.55	−2.64
135800.0	93	66.48	−4.57
135849.3	94	66.50	−1.9
135888.5	95	66.33	−8.4
136038.6	98	66.61	10.07
136115.5	100	66.37	−2.49
136153.4	101	66.26	−5.19
136194.0	102	66.22	−4.24
136235.6	103	66.23	−2.20
136273.5	104	66.17	−3.49
136314.2	105	66.19	−1.41
136352.7	106	66.18	−0.94
136385.9	107	66.03	−5.12
136423.5	108	66.03	−4.23

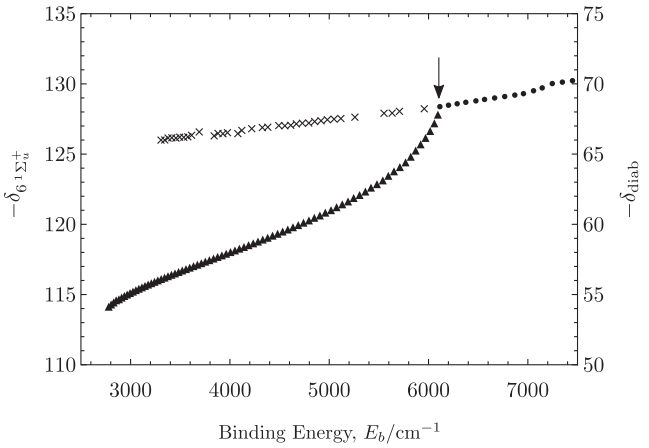

Fig. 3. A comparison of quantum defects for vibrational levels of the outer-well of the $6\,^1\Sigma_u^+$ state (left-hand scale, black triangles) predicted by Staszewska and Wolniewicz [14] to those of the $B''\bar{B}\,^1\Sigma_u^+$ state (right-hand scale, black circles) and observed resonances above the $(1s, 3l)$ dissociation limit (right-hand scale, crosses). Note that the vibrational numbering for the $6\,^1\Sigma_u^+$ state starts at $v' = 0$, while that of the observed above-threshold resonances starts at $v' = 61$ (see Table 1).

the outer well have yet been reported we instead calculate quantum defects using theoretically determined vibrational energies derived from an adiabatic potential energy curve [14]. Fig. 3 plots these quantum defects vs. binding energy for the $v' = 0$—76 vibrational levels of the outer well of the $6\,^1\Sigma_u^+$ state.

3. Discussion

Fig. 2 shows that the observed resonances above the $(1s, 3l)$ threshold can be considered as a continuation of the HR series seen in the $B''\bar{B}\,^1\Sigma_u^+$ state below the dissociation limit. Three linked linear regions are evident in Fig. 2. The first region, $E_b \approx 8500$—$17,000\ \mathrm{cm}^{-1}$, corresponds to the vibrational levels of the outer-well $\bar{B}\,^1\Sigma_u^+$ state below the double-well barrier, and its linearity is a characteristic of HR behaviour seen in a wide range of other ion-pair states [1–4,12]. The second region, $E_b \approx 6000$—$8500\ \mathrm{cm}^{-1}$, includes levels of the $B''\bar{B}\,^1\Sigma_u^+$ state above the double-well barrier, but below the $(1s, 3l)$ threshold. It also shows linearity with several individual level perturbations which have been discussed previously in Ref. [11]. The third region to the left of the arrow ($E_b = 3300$—$6000\ \mathrm{cm}^{-1}$) comprises the resonances observed above the $(1s, 3l)$ threshold [10,11] and are listed in Table 1.

The downward displacement in quantum defect and change in slope at $E_b \approx 8500\ \mathrm{cm}^{-1}$ is due to the dramatic widening of the potential energy curve for levels with $v' \geqslant 36$ that have energies above the top of the double-well barrier. The quantum defects of the observed resonances above the $(1s, 3l)$ threshold join smoothly onto the levels below it, indicating that the crossing at $E_b \approx 6000\ \mathrm{cm}^{-1}$ of the ion-pair potential energy curve and the $3p$ asymptote is diabatic. It involves a much weaker interaction than the less diabatic curve crossing of the $(2s\sigma, 2p\sigma)$ doubly-excited electronic state with the B'' $(1s\sigma, 4p\sigma)$ electronic Rydberg state, which creates the double-well barrier. The relative strength of the interactions in the two curve crossing regions is manifest in the behaviour of the slopes in Fig. 2. The quantum defects near $E_b \approx 6000\ \mathrm{cm}^{-1}$ maintain the same slope through the diabatic crossing, whereas near the double-well barrier at $E_b \approx 8500\ \mathrm{cm}^{-1}$, the slope changes considerably.

The calculated resonance structure above the $(1s, 3l)$ limit reported by Kirrander and Jungen [13] agrees very well with the measured energies, as listed in Table 1. A HR analysis of the theoretical results shows that the calculated resonances fall on the same straight line as the observed resonances, provided that a small adjustment is made as follows; the first two calculated resonances are split by only $25\ \mathrm{cm}^{-1}$, compared with an average spacing of $\sim 75\ \mathrm{cm}^{-1}$. The best agreement with the HR model is obtained if the average term-value for these two resonances is used, suggesting that this resonance is perturbed by an interloping state, resulting in two resonances in the *ab initio* calculation.

We considered whether the resonances observed above the $3p$ limit could be due to excitation, either direct or indirect, of levels of the outer well of the $6\,^1\Sigma_u^+$ state. The barrier separating the inner and outer wells is extremely broad with a flat top, and it essentially isolates the outer well from the inner well making any tunneling between them extremely weak. Further, the minimum of the outer well of the $6\,^1\Sigma_u^+$ state ($R_e \sim 34\ a_0$, or 17 Å) is displaced well beyond that of the $B''\bar{B}\,^1\Sigma_u^+$ state ($R_e \sim 11\ a_0$, or 5.9 Å). In fact, the overlap of vibrational wave functions in the outer well of the $6\,^1\Sigma_u^+$ state with any other states at lower energy will be very small, making direct excitation in the experiments highly unlikely.

The behaviour of the $6\,^1\Sigma_u^+$ state HR quantum defects also argues against identifying the observed resonances with the $6\,^1\Sigma_u^+$ state. Shown in Fig. 3 are the $6\,^1\Sigma_u^+$ state quantum defects with the left-hand axis using numbering that assumes that the first outer-well level is assigned $v' = 0$. We see that they are large (115–122), consistent with the large excluded volume of phase space that is formed by the barrier at $\sim 15a_0$ (8 Å). To make a direct comparison the right-hand axis shows the HR quantum defect values adopting a vibrational numbering that continues consecutively from the $v' = 59$ level of the $B''\bar{B}\,^1\Sigma_u^+$ state. Irrespective of the chosen absolute vibrational numbering, the HR quantum defects of the observed levels above and below the $n = 3$ threshold continue smoothly with the same slope $(8.2 \times 10^{-4}/\mathrm{cm}^{-1})$, whereas those for the vibrational levels of the $6\,^1\Sigma_u^+$ state do not, exhibiting a dramatic change in slope above the threshold $(3.15 \times 10^{-3}/\mathrm{cm}^{-1})$.

As explained by Koelemeij et al. [18] who used a Landau-Zener treatment to quantify the interaction between the four states ($B/\bar{B}\,^1\Sigma_u^+, 4\,^1\Sigma_u^+, 5\,^1\Sigma_u^+$, and the $6\,^1\Sigma_u^+$) that meet at the $(1s, 3l)$ dissociation limit, all of the vibrational levels of the outer well of the $6\,^1\Sigma_u^+$ state, perhaps with the exclusion of the $v' = 0$ level, are expected to be rapidly predissociated. The interaction matrix H_{12} at the crossing ($R \approx 36\ a_0$, 19 Å) in the diabatic basis is equal to half of the closest separation of the $B''\bar{B}\,^1\Sigma_u^+$ and the $6\,^1\Sigma_u^+$ potential energy curves [21]. Here, $H_{12} \sim 20\ \mathrm{cm}^{-1}$. (This value is quite small when compared to the interaction matrix element of the avoided crossing of the $B\,^1\Sigma_u^+$ curve and the $B''\bar{B}\,^1\Sigma_u^+$ curve ($H_{12} \sim 3000\ \mathrm{cm}^{-1}$) at lower energy and smaller internuclear separation studied previously [12]). The weak interaction between the four states that meet at the $(1s, 3l)$ dissociation limit can also be gauged by the minimal displacement in quantum defect of the highest vibrational level ($v' = 59$) of the $B''\bar{B}\,^1\Sigma_u^+$ state located just $15\ \mathrm{cm}^{-1}$ below the crossing.

A consequence of this weak interaction energy, corresponding to a very weakly avoided crossing, is that passing through the crossing at $36\ a_0$ at any but the slowest radial velocities will be diabatic in nature and only more so as v' increases. In an adiabatic picture of the potential energy curves in this region, vibrational levels of the outer well of the $6\,^1\Sigma_u^+$ state would have to change electronic configuration at every passage through the curve crossing to remain in the outer well and avoid following the $3p$ asymptote. The observed diabatic nature of the curve crossings in this region

results in strong predissociation for vibrational levels of the outer well of the $6\,^1\Sigma_u^+$ state and stable ion-pair vibrational character of the resonances observed above the $(1s, 3l)$ threshold. The outer well of the $6\,^1\Sigma_u^+$ state thus plays at best a minor role in the dynamics of the resonances considered here, perhaps only in a narrow energy region just above the $3p$ crossing.

Similar diabatic behaviour in the *gerade* $H\bar{H}\,^1\Sigma_g^+$ state has been noted by Kirrander [16]. This situation is also similar to the classic crossing of the $B\,^3\Pi_0^+$ and $B'\,(0^+)$ states in IBr [22,23] but with a weaker interaction energy. It is interesting to note that in their original proposal pointing to Rydberg behaviour in ion-pair states, Asaro and Dalgarno [1] were also able to follow an ion pair progression through an avoided crossing in a model potential.

The continued strength of the $B''\bar{B}\,^1\Sigma_u^+ \leftarrow EF\,^1\Sigma_g^+$ transition above the $B''\bar{B}$ barrier requires comment. If, as we propose, the diabatic picture is the better first-order description of the spectrum, the probe stage of the excitation scheme used by Ekey and McCormack [10] and Chartrand et al. [11] involves a one-electron promotion from the $\sigma_g^2 + \sigma_u^2$ configuration of the outer well of the $EF\,^1\Sigma_g^+$ state, $R_e = 4.5\ a_0$ (2.4 Å), to the predominantly $\sigma_u^1 2s^1$ configuration of the inner wall of the diabatic $B''\bar{B}\,^1\Sigma_u^+$ state, where we have denoted the two states of the H_2^+ core as $\sigma_{g,u} = 1s_A \pm 1s_B$. Higher $np\sigma_g$ configurations will be mixed in as the $\sigma_g^1 4p^1, 4f^1$ states are crossed at higher energies (Fig. 1), but the transition remains a strong one because of the low principal quantum number of the dominant $n = 2$ configuration, $\sigma_u^1 2s^1$, in the Franck-Condon range of 4–6 a_0 (2–3 Å) of the $B''\bar{B}\,^1\Sigma_u^+$ state.

It is interesting to consider what lies at higher energies, beyond the HR resonances discussed here. The density of states in a Coulomb potential increases rapidly and becomes infinite as dissociation to free ion-pairs is approached. It will be difficult to access this region ($E_b = 0$—$3000\ \mathrm{cm}^{-1}$) by transitions directly from the ground state or through intermediate states using optical double resonance techniques. However, as noted above, access is known to be possible through electronic Rydberg states which are coupled to many of the ion-pair states; this approach is the basis of the Threshold Ion-pair Production Spectroscopy (TIPS) [24] and Zero Ion Kinetic Energy (ZIKE) techniques [25,26]. This high energy region, where HR states are found to be long-lived ($\tau \sim 10^{-6}$ s), can also be studied using pulsed excitation techniques to prepare a coherent superposition of states and observing the evolution of the wave packets thus produced [27,28].

4. Conclusion

A quantum defect analysis of all the available data on the $B''\bar{B}\,^1\Sigma_u^+$ state of H_2 suggests that essentially diabatic behaviour persists throughout the energy range in which at least two avoided crossings are traversed. These crossings are marked by local perturbations and a clear change in gradient of the $\delta(E_b)$ vs. E_b plot as the vibrational motion penetrates to smaller radial separations. This analysis also reveals that the resonance features observed above the $3p$ asymptote should not be associated with the vibrational levels of the outer well of the $6\,^1\Sigma_u^+$ state, emphasizing the inaccessibility of this state from the intermediate vibronic levels used in current multiphoton excitation schemes and consistent with analysis of the predissociative nature of these levels.

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