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- FREQUENCY MIXING IN NONLINEAR CRYSTALS: AN EFFICIENT WAY TO GENERATE TUNABLE UV-LASERLIGHT
- TUNABLE COHERENT VUV-RADIATION BY NONRESONANT FREQUENCY MIXING OF PULSED LASERLIGHT IN GASES
- TUNABLE VUV-RADIATION (PART II): TWO PHOTON RESONANT SUM- AND DIFFERENCE FREQUENCY MIXING IN RARE GASES AND METAL VAPORS

R. HILBIG
Fakultaet fuer Physik
Universitaet Bielefeld
4800 Bielefeld
Fed. Rep. Germany

FREQUENCY MIXING IN NONLINEAR CRYSTALS
- AN EFFICIENT WAY TO GENERATE TUNABLE UV-LASERLIGHT -

The method of frequency conversion of tunable visible laserlight into UV-laserradiation with the help of birefringent crystals will be mentioned in this talk. The basis for such a frequency mixing is a non-linear medium which is polarized by an incident electromagnetic wave with an amplitude $\vec{E}$.

For large values of the optical electric field, such as those available from the laser sources, the induced optical polarization can be represented as a series expansion /1/

$$\vec{P} = \varepsilon_0 [\chi^{(1)} \vec{E} + \chi^{(2)} \vec{E}\vec{E} + \chi^{(3)} \vec{E}\vec{E}\vec{E} + \dots]$$

where $\chi^{(2)}$, $\chi^{(3)}$, etc. are the non-linear optical susceptibilities of the medium and are responsible for a large variety of non-linear optical phenomena. Most of the interesting non-linear effects arise from the terms of electric polarization that are quadratic or cubic functions of the electric field amplitudes. The quadratic polarization gives rise to the phenomena of second harmonic generation (SHG) linear electro-optic or Pockel's effect, and parametric generation /1/.

For the case of a light wave of angular frequency ω, which is incident upon such a medium, - this is the special case of second harmonic generation (SHG) - the second order polarization at the harmonic frequency is given by /2/

$$P_i(2\omega) = \varepsilon_0 \sum_{j,k=1}^{3} d_{ijk}(-2\omega; \omega, \omega)\, E_j(\omega) \cdot E_k(\omega)$$

The SHG coefficient $d_{ijk}(2\omega)$ is a third rank tensor. Because of some symmetry properties $d_{ijk}(2\omega)$ can be written in a contracted form in which the suffices j and k are replaced by a single suffix l.

In the contracted form the d_{il}'s are 18 in number and the components of the second order polarization at the harmonic frequency of 2ω can be written in the matrix form /3/.

$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \varepsilon_0 \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_yE_z \\ 2E_xE_z \\ 2E_xE_y \end{pmatrix}$$

The number of nonvanishing, independent elements of the second harmonic tensor depends upon the point group symmetry of the medium. Crystals of the class $\bar{4}2m$ have only three such coefficients; these are d_{14}, d_{25} and d_{36}. Normally only two of them are independent (d_{14} and d_{25} are equal). In certain cases, the number of non-vanishing elements of the nonlinear optical tensor is further reduced by an additional symmetry condition. [For the class $\bar{4}2m$ all independent coefficients are equal.] /3/

Such a polarization generates a wave of frequency 2ω, the connection is given by the maxwell-equation. This equation can be solved with the help of a small signal approximation. The second harmonic power $P_{2\omega}$ generated by a plane wave of angular frequency ω and power P_ω incident along a principal axis of a plane parallel slab of thickness L of a nonabsorbing nonlinear crystal is given by /4/

$$P_{2\omega} = \frac{128\,\pi^3 c_1\, d_{ije}^2\, (P_\omega)^2\, \omega^2\, L^2}{n_{2\omega}\, n_\omega^2} \left(\frac{\sin(L\Delta k/2)}{(L\Delta k/2)}\right)^2$$

where

c = speed of light of free space

n_ω = refractive index of the crystal at the fundamental wavelength

$n_{2\omega}$ = refractive index of the crystal at the second harmonic wavelength

$\Delta k = (k_{2\omega} - 2k_\omega)$, the wave vector mismatch between the free harmonic and the bound waves in the crystal.

In general, because of dispersion in the medium, $\Delta k \neq 0$. That's why the second harmonic power undergoes periodic oscillations /3/. The period of the oscillations is given by the coherence length $l_{coh} = \pi/\Delta k$. For normal incidence we get /2/

$$l_{coh} = \frac{\lambda}{4(n^{2\omega} - n^\omega)},$$

where λ is the free-space wavelength of the fundamental wave.

It follows that for efficient second harmonic conversion, the wave vector mismatch Δk between the interacting waves should be zero. This is termed phase matching.

For a phase-matched frequency conversion the small signal approximation is normally broken. For this case we get the following result for SHG /1,11/.

$$P_{2\omega}(L) = P_\omega(0)\, \tanh^2\left(\frac{L}{l_{SH}}\right) \quad ; \quad l_{SH}^{-1} = \frac{4\pi\omega^2 d_{ik}}{kc^2} E_\omega(0)$$

Because of the dispersion of the refractive index between the fundamental and the second harmonic wavelengths, phase matching is difficult to achieve in an isotropic crystal. However, in an anisotropic crystal it is often possible to obtain $\Delta k = 0$ by a suitable choice of direction of propagation and polarization. Depending upon the choice of polarization, two types of phase matching in birefringent crystals are possible /1,4/

1) angle-tuning or critical tuning:

Phase matching is optimized by tuning the crystal relative to the wavevector of the light.

2) temperature-tuning or 90° index matching:

For light incident under 90° to the optical axis phase matching is realized for a certain temperature of the crystal.

The crystals ADP, KDP, KD*P, KB_5 and urea are of most interest for the generation of tunable UV-radiation by frequency doubling of pulsed dye laser radiation. Some properties of these materials are listed in table 1. The UV-spectral range where a critical phase matching for SHG is possible is shown in figure 1.

The KDP and the KD*P can be used in the range λ_{UV} = 252 - 400 nm, the ADP from 250 nm to 400 nm. If the power density of the incident visible laserlight is greater than about 5 MW/cm², the efficiency η for SHG of typical 15 - 30 % is nearly independent of the wavelength /5/.

A frequency-doubling of visible laserlight generates in a phase-matched KB_5-crystal UV-radiation with λ_{UV} = 217 - 315 nm. Because of the little nonlinear coefficient η is strongly wavelength dependent (η = 0.5 - 8 %) /6/.

In urea - this crystal is very hard to grow with sufficient optical quality - a phase matched SHG is possible for λ_{UV} = 238 - 400 nm /7/.

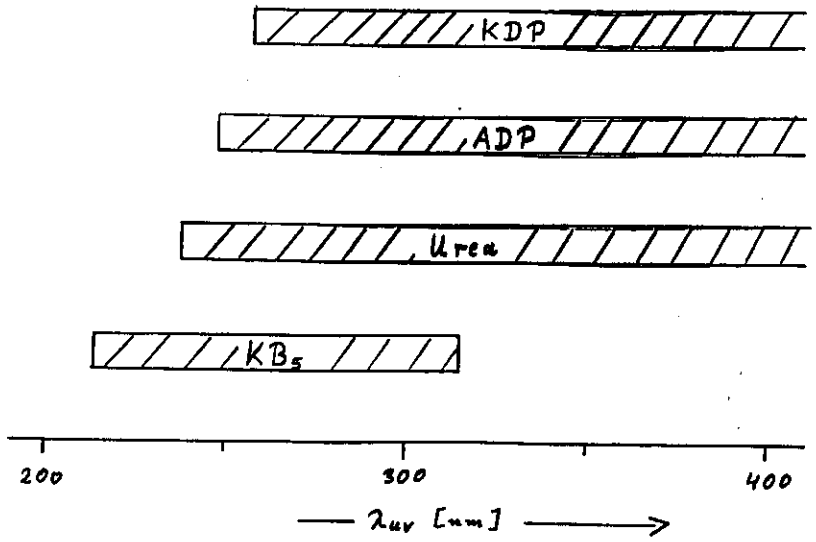
Besides SHG the sum frequency mixing of light with ω_1 and ω_2 is a useful method for the generation of UV-light. Tunable UV-radiation is generated for example by a 90° incident matched sum frequency mixing with $\omega_{UV} = \omega_1 + \omega_2$ in KB_5, where ω_1 and ω_2 are both tunable (λ_{UV} = 186 - 217 nm) /8/. Another possibility is for example the generation of the sum frequency $\omega_{UV} = \omega_1 + \omega_2$ in KDP or ADP by critical tuning. Here is only ω_2 can be a fixed frequency and only ω_2 must be variable /9/. In a KDP crystal the mixing $\omega_{UV} = \omega_1 + \omega_2$, where ω_2 is the frequency of a Nd-YAG laser, generates UV-light with λ_{UV} = 216 - 400 nm /10/.

The just described methods (SHG and sum frequency mixing in crystals) are really a powerful tool to generate tunable UV-radiation. This can be demonstrated, for example, for a commercial Nd-YAG laser pumped dye laser system (Quanta Ray).

Table 1 : Selected nonlinear crystals

Material	Formula	Symmetry	Nonlinear coefficient d_{ij} (relative to KDP)	Damage threshold
ADP	$NH_4H_2PO_4$	$\bar{4}2m$	1,2	> 400 MW/cm²
KDP	KH_2PO_4	$\bar{4}2m$	1,0	> 400 MW/cm²
D-KDP (KD*P)	KD_2PO_4	$\bar{4}2m$	1,1	> 400 MW/cm²
KPB (KB_5)	$KB_5O_8/4H_2O$	$mm2$	0,03 0,002	1000 MW/cm²
Urea	$(NH_2)_2CO$	$\bar{4}2m$	2,8	≈ 3000 MW/cm²

Figure 1 : Tuning range for critical tuning



Pumped by the second harmonic of the Nd-YAG laser the dye laser can be operated in the range between $\lambda = 540\,nm - 900\,nm$. Figure 2 shows the tuning behavior and the pulse power of this laser system. In the laser-dyes range $\lambda = 540$-$670\,nm$ pulse powers up to 12 MW are generated. With the help of the dyes Fluorescein 27 in a basic solution, the Rhodamines 6G, 610 base, 620, 640 and DCM the whole spectral range is covered. If you pump the dye laser with the third harmonic at $\lambda = 355\,nm$ (this harmonic is generated by frequency mixing the second harmonic and the fundamental of the Nd-YAG laser in a second KD*P-crystal with a pulse energy of 150 mJ/pulse) you can also generate laserlight between 410 nm and 660 nm with the help of the coumarin dyes and the dye Stilben 420.

A generation of tunable UV-radiation is for example possible with the help of this commercial wavelength extender WEX 1 (Quanta Ray). If the laser frequency changes the crystal is automatically turned to the correct angle θ_{Pm}. The so generated pulse power and the tuning range of the UV-radiation is also shown in figure 2. Tunable UV-light is generated for $\lambda_{UV} = 260 - 340\,nm$ with pulse powers up to 3 MW. In the whole spectral range the conversion efficiency is about 20%.

But besides the frequency doubling also a sum frequency mixing in KDP-crystals is appropriate for the generation of UV-light (as we have seen before). Therefore the rest of the fundamental light of the Nd-YAG laser ($\lambda_I = 1.064\,\mu m$) can be used as a powerful source at fixed frequency $\omega_2 = \omega_I$. The light of variable frequency ω_1 can either be the visible light of the dye laser or the frequency doubled light at $\omega_{UV} = 2\omega_L$.
The sum frequency $\omega^*_{UV} = \omega_L + \omega_I$ is generated between 340 nm and 410 nm. The frequency mixing $\omega'_{UV} = \omega_{UV} / \omega_I$ provides tunable UV-radiation of shorter wavelength $\lambda_{UV} = 216 - 255\,nm$ (figure 10). The conversion efficiency with respect to the power of the visible laser light is about 20% (ω^*_{UV}) or about 5% (ω'_{UV}). The generated UV-powers are of the order of 2 MW or 0.5 MW. (We have generated about 1 MW pulse power around 227 nm with this same system).

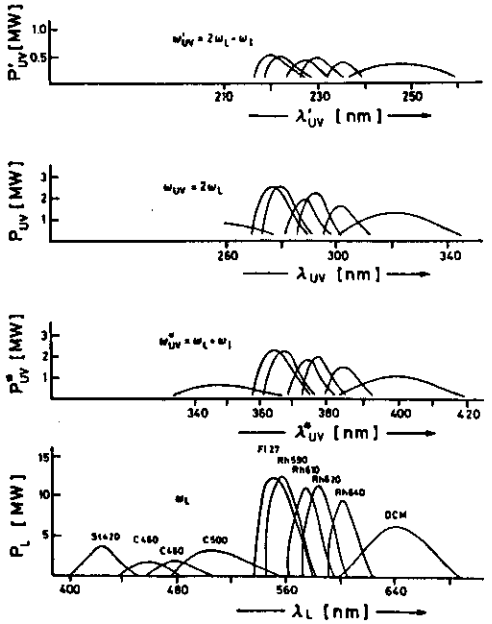


Fig 2

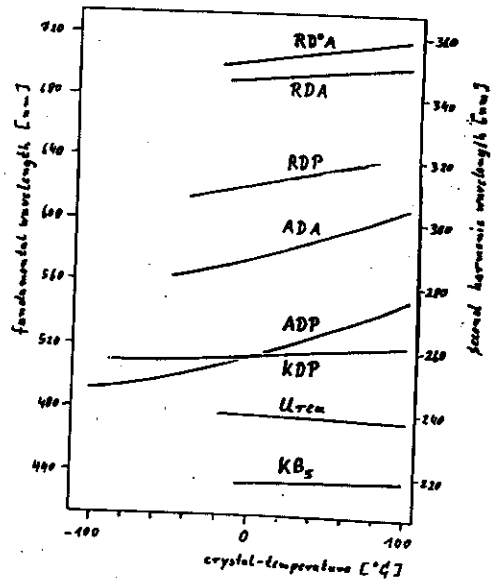


Fig. 2

For a frequency doubling of cw - laserlight normally 90° incident matching is used. Figure 3 shows the ranges which are covered by temperature tuning under 90° incident matching conditions for some crystals. The ADP is seen to be the most appropriate medium for such a temperature tuning. A frequency doubling is possible for light of wavelength $\lambda = 486 - 532$ nm ($\lambda_{UV} = 243 - 266$ nm). The KB_5, KDP and other crystals are improper for a temperature tuning.

With the help of for example intracavity frequency doubling /11/ or an external ring cavity /12/ even cw - laserlight can be frequency doubled with an efficiency of about 1%. (Up to 50 mW have been generated as a second harmonic power /11/.)

It has been shown that frequency doubling and frequency mixing in appropriate birefringent crystals is an excellent method to generate efficiently tunable UV - laser - radiation. This is true for pulsed as for cw - radiation.

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2. TUNABLE COHERENT VUV-RADIATION BY NONRESONANT FREQUENCY MIXING OF PULSED LASERLIGHT IN GASES

This contribution reports on the generation of tunable vacuum ultraviolet in the spectral region between 100 nm and 200 nm as well as in certain ranges of wavelengths below 100 nm.

Methods which are well suited for the generation of tunable coherent VUV are third harmonic generation and third order frequency mixing of intense dye laser radiation.

In the case of third harmonic generation laser light of the frequency ω_1 is converted in an appropriate nonlinear medium to light of the frequency $\omega_3 = 3\omega_1$. Starting with light of the frequencies ω_1 and ω_2 sum- and difference frequency mixing provides radiation with the frequency $\omega_3 = 2\omega_1 \pm \omega_2$.

For such frequency conversions the nonlinear medium has to be optically isotrop and has to be transparent in the VUV. For these reasons rare gases and metal vapors or mixtures of rare gases and metal vapors are very appropriate.

An electromagnetic field, which is incident upon such a medium, induces a polarisation of this form /1/:

$$\vec{P} = \chi^{(1)}\vec{E} + \chi^{(2)}\vec{E}\vec{E} + \chi^{(3)}\vec{E}\vec{E}\vec{E} + \ldots = \vec{P}^{(1)} + \vec{P}^{(2)} + \vec{P}^{(3)} + \ldots$$

For an isotropic medium the polarisation $\vec{P}^{(2)}$ in second order is identically zero /2/. So the first nonlinear interaction of the wave with the medium is given by

$$\vec{P}^{(3)} = \chi^{(3)}\vec{E}\vec{E}\vec{E}$$

For an electromagnetic field $\vec{E}$, which consists of a limited number of different frequency components, there will be induced a nonlinear polarisation with frequency components $\vec{P}^{(3)}(\omega_4)$. The frequency ω_4 can be different from the irradiated frequencies ω_i. Such a polarisation $\vec{P}^{(3)}(\omega_4)$ forms an electromagnetic wave $\vec{E}(\omega_4)$, the connection between $\vec{P}^{(3)}(\omega_4)$ and $\vec{E}(\omega_4)$ is given by the maxwell-equations /1/.

For third harmonic generation in gases for example the conversion efficiency η for the conversion of the focused laserradiation to VUV-radiation is given by this equation /7/:

$$\eta = \frac{P_4}{P_1} = \frac{8.214\cdot 10^{-3}\cdot n_4^2}{\lambda^4 \cdot n_1^3} \cdot N^2\left(\chi^{(3)}(3\omega)\right)^2 P_1^2 \cdot F_1\left(b\Delta k, \frac{b}{L}, \frac{f}{L}\right)$$

where

$\lambda = 2\pi c_i / \omega$,

N is the density of the medium per unit volume,

$\chi^{(3)}(3\omega)$ is the atomic nonlinear susceptibility in third order,

b is the confocal parameter,

$\Delta k = k_4 - 3k_1 = 6\pi(n_4 - n_1)/\lambda$ is the wavevector mismatch and n_i is the index of refraction of the medium at ω_i.

If the laserradiation is focused into the middle of a gas cell, which length L is much greater than b, F_1 is given by an analytic expression /3/:

Sum frequency generation $\omega_4 = \omega_1 + \omega_2 + \omega_3$ (Frequency tripling $\omega_4 = 3\omega_1$)

$$F_1(b\Delta k; 0; 0.5) = \begin{cases} \pi^2 (b\Delta k)^2 \exp[b\Delta k] & \text{for } \Delta k < 0 \\ 0 & \text{for } \Delta k \geq 0 \end{cases}$$

F_1 is equal to zero for $b\Delta k > 0$. That means in a so called positive dispersive medium a sum frequency mixing is not possible at all. The generation of a sum frequency can only be done in a negative dispersive region of the used medium. If $b\Delta k = -2$ phase-matching is best.

Besides a large power of the laserlight – output powers of several MW are today possible even with dyelasers /4,5/ – the third harmonic generation needs a negative dispersive medium. The condition $\Delta k < 0$ is of course a severe limitation on the spectral regions in which rare gases, for example, can be used for frequency tripling.

Figure 1 shows the negative dispersive regions for the rare gases Neon, Argon, Krypton and Xenon and for the metal vapor mercury. – These gases are of most interest because they are experimentally easy to handle (compared with other metal vapors). –

For longer wavelength than the cutoff of LiF-windows (this is the material with the shortest cut-off-wavelength) the rare gases Xe and Kr and the metal vapor Hg are negative dispersive in the alkaline areas. Frequency tripling of dye laser radiation in the negative dispersive regions of Xe and Kr has been investigated in detail by many groups /6,7/.

The longest wavelength range in which the rare gas Krypton is negative dispersive extends from about 120.3 to 123.6 nm. This range has attracted some attention because it contains the L_α - wavelength of the H-atom (λ_{VUV} = 121.567 nm). In fact frequency tripling in Kr has been investigated by several research groups to generate L_α /8/. The generated power of L_α was typically a few watts. ($\eta \approx 10^{-6}$).

Beside the THG in pure Kr frequency tripling in Kr - Kr mixtures has been investigated in detail /8/. In such a phase matched rare gas mixture the conversion efficiency was increased by more than two orders of magnitude. (The largest power in a Kr - Kr mixture was 80 W /9/.)

That a nonresonant THG of visible laser light in mercury vapor is also very interesting for the generation of tunable VUV-radiation is demonstrated in figure 2. If the laser is operated with the coumarine dyes and stilben (λ_L = 425 - 545 nm) tunable VUV-radiation is generated for λ_{VUV} = 142 - 181 nm with output powers of up to 1 W ($\eta \approx 10^{-6}$). It is remarkable that in the whole spectral region of λ_{VUV} = 141 - 172 nm the mercury pressure has not been changed /10/.

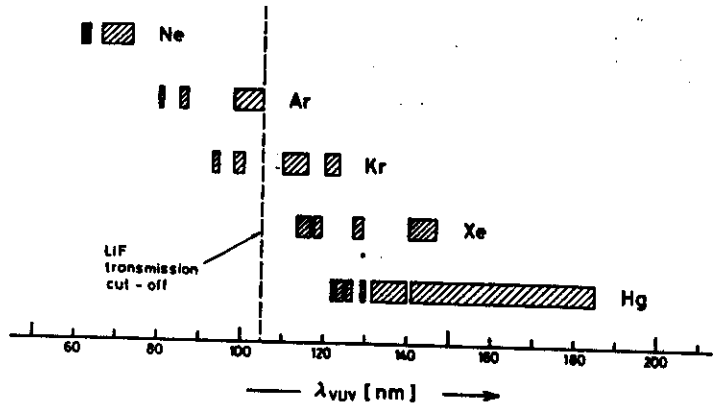

Fig. 1 Spectral regions with negative mismatch ΔK for frequency tripling ($\omega_{VUV} = 3\omega_L$) in Ne, Ar, Kr, Xe and Hg.

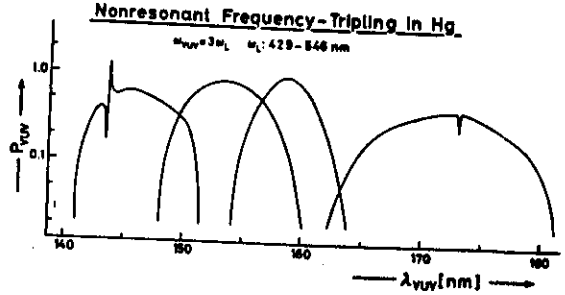

Fig. 2:

Of great interest is the spectral region of the VUV, which lies outside the transmission range of LiF - material, in the following termed XUV. The generation of tunable XUV-radiation is for example possible by third harmonic generation in these negative dispersive regions of Ar and Ne (see figure 1).

Frequency tripling of UV dye laser radiation in Ar for example generates XUV between 96 nm and 105 nm. With P_{UV} in about 2 MW the XUV power is between 1 and 10 W, for $\eta \approx 5 \cdot 10^{-6}$ /11/. If the dye laser system is operated with conversion 40% and this light is frequency-doubled ($P_{UV} \approx 1$ MW), XUV light is also generated in the range $\lambda_{XUV} = 85.6 - 87$ nm ($\eta \approx 10^{-5}$).

Experimental results obtained for third harmonic generation in the negative dispersive region at the high energy side of the $2p-3s'[\frac{1}{2},1]$ transition of Ne are displayed in figure 2. With pulse powers of $P_{UV} = 0.07 - 0.32$ MW (2k 65) or $P_{UV} = 0.07 - 0.$ (FL 27) the third harmonic power P_{XUV} is typically 0.1 - 0.4 W /12/.

These experiments demonstrate third frequency tripling of intense dye laser radiation provides an effective method of generation VUV-radiation. However phase matching conditions restrict such sum-frequency mixing to spectral regions of negative phase-mismatch (Δk /13/.

In contrast to the sum frequency the difference frequency can be generated in a medium with $\Delta k \geq 0$ /13/. Since this conversion is, in principle, not restricted by the dispersion of the medium it should be of good advantage for the generation of narrowbanded VUV radiation, which is tunable continuously in the 105 - 200 nm spectral range.

The tuning range of the VUV which can be generated with the present dye laser systems by difference frequency mixing is summarized in figure 4. With the help of the shown conversion schemes nearly the whole VUV-range can be covered. These schemes also offer the advantage of requiring only one dye laser system for gene-

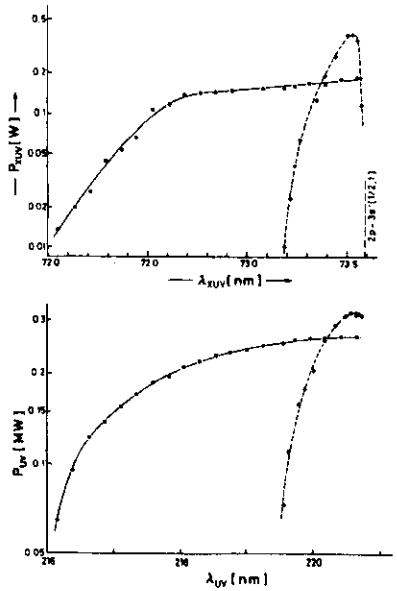

Fig. 3. Nonresonant frequency tripling in the negative dispersive region at the high energy side of the $2p-3s'[1/2, 1]$ transition. /12/

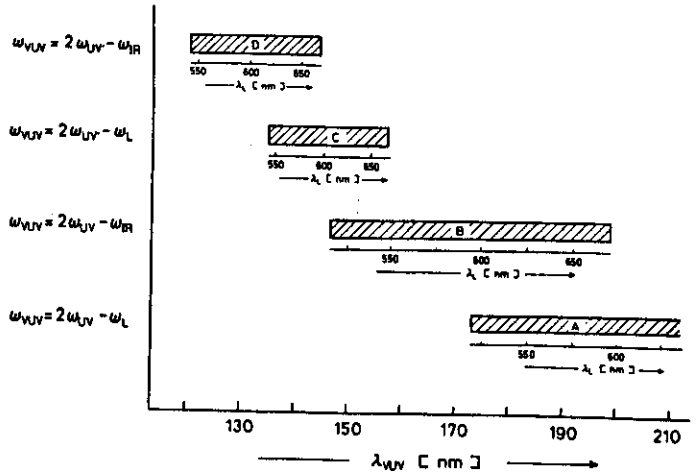

Fig. 4: Spectral range of the VUV which can be covered by the listed difference frequencies. (ω_L: tunable Dyelight with wavelength λ_L; $\omega_{UV} = 2\omega_L$; ω_{IR} = ...

In Xe, for example, the frequency mixing process $\omega_{VUV} = 2\omega_{UV} - \omega_{IR}$ (ω_{UV} is the second harmonic frequency of a tunable dye laser, ω_{IR} is the fundamental of the Nd-YAG pump laser) generates continuously tunable VUV-light for $\lambda_{VUV} = 155 - 199$ nm (figure 5). An exception is given for $\lambda_{VUV} = 165 - 169$ nm where P_{VUV} is attenuated for some wavelength. These attenuations occur if the sum of ω_{VUV} and ω_{UV} coincides with the transition frequency of a two photon resonance. Around these wavelength tunable VUV-radiation can be generated in Kr, but the conversion efficiency is nearly a factor of 4 less than in Xe /13/.

This example demonstrate that the difference frequency mixing is well suited for the generation of tunable VUV-radiation. But that the choose of the rare gases is very important is demonstrated once more in figure 6. There P_{VUV} is shown for the difference frequency $\omega_{VUV} = 2\omega'_{UV} - \omega_{IR}$ in the range $\lambda_{VUV} = 120 - 179$ nm ($\omega'_{UV} = \omega_{UV} + \omega_{IR}$)

In Kr the generation of continuously tunable VUV is possible. But in Kr as in Xe the VUV-power is attenuated by absorption by resonance lines of the atoms and by dimers for certain wavelength. Besides this attenuations there also exists a resonant enhancement of P_{VUV} for each wavelength λ_{VUV} ($\omega_{VUV} = 2\omega'_{UV} - \omega_{IR}$) where $2\omega'_{UV}$ coincides with a two photon resonance /13/.

In conclusion one can say that the generation of tunable VUV-radiation by a non-resonant sum- or difference frequency mixing (in second order) in gases and metal vapors is possible today in the whole spectral range between 120 nm and 210 nm as well as in large portions between 70 nm and 120 nm with conversion efficiencies of 10^{-6} to 10^{-5}. The experimental handling of such a VUV-source is very easy. So it has become a useful tool at hand for spectroscopic applications /14/.

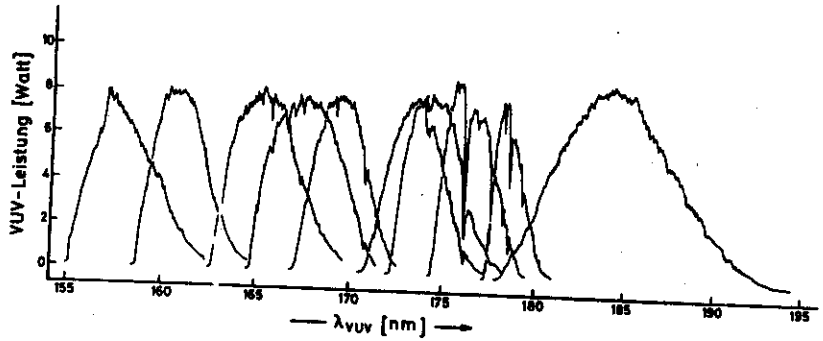

Fig. 5: Tuning characteristic of the difference frequency $\omega_{VUV} = 2\omega_{UV} - \omega_{IR}$ in Xe.

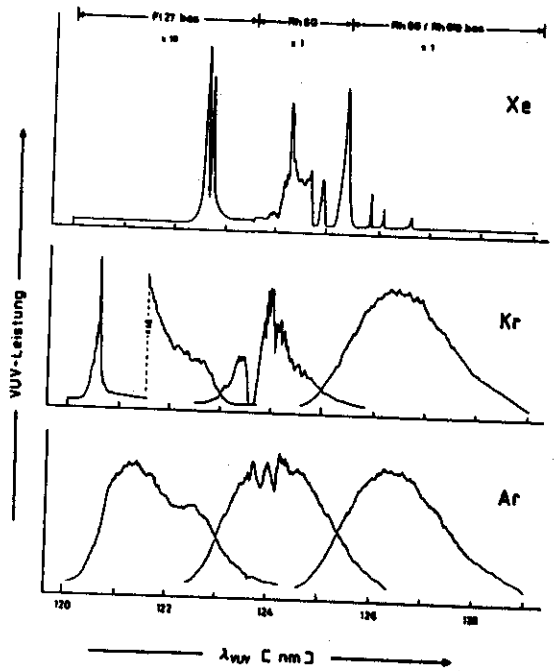

Fig. 6: The difference frequency $\omega_{VUV} = 2\omega'_{UV} - \omega_{IR}$ in Xe, Kr and Ar.

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3. TUNABLE VUV-RADIATION (PART II): TWO PHOTON RESONANT SUM- AND DIFFERENCE FREQUENCY MIXING IN RARE GASES AND METAL VAPORS

The first contribution about the generation of tunable VUV-radiation has been engaged in nonresonant frequency conversion of powerful dye laser radiation. The conversion efficiency of such a nonresonant frequency mixing in rare gases is typical between 10^{-6} and 10^{-5} even for optimised phasematching conditions. The generated power is of the order of 1 - 10 W. The conversion efficiency is so low because of the small nonlinear coefficient of rare gases.

In contrast to rare gases metal vapors have a larger nonlinear susceptibility in particular if it is enhanced by a two-photon resonance or autoionizing states. Two photon enhanced frequency conversion in metal vapors provided efficiencies of 10^{-3} to 10^{-4} with laser pulse powers of only 10 to 100 kW /11,21.

Compared to metal vapors the experimental handling of rare gases is very simple. However, efficient frequency conversion in rare gases requires laser pulses in the UV-spectral range and of at least megawatt pulse power which are today achievable /3,4/. Because the two photon resonances of rare gases have a very large transition frequency, even the difference frequency mixing generates light in the VUV. Such a frequency conversion is not restricted by phasematching conditions (as for example the wave frequency), so it provides a VUV radiation source which is experimentally simple, reliable in operation and is capable to generate VUV at wavelength in the range between 70 and 200 nm.

The conversion efficiency for such a frequency mixing process is a well known expression. For a frequency tripling, for example, η is given by /5/:

$$\eta = \frac{P_{VUV}}{P} \sim N^2 \left[\chi^{(3)}(3\omega)\right]^2 P^2 F_1\left(b\alpha k, \frac{b}{L}, \frac{\xi}{L}\right)$$

So η is proportional to the square of the density N, of the nonlinear susceptibility $\chi^{(3)}(3\omega)$ and of the power P of the incident light. For a gaussian beam the phase-matching factor F_1 is given by the following expression /5/:

$$F_1(b\Delta k, 0, 2.9) = \begin{cases} 0 & \Delta k \geq 0 \\ \pi^2 (b\Delta k)^2 \exp(i b\Delta k) & ; \Delta k < 0 \end{cases}$$

F_1 is zero however if $\Delta k \geq 0$. Thus, efficient third harmonic generation requires a nonlinear medium which is negative dispersive. This restriction for the generation of a new frequency is not given for a difference frequency, which can be generated in positive as well as in negative dispersive media.

For a frequency tripling the nonlinear susceptibility $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ is given by 4 terms, over which must be summed /6/

$$\chi^{(3)}(-3\omega;\omega,\omega,\omega) = \frac{N}{\hbar^3 \varepsilon_0} \sum_{gabc} \rho(g) \times \left(\frac{\mu^*_{ga}\,\mu_{ab}\,\mu_{bc}\,\mu_{cg}}{(\Omega_{ag}-3\omega)(\Omega_{bg}-2\omega)(\Omega_{cg}-\omega)} \right.$$

$$+ \frac{\mu_{ga}\,\mu^*_{ab}\,\mu_{bc}\,\mu_{cg}}{(\Omega_{ag}+\omega)(\Omega_{bg}-2\omega)(\Omega_{cg}-\omega)}$$

$$+ \frac{\mu_{ga}\,\mu_{ab}\,\mu^*_{bc}\,\mu_{cg}}{(\Omega_{ag}+\omega)(\Omega_{bg}+2\omega)(\Omega_{cg}-\omega)}$$

$$\left. + \frac{\mu_{ga}\,\mu_{ab}\,\mu_{bc}\,\mu^*_{cg}}{(\Omega_{ag}+\omega)(\Omega_{bg}+2\omega)(\Omega_{cg}+3\omega)} \right)$$

where $\mu_{ij} = \varepsilon Q_{ij}$ ($\varepsilon = \varepsilon_\omega = \varepsilon_{3\omega}$ for a tripling of linear polarised light /7/)

Ω_{ij} are the transition frequencies ; $\Omega_{ij} = (E_i - E_j)/\hbar$,

Q_{ij} are the matrix elements $\langle i|Q|j\rangle$ between the stationary states $|i\rangle$ and $|j\rangle$,

ε_i are the unit vectors of the electric field $\vec{E}_i$; $\varepsilon_i = \vec{E}_i / |\vec{E}_i|$,

$\rho(g)$ is the unperturbed diagonal density matrix element for state g

If only the ground state of the used nonlinear medium is populated, the first term of the sum makes the main contribution to $\chi^{(3)}(3\omega)$. The functional dependence of this term on the energie differences between the frequency ω of the incoming

light and the transition frequencies Ω_{ij} of the nonlinear medium is given in figure 1. The ΔE_i are also demonstrated there. While ΔE_i increase the nonlinear susceptibility. But for ΔE_a or ΔE_c is equal to zero the generated VUV or the incoming laser radiation will be absorbed by the medium. So normally two-photon resonances - that means ΔE_b is zero - are used to enhance the nonlinear susceptibility /6/.

Such an enhancement of $\chi^{(3)}(3\omega)$ also increase the efficiency of a frequency conversion. But not only $\chi^{(3)}(3\omega)$ but also $\chi^{(3)}(\omega)$ is increased by the two photon resonance. So $\vec{P}^{(3)}(\omega) = \chi^{(3)}(\omega) \cdot E_1^* E_1 E_1$ is a power dependent additional part to the linear polarisation $\vec{P}^{(1)}(\omega)$. So the real part of $\chi^{(3)}(\omega)$ describes a (power dependent) change of the linear index of refraction n /6/.

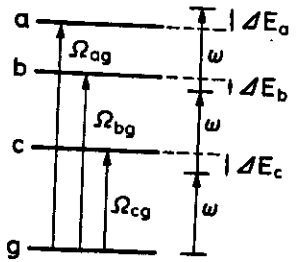
The imaginary part of $\chi^{(3)}(\omega)$ describes the two photon absorption. If this absorption cannot be neglected - this is the normal case for an efficient resonant frequency conversion - it leads beside the depletion of the fundamental wave at ω to a change of the population density of the ground state and the two photon level and even because of the decay of this level to a change of population for those states which lie between the ground state and the two photon state.

For a reliable quantitative calculation the different contributions to the induced polarisation cannot be considered separated because of the coupling of the nonlinear interactions. Such a calculation is only possible with the help of a computer simulation /8/. But experimental results give more information about the procedure to optimize the efficiency of a two photon resonant sum- and difference frequency mixing /9/.

For a resonant frequency conversion you normally need two laser systems. One with light of frequency ω_1 that is fixed to the two photon resonance, and a second with a tuneable frequency ω_2. But for the investigation of the interaction mechanisms in Xe ω_1 was given by the fundamental of the frequency-doubled dye laser with frequency ω_1 /9/.

Figure 2 shows the resonant enhancement of the VUV power at $2\omega_1 - \omega_2$ in the vicinity of the two photon resonance $6p - 6p$. The wavelength of the VUV is 170.6 nm.

Nonlinear Susceptibility $\chi^{(3)}(3\omega)$



$$\chi^{(3)}(3\omega) = \frac{1}{\hbar^3} \sum_g \sum_{abc} \mu_{ga}\, \mu_{ab}\, \mu_{bc}\, \mu_{cg}\, \rho_{gg}\, A_{abc}$$

$$A_{abc} = \frac{1}{\underbrace{(\Omega_{ag}-3\omega)}_{\Delta E_a}\ \underbrace{(\Omega_{bg}-2\omega)}_{\Delta E_b}\ \underbrace{(\Omega_{cg}-\omega)}_{\Delta E_c}} + \ldots.$$

Fig. 1:

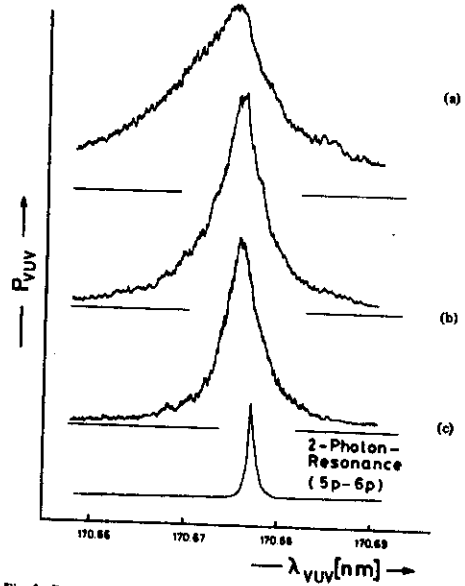


Fig. 3. Resonant enhancement of the VUV output power P_{VUV} at $\omega_{VUV} = 2\omega_{UV} - \omega_D$ ($\omega_D = \omega_{UV}/2$) as a function of the detuning of ω_{UV} from the two-photon resonance $5p-6p[\frac{1}{2}, 2]$. The Xe pressure is 30 torr. (a) The UV input power $P_{UV} = 30$ kW, (b) $P_{UV} = 10$ kW, (c) $P_{UV} = 5$ kW. Each of the three curves is displayed at a different scale.

Obviously the spectral range of the resonant enhancement increases with increasing input power. The spectral distribution is nonsymmetric and the optimum VUV output is spectrally shifted towards shorter wavelengths. The nonsymmetric broadening is caused by a corresponding power broadening of the two photon resonance.

However in contrast to the resonant enhancement the two photon excited fluorescence exhibits no measurable shift. An explanation for this difference is obtained by considering the contribution of the different saturation mechanisms (like two-photon excitation and ionisation) to the change of the index of refraction.

The result is shown in figure 3. The phase mismatch changes considerably in the vicinity of the two photon resonance. As expected the variation of ζ is strongly power dependent. For sufficiently large detunings the measured mismatch approaches the value calculated from the refractive index. At resonance the mismatch is large. Therefore a smaller Xe pressure is required for optimum phase matching. At large detunings the mismatch is considerably smaller and optimum VUV output requires a correspondingly higher pressure.

Figure 4 shows the resonant enhancement of the VUV for different pressures. Because of the large mismatch at the center of the two photon resonance optimum phase matching is obtained at low gas pressures. At higher pressures the phasematching is broken at the center of the resonance. For sufficiently large detunings the mismatch is smaller and optimum VUV is observed at higher Xe pressure.

These results have shown that the limitation of the conversion efficiency η is mainly given by the change of the phase matching conditions (figure 3) and by the decrease of $\chi^{(3)}(2\omega_1 - \omega_2)$ through power broadening of the resonance (figure 2) and through excitation of the two photon state. But there also exist limitations of η which depend on the laser with frequency ω_2.

For the generation of tunable VUV this frequency ω_2 has to be tuned. If ω_2 is in the spectral range of 300 - 700 nm the VUV is in the range of 190 to 220 nm. An example

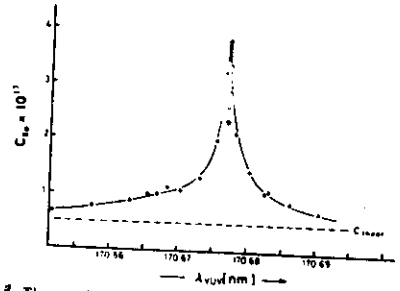


Fig. 3. The atomic contribution C_{Xe} to the phase mismatch Δk. +: P_{UV} = 30 kW; Δ: P_{UV} = 15 kW; O: P_{UV} = 10 kW; and ∘: P_{UV} = 5 kW. /8/

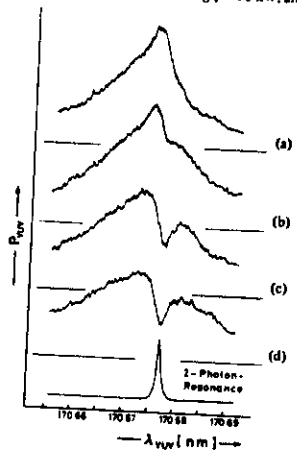


Fig. 4. The resonant enhancement of P_{VUV} measured in the vicinity of the two-photon resonance for the same input power P_{UV} = 30 kW, but different pressures p_{Xe}. (a) p_{Xe} = 34 torr, (b) p_{Xe} = 52 torr, (c) p_{Xe} = 103 torr, and (d) p_{Xe} = 150 torr. /9/

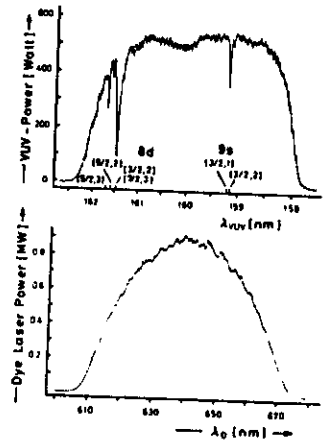


Fig. 5. Tunable VUV generated by difference frequency mixing $\omega_{VUV} = 2\omega_{UV} - \omega_D$. The pressure p_{Xe} = 22 torr is adjusted for optimum VUV output at λ_{VUV} = 160 nm. /9/

is shown in figure 5. ω_2 is tuned between 610 and 670 nm. The VUV has a wavelength of 158 - 162 nm. Two features are obvious. First the VUV is not proportional to the dye laser power and at several wavelengths the VUV shows resonance-like attenuations.

These attenuations occur when the sum-frequency $2\omega_1 + \omega_2$ coincides with the excited states 7s and 8d in Xe. The two- and three photon resonant excitation and ionisation reduces the conversion efficiency. The conversion efficiency is also reduced by phase-matched generation of VUV at the sum which causes the minimum at 160 nm /9/.

In principle it has been shown in Xe that the two photon resonant difference frequency mixing is well suited to generate tunable VUV radiation with output powers of the order of 1 kW.

In Kr the first two photon-resonance $4p - 5p\,[5/2,2]$ is well suited for an enhancement of the conversion efficiency. For the excitation of this level we need laser radiation with λ_R = 116 nm. The resonant mixing $\omega_{VUV} = 2\omega_R - \omega_2$ (with λ_2 = 270 - 730 nm) generates widely tunable radiation as shown in figure 6 /9/. Tuning for example the dye laser in the range λ_L = 540 - 730 nm the conversions $2\omega_R - \omega_L$, $2\omega_R - (\omega_L + \omega_{SR})$ and $2\omega_R - (2\omega_L)$ generate VUV at λ_{VUV} = 127.5 nm - 134.5 nm, 145.5 nm - 155 nm and 155 nm - 181 nm, respectively. Radiation at λ_{VUV} = 135 - 145 nm is produced by $2\omega_R - \omega_L$ with λ_L = 428 - 548 nm which is in the tuning range of coaxial dye lasers. The tuning curves displayed in figure 6 are measured at input powers P_R and P_L of about 70 kW. At optimum conditions an input of P_R = 100 kW and P_L = 1 MW generates VUV pulses close to 0.5 kW.

Beside Xe and Kr mercury is a very interesting conversion medium for resonant sum- and difference frequency mixing because it is - compared with other metal vapors - easy to handle and the two photon resonances are capable with the frequency doubled radiation of pulsed dye lasers /11/. Exciting the 6s - 7s transition of mercury the sum-frequency $\omega_{VUV} = 2\omega_R + \omega_2$ lies in the range of the Rydberg states. Tuning for example the dye laser between 480 nm and 550 nm VUV radiation is observed above the ^3P and ^1P levels for n = 12 - 26 (figure 6). This tuning characteristics cannot be altered significantly by phase matching with a rare gas /11/.

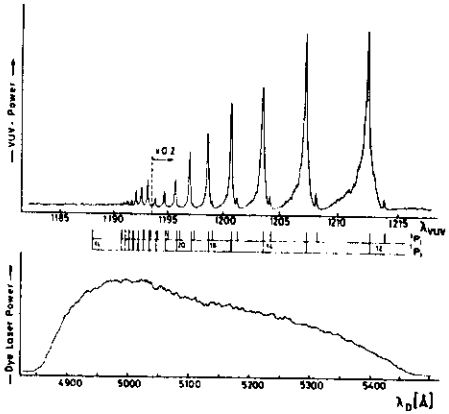


Fig. 6. Resonant enhancement of the VUV generated at the sum frequency $\omega_{VUV}^{+} = 2\omega_{UV} + \omega_D$ (ω_{UV} is tuned to the $6\,^1S_0$–$7\,^1S_0$ resonance) in the vicinity of the $n\,^{1,3}P_1$ Rydberg levels (n = 12–26). Radiation at ω_D is provided in the range λ_D = 4900–5450 Å by a Coumarin 500 dye laser. (P_{UV} = 100 kW, P_D ≈ 200 kW, p_{Hg} = 1 torr, p_{Ar} = 2.5 torr.)

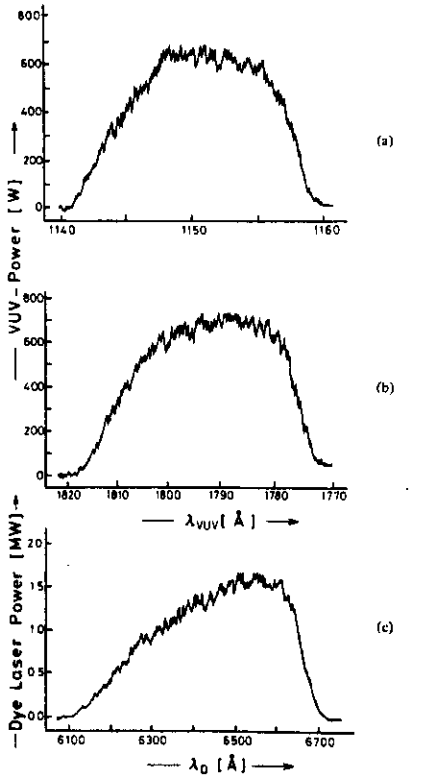


Fig. 7. Resonant frequency mixing $\omega_{VUV}^{+} = 2\omega_{UV} \pm \omega_D$ (ω_{UV} is resonant with the $6\,^1S_0$–$6\,^1D_2$ two-photon transition, ω_D is tuned in the range λ_D = 6100–6700 Å) generates continuously tunable VUV at (a) λ_{VUV}^{+} = 1140–1160 Å and (b) λ_{VUV}^{-} = 1770–1820 Å. The additional parameters are (a) P_{UV} = 0.8 MW, p_{Hg} = 1.5 torr, p_{Kr} = 1 torr and (b) p_{Kr} = 123 torr.

If the 6s - 6d resonance is excited the sum frequency $2\omega_1 + \omega_2$ as well as the difference frequency $2\omega_1 - \omega_2$ lies in VUV. $\omega_{VUV}^{(-)}$ is generated at wavelengths shorter than the first mercury resonance (λ = 185 nm); the sum frequency is above the ionization limit. There results a smooth tuning of the sum- and difference frequency /11/.

In the example shown in figure 7 the dye laser is tuned between λ = 600–670 nm. The sum is in the range λ_{VUV} = 111–116 nm and the difference frequency is between 177 nm and 182 nm. The output power was typically 600–700 watts.

The first shown results demonstrate that a resonant frequency conversion in rare gases and metal vapors can generate radiation in nearly the whole spectral region of the VUV. The conversion efficiency can be as high as several % even with input powers less than 1 MW. Best besides the generation of pulsed VUV-light cw-radiation can be generated by a resonant frequency mixing /12/.

Single frequency cw coherent VUV radiation is generated for the first time by tripling the frequency of a stabilized dye ring laser in Hg. Tuning λ_L to the Hg two-photon resonance $3\,^1S_0$ - $3\,^1D_2$ (λ_L = 430.88 nm) a laser power of P_L = 0.2 W generated VUV-radiation (λ_{VUV} = 143.6 nm) of more than $1.2 \cdot 10^5$ photons/sec ($P_{VUV} = 1.8 \cdot 10^{-13}$ W) /13/. The generated third harmonic is tunable over the broadened resonance profile (figure 18). Best with two dye lasers operated at the wavelengths λ_1 = 430.88 nm and λ_2 = 430–600 nm the resonant frequency mixing $\omega_{VUV} = 2\omega_1 + \omega_2$ will generate continuously tunable radiation at λ_{VUV} = 140–157 nm /14/.

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