

Observation of Triplet nd Autoionizing Rydberg States in H_2

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Single-photon laser spectroscopy of H_2 from the metastable $c^3\Pi_u$ state has been used to study triplet nd autoionizing Rydberg states, $n \approx 10$ –20. We observe a new and extensive spectrum which shows a well-resolved fine structure due to interaction of the Rydberg electron with the extended cord. An *ab initio* Hund's case- d model is shown to predict the transition frequencies in isolated portions of the spectrum. In general, however, extensive channel interactions will necessitate a multichannel quantum-defect-theory analysis.

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Photoionization of H_2 is one of the most fundamental molecular processes, and it has received considerable theoretical and experimental attention. In particular, Herzberg and Jungen¹ and later Dehmer and Chupka² studied, with resolution $\approx 2.5 \text{ cm}^{-1}$, the singlet np autoionizing Rydberg series accessible via vacuum ultraviolet (vuv) absorption from the H_2 ground state. Their work has elicited substantial theoretical response^{3–7} which has attempted to understand the mechanism of molecular autoionization and to analyze the observed spectra within the framework of multichannel quantum-defect theory (MQDT). MQDT has been remarkably successful at describing this highly complex situation with a small number of experimentally determined parameters. However, MQDT has also predicted spectral structure as yet unseen for lack of resolution in the vuv absorption measurements, and it has been confined, for lack of experimental data, exclusively to the np series.

Laser spectroscopy of the high Rydberg states of H_2 can provide major new and more stringent tests of the current theory by improving the resolution and opening new channels for measurements. The first such experiments have very recently been reported. Bjerre, Kachru, and Helm⁸ observed the singlet np Rydberg series by multiphoton excitation from the ground state. Their work demonstrated a greatly improved resolution over the previous vuv measurements. Welge and Rottke⁹ used essentially the same technique to open the singlet ns and nd Rydberg channels to study, observing n up to 75. Sturru, Sobol, and Lundeen¹⁰ have studied high angular momentum states ($L = 3$ –6) in the nonautoionizing $v = 0$, $n = 10$ level. Finally, several groups have reported unpublished observations of triplet nd ¹¹ and nf ¹² autoionizing Rydberg series.

We here report on our laser spectroscopy measurements of the triplet nd autoionizing Rydberg states of H_2 . Our resolution is a factor of 5 better than that of the vuv measurements of singlet states. The observed spectrum is extensive and will require careful, detailed analysis. This paper presents our initial results and

describes the use of an *ab initio* model for calculating the Rydberg energy levels and assigning the spectrum; more complete measurements and analysis will be published later. This demonstration of the controlled preparation of Rydberg states in H_2 also opens the door for many future studies of the highly excited states of this fundamental molecule.

The high Rydberg states of molecules have been little studied in comparison with atoms. For sufficiently high excitation the molecular properties must become quasiatomic and be well described by Hund's coupling case d of molecular physics. Other than H_2 , where even the $n = 4$ states are close to case d , only a small number of molecules have been studied in Rydberg states high enough to exhibit case- d behavior. Both the early onset of case- d behavior and the fact that the properties of H_2 , the prototype of molecular physics, are generally not well known from first principles (unlike the hydrogen atom with respect to atomic physics) make H_2 the natural choice for studying the essential features of Rydberg molecules.

We also note the fairly small number of studies of the triplet states of H_2 . Recent studies of the triplet states include high-resolution laser spectroscopy of the $n = 3, 4$ s and d states from the $c^3\Pi_u$ state,^{13,14} and a laser photodissociation measurement of $n = 3$ states.¹⁵ Other than the $np\pi$ states, which are known to $n = 7$ from Dieke's classical emission work,¹⁶ the triplet states have been known only to $n = 4$. This seems quite remarkable to us, considering the fundamental importance of H_2 and the vast number of H_2 experiments performed over the past several decades. This work reported here will add significantly to our knowledge of the triplet states of H_2 .

Our technique is laser spectroscopy of a thermal beam of metastable $2p\pi$, $c^3\Pi_u$ molecules. The even- N rotational levels of parahydrogen and the odd- N levels of orthohydrogen have radiative lifetimes $> 100 \mu\text{s}$,¹⁷ allowing them to traverse the length of our apparatus with little loss. The metastable beam is formed by electron impact on an effusive H_2 beam, and the metastable molecules (predominantly in states

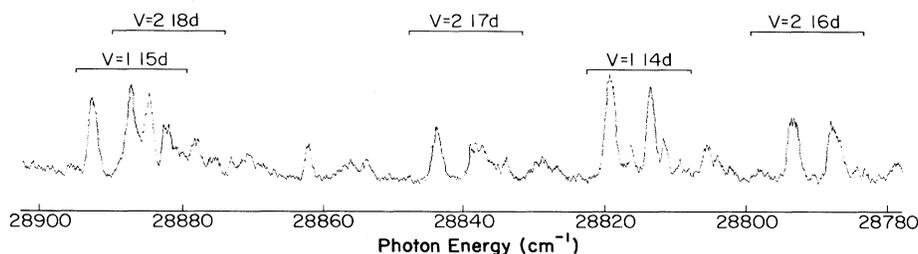


FIG. 1. A portion of the photoionization spectrum of the metastable $c^3\Pi_u$ state of H_2 , near 347 nm, showing transitions to nd autoionizing Rydberg states.

$\nu = 0-2$, $N = 1-3$) are then single-photon excited by a frequency-doubled pulsed dye laser (50-kW pulses, $\lambda \sim 340$ nm) to autoionizing nd Rydberg states. Photoions are extracted from the beam by a weak electric field (< 10 V/cm) and then accelerated into a Channeltron detector.

We have found a rich spectrum which extends from 28 000 to 30 000 cm^{-1} and contains several hundred lines. Figure 1 shows a typical portion of the spectrum. The major features of the spectrum can be identified as $\Delta\nu = 0$ transitions from levels $\nu = 1, 2$ of $c^3\Pi_u$ to nd states, $n \approx 10-20$, converging to various rovibrational levels of the H_2^+ core. Franck-Condon factors for the nearly parallel potential curves of final and initial states suppress $\Delta\nu \neq 0$ transitions, and the $\nu = 0$ Rydberg states are either below the ionization limit, and thus not seen, or autoionize only weakly through rotational preionization.

The observed structure within each group is due in part to the rotational structure of the lower level and also, more interestingly and importantly, to the interaction of the Rydberg electron with the extended, nonspherical core. This is described further below. An important factor in keeping the spectrum well resolved is that only the $N = 1-3$ rotational levels (there is no $N = 0$ in a Π state) have substantial population at room temperature. Finally, we note that in this region of the spectrum the background is almost entirely electronic noise, with direct photoionization to the continuum not observed. The weakness of the open channel explains why the lines have a symmetrical profile rather than the Beutler-Fano profile commonly seen in autoionization.

Observed linewidths range from the laser linewidth of 0.5 cm^{-1} to about 1.0 cm^{-1} . At this stage we cannot say whether the larger widths are due to autoionization or to possible saturation effects or detector nonlinearity. It is noteworthy that we have not observed any exceedingly broad lines (≥ 5 cm^{-1}) such as were seen among the np levels. This most likely reflects the smaller core penetration of the d orbitals. We also note that we have not yet seen any lines identified as transitions to the ns Rydberg series. This is not

surprising at the present level of resolution and signal-to-noise ratio, since $2p \rightarrow ns$ oscillator strengths are, for large n , roughly a factor of 30 smaller than for $2p \rightarrow nd$.

Figure 2 shows a more limited region of the spectrum. Its well-resolved structure and relatively good isolation have permitted a fairly straightforward analysis. Rydberg states of H_2 are well described by the seldom-used Hund's coupling case d . Case d is an essentially atomic model, with the Rydberg electron's angular momentum L adding vectorially to the rotational angular momentum R of the H_2^+ core to give total angular momentum (exclusive of spins) $N = L + R$. Note the different usage of N in Hund's case- b ($c^3\Pi_u$) and case- d (Rydberg states) notation. Interaction of the electron with the finite size of the core separates levels of differing N , providing a fine structure. The molecular spin-orbit interaction is unresolvable in this work. The structure, then, is an nL Rydberg series

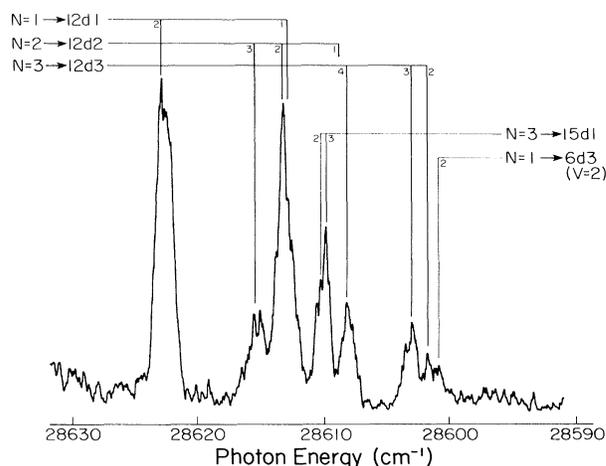


FIG. 2. Photoionization spectrum of H_2 near the $c^3\Pi_u$, $\nu = 1$, $N \rightarrow \nu = 1$, $12dR$ transitions. N for the upper state is shown next to each transition. The $\nu = 1$, $15d1$ and $\nu = 2$, $6d3$ states perturb the spectrum, as described in the text.

converging to each rovibrational level (ν, R) of the core, with each n exhibiting fine structure (different N) due to the electron-core interaction. Levels above the ionization limit ($\nu=0, R=0$) are able to autoionize, with $\Delta\nu=1$ vibrational autoionization being the dominant, but not exclusive, process. Notation for the Rydberg levels is ndR , showing the rotation level R of H_2^+ to which the nd series is converging.

Eyler and Pipkin¹⁴ have formulated an *ab initio* case- d model of H_2 , and it has been applied successfully at lower values of n .^{10, 14, 18} In this long-range interaction model the molecular energy is due to the core's rovibrational energy, the Rydberg electron's binding energy $-R/n^2$, and the electron's interaction energy with the core's quadrupole moment and polarizability. The interaction Hamiltonian is expressed in molecule-fixed coordinates as

$$H_{\text{int}} = -\frac{e^2\alpha}{2r^4} - \left(\frac{e^2\gamma}{3r^4} + \frac{eQ}{r^3} \right) P_2(\cos\theta).$$

Here Q , α , and γ are, respectively, the core's quadrupole moment, isotropic polarizability, and anisotropic polarizability. All are functions of the internuclear separation. This electron-core interaction allows perturbations between levels with $\Delta N=0, \Delta R=0, \pm 2$.

It is important to recognize that this long-range

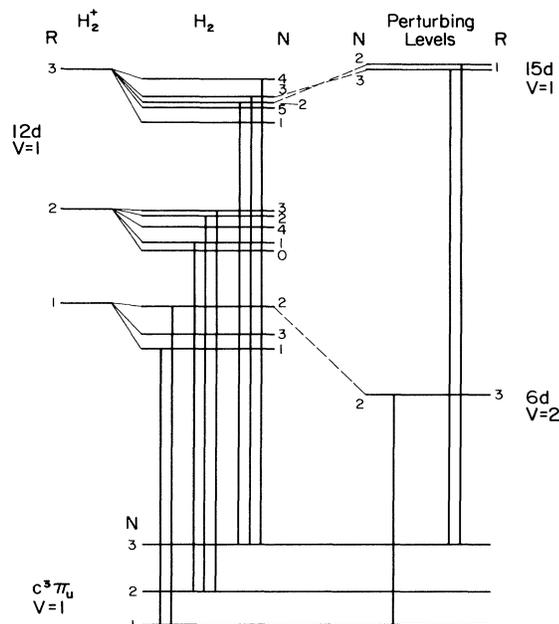


FIG. 3. Energy levels of H_2 relevant to the spectrum of Fig. 2. The fine structure is greatly enlarged relative to the separation between H_2^+ rotational levels. Perturbations are denoted by dashed lines, and allowed transitions are shown as vertical lines.

model does not allow for core penetration of the Rydberg electron. This is due to the setting of $r_{<}/r_{>} = r_{\text{core}}/r_{\text{Ryd}}$ whenever it occurs in the multipole expansions that lead to H_{int} . Consequently, this model would not be expected to work, and indeed does not for the previously studied np Rydberg series since core penetration of the p electron is not negligible. For higher angular momentum states, however, core penetration is minimal and the long-range model gives good agreement with observation. Its advantages are twofold. First, it is a completely *ab initio* model, requiring only the H_2^+ rovibrational energy, wave functions, and the parameters Q , α , and γ . These can all be accurately calculated for one-electron H_2^+ . This approach is in contrast to MQDT, which parametrizes spectral data in terms of a small number of *experimentally* determined parameters. Second, this model is fairly intuitive and, if its limitations are kept in mind, gives a straightforward physical picture of the important interactions in highly excited molecules.

We have used this model, including perturbations, to predict the spectrum of Fig. 2 which, on the basis of the electron's Rydberg energy alone, can be identified as arising primarily from $\nu=1$ transitions to $12d$ levels. Figure 3 shows the relevant $12d$ levels as well as three perturbing levels. The two $N=2$ perturbations produce relatively small energy shifts ($< 1 \text{ cm}^{-1}$), but the $N=3$ shift is $\approx 3 \text{ cm}^{-1}$. Several more distant perturbers produce smaller effects. Comparison of Figs. 2 and 3 show that all transitions are observed except that to $12d2, N=1$, which is expected to be weak.

Our calculation procedure was to evaluate diagonal and off-diagonal matrix elements for all nd Rydberg states ($n < 25$) within $\approx 100 \text{ cm}^{-1}$ of the observed $12d$ levels. The energy matrix was then diagonalized to give the perturbed energy levels. Possible $s-d$ per-

TABLE I. Observed and calculated transition frequencies for the spectrum of Fig. 2. All levels have vibration quantum number $\nu=1$ except where noted.

$c^3\Pi_u$	Transition Rydberg	Frequency (cm^{-1})		
		Obs.	Cal.	Diff.
$N=1$	$12d1, N=1$	28 613.0	28 612.7	0.3
	$N=2$	28 622.4	28 621.2	1.2
	$6d3, N=2, \nu=2$	28 600.6	28 599.9	0.7
$N=2$	$12d2, N=1$	· · ·	28 609.2	· · ·
	$N=2$	a	28 612.1	· · ·
	$N=3$	28 615.2	28 614.2	1.0
$N=3$	$12d3, N=2$	28 601.6	28 601.9	-0.3
	$N=3$	28 602.9	28 603.1	-0.2
	$N=4$	28 607.9	28 608.2	-0.3
	$15d1, N=2$	28 610.3	28 609.7	0.6
	$N=3$	28 609.9	28 609.2	0.7

^aBlended with stronger line.

turbations have not been included. Morse functions, which should be acceptably accurate for low vibrational quantum numbers, were used to calculate the matrix elements of Q , α , and γ . Finally, Dieke's energy levels¹⁶ for $c^3\Pi_u$, corrected by -149.6 cm^{-1} ,¹⁹ were used to predict the transition frequencies.

Calculated and observed transition frequencies are shown in Table I. If the transitions to $\nu=1$, $12d1$, $N=2$ and $\nu=2$, $6d3$, $N=2$ are omitted, for reasons noted below, the calculated frequencies are systematically about 0.3 cm^{-1} smaller than the observed frequencies, and the rms difference is about 0.6 cm^{-1} . Possible random errors, including wavelength calibration and calculational uncertainties, are estimated to give a probable error of $\pm 0.4\text{ cm}^{-1}$, slightly less than the observed 0.6-cm^{-1} rms difference. With regard to the 0.3-cm^{-1} shift between calculated and observed frequencies, we note that Eyler, Short, and Pipkin, in preliminary analysis of two-photon transitions from $c^3\Pi_u$ to nf Rydberg states,¹² also find frequencies calculated by this model to be systematically about 0.2 cm^{-1} smaller than observed. These findings suggest that either the ionization potential of H_2 or the $c^3\Pi_u$ energy levels may be in error.

The motivation for not including $12d1$, $N=2$ and $6d3$, $N=2$ is that $n=6$ is not high enough for an accurate determination of the $6d3$, $N=2$ level. Eyler and Pipkin¹⁴ found this long-range model to be good to only a few inverse centimeters for the $4d$ levels. Since the effects of Q , α , and γ decrease like n^{-3} , the possible uncertainty in $6d3$, $N=2$, and thus the uncertainty in the shift of $12d1$, $N=2$ caused by the nearby $6d3$, is much larger than for the other levels.

We conclude that the long-range model produces good, but not excellent, agreement with observation. The level of agreement is consistent, when scaled as n^{-3} , with the $n=4$ study of Eyler and Pipkin.¹⁴ It is certainly true that the inclusion of off-diagonal elements, which induces shifts as large as 3 cm^{-1} , is essential for achieving agreement. Indeed, the spectrum could not be assigned until the perturbations were considered. The difficulty is that the number of possible perturbers becomes exceedingly large as n increases. This is hardly new, of course, and accounts for the success and popularity of the MQDT approach to Rydberg series. We expect that MQDT can be effective for analyzing these data, especially after more detailed measurements are made on the shapes and widths of the autoionization profiles, and we are proceeding with such an analysis. The long-range model, however, will still prove exceedingly valuable

for the initial assignment of transitions.

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