

EXCITATION OF H₂ USING CONTINUOUSLY TUNABLE COHERENT XUV RADIATION (97.3–102.3 nm)

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Broadly tunable XUV radiation from 97.3 to 102.3 nm has been generated by frequency tripling the second-harmonic output of a Nd:YAG-pumped dye laser in a pulsed argon source. About 7×10^9 photons per shot in a 1.7 cm^{-1} bandwidth are produced, corresponding to a conversion efficiency of $\approx 10^{-6}$. Four bands of the Lyman system and two bands of the Werner system of molecular hydrogen were excited. Detection of H₂ densities of $\approx 2 \times 10^8$ molecules/cm³ in a (*w*, *J*) level was accomplished using laser-induced fluorescence.

1. Introduction

Since the demonstration by Franken et al. [1] of frequency upconversion in a non-linear medium, numerous non-linear techniques have been described that seek to generate coherent radiation in the VUV and below the lithium fluoride cutoff (104 nm), in the XUV [2–6]. In spite of the impressive results reported to date, the lack of extensive tunability and the complexity of the laser schemes used have hindered wide application of VUV and XUV sources to studies of chemical physics. Recently Kung [7] and Bokor et al. [8] have reported relatively simple arrangements for generating VUV and XUV radiation using a pulsed jet source as the non-linear medium. Kung has frequency tripled 355 nm light in Xe, producing 4.7×10^{11} photons per shot at 118.2 nm, while Bokor et al. generated the third and higher odd-order harmonics of a picosecond excimer laser (KrF) to achieve coherent XUV radiation. In this letter we report an extension of this technique to the generation of continuously tunable XUV, which has enabled us to detect H₂ in a quantum-state-specific manner via excitation of Lyman and Werner transitions, with a detection limit of $\approx 2 \times 10^8$ molecules/

cm³. Our scheme involves frequency tripling the second harmonic of a dye laser in argon gas, which is injected via a pulsed valve.

2. Experimental

Fig. 1 displays a schematic drawing of the apparatus. A frequency-doubled Nd:YAG-pumped dye laser (Quanta-Ray, DCR-1A/PDL/WEX system) operated at 10 Hz is focused onto the non-linear medium with a fused silica lens (20 cm focal length) held on an XYZ translation stage. Between 3 and 14 mJ of UV energy are obtained in a ≈ 4 ns pulse, over the range 307–292 nm, which is covered in two stages using rhodamine 640 and kiton red dyes (Exciton). The gaseous non-linear medium is admitted through a piezoelectrically driven valve (Lasertechnics model LPV) opened synchronously with the firing of the laser by a 200 μ s, 100 V driver pulse. In general, for third-harmonic generation, this is operated as a pulsed free jet whereby the laser is focused as close as possible (≈ 0.2 mm) to the 1.0 mm nozzle. As has been shown by Kung [7] this scheme permits frequency tripling for both positively and negatively dispersive media. A number of

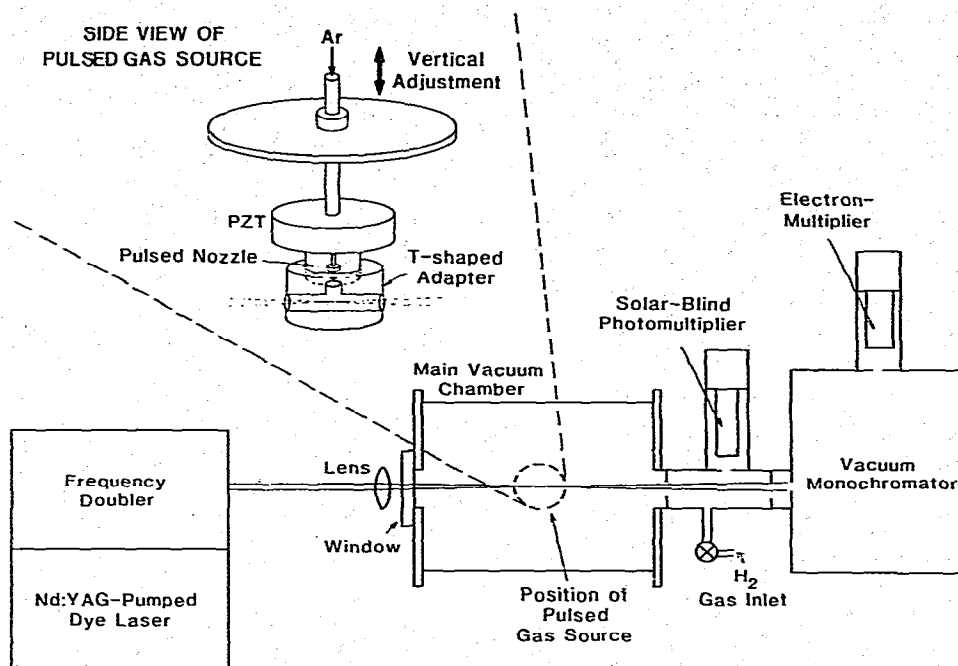


Fig. 1. Experimental apparatus.

gases have been employed by us, including Ar, Kr, Ne, Xe and H_2 . Of these, Ar yields the highest conversion efficiency in this region by more than an order of magnitude. Since Ar is negatively dispersive over the range 96.9–104.7 nm [9], we have modified the simple nozzle geometry to produce a more extensive interaction region. This has been accomplished by addition of a T-shaped adapter machined from a Teflon block which fits over the nozzle source and directs gas into a 0.3 mm diameter, 30 mm long tube (see inset in fig. 1). For Ar this produces an increase of ≈ 3.5 in the conversion efficiency and substantially relaxes alignment constraints. Here the laser beam is focused within the open adapter tube, passing axially through it. We note that positively dispersive media might produce less conversion for this case. The T-shaped adapter and Ar gas were employed in obtaining all results reported here.

The pulsed valve assembly is mounted on a vacuum chamber, 35 cm long, 24 cm diameter, fitted with an ionization gauge for pressure measurements. The chamber is exhausted by a liquid-nitrogen-trapped 6" diffusion pump (NRC model 184). For a typical reservoir pressure of 5 atm, the arrangement gives pressures

of 5×10^{-5} Torr with the valve operating at 10 Hz. When not pulsing, the pressure is 1×10^{-5} Torr due to a continuous leak through the valve which is present at optimum throughput conditions. The pressure is less than 10^{-6} Torr when the nozzle reservoir is evacuated. Ultimate optimization of the gas source is facilitated by raising and lowering the entire source assembly with respect to the laser beam axis.

The third-harmonic XUV radiation is detected by an electron multiplier (EMI model D233) mounted at the exit of a 0.3 m vacuum monochromator (McPherson model 218). An additional liquid-nitrogen-trapped 2" diffusion pump (NRC model 189) serves to maintain a vacuum of less than 10^{-5} Torr in the monochromator at all times.

Absorption of the XUV radiation by molecular hydrogen is observed by adding H_2 to the main chamber via a variable leak valve (Granville-Phillips model 203-015). Fluorescence excitation from H_2 is detected by a solar-blind photomultiplier (EMI model G26L315) which is sensitive to radiation in the range 115–180 nm. The photomultiplier is mounted at right angles to the laser beam on a 10 cm diameter, 15 cm long tube which runs between the main chamber and the mono-

chromator entrance slits (see fig. 1).

A boxcar integrator (PARC model 162/165) is utilized to process the fluorescence signals and the XUV power. These are displayed on a dual pen recorder (Gould model 2200). A 1 GHz oscilloscope (Tektronix model 7104) is employed to monitor the signals in real time and to preamplify the output of the photomultiplier.

All gases are of research purity ($>99.99\%$) and are used without further purification.

3. Results

3.1. Characterization of the XUV source

Using the pulsed source described above with a reservoir pressure of 5 atm, we find efficient third-harmonic generation between 97.3 and 102.3 nm. This corresponds to the full tuning range accessible with the two dyes employed and does not reflect limitations of the scheme. Without correcting for the (unknown) spectral response of the monochromator/electron multiplier detection system, we find for constant incident power that the conversion efficiency is roughly constant from 100 to 102.3 nm, but falls by a factor ≈ 3 in going from 100 to 97.3 nm. Studies of the power dependence of the conversion efficiency reveal that the XUV radiation increases with the cube of the incident laser power, within experimental uncertainties.

We have used this laser-generated XUV radiation to excite the Lyman, $B^1\Sigma_u^+ - X^1\Sigma_g^+$, and Werner, $C^1\Pi_u - X^1\Sigma_g^+$, systems of H_2 . Our main objective in these studies has been to assess the value of the system described as a sensitive quantum-state-specific detector of H_2 . However we have also used this excitation to determine two important parameters of the XUV source, namely, the spectral bandwidth and the number of photons generated per laser shot.

The bandwidth of the XUV radiation is readily extracted from the linewidths of individual Lyman and Werner transitions. We measure these linewidths to be 1.9 cm^{-1} (fwhm) at $\approx 100000 \text{ cm}^{-1}$. The Doppler width of H_2 at 300 K is 0.88 cm^{-1} , from which we infer a bandwidth of $\approx 1.7 \text{ cm}^{-1}$ (fwhm) in the XUV. Since the XUV bandwidth in third-harmonic generation is $3^{1/2}$ times larger than that of the incident laser [10], the bandwidth can be narrowed significantly, if

desired, by inserting intracavity etalon(s) into the dye laser oscillator.

An estimate of the number of XUV photons produced by each laser shot is obtained by careful extrapolation of the fluorescence signals detected by the solar-blind photomultiplier tube. Tuning the laser to the R(1) line of the (7,0) Lyman band and setting the pressure of H_2 gas to produce 15% absorption over the 38 cm path length between the nozzle and the monochromator gave a $400 \mu\text{A}$, 30 ns (fwhm) output pulse. Using our knowledge of the collection geometry (2.5 cm observation length at a solid angle of 0.029 sr), the factory calibration for the photomultiplier gain (1×10^6 at 2436 V) and spectral sensitivity curve, together with the published Franck-Condon factors [11,12], we estimate that the average number of photons produced per laser shot is $\approx 7 \times 10^9$, to within a factor 2, corresponding to a conversion efficiency of $\approx 8 \times 10^{-7}$ at 101.34 nm.

3.2. Excitation and detection of H_2

The upper trace in fig. 2 shows the absorption spectrum in the region of the (7,0) Lyman band of H_2 taken at $\approx 5 \times 10^{-5}$ Torr, obtained with the tunable source described in section 3.1. Assignment of the absorption peaks is based on work reported by Dabrowski and Herzberg [13]. The background signal, which corresponds to the unattenuated XUV radiation, serves to illustrate the general flatness of the XUV power curve in this region of the spectrum. The lower trace in fig. 2 depicts the fluorescence excitation spectrum of H_2 in the same region. Although the pressure of H_2 used in this case was only 4×10^{-6} Torr, the signal-to-noise ratio is clearly superior to that of the absorption spectrum. From here on, all reported measurements refer to this laser-induced fluorescence (LIF) technique.

We find that it is sufficient to use one dye (rhodamine 640) to record the entire branch structure of a number of bands. Fig. 3 shows the fluorescence excitation spectrum from 100.8 to 101.3 nm of the H_2 C-X (0,0) band at room temperature. The P-, Q- and R-branch transitions are clearly evident. Superimposed in this region are the P(3) and P(4) transitions of the B-X (8,0) band, which are also observed in this experiment. It should be pointed out that, at room temperature (293 K), population in the $v'' = 0, J'' = 4$ level is 0.38% of the total population. Observation of transi-

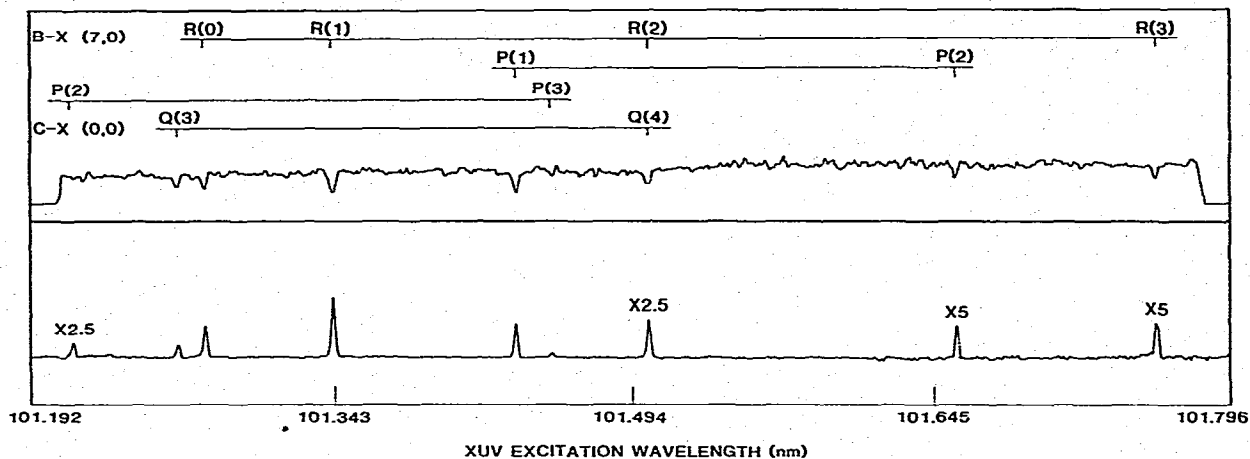


Fig. 2. H_2 absorption (upper trace, 5×10^{-5} Torr) and fluorescence excitation (lower trace, 4×10^{-6} Torr) spectra in the region 101.2–101.8 nm.

tions originating from this level therefore implies with the present apparatus a detection sensitivity of $\approx 2 \times 10^8$ molecules/cm³ in this (v'' , J'') level. Table 1 summarizes the transitions of H_2 that were observed using the two dyes rhodamine 640 and kition red. Note that these represent the strongest bands of the Lyman and Werner systems.

4. Discussion

4.1. Conversion efficiency

Miles and Harris [14] have discussed the conversion efficiency, P_3/P_1 , for third-harmonic generation in an isotropic medium, where P_3 and P_1 are the generated and incident powers, respectively. In general, the conversion efficiency depends on the density N (cm⁻³), the third-order susceptibility $\chi^{(3)}(\omega_3)$ in esu at the frequency $\omega_3 = 6\pi c/\lambda_1$ where λ_1 is the wavelength (cm) of the fundamental, the incident power, P_1 , in W, and a dimensionless phase mismatch integral that accounts for the effects of focusing and dispersion. When the confocal parameter is much larger than the interaction length, then it can be shown that the maximum conversion efficiency is given by [9, 14]

$$P_3/P_1 = (8.323 \times 10^{-3}/\lambda_1^2)(NL_c)^2 \chi^{(3)}(\omega_3)^2 (P_1/A)^2, \quad (1)$$

where A is the area (cm²) of the focused beam and L_c is the coherence length (cm) defined in terms of the wavevector mismatch Δk by

$$L_c = \pi/\Delta k = \lambda_1/6(n_3 - n_1). \quad (2)$$

Here n_3 and n_1 are the refractive indices of the medium at the generated and incident wavelengths.

We measure P_1 to be 2.3×10^6 W and A to be 2.5×10^{-5} cm². Using for NL_c the calculated value

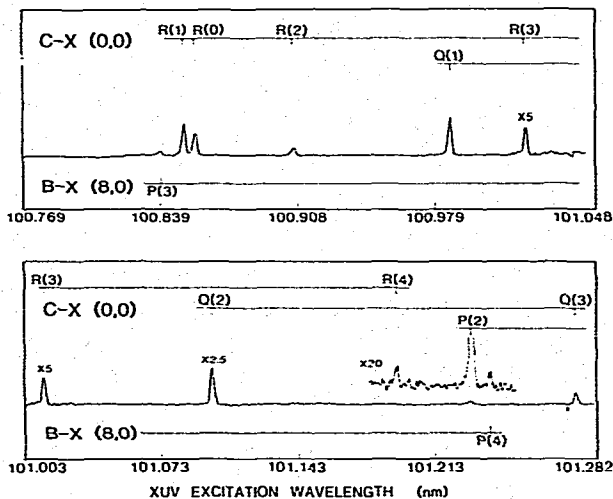


Fig. 3. Fluorescence excitation spectrum of room-temperature H_2 at 4×10^{-6} Torr in the region 100.8–101.3 nm.

Table 1
Observed H₂ line positions (cm⁻¹) a)

J''	B ¹ Σ _u ⁺ -X ¹ Σ _g ⁺								
	(7,0)		(8,0)		(9,0)		(10,0)		
	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	
0		98734.03					100868.11 c)		101890.99
1	98586.84	674.39	99670.64		100723.88		804.25 c)	101746.15	825.74
2	379.53	524.36 c)	463.23	99602.72	515.00		649.29	536.65	667.88
3	086.70	287.08	167.78	362.30			404.08		
4			98788.76						

J''	C ¹ H _u -X ¹ Σ _g ⁺					
	(0,0)			(1,0)		
	P(J)	Q(J)	R(J)	P(J)	Q(J)	R(J)
0			99151.92			101457.75 b)
1		99032.22	156.94		101337.83	455.79 b)
2	98797.36	98917.78	105.04		216.81	394.63
3	569.86	747.82	98996.94		037.93	271.00
4		524.12 c)	832.08		100804.64 c)	

a) Values taken from Drabrowski and Herzberg [13]. b) Not truly resolved. c) Blended.

[9] of 3.14×10^{17} cm⁻² and estimating for $\chi^{(3)}(\omega_3)$ in argon at 101.3 nm the value of 2×10^{-35} esu, eq. (1) yields a maximum conversion efficiency of 3×10^{-6} . With our input power, this corresponds to a maximum of 1.2×10^{10} XUV photons per laser pulse. This should be compared to the experimentally determined estimate of 7×10^9 photons. We conclude that close to the maximum conversion efficiency has been achieved for the conditions of this experiment. This conversion efficiency is limited at the present by the UV power available, the quality of the UV beam, and the physical constraint of having a focal length of 20 cm because of the dimensions of the current vacuum chamber. It is by no means the theoretical limit for this third-harmonic generation process. For example, phase matching under tight focusing is expected to increase markedly the conversion efficiency compared to the plane-wave limit.

4.2. LIF detection of H₂

It is evident that the simple scheme described here can generate broadly tunable, narrow-band radiation

below 104 nm without the need for extensive differential pumping. Furthermore, we have demonstrated that this radiation can be used to detect sensitively the population in individual quantum states of H₂. The present LIF detection limit of $\approx 2 \times 10^8$ molecules/cm³ in a (ν'' , J'') level is restricted by interference from scattered light which prevents us from operating the solar-blind photomultiplier at higher gain. With the use of more extensive baffling we estimate that the detection of H₂ densities as low as 10^7 molecules/cm³ might be achieved with the present straightforward detection electronics. Further improvements could be readily realized by increasing the conversion efficiency through the use of higher UV power and tighter focusing.

To deduce relative populations for individual quantum levels from LIF signals requires consideration of a number of factors. These include transition line strengths, polarization and power saturation effects and the detection response as a function of emission wavelength. Nevertheless, a simple preliminary analysis of the line intensities of the B-X (7,0) band shows that the rotational populations follow the expected Boltzmann dis-

tribution for room-temperature H_2 . This result encourages us to believe that the present technique can be widely applied to follow the internal-state population distributions of H_2 in a large number of interesting studies.

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