

Resonant Ionization Spectroscopy in the XUV Spectral Region

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Abstract. An XUV-laser source, tunable in the range 54-100 nm, is designed for on-line resonant ionization detection of atomic and molecular species at low densities. The system is used for sensitive detection of He and Ne atoms, and H₂, F₂, N₂ and CO molecules.

Laser ionization of atoms and molecules in the gasphase is usually achieved by using lasers in the visible and uv-regions of the spectrum. The discovery of new non-linear crystalline materials extended the available domain in which powerful UV-pulses (of over 1 mJ) are available for multi-photon RIS-studies towards 200 nm. Species with low ionization thresholds and suitable intermediate states may be sensitively detected, particularly when a 1+1 resonance enhanced multi-photon (REMPI) scheme is applicable, such as for the NO molecule. In less favorable examples more photons are required in m+n REMPI-schemes. An alternative approach is to generate extreme ultraviolet (XUV) radiation, that is incorporated in a sensitive 1 XUV + 1 UV REMPI scheme. Particularly for the resonant excitation of small atoms and molecules wavelengths in the windowless regime are suitable. In the following paragraphs we first discuss some aspects of the generation of XUV-light; then the tunable XUV-laser source in the set-up for RIS-studies is described; finally some applications of the XUV-laser used for the resonance excitation of atoms and sensitive state-selective detection of molecules are presented.

On the production of XUV-light

Throughout the years a number of techniques have been explored for the production of electromagnetic radiation in the extreme ultraviolet, which is commonly defined as the range below the lithium-fluoride cutoff at $\lambda=105$ nm. In the past the Hopfield continuum in the 60-100 nm region, obtained from a discharge in helium, was developed into a widely used spectroscopic light source. At present synchrotron radiation sources, that appeared as a by-product of accelerator technology, are in use at various places in the world for studies in atomic and molecular spectroscopy in the VUV, XUV, röntgen and X-ray domain. Although the resolving power is generally limited, sub-cm⁻¹ resolution has been reported in XUV-spectroscopic studies at synchrotrons [1]. Lasers have been employed for the generation of XUV-light through different methods. True XUV-lasers, in which stimulated emission is amplified from a population inversion on an atomic transition, have been devised [2], but these lasers operate at fixed wavelengths. Broadband XUV-radiation is generated by focussing high-power pulsed lasers on to solid targets. A review on these laser induced plasma sources and their use for XUV-spectroscopy was given by Costello et al. [3]. The classical discharge source, synchrotrons and laser induced plasma sources are useful tools for spectroscopic studies in the XUV-domain. In their application these techniques have in common that the resolving power is determined by a secondary dispersive element.

In contrast, in nonlinear upconversion processes short wavelength radiation is produced with coherence properties that depend on the characteristics of the incoming fields. Since optical third harmonic generation in gases was first demonstrated [4] a great number of studies have been performed on the characterization of nonlinear wave-mixing processes and the optimization for the generation of coherent XUV-light. Here we recall that the intensity $I_{n\omega}$ obtained in an harmonic conversion process is proportional to:

$$I_{n\omega} \propto I_{\omega}^n N^2 |\chi^{(n)}(n\omega)|^2 F(L, b, f, \Delta k)$$

where I_ω is the intensity of the fundamental and N the density of the medium. The so-called phase-matching function $F(L,b,f,\Delta k)$ is dependent on the focussing conditions of the incident laser beam (length of medium L , the confocal parameter b , focal length f and the exact location of the focus with respect to L) and the dispersion Δk of the medium. The conversion efficiency is dependent on the nonlinear susceptibility:

$$\chi^{(n)}(n\omega) \propto \rho_{\text{states}} \sum_{i,j,k,m} \frac{\langle i|\mu|j\rangle \langle j|\mu|k\rangle \langle k|\mu|m\rangle \langle m|\mu|i\rangle}{(\omega - \Omega_{ij} - i\Gamma_j)(2\omega - \Omega_{jk} - i\Gamma_k)(3\omega - \Omega_{km} - i\Gamma_m)}$$

where Ω represent quantized transitions in the medium, Γ the damping coefficients of excited states and $\langle i|\mu|j\rangle$ transition dipole matrix elements. The summation is over all quantum states of the atoms/molecules in the medium and ρ the relative density of populated states. Similar equations may be given for wave-mixing processes involving multiple incident frequencies. The resonance denominators allow for the possibility of resonance enhancement and this phenomenon is often used in two-photon resonance enhanced sumfrequency mixing processes for the efficient generation of XUV [5]. These resonant processes have the advantage of relatively high conversion efficiencies ($\eta \sim 10^{-4}$) and rather flat XUV-tunability curves. Straightforward harmonic generation has the advantage that only a single tunable laser is required.

In sumfrequency mixing as well as harmonic generation usually noble gases are used as nonlinear media. In a series of experiments we have investigated third harmonic generation in molecular media. Resulting tripling efficiencies in the range 97.3-99.7 nm, obtained by scanning a frequency doubled dye laser through a single dye gain curve, are displayed in Fig. 1. A quantitative analysis of the tripling curves would involve a detailed knowledge of the spectroscopy and the dispersion characteristics of the media. The XUV-intensity will be strongly influenced by processes of molecular photodissociation, ionization and absorption at all harmonics in the focal interaction zone. Moreover the formation of clusters as well as the population distribution over the states will vary in a complicated way over the interaction zone in case of molecular beam expansions. Also at high incident laser intensities saturation of some of the processes mentioned will play a role. These processes determine the non-linear susceptibility as well as the phase-matching function and make a simulation of the XUV-yield in molecular media an entangled problem.

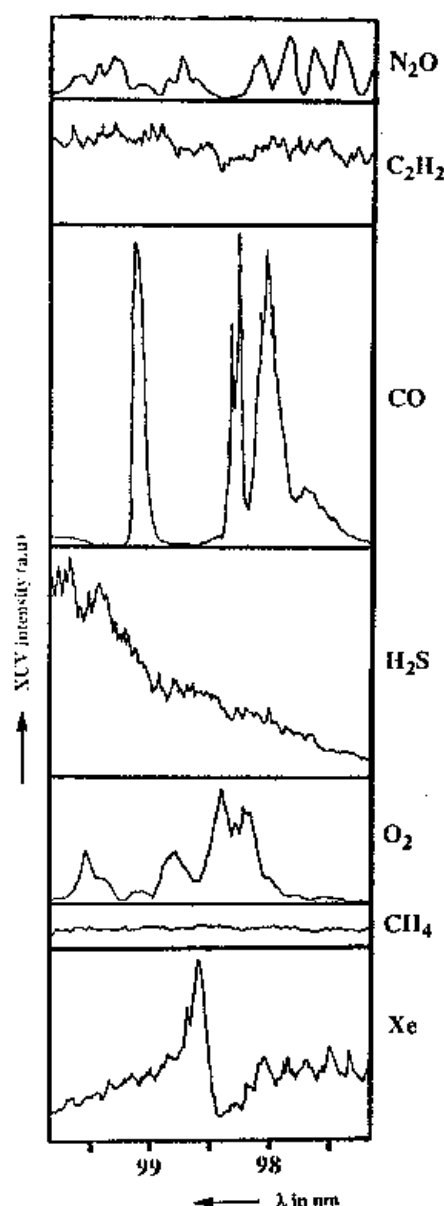


Fig. 1: Efficiency curves for third harmonic generation using various gases as nonlinear medium in a pulsed gas jet; XUV intensities given on the same relative vertical scales. Experimental conditions: focal length $f=15$ cm, confocal parameter $b=8$ mm, nozzle diameter $L=1$ mm, backing pressures of approx. 3 Bar. Laser pulses 10 mJ/pulse at the UV-fundamental in 5 ns pulses. The wavelength range corresponds to the gain curve of a Nd-YAG pumped frequency doubled dye laser operating on Rhodamine 610.

EXPERIMENTAL SETUP

The experimental configuration of the XUV-laser source is schematically shown in Fig. 2. From a laser setup we obtain tunable UV-pulses in the wavelength range 210-300 nm. XUV-light in the range 70-100 nm is then produced by third harmonic generation in pulsed gas jets [7] that are produced by a home-built piezo-electrically tuned valve. Absolute XUV-intensities can only be roughly estimated at 10^{10} photons/pulse in the range 90-100 nm and much lower at shorter wavelengths. The range 54-60 nm is reached by fifth harmonic generation, after frequency doubling of red/yellow dye lasers, with intensities on the order of 10^4 photons/pulse. Our XUV-laser spectrometer is designed to be used on-line for RIS-studies. In between the XUV-production zone and an XUV/UV separation monochromator, the overlapping light beams diverge into an interaction zone (0.1 cm^3), where they are crossed perpendicularly with a atomic/molecular beam. Via 1 XUV + 1 UV two-photon ionization probe particles are resonantly ionized, thus providing a sensitive detection scheme.

Most of the measurements were performed using a commercial grating based pulsed dye laser (Quanta-Ray PDL-3). The bandwidth of the XUV-source is directly related to the width of this system and is in the range $0.2\text{-}0.4 \text{ cm}^{-1}$, depending on specific wavelength and pumping rate of the dye laser [6]. Recently we have constructed a laser based on the principle of pulsed-dye-amplification, starting from a narrowband continuous wave ring dye laser pumped by an argon-ion laser. Our design of a PDA-laser differs somewhat from other setups [8], in that the amplification stages are separated by more than the length corresponding to the pulse duration of the pump laser. By this method and using a powerful Nd-YAG-laser ($>600 \text{ mJ/pulse}$ at 532 nm) tunable UV-pulses of 70 mJ/pulse were produced with a bandwidth a factor of 20 narrower than the grating based pulsed dye laser. Third and fifth harmonics were generated while using this system. A disadvantage is its limited continuous tunability (1 cm^{-1} in the visible).

APPLICATION TO RIS-STUDIES

In this paragraph some applications of the XUV-laser will be given in resonant ionization studies of atoms and molecules. In all experiments the particle density in the skimmed beam at the location of the interaction zone is below 10^{11} cm^{-3} . In view of the large signal-to-noise ratios obtained it is inferred that the detection efficiency of 1 XUV + 1 UV ionization schemes may well compete with the most efficient REMPI schemes. Sensitive detection schemes for RIS-probing of various species by means of an XUV-laser have been listed in Table I.

For molecular fluorine a detection limit of 5×10^7 molecules per cm^3 was determined for resonance ionization via a $C^1\Sigma^+$ valence state reached at 96.1 nm [9]. This value was obtained under conditions that were not fully optimized for noise reduction and UV intensities of 20 mJ/pulse ; we expect under optimized conditions an order of magnitude lower detection limit. An interesting observation is that 1 XUV + 1 UV ionization is markedly different from 3+1 REMPI, where the same excited quantum states may be probed. In 3+1 REMPI only Rydberg states are observed [10], while in 1+1 both Rydberg and valence states are observed. The mechanisms causing this discrepancy have not been fully clarified yet.

TABLE I: Efficient Resonance Ionization Schemes for 1 XUV + 1 UV photoionization

Species	Intermediate state	Excitation wavelength (In nm)
H ₂ , D ₂	B ¹ Σ _u ⁺ , v=8-10	95-98
N ₂	c ₄ ¹ Σ _u ⁺ , v=0	95.8
F ₂	C ¹ Σ _u ⁺ , v=n+26	96.1
HF, DF	C ¹ Π, v=0	95.1 and 95.0
CO	L ¹ Π, v=0	96.8
Ne	3s and 3s'	74.5 and 73.5
He	1s2p ¹ P	58.4

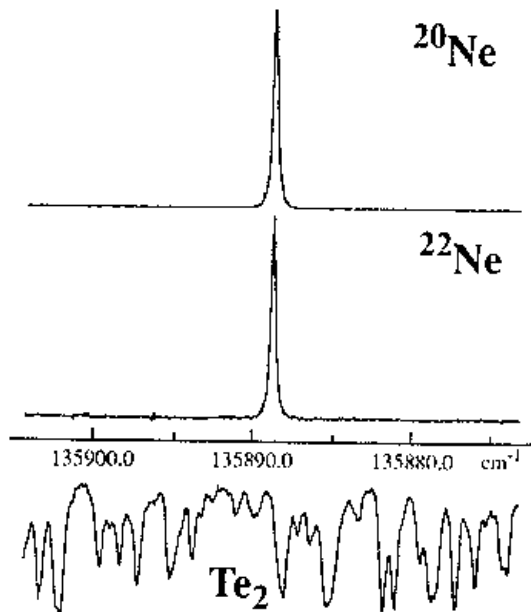


Fig. 3: Recording of the $2p^6-2p^5 3s'[1/2]_1$ transition in neon at 73.6 nm. Spectra for ^{20}Ne and ^{22}Ne were obtained simultaneously in a single wavelength scan with two gated integrators set at different ion masses. The spectra were recorded at a pressure in the interaction zone of 3×10^{-7} mbar from a natural isotopic sample (90% ^{20}Ne and 10% ^{22}Ne). The Te_2 spectrum, recorded at the fundamental wavelength (442 nm), is used for absolute frequency calibration.

The wavelength range 70-90 nm can in principle be covered by frequency tripling of frequency doubled blue dye lasers. As the UV-output of Nd-YAG lasers, required for pumping of blue dyes, is lower than the green output, and the blue dyes are less efficient than Rhodamine dyes, the tunable UV intensities are limited to 6-7 mJ/pulse. Hence the generated XUV will be less intense than in the range 90-100 nm. However, xenon and krypton have strong two-photon resonances to be used for resonance enhanced third harmonic generation in this range. Particularly the $6p'[1/2]_0$ state in xenon gives a large third harmonic yield. At the wavelength position of the $2p^6-2p^5 3s'[1/2]_1$ resonance transition in neon at 73.6 nm the XUV-intensity is a factor of 100-1000 less than on this xenon two-photon resonance, but it is high enough to record high signal-to-noise spectra as shown in Fig 3. From the simultaneous measurement of ^{20}Ne and ^{22}Ne an accurate value for the transition isotope shift could be determined [11].

Tunable radiation in the range 54-60 nm is produced by fifth harmonic generation after frequency doubling of the efficient Rhodamine dye lasers. Although the XUV-yields in this domain are estimated too be as low as 10^4-10^5 photons/pulse, nevertheless a 1 XUV + 1 UV photoionization recording of the He resonance line at 58.4 nm could be recorded [12]. In Fig. 4 a simultaneous recording of a spectrum of the absorption spectrum of I_2 at the dye laser fundamental at 584 nm, used for calibration, and a spectrum at the tenth harmonic of the He-line at 58.4 nm are displayed. From accurate calibration procedures the transition frequency could be determined at $171134.89 \pm 0.03 \text{ cm}^{-1}$.

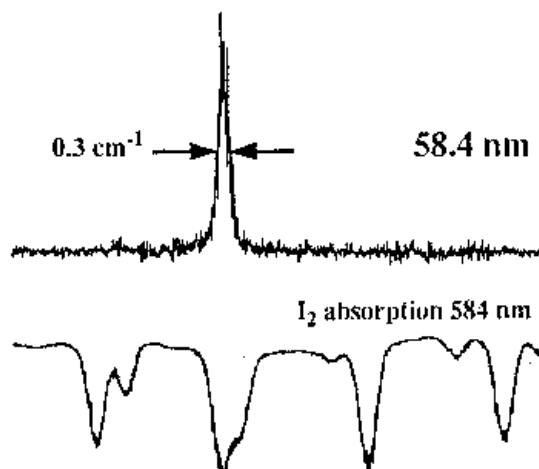


Fig. 4: Recording of a 1 XUV + 1 UV photionization spectrum of the resonance line of ^4He . The I_2 -absorption spectrum is used for absolute calibration of the frequency.

The detection efficiency of the 1 XUV + 1 UV resonance ionization method, applied to molecular species, is largely determined by possible competing processes of dissociation of the excited states. In cases, where the rotational structure of a bound state is coupled to dissociating continua this phenomenon is called predissociation. The predissociation process implies a life-time shortening of the excited states, which can be experimentally probed by linewidth measurements of the individual resonances. As a by-product of the competing process the RIS-signal intensities are strongly reduced. In the studies on H₂ [13], F₂ [9] and HF [14] no broadening effects related to predissociation were found. For N₂ [15] and CO [16] an XUV-laser was used for a detailed study of the predissociation effects in the excited states. For CO, see also Fig. 5, predissociation rates were found to depend on rotational state, parity and isotope [16].

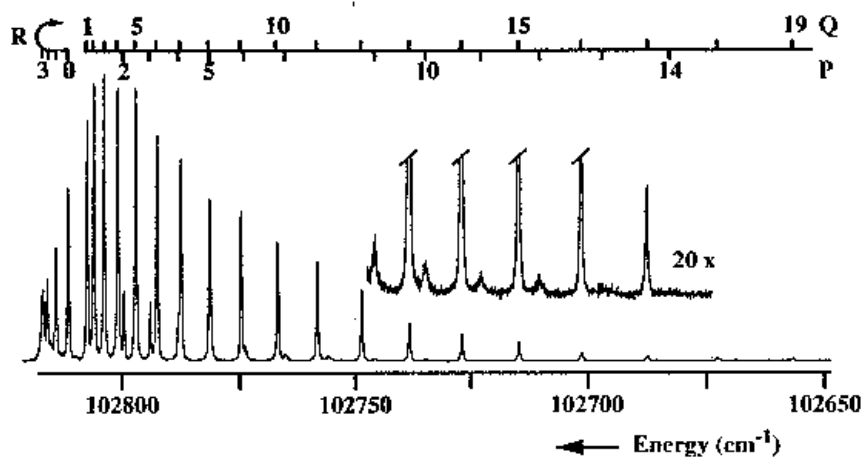


Fig. 5: Spectrum of the $(3\sigma)W^1\Pi-X^1\Sigma^+$ (0,0) band of $^{12}\text{C}^{16}\text{O}$. The P-lines show strong broadening at high J states, accompanied by a relative intensity decrease. The Q-lines, probing a different parity component, do not show this behaviour.

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