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P H Y S I C A L   R E V I E W   L E T T E R S

Observation of a Rydberg Series in H⁺H⁻: A Heavy Bohr Atom

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We report on the realization of a *heavy* "Bohr atom," through the spectroscopic observation of a Rydberg series of bound quantum states at principal quantum numbers $n = 140$ to 230. The system is made heavy by replacing an electron inside a hydrogen atom by a composite H⁻ particle, thus forming a H⁺H⁻ Coulombically bound system obeying the physical laws of a generalized atom with appropriate mass scaling.

Bohr developed the atomic model by imposing an *ad hoc* quantization condition on the angular momentum of an electron orbiting in the Coulombic potential of a positively charged nucleus [1]. The same solutions for the level energies are found by solving the Schrödinger equation for a quantum system bound by a $1/r$ potential; Rydberg states are represented by [2]

$$E_n = E_{\lim} - \frac{R_A}{(n - \delta)^2}, \qquad (1)$$

where R_A is the atomic Rydberg constant and n is the principal quantum number. For atoms with an extended core, i.e., all atoms other than hydrogen, a quantum defect δ should be included. The wide variety of atomic and molecular realizations of Rydberg systems all have in common that the fundamental scale factor, the Rydberg constant, is essentially the same, because it is governed by the mass of the electron bound to a much heavier core: $R_A = (\mu/m_e)R_\infty$; for all these systems the reduced mass of the electron μ is close to m_e. Only few exotic systems like muonium ($\mu^+ e^-$) [3] or positronium ($e^+ e^-$) [4] provide a different scale factor, the latter having exactly $R_\infty/2$.

Ion-pair systems bound by their Coulombic $1/r$ potential provide a realistic extension of the Rydberg concept to heavier systems. Initially the process of ion-pair formation above threshold was investigated by Chupka *et al.* [5] measuring $H_2 + h\nu \rightarrow H^+ + H^-$. Hepburn and co-workers used the existence of long-lived bound states immediately below the ion-pair limit in their threshold ion-pair production spectroscopy (TIPPS) to determine accurate values of ion-pair dissociation thresholds, applied amongst others to the H⁺H⁻ system [6]. Later Reinhold and Ubachs demonstrated the existence of bound heavy Rydberg states of the H⁺H⁻ system through the probing of wave-packet dynamics in the densely structured quantum region several cm⁻¹ below threshold [7]. These time-domain observations of heavy Rydberg states, conceptually analogous to observations of electronic wave packets [8], reveal the characteristic signatures of such states without resolving individual quantum states.

We report on the first experimental observation of a *frequency-resolved* quantum series of heavy Rydberg states in the H⁺H⁻ system, here referred to as a heavy Bohr atom. Two-step laser excitation is performed, starting in the ground state of the neutral H_2 molecule, using an extreme ultraviolet (XUV) pulsed laser source in the first step, populating an intermediate state in the molecule: the $C^1\Pi_u$, $v = 3$, $J = 1$ state in parahydrogen or the $B^1\Sigma_u^+$, $v = 12$, $J = 0$ state in orthohydrogen. A second laser, tunable in the ultraviolet region then further excites the molecule towards the energetic region where the heavy Rydberg states are expected. A sketch of the experimental arrangement is presented in Fig. 1. The use of such a laser-based XUV source in a double-resonance excitation scheme, including the XUV spatial filtering method,
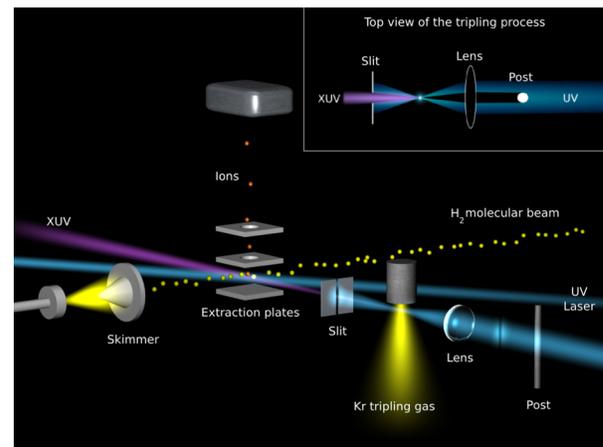
FIG. 1 (color online). Experimental setup. An H_2 molecular beam is perpendicularly intersected with a beam of XUV radiation, obtained via third harmonic generation of a pulsed UV-laser beam underneath the orifice of a pulsed valve in krypton gas. The XUV radiation is geometrically filtered from the incident fundamental UV beam by selecting the phase-matched k_{XUV} vector in a UV-dark region imposed by a post placed in the incident laser beam (see inset). H⁺ and H_2^+ are extracted from the interaction region by a pulsed electric field for signal detection.

were described by Reinhold *et al.* [9] (see also the inset of
Fig. 1). Signal is detected by probing H_2^+ ions produced in
the two-step excitation process. Alternatively, signals were
detected (although weaker) by probing H^+ ions, which are
produced via dissociation of the H_2 molecule. In the latter
channel excited H atoms are formed, which are subse-
quently ionized to form H^+ by the UV radiation from the
second laser. The energetic region under investigation
($134\,000$–$138\,000$ cm^{-1}) is above the $n = 2$ and $n = 3$
dissociation limits in H_2 and both dissociative decay chan-
nels were experimentally observed. Level energies ac-
cessed in the two-step excitation process are derived
from the well-determined intermediate levels [10] and
from calibration of the second tunable laser.

Figure 2 displays the fundamental discovery of the
present study. A long series of regularly spaced resonances
is observed in an energy window of some 2000 cm^{-1}.
These resonances visibly follow the pattern of a
Rydberg-like series indicated and numbered in the figure.
However, the Rydberg series is not as "clean" as usually
observed in atoms; the intensities, widths, and line shapes
vary across the series superimposed on a structured con-
tinuum, while some unassigned resonances are present as
well. The series of quantum states with a Rydberg *electron*
bound by an H_2^+ molecular core in quantum states $v^+ = 7$
and $N^+ = 0$, 2, or 4 (only *even* rotational quantum num-
bers for para-H_2), expected in this energy range, do not
match the observed features. Alternatively, the series can
be fitted to an equation for *heavy* Rydberg states:

$$E_n = E_{IP} - \frac{R_h}{(n - \delta)^2}, \qquad (2)$$

where R_h denotes the Rydberg constant for the H^+H^-

heavy Bohr atom. While in the experiment the $X^1\Sigma_g^+$, $v = 0$, $N = 0$ ground level of the neutral H_2 molecule is taken
as the zero energy level, the H^+H^- (ion-pair) dissociation
limit E_{IP} can be determined from a thermodynamic cycle
[11], thus including the values for the ionization energy of
the neutral H_2 molecule, the dissociation energy of the H_2^+
ion and the electron affinity of the H atom, yielding $E_{IP} =$
IE(H_2) + D_0(H_2^+) − EA(H) and resulting in $E_{IP} =$
$139\,713.83$ cm^{-1}. The Rydberg constant for the heavy
Bohr atom H^+H^- can be obtained by replacing the elec-
tron by an H^- particle, yielding the scaling factor
$(\mu/m_e) = 918.5761$ [11]. Note that the Bohr radius for
the heavy system is $a_0^h = 5.7 \times 10^{-14}$ m. Based on the
numbers for E_{IP} and R_h the observed Rydberg series in
parahydrogen can be assigned to principal quantum num-
bers n between 161 and 230 (with a gap between $n =$
205–225). A fit to Eq. (2) yields a value for the quantum
defect of $\delta = 0.05$.

The observations displayed in Fig. 3 add to the findings.
They show that the heavy Rydberg series can be observed
at even lower energies, where states of $n = 140$–150 are
located, that the $B^1\Sigma_u^+$ intermediate state of valence char-
acter can be used, as opposed to the $C^1\Pi_u$ state of mo-
lecular Rydberg character, and that the series can also be
observed in ortho-H_2, as opposed to para-H_2 in Fig. 2. A
remarkable observation features at excitation energies
above $135\,500$ cm^{-1}, where the assignment in terms of
Rydberg states in the heavy Bohr atom ceases to match.
From the more detailed upper part of Fig. 3 it becomes
clear that in this energy range the ordinary or electronic
Rydberg states converging to the $v^+ = 6$, $N^+ = 1$, 3 limits
in the ortho-H_2^+ core are excited. Also, some effects of
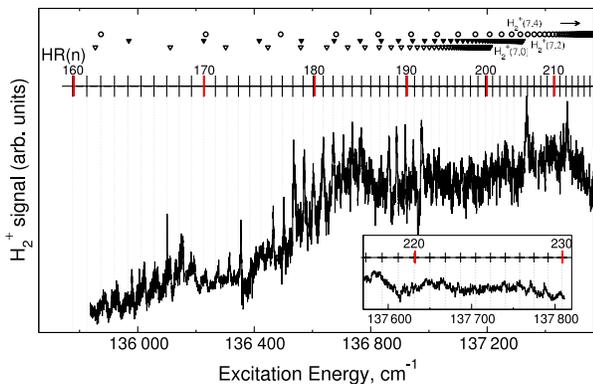mutual interaction between these Rydberg series, a well-

FIG. 2 (color online).   Characteristic spectrum after two-step
laser excitation via C-X (3,0) R(0) in the para-H_2 molecule. The
markers and dotted lines show the predicted positions in the
heavy Bohr atom between $n = 161$ and $n = 230$ in the H^+H^-
system. In the range between $n = 205$–225 the series is inter-
rupted and overlaid by resonant structures, but appears again for
$n = 225$. The Rydberg series converging to the H_2^+ ($v^+ = 7$,
$N^+ = 0$, 2, and 4) states of the ion are denoted with open
triangles, full triangles, and open circles, respectively.

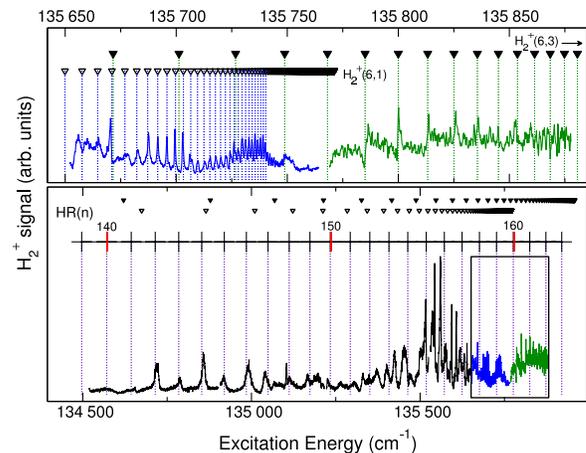FIG. 3 (color online).   Lower panel: Characteristic spectrum
after two-step laser excitation via B-X (12,0) P(1) in the
ortho-H_2 molecule, showing $n = 140$–162 Rydberg states in
the heavy Bohr atom. In the upper panel the part of the spectrum
between $135\,650$ and $135\,880$ cm^{-1} is enlarged, showing the
electronic Rydberg series converging to the H_2^+ ($v^+ = 6$, $N^+ =$
1, 3) states of the ion.

known feature in molecular Rydberg series [12], seem to be present.

From the perspective of *electronic* Rydberg spectroscopy, an intermediate state with a $2p$ electron, $2p\sigma$ in case of the $B^1\Sigma_u^+$ state and $2p\pi$ in case of the $C^1\Pi_u$ state, should give rise to ns and nd series, as are indeed observed [13] in such excitation schemes in H_2. Considering the angular momenta in a Hund's case (d) framework, mutually interacting ns and nd Rydberg series converging to several allowed N^+ series limits are expected. This is indeed observed in Fig. 3 with series converging to $N^+ = 1$ and 3, for $v^+ = 6$ in the ortho-ion core. We observed the same phenomenon in parahydrogen, when exciting via the $B^1\Sigma_u^+$, $v = 12$, $J = 1$ intermediate state in the energetic region near $135\,600\,\text{cm}^{-1}$ (not shown here), where Rydberg series converging to $N^+ = 0$, 2, and 4, for $v^+ = 6$ in the para-ion core are observed. However, the observed spectral lines, indicated by HR(n) in Figs. 2 and 3, are not associated with *electronic* states, but with excitations in the heavy H^+H^- system.

An elucidating connection can be made between the quantum numbers that characterize the heavy Bohr atom, principal quantum number n, and angular momentum quantum numbers ℓ or J, and the usual molecular quantum numbers v and J associated with an intramolecular potential-energy curve (in this case $1/R$). This connection was established by Pan and Mies [14] to be $n \leftrightarrow v + J + 1$. It can be understood by considering the number of *radial nodes* in the wave function, v in the molecular system and $n - \ell - 1$, or $n - J - 1$ in the Rydberg system. In the present experiment for orthohydrogen only a $J = 1$ state is excited ($J = 0$ in the intermediate state); hence, a single n series in the heavy Bohr atom results through jumps in the v quantum number. In parahydrogen (a $J = 1$ intermediate state) $J = 0$ and 2 states can be excited, when applying the $\Delta\ell = \Delta J = \pm 1$ (Laporte) selection rule in the heavy Bohr atom. Hence, *two* series might be expected, possibly with different quantum defects δ_J. Since this H^- particle is in a unique $^1S_0$ state, there exists only a *single* series limit (neglecting hyperfine structure).

In the potential-energy diagram (Fig. 4) a distinction is made between a short-range regime ($R < 12a_0$), where the covalent states in the H_2 molecule and the electronic Rydberg states are located, and a long range regime ($R > 12a_0$). At $\approx 10a_0$ the ion-pair potential undergoes a strong interaction ($\approx 3000\,\text{cm}^{-1}$) with a dissociative state, thus giving rise to the characteristic double-well states in H_2, the $H\bar{H}^1\Sigma_g^+$ state in the g manifold [15] and the $B''\bar{B}^1\Sigma_u^+$ state in the u manifold [16]. Heavy Rydberg states with small principal quantum numbers, thus having bond lengths of the order of the scaled Bohr radius, are unphysical because the H^- ion itself is larger. Therefore, the principal quantum number n of the lowest essentially pure ion-pair state in H^+H^- is given by $R = n^2 a_0^h \approx 12a_0 \approx 6 \times 10^{-10}$ m, i.e., $n \approx 100$.
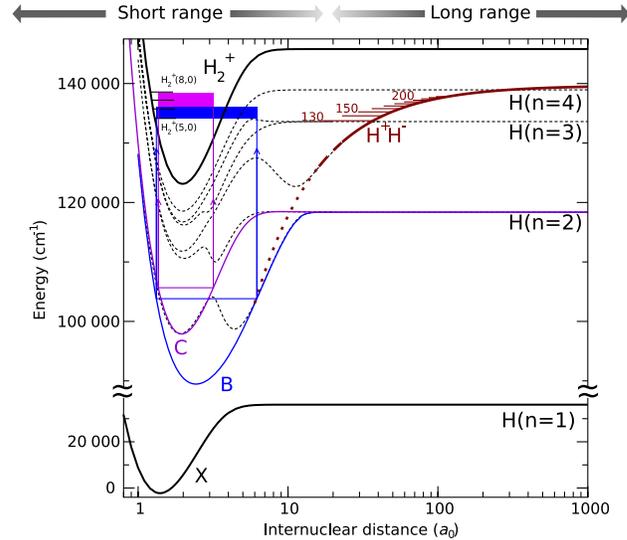

FIG. 4 (color online). Potential-energy diagram of the H_2 molecule with distinction between two separated regimes: for $R < 12a_0$ the range of internuclear distances where covalently bound states and the electronic Rydberg states converging to H_2^+ (v^+, J^+) dominate (dashed lines representing the potential curves of *gerade* symmetry in this region [15]), and the range $R > 12a_0$ where H^+H^- heavy Rydberg states exist. The H^+H^- Coulomb potential is shown in dark (red) and extended to smaller R by dots. Intermediate energy levels in the B and C states (at $\sim 105\,000\,\text{cm}^{-1}$ excitation) are indicated and their accessible Franck-Condon ranges mapped (boxes).

All presently observed heavy Bohr atomic states fall in the energetic range between the $H(1s) + H(3\ell)$ and $H(1s) + H(4\ell)$ dissociation energies (see Fig. 4). Below $n = 130$ a perturbation in the heavy Rydberg series is expected, by about $60\,\text{cm}^{-1}$ at $36a_0$, due to the avoided crossing with $H(3\ell)$ [17]. In this range and above $n = 250$, where another crossing with $H(4\ell)$ occurs (presumably with a strength of only a few cm^{-1}), the series in the heavy Bohr atom indeed dies out. Unresolved heavy Rydberg states were shown to exist above the $n = 4$ threshold by wave-packet experiments [11].

Photoexcitation of molecular states is governed by the Condon principle: Electronic orbitals are excited by the optical transition during which the nuclei remain essentially fixed in space. As a result, the strengths of transitions are governed by the square of the overlap integral of the initial and final rovibrational wave functions of nuclear motion (the Franck-Condon factor):

$$I_n = \left| \int \Psi_n^*(R)\Psi_{B,C}(R)dR \right|^2. \tag{3}$$

By far the main part of the nuclear wave function of the heavy Rydberg states is at large internuclear distance (e.g., the outer turning point for $n = 200$ is $R \approx 90a_0$), while the lower state is confined to $R < 6a_0$. The Franck-Condon factor of the transition should therefore be extremely

small; further, excitation from the C state (which is confined to $R < 3a_0$) should be much weaker than from the B state, but this is not observed. From this we conclude that the heavy Rydberg states are not directly excited from the prepared intermediate B and C states via their Franck-Condon overlap.

We invoke the mechanism of a *complex resonance* [18] to resolve this issue. A superposition quantum state:

$$\Psi_c = \Psi_{hR}(n) + \sum_{v^+, J^+} \Psi(H_2^+, v^+, J^+; e^-) + \sum_{diss} \Psi(H, H^*)$$
(4)

with mixed character of electronic Rydberg channels (some 20 of those) associated with a $\Psi(H_2^+, v^+, J^+)$ core representing the ionization continua above each limit and a bound series below, dissociative continua (both $n = 2$ and $n = 3$ channels), and a series of Bohr atomic states $\Psi_{hR}(n)$; in excitation the latter have a zero transition dipole moment. A crucial ingredient in the complex resonance model is a broad interloper state for which the transition dipole moment is large; a low n Rydberg state converging to a higher lying limit $H_2^+(v^+)$, hence a state in which v^+ is significantly larger than 6, takes on this role. As shown for another transition scheme in the H_2 molecule [18], under such conditions quantum interferences via different but indistinguishable pathways can lead to excitation of narrow series (in the example of [18] electronic Rydberg states), while excitation of the associated bound states may result in autoionizing decay. This closely matches the situation in the present experiment, although the number of channels is much larger than in an idealized example. The interpretation in terms of a complex resonance explains the occurrence of underlying (possibly structured) continua in the spectrum, the variation of widths over the bound series, and the variation of asymmetry in the line shapes exhibiting differing Fano parameters. At the same time it provides an explanation for the fact that H^+H^- heavy Bohr atomic states are *excited*, while signal is *detected* in another channel, such as H_2^+. A detailed quantitative analysis is beyond the scope of the present Letter.

It is interesting to note that the $p\bar{p}$ matter-antimatter protonium system [19] exhibits nearly the same Rydberg constant as the H^+H^- system. Hence both systems have a similar energy level structure. In H^+H^- the electrons have the positive effect to mediate a complex resonance, thus providing optical access to the series of heavy quantum states, a phenomenon which does not occur in $p\bar{p}$.

In conclusion, we have observed a frequency-resolved series of quantum resonances in a heavy Rydberg system by two-step excitation. In principle such series should be observable in any A^+B^- diatomic molecule, or in $A^+(BC)^-$ polyatomic molecules [14], as long as the negative particle is bound (which would exclude, e.g., N^-). In such systems a heavy Rydberg series is associated with each quantum state (rotational, vibrational, electronic, and fine structure) in either of the two constituting particles. The presently studied H^+H^- system is the simplest, not only because H_2 is the simplest neutral molecule, but, in particular, since H^- in the $^1S_0$ state has no internal structure and therefore only a single Rydberg series limit exists, making the system truly a heavy *Bohr atom*.

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