PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Infrared Picosecond Pulses and Applications

W. Kaiser, A. Fendt, W. Kranitzky and A. Laubereau

Phil. Trans. R. Soc. Lond. A 1980 **298**, 267-271
doi: 10.1098/rsta.1980.0250

Phil. Trans. R. Soc. Lond. A **298**, 267–271 (1980)
Printed in Great Britain

Infrared picosecond pulses and applications

By W. Kaiser, A. Fendt, W. Kranitzky and A. Laubereau
Physik Department der Technischen Universität München, Arcisstrasse 21,
8000 *München* 2, *Germany*

By using the three-photon parametric process, tunable infrared pulses between 2500 and 7000 cm^{-1} can be generated with $LiNbO_3$ crystals. By varying the time delay between the pump pulse and a signal input pulse the duration of the i.r. pulses may be changed. I.r. pulses as short as 0.5 ps have been experimentally observed.

The dynamics of vibrational modes of polyatomic molecules was studied by using a two-pulse system. A first i.r. pulse excites a specific molecular vibration while a second properly delayed pulse monitors the instantaneous state of the vibrational system. Two types of experiments are discussed, those where the anti-Stokes Raman scattering or a fluorescence signal is observed.

The three-photon parametric process offers the possibility to generate frequency tunable pulses of picosecond and subpicosecond duration. In particular, infrared pulses between 2500 and 7000 cm^{-1} may be produced with pump pulses of 9400 cm^{-1} (Nd-doped glass or crystals) by using $LiNbO_3$ crystals as nonlinear material (Laubereau *et al.* 1974). Signal and idler emission is readily observed with a conversion efficiency of 1–3% in a single-path generator for pump intensities of approximately 10^{10} W/cm^2 (depending upon the total length of the crystals). In our experiments, the parametric generator consists of two properly orientated $LiNbO_3$ crystals separated by roughly 50 cm (see figure 1). The signal radiation of the first crystal serves as an input for the parametric amplification in the second specimen. In this way, the divergence of the parametric light is very small and the resulting bandwidths of the signal and idler become optimally narrow. Figure 2 shows quite convincingly the importance of a small beam divergence in the parametric process (Seilmeier *et al.* 1978*a*). The frequency differences, $\Delta\nu$, of idler waves generated in a collinear and in an off-axis beam are calculated as a function of the off-axis angle, α. For α of 3 mrad and for an idler frequency of 3000 cm^{-1} the spectral contribution to the bandwidth is $\Delta\tilde{\nu} = 5$ cm^{-1}. Note the rapid increase of $\Delta\nu$ with α and with idler frequency.

We have made a detailed study of the bandwidth and pulse duration of our infrared pulses. The signal around 6400 cm^{-1} was up-converted in a nonlinear crystal and the spectral properties of an individual pulse were studied. In addition, an autocorrelation measurement provided the duration of the signal pulses. The spectral properties of the idler pulse were measured directly around 3000 cm^{-1}. Our experimental observations are summarized as follows. For idler and signal pulses of 3000 and 6400 cm^{-1}, respectively, we find a frequency width of 8 cm^{-1} and a pulse duration of 3 ps, i.e. a favourable product of 0.7 for bandwidth times time. The divergence of the parametric radiation is 3 mrad for a laser divergence of 0.5 mrad. Intensity values of approximately 1 GW/cm^2 are readily achieved in the parametric beam.

More recently, we have demonstrated efficient generation of subpicosecond pulses in the infrared (Fendt *et al.* 1979). The novel system is depicted in figure 3. The first two $LiNbO_3$

crystals at the lower left of the picture represent the (narrow band) parametric single path generator discussed above. A small part of the signal pulse is subsequently amplified in a third $LiNbO_3$ crystal, generating an intense idler pulse at longer wavelength. Of special interest are the results where a well defined time delay, t_d is introduced between the input signal and the pump pulse in the amplifier crystal. Varying t_d leads to substantial changes in the duration of the signal and idler pulse. Very short infrared pulses are obtained when an asymmetrically

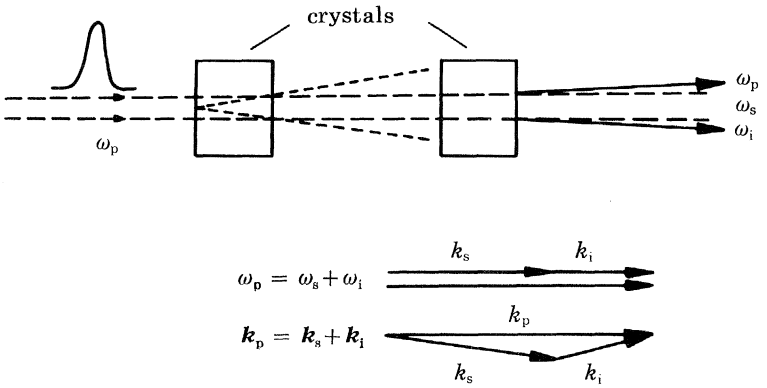

FIGURE 1. Schematic of the single path parametric generator consisting of two nonlinear crystals (e.g. $LiNbO_3$). The parametric emission of the first crystal serves as an input to the second specimen.

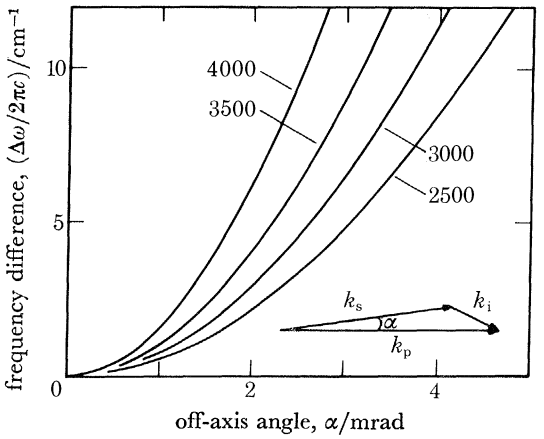

FIGURE 2. Type I phase-matching of $LiNbO_3$ with pump frequency of 9455 cm^{-1}: frequency difference between collinear and off-axis radiation for various idler frequencies (in the forward direction). Inset: the wavevector diagram shows the angle α for non-collinear phase-matching.

shaped laser pump pulse is used. Signal pulses ($\tilde{\nu}_s = 6550\ cm^{-1}$) as short as 0.5 ps were measured for delay times of 8.5 ps. In figure 4, computer calculations of pump pulse and amplified signal pulse are shown for different delay times between the two pulses. Shorter signal pulses are generated for larger delay times. Of special interest for practical application are the favourable energy conversion efficiencies obtained in the amplifier–generator system. Experimental data are presented in figure 5, where the energy conversion efficiency is 15% for $t_d \approx 0$.

We have used tunable idler pulses produced in a two-crystal generator for the investigation of vibrational modes of polyatomic molecules. In a first step, a specific molecular vibration is excited by an intense short pulse at frequency ν_1 by means of resonant infrared absorption. A second pulse, delayed with respect to the first, monitors the instantaneous state of the excited vibrational system. Two types of probing experiments should be outlined here.

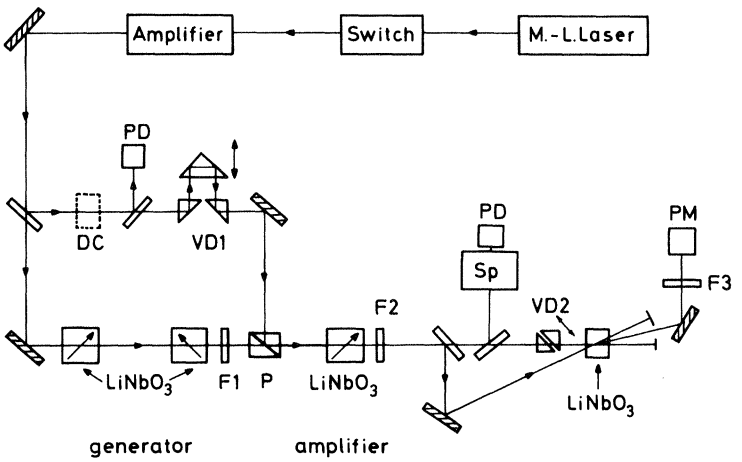

FIGURE 3. Parametric generator–amplifier system for the generation of infrared pulses of tunable frequency and variable pulse duration. Lower right: the autocorrelation set-up analyses the pulse duration of the signal pulse.

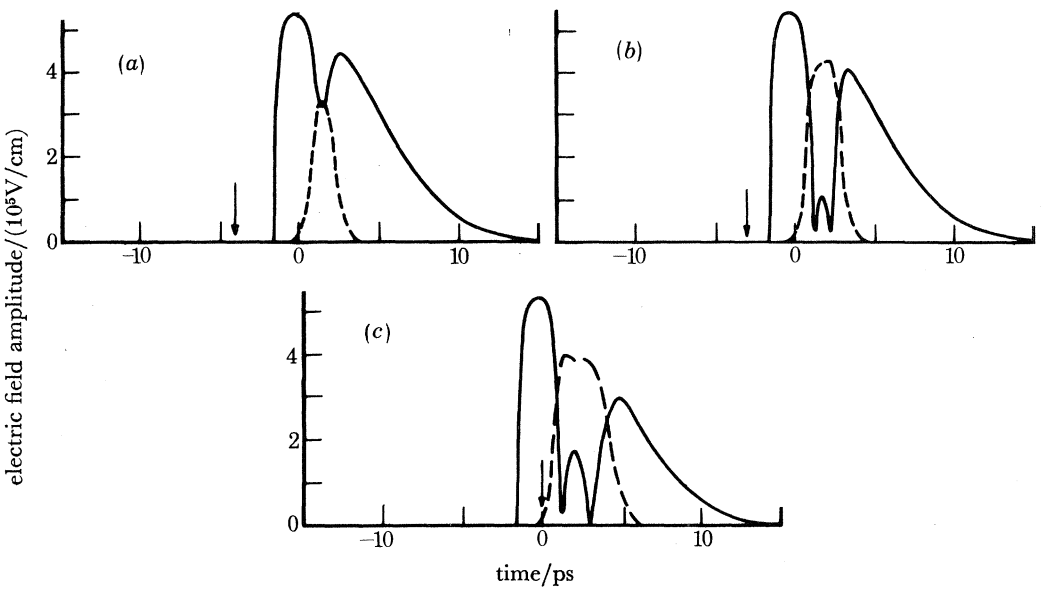

FIGURE 4. Calculated pulse shapes in parametric interaction. (*a*)–(*c*), The effect of a delay time t_d between the pump pulse and input signal pulse (marked by an arrow). The duration and amplitude of the amplified signal pulse depends upon t_d.

(i) The observation of the spontaneous anti-Stokes Raman scattering (at 90°) of the probe pulse allows the study of the instantaneous occupation of the vibrational energy states. We found time constants between approximately 1 and 100 ps for C–H stretching modes in a number of polyatomic molecules, e.g. $CHCl_3$, CH_2Cl_2, CH_3CCl_3, or CH_3I. It turned out that

the vibrational relaxation times depend critically upon the vibrational energy states of the individual molecules. Fermi resonance with overtones or combination modes and rotational motion of part of the molecule favour rapid decay of vibrational energy (Laubereau *et al* 1978).

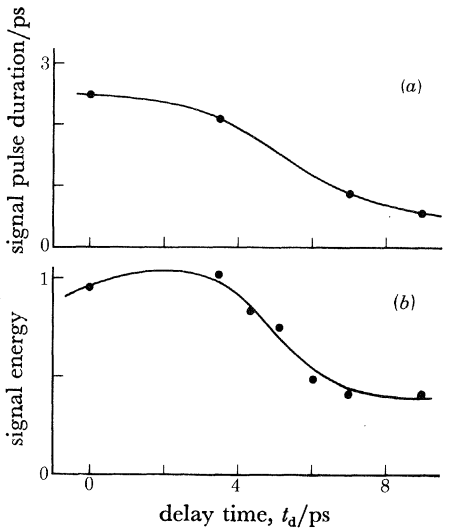

FIGURE 5. Parametric amplification with shaped laser pulses. (*a*) Measured duration of the amplified signal pulse plotted against delay time, t_d, between pump pulse and input signal. A significant pulse shortening is observed for delayed signal pulses. (*b*) Energy of the signal pulse plotted against delay time, t_d. The energy conversion efficiency is 15% for $t_d \approx 0$.

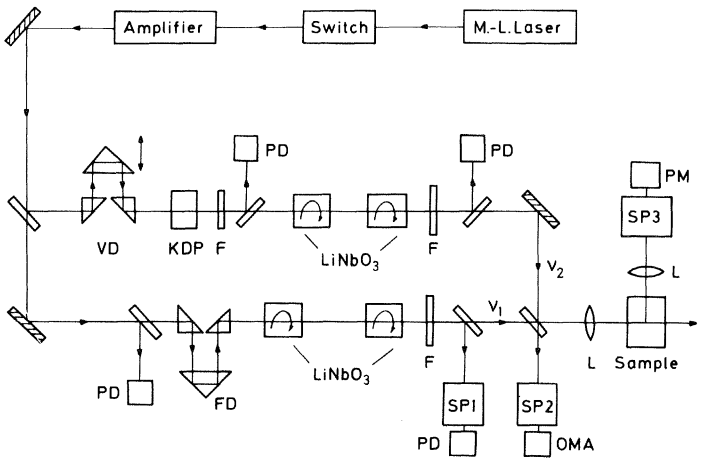

FIGURE 6. Schematic of experimental system with two parametric generators. The tunable infrared pulse (ν_1) is produced in the lower, the tunable visible pulse (ν_2) in the middle beam, with the use of two $LiNbO_3$ crystals each. The two pulses traverse the sample collinearly with adjustable time delay.

(ii) In very dilute systems we successfully used a fluorescence probing technique (Seilmeier *et al.* 1978*b*). The frequency of the probing pulse is made tunable by a second parametric generator and the vibrationally excited molecules were promoted to the bottom of the first excited singlet state from where they fluoresce. Figure 6 presents schematically part of the experimental system. In the lower beam the infrared frequency at ν_1 is generated while the second part of the laser pulse is converted to the second harmonic (green) frequency in the

KDP crystal and subsequently converted to a red pulse of frequency ν_2 by means of a parametric process. Tuning the pulse frequencies ν_1 and ν_2, one obtains interesting spectra which give information on the states contributing predominantly to the two-pulse excitation process. The relevant matrix element for the total transition of the molecule into S_1 may be written as a product of an infrared transition and a Franck–Condon factor. The intermediate vibrational states are thought to be mixed states containing skeletal modes of the molecules. These skeletal modes are known to have large Franck–Condon factors since they couple well to the π-electrons of the chromophore. When the infrared frequency ν_1 is tuned to 2970 cm^{-1} we find a lifetime of 6 ± 1 ps for the excited molecules (e.g. Coumarin 6). Recent measurements strongly suggest that this time constant is related to the CH_3 stretching mode which has a strong i.r. absorption at this wavelength.

In summary, the parametric process proves to be a useful tool for the generation of ultrashort pulses over a wide frequency range. Numerous dynamic investigations are possible with such pulses.

References (Kaiser *et al.*)

Fendt, A., Kranitzky, W., Laubereau, A. & Kaiser W. 1979 *Optics Commun.* **28**, 142–146.
Laubereau, A., Greiter, L. & Kaiser W. 1974 *Appl. Phys. Lett.* **25**, 87–89.
Laubereau, A., Fischer, S. F., Spanner, K. & Kaiser, W. 1978 *Chem. Phys.* **31**, 335–344.
Seilmeier, A., Spanner, K., Laubereau, A. & Kaiser, W. 1978*a* *Optics Commun.* **24**, 237–242.
Seilmeier, A., Kaiser, W., Laubereau, A. & Fischer, S. F. 1978*b* *Chem. Phys. Lett.* **58**, 225–229.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES