Precision Spectroscopy of the *nf* Triplet Rydberg States of H_2 and Determination of the Triplet Ionization Potential

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Several triplet Rydberg *f* states in molecular hydrogen were observed with a resolution of about 50 MHz under stepwise excitation. Extrapolation of the energy intervals to the Rydberg series limit gives a precise value for the ionization energy for H_2 relative to the lowest triplet bound state, the $c(2p)\,^3\Pi_u$ state, and an improved value for the ionization potential of the H_2 molecule in the ground state. The new value for the ionization potential is in excellent agreement with *ab initio* calculations and confirms the Lamb shift in the ground state of H_2.

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The Rydberg *f* states of H_2 are of particular interest because they exhibit essentially no penetration of the Rydberg electron into the $H_2{}^+$-ion core about which it orbits. The only existing observations are of the $5g$-$4f$ transitions in infrared emission,[1,2] and of several microwave intervals in the $n=10$ manifold.[3] Extensive series of Rydberg *d* states have recently been observed using laser spectroscopy, but a detailed analysis of the energy levels is difficult because of the limited experimental resolution of the pulsed lasers used, and especially because of the effects of perturbations between different Rydberg series.[4,5]

This Letter reports the first observation of an extended series of Rydberg *nf* states in H_2, with principal quantum numbers ranging from $n=10$ to $n=19$. By using two cw dye lasers to excite these levels stepwise from the metastable $c(2p)\,^3\Pi_u$ state, we have been able to determine the $(2p)\,^3\Pi_u \rightarrow (nf)\,^3(\ldots)$ energy intervals to a precision of 0.01 cm^{-1}. Comparisons with *ab initio* calculations of the energy levels allow an accurate extrapolation to the Rydberg series limit. In this manner we have obtained an improved value for the ionization limit of H_2 relative to the metastable $c(2p)\,^3\Pi_u$ state and a new value for the ionization potential relative to the $X(1s\sigma)\,^1\Sigma_g^+$ ground state. This is of particular interest because a new, highly precise calculation of the dissociation energy of H_2, which does not agree well with experiment, can be combined with calculations on the $H_2{}^+$ ion to give a new theoretical value for the ionization potential. In addition, the experimental resolution is sufficient to resolve the natural linewidths of these states due to autoionization, which are typically about 0.3 GHz. The autoionization arises from the weak coupling between the Rydberg electron and the vibrational motion of the $H_2{}^+$ core, which is the $v=1$ vibrational level for all the observed levels. These autoionization rates and a comparison with *ab initio* calculations will be described in a separate publication.

Figure 1 shows a partial energy-level diagram for molecular hydrogen and the transitions used to excite the molecules up into the *nf* triplet Rydberg states. The apparatus[6] was a modification of that used earlier to study the $n=3$ and $n=4$ *s* and *d* triplet levels in H_2. Electron bombardment excited H_2 molecules in a thermal beam into the $2p$ metastable state. An initial excitation from the metastable state to the $3d$ manifold was provided by the output (near 600 nm) from a Coherent 599 dye laser. The output (near 820 nm) of a Coherent 699 ring laser with Styryl 9 dye excited the molecules from the $3d$ manifold into the *nf* Rydberg states. An ultraviolet-sensitive photomultiplier was employed to detect the radiation from the $3d$ state and a Channeltron to detect the electrons emitted when the molecules in the *nf* Rydberg states autoionized.

The measurements were made by setting the CR-599 laser on the $(2p)\,^3\Pi_u \rightarrow (3d)\,^3\Sigma$ transition and

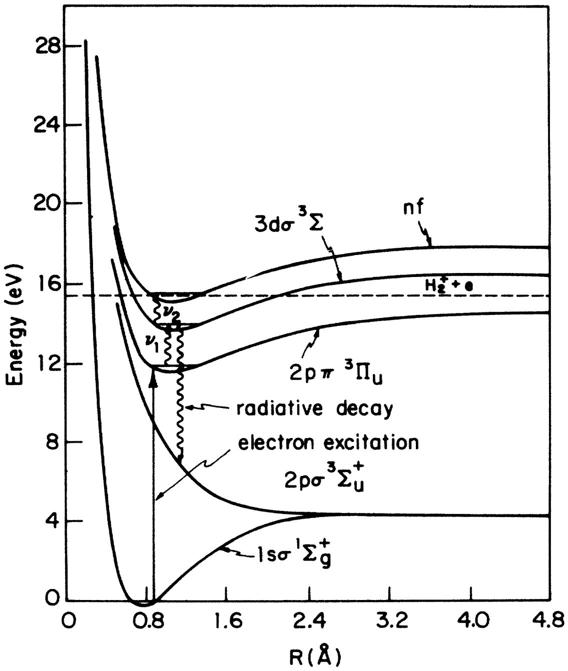

FIG. 1. Energy-level diagram for selected states of molecular hydrogen showing the technique used to excite high-lying *nf* Rydberg states.

scanning the CR-699 laser. The wavelength of the radiation from the CR-699 laser was measured by observing the absorption in a high-temperature iodine cell and using the atlas of iodine lines compiled by Gerstenkorn *et al.*[7] Figure 2 shows a typical scan of the molecular hydrogen and iodine lines for parahydrogen.

For parahydrogen we observed the sequence

$$(2p)\,{}^3\Pi_u, v=1, N=2 \rightarrow (3d)\,{}^3\Sigma, v=1, N=2 \rightarrow (nf)\,{}^3(\;.\;.\;.\;), v=1, R=0, N=3.$$

For orthohydrogen we observed the sequences

$$(2p)\,{}^3\Pi_u, v=1, N=1 \rightarrow (3d)\,{}^3\Sigma, v=1, N=1 \rightarrow (nf)\,{}^3(\;.\;.\;.\;), v=1, R=1, N=2,$$

$$(2p)\,{}^3\Pi_u, v=1, N=1 \rightarrow (3d)\,{}^3\Sigma, v=1, N=1 \rightarrow (nf)\,{}^3(\;.\;.\;.\;), v=1, R=3, N=0\text{–}2.$$

The quantum number R characterizes the rotation of the molecular core; the quantum number N describes the total angular momentum exclusive of spin. In this Letter we report only the measurements of the $(nf)\,{}^3(\;.\;.\;.\;)$ states with $R=0$ and $R=1$.

Table I summarizes the measured intervals for all the transitions to the $(nf)\,{}^3(\;.\;.\;.\;)$, $R=0$, $N=3$ levels observed for parahydrogen. Table II summarizes the measured intervals for all the transitions to the $(nf)\,{}^3(\;.\;.\;.\;)$, $R=1$, $N=2$ states of orthohydrogen. The uncertainty of the measurements is about 0.01 cm^{-1} and is limited by the nonlinearities in the scan, undetected mode hops in the CR-699 ring laser, and asymmetries in the iodine lines.

Tables I and II also show the values for the reciprocal wavelengths of the transitions predicted by an *ab initio* calculation based on the long-range model which takes into account the polarizability and quadrupole moment of the $H_2{}^+$-molecular-ion core. There were two parts to this calculation. For the first part the technique used earlier for the treatment of the $4d$ triplet states of H_2 was employed to calculate the energy levels for each nf triplet Rydberg state. First-order energies were calculated using the explicit formulas in Ref. 6. For the second part, perturbations from both nearby and distant Rydberg states were included using second-order perturbation theory.

The polarizabilities were taken from the calculations of Bishop and Cheung,[8] which appear to be more accurate than those used in Ref. 6. The quadrupole moments were taken from Karl *et al.*[9] Both the polarizabilities and quadrupole moments were interpolated between tabulated internuclear separations using seven-point Lagrange interpolation. The resulting moment functions were integrated between numerically determined $H_2{}^+$ vibrational wave functions, both for diagonal and off-diagonal matrix elements. The accuracy of the resulting averaged constants is estimated to be a few tenths of one percent. The vibrational and rotational energy levels for the $H_2{}^+$ core were taken from the calculations of Bishop and Cheung.[10]

The second-order perturbations were calculated us-

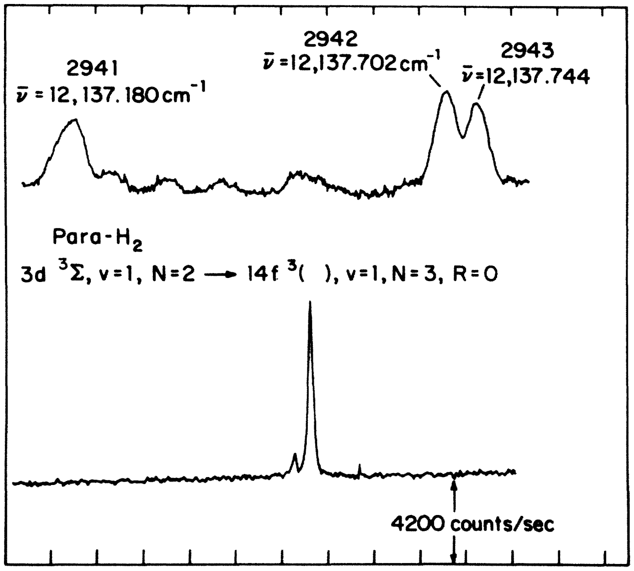

FIG. 2. Typical scan for parahydrogen showing the $(3d)\,{}^3\Sigma \rightarrow (14f)\,{}^3(\;.\;.\;.\;)$ transition (lower trace) and the iodine lines (upper trace) used to measure the reciprocal wavelength of the lines. The four-digit numbers above the iodine lines are the identification numbers from the iodine atlas.

TABLE I. Comparison of the measured and predicted intervals for the $3d\,{}^3\Sigma$, $v=1$, $N=2 \rightarrow nf^3(\;.\;.\;.\;)$, $v=1$, $R=0$, $N=3$ transitions in parahydrogen. The measured intervals were determined through the use of the iodine atlas (Ref. 7) and the uncertainties are estimated to be less than 0.01 cm^{-1}. The $15f$ level was omitted in the calculation of the average difference between experiment and theory.

n	Measured interval (cm^{-1})	Quad.-pol. model (cm^{-1})	Second-order corr. (cm^{-1})	Predicted interval (cm^{-1})	Expt.−theory (cm^{-1})
12	11 935.01	11 934.69	−0.078	11 934.61	0.40
13	12 047.96	12 047.55	0.024	12 047.57	0.39
14	12 137.53	12 137.09	0.057	12 137.15	0.38
15	12 209.51	12 209.32	−0.230	12 209.09	0.42
16	12 268.82	12 268.43	0.015	12 268.45	0.37
17	12 317.84	12 317.42	0.047	12 317.47	0.37
18	12 358.82	12 358.82	−0.001	12 358.47	0.35
Ave.					0.38(2)

TABLE II. Comparison of the measured and predicted intervals for the $3d\,^3\Sigma$, $v=1$, $N=1 \rightarrow nf\,^3(\ldots)$, $v=1$, $R=1$, $N=2$ transitions in orthohydrogen. The measured intervals were determined through the use of the iodine atlas (Ref. 7) and the uncertainties are estimated to be less than 0.01 cm^{-1}. The $13f$ and $15f$ levels were omitted in the calculation of the average difference between experiment and theory.

n	Measured interval (cm^{-1})	Quad.-pol. model (cm^{-1})	Second-order corr. (cm^{-1})	Predicted interval (cm^{-1})	Expt.−theory (cm^{-1})
12	12 016.53	12 016.05	0.067	12 016.12	0.41
13	12 129.70	12 129.13	0.024	12 129.15	0.55
14	12 219.31	12 218.83	0.046	12 218.88	0.43
15	12 291.87	12 291.18	0.366	12 291.55	0.32
16	12 350.84	12 350.38	0.034	12 350.42	0.42
17	12 399.88	12 399.44	−0.001	12 399.44	0.44
18	12 441.01	12 440.55	0.025	12 440.58	0.43
19	12 475.79	12 475.33	0.017	12 475.35	0.44
Ave.					0.43(1)

ing the same scheme as Sturrus, Sobol, and Lundeen.[3] Only perturbations caused by the polarizability and quadrupole interactions were included, and hydrogen-atom energies were used to approximate the electronic energies of the perturbing states. All *np*, *nf*, and *nh* states with $3 \leqslant n \leqslant 25$, $-1 \leqslant \Delta v \leqslant 1$, and $-2 \leqslant \Delta R \leqslant 2$ were included. The hydrogenic approximation is expected to be excellent except for the *np* states, which are known to exhibit significant core interaction. Unfortunately the spectrum of the triplet *np* Rydberg states is very poorly known so that accurate energy levels and phase shifts of the radial electronic wave functions could not be determined. This was the major source of uncertainty in these calculations.

The value for the ionization energy of hydrogen was initially assumed to be 124 417.20 cm^{-1}. This value was determined by Herzberg and Jungen[11] from an analysis of the singlet levels of H_2 and their estimated error was 0.4 cm^{-1}. To calculate the transition intervals the energy levels for the $(2p)\,^3\Pi_u$, $v=1$, $N=2$ state of parahydrogen (97 395.57 cm^{-1}) and the $(2p)\,^3\Pi_u$, $v=1$, $N=1$ state of orthohydrogen (97 280.54 cm^{-1}) were obtained by adding the correction given by Miller and Freund[12] for the position of the triplet levels with respect to the singlet levels (−149.6 cm^{-1}) to the respective values given by Crosswhite[13] (97 545.17 and 97 430.14 cm^{-1}). The interval between the $(2p)\,^3\Pi_u$ levels and the $(3d)\,^3\Sigma$ levels for parahydrogen [16 515.46(1) cm^{-1}] was taken from the measurements of Lichten, Wik, and Miller.[14] We measured the $(2p)\,^3\Pi_u \rightarrow (3d)\,^3\Sigma$ interval for orthohydrogen and obtained 16 603.27(1) cm^{-1}; this agrees well with the value 16 603.24 cm^{-1} given in the Crosswhite compilation. Tables I and II show for each level the results for both parts 1 and 2 of the calculation.

Tables I and II summarize the predicted energy levels and the differences between the measured and experimental values. For those levels where the second-order correction is large, it is due primarily to one close-lying level. For those levels where the calculation can be trusted the differences between the measured and theoretical intervals is consistent with the single value (0.38 ± 0.02) cm^{-1} for parahydrogen and the single value (0.43 ± 0.01) cm^{-1} for orthohydrogen. The near equality of the two average differences indicates that the value used for the ionization potential in the initial calculation is not correct. A similar analysis for the $nf\,^3(\ldots)$, $v=1$, $R=3$, $N=0$–2 levels showed more variation. In all cases there were close-lying perturbing levels which made the predictions unreliable.

These data can be used to determine a more precise value for the ionization potential (IP) of the $(2p)\,^3\Pi_u$ state. The values obtained are

$$\mathrm{IP}((2p)\,^3\Pi_u, v=1, N=1, J=2) = 27\,137.09(2)\ \mathrm{cm}^{-1},$$

$$\mathrm{IP}((2p)\,^3\Pi_u, v=1, N=2, J=3) = 27\,022.01(2)\ \mathrm{cm}^{-1}.$$

By using the accurate $c(2p)\,^3\Pi_u \rightarrow a(2s\sigma)\,^3\Sigma_g$ intervals of Dabrowski and Herzberg[15] these values can be referred to the $N=1$, $v=0$ and $N=2$, $v=0$ levels of the $a(2s\sigma)\,^3\Sigma_g^+$ state. The *a*-state term values can be obtained from Freund *et al.*[16] by using the rotational intervals from Crosswhite's tables.[13] This yields two values for the ionization potential of H_2,

$$\mathrm{IP}((1s\sigma)\,^1\Sigma_g^+) = \begin{cases} 124\,417.53\ \mathrm{cm}^{-1}\ \text{(orthohydrogen)}, \\ 124\,417.50\ \mathrm{cm}^{-1}\ \text{(parahydrogen)}. \end{cases}$$

The average value, 124 417.51 ± 0.22 cm^{-1}, has an uncertainty dominated by the uncertainty in the vacuum-ultraviolet intervals that link all excited states to the ground state. This agrees well with the value 124 417.2(4) determined by Herzberg and Jungen,[11] and with their tentative new value of 124 417.5 cm^{-1}.[17] The discrepancy in the average differences between the measured and calculated values in Tables I and II can be traced to variations in the term table for the $c(2p)\,^3\Pi_u$ state given by Crosswhite which are removed by using the measurements of Dabrowski and Herzberg.

A new theoretical value for the ionization potential can be obtained by combining the precise calculations of Bishop and Cheung[10,18] for the ground state of H_2^+ with the very recent calculation by Kolos, Szalewicz, and Monkhorst[19] of the dissociation energy of H_2. From their results one obtains the value, including relativistic and radiative corrections,

$$\mathrm{IP}((1s\sigma)\,{}^1\Sigma_g^+) = 124\,417.503\ \mathrm{cm}^{-1}.$$

The accuracy appears to be limited mainly by the calculation of the H_2 ground state, and is estimated to be about 0.1 cm^{-1}. This value is in good agreement with the new experimental value. The existence of the Lamb shift for the ground state of H_2, about 0.7 cm^{-1}, is clearly confirmed by these new results. The excellent agreement is particularly interesting in view of the poor agreement of the dissociation energy with experiment.[19]

This preliminary experiment indicates that laser spectroscopy can be used to study in detail the high-lying Rydberg states of the hydrogen molecule. One cannot only measure with precision the positions of the levels but one can also study the decay mechanisms by measuring the natural linewidths. Preliminary studies indicate that the lifetimes of the levels agree with the predictions of a variation of the long-range model used here to calculate the position of the energy levels.

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