High-resolution three-photon spectroscopy and multiphoton interference in molecular hydrogen

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Under favorable circumstances, a pulse-amplified cw dye laser can be used to excite three-photon resonant, four-photon transitions without significant power broadening. We have used this technique to make precise vacuum ultraviolet measurements, and to observe the cancellation of three-photon resonances due to third-harmonic generation at much lower number densities than has previously been possible. Three transitions to the B and C states of molecular hydrogen near 100 000 cm^{-1} have been measured with an accuracy up to 0.04 cm^{-1}, twice that of previous measurements.

Decades after the advent of laser spectroscopy, the most precise measurements of vacuum ultraviolet (vuv) intervals are still, with only a few exceptions, those made by classical instruments such as monochromators.[1-6] The principal obstacle to extending the precision of single-mode lasers to the far ultraviolet has been the fact that the wavelengths cannot be generated directly by narrow-band lasers, so transitions above 25 000 cm^{-1} must be studied by nonlinear techniques. Spectroscopy involving two-photon absorption is a common technique, and, combined with frequency doubling, has pushed the limits of precise spectroscopy above 90 000 cm^{-1}.[2-6] To go much farther into the ultraviolet requires higher-order nonlinear techniques: four-wave mixing or three-photon absorption. While both of these techniques are widely practiced, they have generally used broadband multimode pulsed lasers. Single-mode lasers have been used only a few times for spectroscopy using third-harmonic generation[1] and never, to our knowledge, have been used for three-photon spectroscopy.

We have studied three transitions in molecular hydrogen to test the feasibility of three-photon spectroscopy for precise measurements and to investigate the phenomenology of narrow-band three-photon transitions. This phenomenology includes both conventional power broadening and novel effects not seen in one- or two-photon transitions. The most striking example is the cancellation of a resonant three-photon transition due to interference with third-harmonic generation. When a transition is allowed in both one and three photons, third-harmonic generation and three-photon absorption can interfere destructively, completely cancelling at resonance in an optically thick sample. To the blue of the resonance, the anomalous dispersion of the bulk sample satisfies the phase-matching conditions for third-harmonic generation, and off-resonant absorption of the third-harmonic radiation produces a weak signal with a broad asymmetric profile. This phenomenon has been widely studied in atoms using broadband lasers,[7,8] and has been observed in a few molecules as well,[9-11] but has not previously been investigated at low number densities because very high laser resolution is required. A simple classical treatment of this effect has been devised by Wynne,[12] and an extensive theoretical analysis has been conducted by Payne and Garrett.[13]

We have chosen the hydrogen molecule both for its simplicity and because it has very strong transitions near 100 000 cm^{-1} between the $X\,^1\Sigma_g^+$ ground state and the $B\,^1\Sigma_u^+$ and $C\,^1\Pi_u$ states. The best previous direct measurements of these intervals, accurate to about 0.1 cm^{-1}, were obtained by Dabrowski using traditional vuv single-photon absorption and emission spectroscopy.[14] A more accurate determination of some other vibrational bands of the B state comes from combining recent measurements by Jungen *et al.* of optical intervals among the excited states with a previous two-photon measurement of the $E,F\,^1\Sigma_g^+ \leftarrow X$ interval.[6,15] The three-photon measurements described here are more accurate than the previous vuv work, but are somewhat less accurate than the results given in Ref. 15.

Several characteristics of the B and C states make them attractive candidates for high-resolution three-photon spectroscopy. ac Stark shifts, always a concern in multiphoton spectroscopy, are expected to be small, first because these transitions have large oscillator strengths, requiring less laser intensity to drive the transitions, and second because there are no one-photon resonances from the X, B, or C states near the wavelengths of the three-photon resonances, so only bound states far from resonance and the continuum can contribute to ac Stark shifts. Finally, since the excited states are ionized by a single additional photon, detecting the resonances is easy. Pratt, Dehmer, and Dehmer have studied such transitions with a resolution limited principally by the multimode laser they used, suggesting that very narrow linewidths are possible.[16]

We have measured three transitions: the $R(1)$ branch of the (3-0) band of $B \leftarrow X$ and the $Q(1)$ and $R(1)$ branches of the (2-0) band of $C \leftarrow X$, with an accuracy of 0.04–0.07 cm^{-1}, twice that of previous measurements.[14]

We are able to obtain large signals without significant power broadening or shifting.

By amplifying the output of a cw single-mode ring dye laser in an excimer-pumped three-stage pulsed amplifier (Lambda Physik FL-2003), we generate 10-nsec pulses with energies up to 14 mJ while avoiding the problems of establishing single-mode oscillation in a pulsed oscillator and measuring its wavelength. The bandwidth of the amplified laser is close to the transform limit of approximately 50 MHz. Even so, the amplified pulse can be shifted in frequency as the gain of the amplifier cell changes during the pulse.[17] While we did not study amplification shifts in this measurement, we have looked for such shifts at three different frequencies, setting upper limits no larger than 20 MHz.[6]

The amplified laser light is frequency doubled in potassium dihydrogen phosphate (KDP), giving up to 1 mJ of doubled light per pulse. A black-glass filter selectively passes the doubled light. The absorption of the visible cw laser in a cell of I_2 vapor at room temperature is acquired simultaneously with the H_2 spectrum and is used as a wavelength reference.[18]

In the molecular-beam apparatus, shown in Fig. 1, we focus the doubled laser light onto a supersonic jet of H_2. A barrier plate maintained at -75 to -900 V accelerates the ions through a skimmer into a fast electron multiplier tube. The detector is only sensitive to ions produced in an area approximately equal to the skimmer aperture, so by aligning the nozzle-skimmer axis perpendicular to the laser beam we eliminate the first-order Doppler shifts, and by choosing the size of the skimmer aperture we define the Doppler width of the signal.

A gated integrator selectively detects H_2^+ or H^+ ions, identifying them by time of flight. The signal is then averaged over ten laser shots and acquired by a computer. An 80% reflecting aluminum mirror $M1$ is introduced when a retroreflected laser beam is required. This mirror and lens $L2$ are adjusted until the foci of the two beams overlap. Except where stated otherwise, the data presented here were acquired without the retroreflected beam.

The supersonic expansion from a pulsed nozzle (Lasertechnics LPV) produces a rovibrationally cold collision-free expansion. 99.995% pure H_2 was used, at a backing pressure of 10–40 psi (gauge). The gas pulse lasts approximately 100 μsec. The number density at the interaction region was varied by moving the nozzle and by reducing the voltage driving it. As it was not feasible to measure the number density, the background pressure of the chamber at a pulse rate of 10 Hz was recorded to give relative number densities within a given run. In previous studies, the Lasertechnics valve has been seen to behave like an ideal nozzle with a diameter about 0.2 times the actual diameter, but this should be regarded only as a rough approximation.[19] The number densities we report are calculated assuming such an expansion with complete rotational freezing (i.e., using an adiabatic exponent of $\frac{5}{3}$).[20] These calculated values should be interpreted as upper limits, since our laser is fired early in the gas pulse, when the density has not yet reached its peak value.

To study the dependence of the spectrum on number density, we varied the distance from the nozzle to the interaction region from 2.2 to 9.5 cm, giving number densities of roughly 1×10^{13}–6×10^{11} cm^{-3}, equivalent to cells at 0.3–0.02 μm Hg at 295 K. To vary the number density within a series of scans, the gas flux in the beam could be reduced by more than an order of magnitude by lowering the voltage driving the nozzle. To check for shifts due to laser intensity, the pulse energy of the laser was varied from 50 μJ to 1 mJ, and both 15- and 35-cm lenses were used to focus the laser.

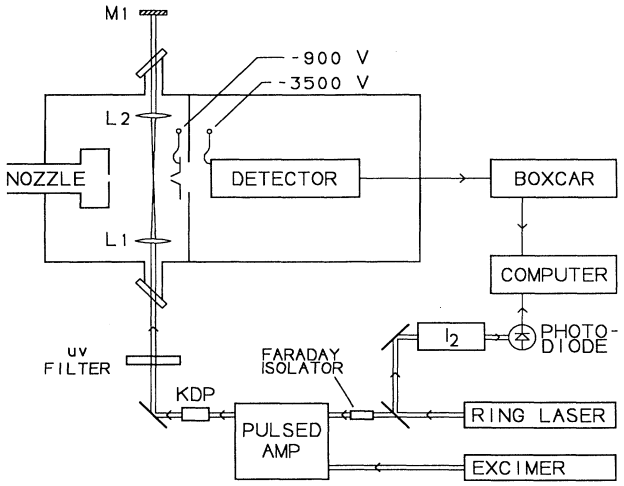

FIG. 1. Apparatus used for three-photon spectroscopy of H_2. Lens $L1$ focuses the frequency-doubled, pulse-amplified laser onto a supersonic expansion of H_2 from the nozzle. Ions are accelerated through the skimmer plate to the detector. Lens $L2$ and mirror $M1$ are introduced when a retroreflected laser beam is required.

Figure 2 shows three scans of the $R(1)$ branch of the $C\leftarrow X$ transition taken at different number densities. Shifting and broadening is evident as the number density of H_2 is increased. At sufficiently low number density we do not see significant variation, but increasing the number density we observe a threshold above which the line

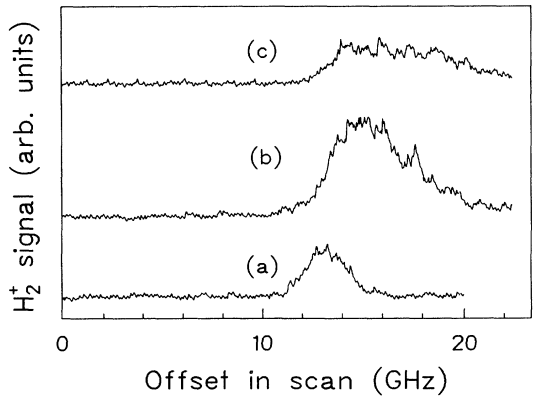

FIG. 2. Shifting and broadening of the $R(1)$ branch of the $C\leftarrow X$ transition with increasing number density ρ (in units of about 10^{11} cm^{-3}): (a) $\rho=3$; (b) $\rho=7$; (c) $\rho=10$. The vertical scale is arbitrary but equal for the three scans.

rapidly shifts and broadens. At the position of the resonance observed at the lowest number density, the signal actually diminishes in size as the number intensity is increased. This effect is also seen in the other transitions, but in $B \leftarrow X$ it is much smaller. The molecular beam is collision free, so this behavior cannot be due to collisional pressure shifts.

The most obvious explanation for this behavior is cancellation of the three-photon signal by third-harmonic generation. This cancellation can occur only if the medium is optically thick at the third-harmonic wavelength, and indeed we see the effect diminish and disappear at sufficiently low number densities. In an optically thick sample, changing the density will affect phase matching for third-harmonic generation, and hence accounts for the shifting and broadening of the observed line.

This explanation is qualitatively reasonable, but a more definite test is also possible. In atomic spectra it has been demonstrated that the three-photon signal reappears at resonance when a counterpropagating laser is introduced. With counterpropagating beams, two excitation routes exist for which third-harmonic generation is forbidden (absorption of two photons propagating in one direction and one in the other), so a strong unshifted transition can be seen.[8,13]

To test for this phenomenon, we retroreflect the laser beam, overlapping the foci of the forward- and backward-propagating beams. This causes a much stronger resonant signal to appear to the red of the previous one, as Fig. 3 shows. This shift is in the same direction as the one observed by reducing the number density. We interpret this behavior as a conclusive sign that the number-density-dependent effects we see are the effect of interference between the resonant three-photon transition and third-harmonic generation in the molecular beam.

A quantitative comparison of the line shape with theoretical treatments is not easily possible, since the experimental parameters are poorly controlled and some of the required molecular properties are not well known. However, the general behavior as the number density is varied is quite similar to previous observations using broadband lasers and much higher number densities, except that here the onset of the effect can be clearly seen. It was previously predicted that with a narrow-band laser, a strong transition, and a reduced Doppler width, this onset should occur at very roughly 10^{12} molecules/cm^3,[13] in good agreement with our observations. One unusual feature of our experiment is that we observe a variation of the threshold number density with laser power. While we did not undertake a systematic study of the interaction between laser intensity and number density, we did observe that the threshold number density decreases substantially as the laser intensity increases. This has not been reported previously, and we have no simple explanation. Since our cooled supersonic beam is nearly collisionless, the collective collisional mechanism used recently to explain similar behavior at very high pressures is probably not applicable.[21]

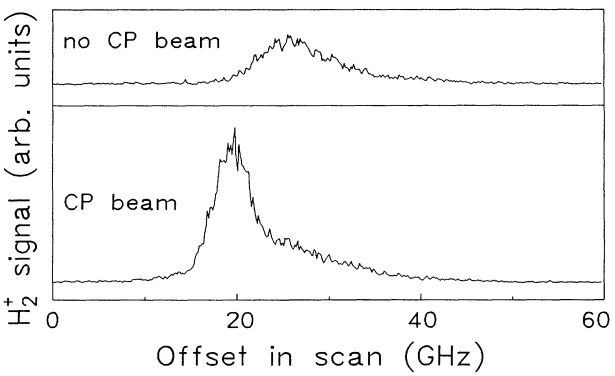

FIG. 3. Appearance of a strong narrow peak in the $R(1)$ branch of the $C \leftarrow X$ transition with the introduction of a counterpropagating (CP) laser beam. The vertical scale on the upper trace has been expanded to make the blue tails on the two traces match.

After moving to a very-low-density region 9.5 cm from the pulsed nozzle, we saw no measurable changes to the positions or widths of the $Q(1)$ and $R(1)$ branches of the $C \leftarrow X$ transition when the number density was further reduced by a factor of 5. Under these conditions, the number density of the interaction region was of the order of 1×10^{11} cm^{-3}, equivalent to that of a cell at approximately 0.004 μm Hg. Reducing the laser intensity to around 6×10^9 W/cm^2 (600 μJ focused with a 35-cm lens) to minimize the ac Stark shift, we obtained conditions under which the line position and width varied only slightly with intensity, allowing us to extrapolate with confidence to both the zero-power and zero-number-density limits. The linewidths of the lowest-intensity data were around 500 MHz, consistent with our estimate of the residual Doppler width defined by the skimmer aperture. The results of the extrapolations are given in Table I. We estimate the uncertainty of the extrapolation as the difference between the lowest power and number-density datum and the extrapolated value. Linear and quadratic extrapolations were consistent with one another within this uncertainty. The results are also consistent with the less-accurate measurements of Dabrowski.[14]

Thus, it is possible to excite transitions in the region of 100 000 cm^{-1} or higher in three photons and retain spectroscopic accuracy superior to that attainable with monochromators. Cancellation of the resonance due to interference with third-harmonic generation has been observed at number densities much lower than in previous work, and the threshold for the onset of this interference is seen to depend on the laser intensity, an effect not hitherto reported. It is possible to avoid the cancellation, but

TABLE I. Measured three-photon transition energies in H_2. Numbers in parentheses in the Energy column represent uncertainties.

Transition	Energy (cm^{-1})
$B \leftarrow X(3\text{-}0)R(1)$	94 032.77(7)
$C \leftarrow X(2\text{-}0)Q(1)$	103 509.38(5)
$C \leftarrow X(2\text{-}0)R(1)$	103 619.99(4)

this requires working at extremely low number density or adding a retroreflected beam, which limits the usefulness of this technique for experiments that require large signals, such as double-resonance spectroscopy. In the future, we plan to study three-photon transitions to the nf Rydberg states. These transitions are forbidden in one photon, so third-harmonic generation cannot occur, and narrow symmetric line shapes should be more easily attainable.

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