Measurement of high Rydberg states and the ionization potential of H_2

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We have measured numerous transitions from the E,F state of H_2 to the singlet np Rydberg states with an accuracy of 0.01 cm^{-1}. The data have been analyzed to obtain values for the ionization potential of H_2 relative to the $v=0$, $N=0$ and 1 levels of the E,F state. By combining these results with previous measurements of the E,F state, a value of 124417.524 ± 0.015 cm^{-1} is obtained for the ionization potential of H_2. This result is in good agreement with previous work but nearly an order of magnitude more accurate, and is very close to the best theoretical value.

As the simplest neutral molecule, H_2 is the system for which fundamental molecular physics can most stringently be tested by the comparison of calculations with experiments and with one another. The accuracy of both theory and experiment for the ground-state energy has improved by more than an order of magnitude in the past twenty years, although the experimental accuracy has fallen somewhat behind.[1-10] It is partially to remedy this situation that we have undertaken a new measurement of the ionization potential.

The theoretical situation has now improved to the point where successive calculations of the adiabatic and nonadiabatic ground-state energies typically differ by 0.01 cm^{-1} or less.[9,10] Since these calculations are so well in hand, the possibility has arisen of making a significant test of the theory of relativistic and radiative corrections. Of the two, the radiative corrections appear to be the more difficult to calculate and are probably of greater physical interest. The ionization potential is determined from the difference between the dissociation energies of H_2 and of H_2^+, so it is the difference between the two radiative corrections that is measured experimentally. This difference is predicted to be 0.378 cm^{-1} (Refs. 7 and 11), which differs by about 0.11 cm^{-1} from the H atom value obtained in the limit of infinite internuclear separation. It follows that the existing agreement of experiment and theory at the level of 0.1 cm^{-1} can be taken as a confirmation of the existence of radiative shifts, but does not test the theory much beyond the level of what can be predicted by counting protons and using H atom values. The situation is somewhat better for measurements of vibrational and rotational spacings within the ground state of the single electron system HD^+, where the agreement of theory and experiment confirms the variation of radiative shifts with internuclear separation, but with deviations between theory and experiment that in some cases approach the size of the small ($\simeq 0.01$ cm^{-1}) radiative shifts.[6,8,12,13]

All experimental determinations of the I.P. of H_2 have been made by Rydberg-series extrapolation, either of the singlet np states[1,3] or of high-l states.[2,4] They are all basically in agreement, although the results for orthohydrogen and parahydrogen differ somewhat in recent measurements by Glab and Hessler made using laser excitation of the np states from the E,F $^1\Sigma_g^+$ state.[3] This paper reports

a new program of measurements of the same series of transitions, using a pulse amplified laser in conjunction with a collimated molecular beam to provide much improved resolution and absolute wavelength accuracy. It is possible to resolve the individual rotational branches of transitions to principal quantum numbers as high as $n=88$, much higher than in previous work. Both the individual transitions and the series limits have been determined with an uncertainty of 0.01 cm^{-1}.

The $v=0$, $N=0$ and 1 levels of the E,F state are excited from the ground state by two-photon transitions. We generate 10-nsec, 50-μJ laser pulses at 202 nm by operating an excimer-pumped dye laser at 606 nm and using frequency doubling in potassium dihydrogen phosphate (KDP) and sum frequency mixing in β-BaB_2O_4.[14] The np Rydberg states are subsequently excited from the E,F state at 397 nm. Since single-mode continuous-wave (cw) dye lasers cannot easily produce this wavelength, we instead operate a cw laser at 794 nm, then pulse amplify and frequency double its output. The resulting 10-nsec pulses have typical energies of 20 μJ and a bandwidth of 0.005 cm^{-1}. The Rydberg states are detected using delayed Stark ionization.

The molecular beam is formed by collimating a supersonic expansion of pure H_2 produced with a pulsed nozzle. The beam passes through two collimating skimmers, giving a residual Doppler width of $\simeq 200$ MHz. The lasers cross the molecular beam 20 cm from the nozzle between two electric-field plates separated by 1 cm. The plates are pulsed with 300 V typically 100–300 nsec after the laser pulses to Stark ionize the Rydberg atoms and collect either ions or electrons. A multiplier tube (EMI 411-1) mounted vertically above the plates detects the charged particles through a mesh-covered hole in the top plate.

The 202-nm pump radiation is focused into the molecular beam using a 50-cm lens. To populate the E,F state efficiently and minimize space charge effects due to the ionization of the H_2 by this light alone, it is necessary to attenuate the pump light to 10 μJ or to defocus the beam slightly. The counterpropagating 397-nm probe radiation is focused with a 50-cm lens. This beam was also defocused slightly to eliminate power broadening of the Rydberg transitions. Most of the data were taken with the probe and pump lasers arriving simultaneously. No measurable shifts were found when the probe was instead

delayed to arrive 10 nsec after the pump.

When ions are detected the double resonance signal is seen as an enhancement over the background ion signal due to the pump beam alone. With electron detection there is essentially no background because the Stark pulse is applied after the 3 eV electrons resulting from photo-ionization by the pump laser have drifted out of the detection area.

A gated integrator is used to acquire the H_2^+ or e^- signal and average it over 10 laser shots. The absorption spectrum of I_2 (at 650°C) and the fringes from a marker interferometer with a free spectral range of 300 MHz are recorded simultaneously to calibrate the data scans. The cw laser power is recorded to normalize the reference data. Data are acquired at 10 to 50 MHz intervals in the scan of the visible dye laser.

Figure 1 shows a scan over the $50p$ transition in orthohydrogen taken while detecting electrons. The narrow 200 MHz linewidth and good signal-to-noise ratio are evident. In orthohydrogen we observed a total of 57 transitions in the $P(1)$, $Q(1)$, and $R(1)$ branches for principal quantum numbers ranging from 41–84. In parahydrogen we observed 20 transitions in the $R(0)$ branch in the range $n = 47$–88.

The transition energies were determined by measuring the separations between the H_2 transitions and I_2 reference lines.[15] Gaussian profiles were fit to the H_2 and I_2 lines. The separation was measured by counting interferometer fringes and using cubic spline interpolation between fringes to correct for laser scan nonlinearities. The uncertainty in measuring the offset from the reference I_2 lines encompasses errors due to the uncertainty in finding the centers of the Doppler-broadened, sometimes asymmetric reference lines (0.003 cm^{-1}), granularity of the data (0.001 cm^{-1}), thermal drift in the reference interferometer (0.0005 cm^{-1}), residual nonlinearity in the laser scan (0.002 cm^{-1}), and possible Doppler shifts arising from nonorthogonality of the laser and molecular beams (0.003 cm^{-1}). All of these are dominated by an overall uncertainty of 0.01 cm^{-1} due to the uncertainty of the absolute I_2 atlas calibration in the 800 nm region.[15]
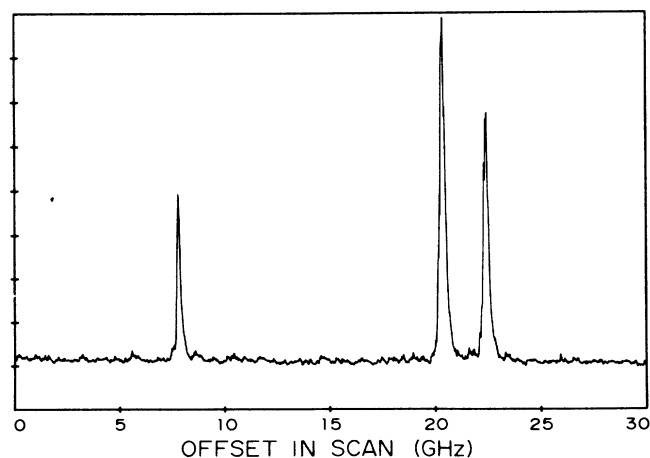
An additional source of experimental error is in the pulsed amplifier, which with high pump powers (50 mJ) can introduce a frequency shift in the laser pulse. To establish an upper limit on this shift we tuned the interferometer between the transmission peaks of the cw and pulse-amplified lasers. We measured the frequency shift to be 8 ± 8 MHz: negligibly small and consistent with zero.

The transitions were assigned by using the best previously available quantum defects and series limits[3,4,7] and calculating the predicted positions of the Rydberg series for each rotational branch. After making numerous assignments in this way we were able to obtain much improved values for the parameters that made the assignment of most of the remaining transitions obvious. Five transitions excited from the $v = 0$, $N = 1$ level near $n = 50$ could not be assigned to the P, Q, or R branches to the np states, and are listed in Table I. Most are quite weak. Their intensities, relative to the main branches, exhibited extreme variation with experimental conditions, suggesting they may be induced by Stark mixing in very small stray fields. No evidence was seen for additional transitions at the highest principal quantum numbers arising from singlet-triplet mixing, although a crude estimate indicates this mixing should become large in orthohydrogen for $n \approx 100$.

After completing the assignments, the series limit of each of the four branches studied was determined using a one- or two-channel quantum defect model. The $P(1)$ $np\Sigma^+$ series and the $Q(1)$ $np\Pi^-$ series are not subject to rotational perturbations and can be fit by a simple Rydberg formula with a constant quantum defect. A least-squares fit to the experimental energies was done for each branch with the series limit and the quantum defect as free parameters.

The analysis of the $R(1)$ series in orthohydrogen and the $R(0)$ series in parahydrogen is more complicated. The $R(0)$ series, which converges to the $N^+ = 0$ level of the ion core, is strongly coupled to the series converging to the $N^+ = 2$ level of the ion core. Similarly, the $R(1)$ series converging to $N^+ = 1$ is coupled to the $N^+ = 3$ series. Two-channel quantum-defect theory describes the behavior of each of these series with only four free parameters: the ionization potentials of the two coupled series, and the quantum defects for the σ and π states.[3,16–18] The rotational intervals in the H_2^+ ion, between $N^+ = 1$ and 3 for orthohydrogen and between $N^+ = 0$ and 2 for parahydrogen, are known to great precision from the calculations of Bishop and Cheung[6] and of Wolniewicz and Poll;[8] the three other parameters were determined by least-squares

FIG. 1. Scan of the $P(1)$, $R(1)$, and $Q(1)$ branches to the $50p$ state.

TABLE I. Unassigned transitions from the $E(v = 0, N = 1)$ state.

n	E (cm^{-1})
47	25 198.20(1)
48	25 200.11(1)
49	25 202.01(1)
50	25 203.80(1)
51	25 205.49(1)

fits to the data. Table II summarizes the results of the fits to the four branches, giving three values for orthohydrogen of the ionization limit from the $v=0$, $N=1$ level of the E,F state to the $v=0$, $N^+ =1$ level of the $X^1\Sigma_g^+$ ground state of H_2^+, and one value for parahydrogen, from $N=0$ to $N^+ =0$. Figure 2 displays the fit residuals.

The relative intensities for the orthohydrogen lines were also calculated approximately by using dipole moments calculated at the internuclear distance $R=2$ a.u. (Ref. 19). The $R(1)$ branch varies considerably in intensity because of the strong interchannel coupling, going through a zero near $n=45$. This intensity variation was seen clearly in the experimental data, though variations caused by changes in laser intensity and by weak predissociation of some of the Rydberg states make quantitative comparison difficult. Similar variations can be seen in earlier measurements at lower principle quantum numbers by Glab and Hessler.[3]

To determine the uncertainty of the ionization limits we must consider both the uncertainty of the transition energies and the possible failure of the two-channel model in extrapolating the Rydberg series. The two principal causes for concern are couplings to additional perturbing states and possible Stark shifts due to stray electric fields. Figure 2 reveals that in the region $n=49$–59 in orthohydrogen, the fit residuals cluster to one side of zero. However, the residuals for all three rotational branches are essentially identical. This does not make sense in the context of a perturbation, since the branches access states that differ both in Λ and in symmetry. A more reasonable explanation can be had by observing that in all cases, the three branches for each principal quantum number were observed in a single scan, and calibrated from a single iodine reference line. Thus, the highly correlated residuals suggest that the calibration is slightly low in this region, perhaps due to a clustering of asymmetric iodine lines. This interpretation is supported by the fact that the $R(0)$ residuals, from data referenced to different iodine lines, show a more random distribution in this region. The estimated uncertainty in measuring the spacing of an H_2 transition from an I_2 peak is 0.005 cm^{-1}, in good agreement with the observed scatter. In sum, there is no indication of deviation from pure two-channel interaction at this resolution.

To test for the presence of stray fields, we applied small dc fields and looked for perturbations of the $59p$ state of orthohydrogen. At 50 mV/cm, we observed additional lines in the spectrum. Without this field we saw no such
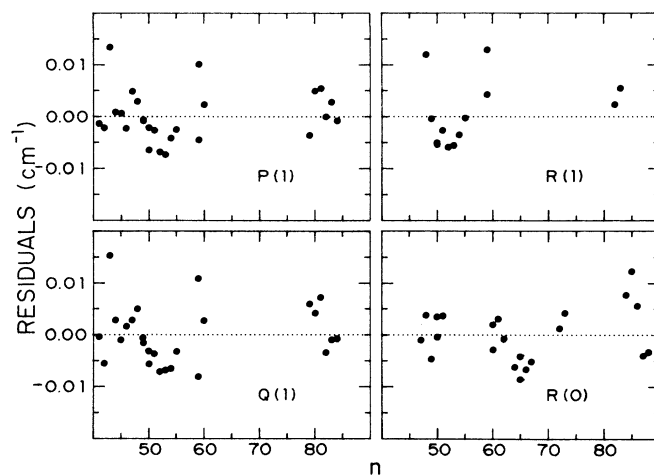

FIG. 2. Residuals from least-squares fits to all identified transitions. Each rotational branch was fit separately.

lines all the way up to $n=84$. By scaling the polarizability as n^7, we establish a limit of 15 mV/cm on stray fields. Assuming such a field and adjusting the data for the Stark shift, the extrapolated series limit does not change. Therefore, the uncertainties in the series limits are dominated entirely by the overall wavelength calibration uncertainty of 0.01 cm^{-1}.

The results of these measurements can be referred to the $v=0$, $N=0$ level of the ground state using the E,F state term energies from Ref. 5, and the H_2^+ rotational interval between $N^+ =0$ and 1 calculated by Bishop and Cheung.[6] A weighted average of the four measurements gives a value of 124417.524 ± 0.015 cm^{-1} for the ionization potential of H_2, which is compared with other recent determinations in Table III. The total uncertainty arises almost entirely from the 0.01 cm^{-1} uncertainties of the E,F state term energies and the 0.01 cm^{-1} uncertainty in the $np \leftarrow E,F$ transitions. Alternately, the data can be interpreted as a set of independent measurements for parahydrogen and orthohydrogen. Comparison of the $N=0$ and $N=1$ results from Table II constitutes a measurement of the difference in the ortho-para splittings between H_2 and H_2^+. The experimental difference of

TABLE II. Experimental quantum defects and series limits for the four Rydberg series, with uncertainties derived from statistical scatter alone.

Branch	Series limit (cm^{-1})	δ_σ	δ_π
$Q(1)$	25 247.526(2)		-0.073
$P(1)$	25 247.531(3)	0.200	
$R(1)$	25 247.543(10)	0.227	-0.072
$R(0)$	25 252.723(3)	0.201	-0.078
Average value for I.P. 124 417.524(4)			

TABLE III. Summary of experimental and theoretical determinations of the ionization potential of H_2, referenced to the $v=0$, $N=0$ ground state.

Herzberg and Jungen[a]	124 417.2(4)
Eyler, Short and Pipkin[b]	124 417.42(15)
Jungen and Herzberg[c]	124 417.5(1)
Glab and Hessler[d]	
parahydrogen	124 417.53(5)
orthohydrogen	124 417.68(5)
Present work	124 417.524(15)
Theory[e]	124 417.501

[a] Reference 18.   [d] References 3 and 5.
[b] References 2 and 5.   [e] Reference 20.
[c] Reference 4.

60.257(9) cm^{-1} is the most accurate direct measurement of the ortho-para splitting made to date and confirms the theoretical value of 60.256 cm^{-1}.[6,10]

By improving the wavelength calibration scheme we soon expect to improve both the present results and those reported in Ref. 5 for the E,F state, probably to the level of 0.003 cm^{-1}. Measurements for the D_2 and hydrogen deuteride (HD) isotopes will also be conducted. The present measurement, together with these expected improvements, will pose a major challenge for molecular theory.

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