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Explosives Detection by LI-MS and Resonance Raman spectroscopy

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Explosives Detection by LI-MS and Resonance Raman spectroscopy

Abstract

This report summarises the experimental development and results from the second year of the FOI strategic project on explosives detection.

Experimental work has been focused on two areas. One is the ESSEX (Extremely Sensitive and Selective Explosive Detector), a trace detection system based on laser ionisation mass spectroscopy (LI-MS). The experimental results on toluene and chlorobenzene are shown to demonstrate the applicability of the technique.

The second is a stand-off system based on Raman spectroscopy. Initial experiments on e.g. the liquid “explosive” nitromethane demonstrate the possibility to obtain identification spectra from 12 meters distance at a detection time of 1second.

Also included are short theoretical descriptions for these techniques.

Keywords

Explosives, detection, mass spectrometry, laser, LI-MS, jet-REMPI, Raman spectroscopy

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Sammanfattning

Denna rapport sammanfattar det experimentella läget efter år två av det strategiska FOI-projektet om explosivämnesdetektion. Arbetet har fokuserats på två områden.

Det ena är ESSEX (Extremely Sensitive and Selective Explosive Detector), en spårmängdsmetod som bygger på en kombination av laserjonisering och masspektrometri. För att demonstrera metodens användbarhet redovisas experimentella resultat från toluen och klorbensen.

Det andra området omfattar en avståndsmetod baserad på Raman-spektroskopi. Inledande försök visar att t.ex. nitrometan, en flytande "explosivämne", kan identifieras på 12 meters avstånd och med en detektionstid på 1 s.

Korta teoretiska beskrivningar för dessa metoder är också inkluderade.

Nyckelord
Explosivämnen, detektion, masspektrometri, laser, LI-MS, jet-REMPI, Raman-spektroskopi

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1 Utökad sammanfattning

Under senare år har terrorism i allt högre grad framträtt som ett betydande hot mot det fredstida samhället. Användandet av explosivämnen är vanligt i terroristsammanhang, det används idag betydligt oftare än de mer uppmärksammade radiologiska, biologiska och kemiska stridsmedlen. Explosivämnen kan också användas för att sprida denna typ av skadliga ämnen.

Också i samband med militära operationer orsakar framför allt IED:er (Improvised Explosive Devices) stora bekymmer och även förluster. Just IED:er är ofta svåra att identifiera, eftersom de kan vara dolda eller kamouflerade. Exempel på IED:er är s k ”roadside bombs”, som placerats försåtligt på, under eller i närheten av vägar.

De ovan nämnda hoten måste tas på allvar, och ett sätt att bemöta dem är att införa känsliga, snabba och pålitliga explosivämnesdetektorer. Detta möjliggör att genomsöka personer eller bagage på flygplatser, i hamnar, vid inpassage till känsliga anläggningar eller vid militära check-points för spår av explosivämnen. Därigenom kan en attack stoppas i ett tidigt skede. Önskvärda egenskaper för dessa detektorer är snabb respons, ”on-line”-insamling, hög känslighet, hög selektivitet och låg falsklarmsgrad. För att uppfylla alla krav behövs sannolikt flera kompletterande metoder. De metoder som finns att tillgå idag är begränsade antingen vad gäller antalet explosivämnen de kan detektera, eller också ligger begränsningen i den tid de behöver för att ge ett noggrant och pålitligt svar.

Denna rapport beskriver de framsteg som under 2006 gjorts inom utvecklingen av två olika tekniker för explosivämnesdetektion. De två teknikerna utgörs av:

- En spårmängdsdetektionsteknik baserad på resonant laserjonisering i kombination med expansionskylning av provet. Detta utgör projektets huvudinriktning.
- En avståndsteknik utgående ifrån resonant Raman-spektroskopi.

Spårmängdsdetektionstekniken benämns ESSEX (Extremely Sensitive and Selective Explosives Detector) och är baserad på tre olika principer; resonant jonisering, masspektometri och kylning av gas via jet-expansion. Grunden för den resonanta joniseringen utgörs av jet-REMPI (Resonance Enhanced Multiphoton Ionisation), men i vissa fall, då ren REMPI inte fungerar, kan ett alternativt joniserings- och detektionsförfarande vara påkallat.

Jet-REMPI ger information om två olika molekylspecifika egenskaper: Molekylens massa och molekylspecifik excitationsenergi. Joniseringen sker i två steg, i sitt enklaste fall med två fotoner av samma färg (våglängd). Den första fotonen exciterar molekylen till ett specifikt tillstånd, den andra fotonen joniserar molekylen. Molekylmassan bestäms sedan med en Time of Flight-masspektrometer (TOF-MS). Den selektiva joniseringen medför att all bakgrund diskrimineras.

Den tvådimensionella karaktären hos mätdata gör det möjligt att utföra avancerad dataanalys och ger hög selektivitet kombinerat med låg risk för falsklarm. Eftersom både molekylmassa och excitationsvåglängd kan bestämmas med hög noggrannhet i detta 2D-diagram kan en omfattande databas skapas, och det finns utrymme att utöka den ytterligare allteftersom nya hotsubstanser blir kända.

Ett antal möjliga hinder för att använda ren REMPI-MS existerar, men vår bedömning är att det i dessa fall finns möjligheter att övervinna hindren genom små modifieringar i metoden. Det kan t ex bli aktuellt att använda två laservåglängder simultant eller att ta hjälp av molekylens fragmenteringsmönster för att genomföra en identifiering. ESSEX utnyttjar REMPI-jonisering i grunden men kan också omfatta dessa små modifieringar i metoden.

Den experimentella utrustning som krävs för ESSEX är en avstämbar laser, en Time of Flight-masspektrometer, en pulsad ventil och en pulsgenerator. Den laser som används är en färgämneslaser som är kontinuerligt avstämbar inom intervallet 205-850 nm. En färgämneslaser kan maximalt avstämmas inom ett intervall av 40 nm utan färgämnesbyte, ett mer tidseffektivt alternativ vore istället en laser av typen OPO (Optical Parametric Oscillator).

Den pulsade ventilen är monterad strax ovanför masspektrometerns laserjoniseringskälla så att den expanderande jeten befinner sig i joniseringskällan. Ventilen sitter monterad på ett rostfritt rör som löper från ventilen och genom en vakuumtät genomföring i jonkammaren ut till en öppen provkopp som rymmer provsubstansen. För att systemet skall fungera optimalt krävs en väl matchad pulssekvens som triggar laserpulsen, ventilens öppningstidpunkt och masspektrometerns jonextraktion. Det är också betydelsefullt för selektiviteten att optimera laserstrålens position i den expanderande jeten.

Införandet av en pulsad ventil för att skapa en jet har gett betydligt bättre spektral upplösning och signal/brusförhållande än det tidigare utnyttjade kapillärinsläppet. Jämförande data som påvisar detta har registrerats för toluen och klorbensen. Toluen har befunnits vara lämpligt att använda vid optimering och injustering av instrumentella fininställningar.

En till ESSEX kompletterande metod är resonant Raman-spektroskopi, denna har potential att användas på längre avstånd, av storleksordningen 100 m. Spontan Ramanspridning är ett välkänt ickeelastiskt spridningsfenomen där våglängden på det infallande ljuset skiftas enligt ett molekylspecifikt mönster. Denna typ av spridning har låg sannolikhet, dvs detektion av Ramansignaler ger låg känslighet. Genom att istället utnyttja resonans, dvs använda en våglängd som matchar en befintlig elektronövergång, kan signalen förstärkas med en faktor 100 till 10^6. Den resonanta Ramansignalen dominerar då över ickeresonanta Ramansignaler från övriga ämnen. Genom att använda en pulsad laser och en väl vald ”gatning” vid upptagning av signalen kan även den betydligt mer långlivade fluorescensen undertryckas.

Metoden testades med befintlig utrustning – en YAG-laser som frekvensdubblas eller – tripplas, ett teleskop av Schmidt-Cassegrain-typ för att samla in det Ramanskiftade ljuset, en optisk fiber samt en spektrometer med tillhörande detektor av typen ICCD (Intensified Charge Coupled Device).

Ramanspektra upptagna på tolv meters avstånd och under 20 s mättid redovisas för isopropylnitrat, nitrobensen, nitrometan och TNT (de första tre i vätskeform och den fjärde i fast form, pressad som cylinder med diametern ca 3 cm och höjden ca 3 cm). En jämförelse med referensspektra tydliggör en god passning. Genom att istället utnyttja resonant Raman förväntas betydligt bättre resultat och därmed möjligheter att detektera lägre koncentrationer på längre avstånd och med kortare mättid.

Sammanfattningsvis har arbetet med ESSEX framför allt varit inriktat på att införa den pulsade ventilen som provinsläpp och att optimera systemet. Detta resulterade i ett förbättrat signal/brusförhållande såväl som bättre upplösning och en reduktion av FWHM (Full Width Half Maximum) med 5 ggr.

Nästa steg blir att kartlägga excitations- och joniseringsscheman för energetiska ämnen. I första hand kartläggs ämnen med högt ångtryck (då värmt provinsläpp saknas) och som förväntas kunna joniseras med fotoner av en våglängd. Ett tillräckligt stort urval av målsubstanser för att kunna verifiera metodens användbarhet kan troligen hittas i denna delmängd.

Ytterligare explosivämnen, som inte kan joniseras med enfärgs-REMPI, kan senare schemabestämmas med ett dubbelt lasersystem, där två våglängder kan användas simultant. Framöver bör också insläppet modifieras så att det kan värmas för att möjliggöra detektion även av molekyler med lågt ångtryck.

Ramanspektroskopi har i de initiala försöken visat sig vara en möjlig metod för avståndsdetektion, och det finns starka förhoppningar om att resonant Ramanspektroskopi kan medföra ytterligare fördelar. Denna metod utgör inte huvudfokus för projektet, men visst arbete bör ändå få fortgå. Det finns beröringspunkter med utvecklingen av ESSEX såtillvida att båda metoderna utnyttjar befintliga elekronövergångar i molekylerna. Detta innebär att samma kartläggningsarbete över tillgängliga resonanta övergångar utgör grundförutsättningar för båda detektionsmetoderna.

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2 Introduction

During the recent years, terrorism has emerged as a prominent threat to society in times of peace. The by far most common form of terrorism uses only conventional explosives and has cost the lives of far more people than the more noticed biological, chemical and radioactive threat substances. Also, explosives could be used to distribute other harmful materials.

The consequences of attacks with explosives are often extensive damage to property as well as people. Examples of well known attacks are the explosion on board Pan Am flight 103 over Lockerbie on December 21 1988 (270 dead), the blasts on three commuter trains in Madrid on March 11 2004 (190 dead and 1500 wounded) and the blasts on a bus and three underground trains in London on July 7 2005 (50 dead).

Common threats for international military operations today are Improvised Explosive Devices (IEDs). These are many times very difficult to reveal in time as they are often concealed, for instance placed as roadside bombs that go off when a vehicle passes. IEDs and roadside bombs constitute a daily problem in troubled spots around the world. Finding roadside bombs before they cause harm is a very tough problem with high demands for long range detection at high speed. A tragic example of roadside bombs connected to the Swedish Armed Forces is the bomb that killed two and wounded three Swedish soldiers in Afghanistan on November 25, 2005.

The existence and employment of sensitive, fast and reliable explosive detection equipment is the most effective weapon against all those threats. Checking people and goods at airports, harbours and at the entrance to areas of general importance or at checkpoints in military troubled areas may lead to the stopping of an attack in an early phase. The desired properties of an explosive detection system are quick response, on-line sampling, high sensitivity (like a dog or better), high selectivity and a low false alarm rate. Furthermore, the system should be able to work all day long and be mobile. If the system should be used to check people, it has to be benign to humans as well. Most likely, a few different techniques have to be combined to build a system which is able to detect all explosives. The techniques available today can detect too few explosives or are too slow for applications with a high sample throughput, so more research in this field is needed.

This report resumes our results with the development of the two following techniques for explosive detection:

- A trace detection technique based on resonant laser ionisation mass spectrometry (LI-MS) combined with sample gas cooling.
- A stand-off detection technique, by which the signal of a standard optical spectroscopic technique, Raman spectroscopy, is enhanced by resonant excitation.

3 Laser Ionisation Mass Spectrometry

The ESSEX system (**E**xtremely **S**ensitive and **S**elective **Ex**plosives Detector) for standoff or remote detection of trace amounts of explosives, being developed at FOI, will employ the laser ionization mass spectrometry (LI-MS) technique based on a special ultra sensitive and selective ionisation scheme. First, an overview of the technique, its advantages and challenges are given and then our own results are shown.

3.1 Description of the technique

3.1.1 Introduction

The combination of three different physical principles; optical spectroscopy, mass spectrometry, and jet expansion of gas, results in a very sensitive and selective detection method. A special case of LI-MS, called jet-REMPI (**R**esonant **E**nhanced **M**ulti **P**hoton **I**onization) was developed to analyze combustion products in a waste incinerator [1] but its generality allows to apply it for the detection of many other substances, amongst those explosives [2]. The generality of the method makes it suitable also for other compounds which are of common interest like chemical warfare agents and narcotics. ESSEX is not restricted to employ jet-REMPI however. In some cases this straightforward detection scheme will not be applicable (see 3.1.4 The challenges of jet-REMPI). When such cases are encountered, alternative ionisation and detection schemes will be employed f.i. by using fragmentation patterns.

3.1.2 The principle of jet-REMPI

Jet-REMPI uses laser ionisation in combination with mass spectrometry (Figure 1) giving information about two different molecular-specific properties: the mass and the energy of a molecular-specific level. The REMPI technique performs the laser ionisation in two steps. The left side in figure 2 shows the simplest form of REMPI, which uses two photons of the same energy. Absorption of a first photon from the laser excites the molecule from the ground state to a known excited state, and the absorption of a second photon ionises the molecule. The mass of the ion is then determined by means of a **T**ime-**o**f-**F**light **M**ass **S**pectrometer (TOF-MS), in which the ions are accelerated by an electric field and the flight time is measured. From the flight time of the ion its mass can be deduced.

The selective ionisation prevents the ionisation of other substances than the one for which the sample is checked at the moment (Figure 2, right side). This eliminates interferences from the background. Scanning the wavelength of the laser therefore results in scanning the sample for different molecules.

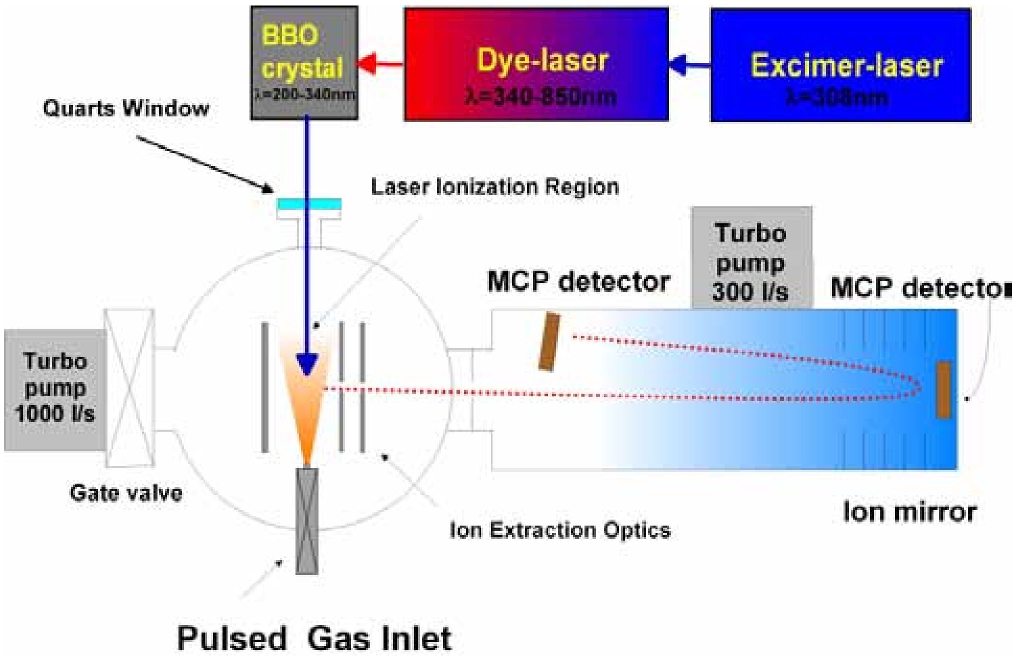

Figure 1 *Experimental setup for jet-REMPI. The sample gas is introduced into the chamber through a pulsed valve (lower left). A frequency doubled laser beam from the dye laser, pumped by an excimer laser, ionises the sample molecules inside a vacuum chamber. The ions are extracted into the TOF-MS (lower right). At the end of the MS an ion mirror reflects the ions towards the detector.*

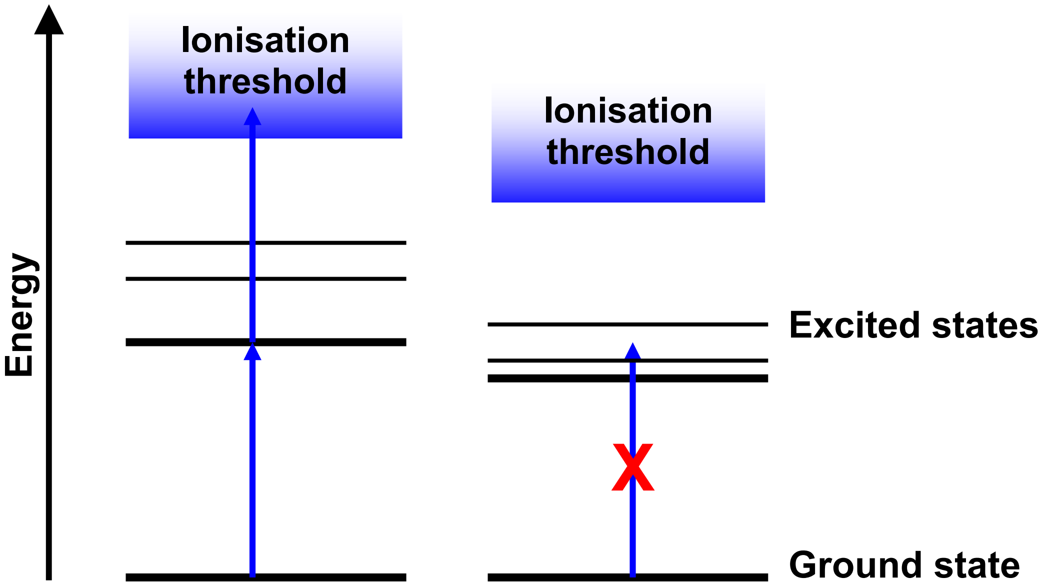

Figure 2 *The principles of REMPI. The left side of the picture shows the objective molecule which has an energetic level matching the laser energy and therefore will be ionised. The right side of the figure shows all other molecules without matching energy levels, hence they do not undergo laser ionisation.*

The word "jet" in jet-REMPI refers to the sample inlet of the mass spectrometer which is realised by a pulsed valve with a high pressure difference. This leads to a strong expansion of the gas inside the vacuum chamber and simultaneous cooling so that the molecules populate only the ground state. The expansion of a gas through a pinhole with the diameter D is shown in Figure 3, left**.** The dependency of the pressure and the temperature of the molecules are shown as well. Both parameters decrease with increasing distance from the inlet. For comparison, pressure and temperature dependency of a gas being introduced through a long channel with the same diameter is shown on the right side of figure 3. The pressure drops linearly from the beginning of the capillary until its end and the gas temperature remains constant, so no cooling takes place.

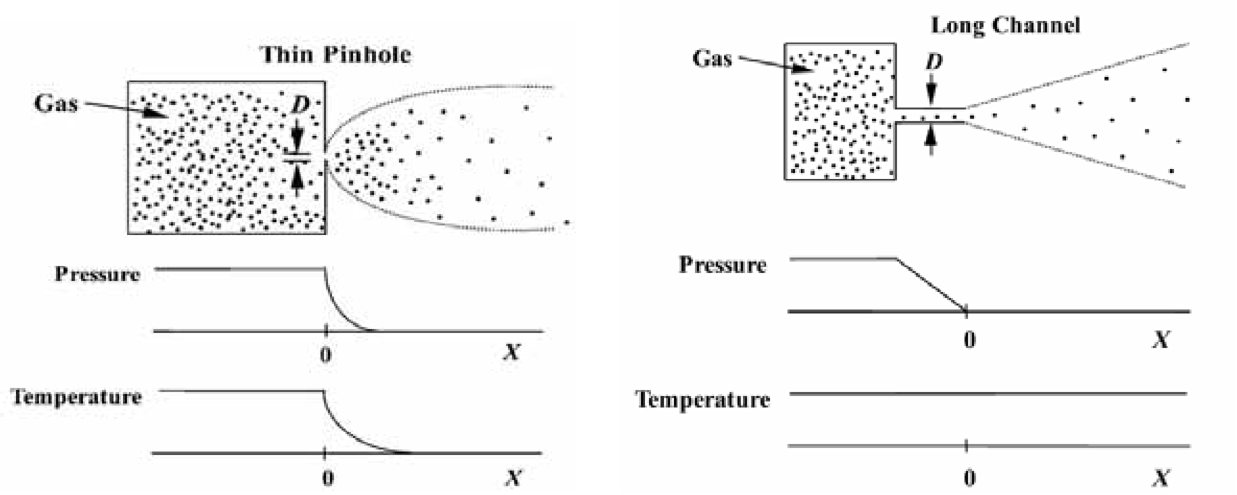

Figure 3 *Supersonic gas expansions through a pinhole (left) and a capillary (right) and related pressure and temperature dependencies (from [3]).*

The results of this cooling technique are very sharp absorption spectra with narrow lines. Narrow lines are a requirement for high selectivity. Figure 4 shows typical jet-REMPI data for different compounds. The received data is two-dimensional, mass and wavelength, which allows unambiguous identification of every compound. The uniqueness of the data for each molecule is presented in Figure 5.

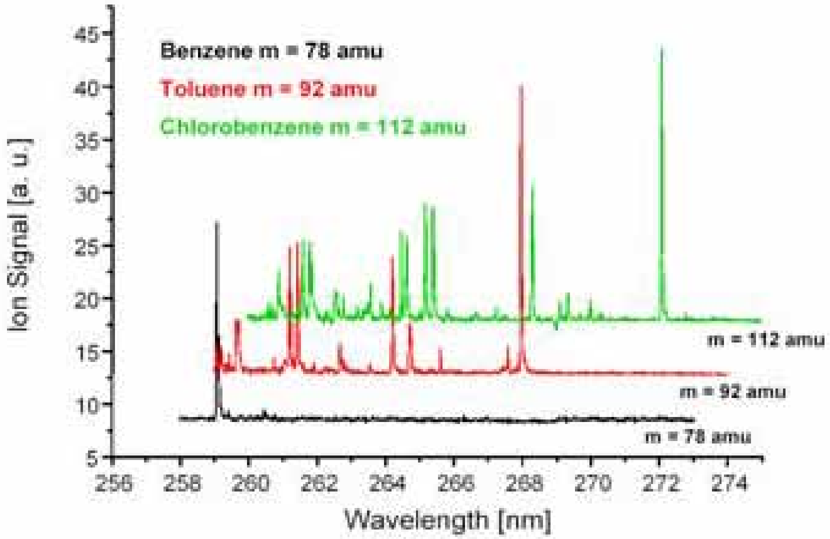

Figure 4 *Typical jet-REMPI spectra for three different molecules. The ion signal depending on the wavelength variation is shown. Figure from SRI.*

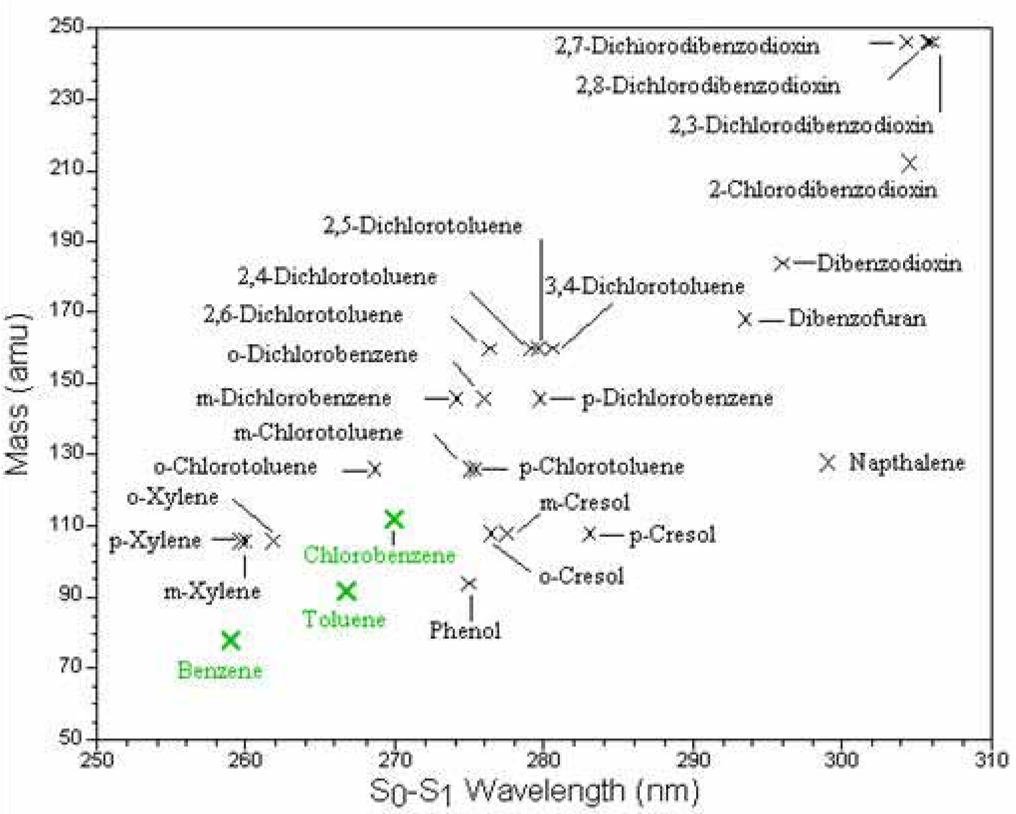

Figure 5 *Each molecule receives a unique position in a mass-wavelength diagram when plotting the corresponding mass and wavelength couple for a specific transition. Here the wavelength for the transition from the ground state S_0 to the first excited state S_1 is indicated. Figure from SRI.*

3.1.3 The advantages of jet-REMPI

The fact that the measured data is achieved in two dimensions results in very high selectivity. This permits good opportunities for advanced data analysis which results in a low risk for false alarms.

The sensitivity of jet-REMPI is in the low ppt-level (parts per trillion, i.e. one among 10^{12}) [4, 5]. The verified detection limit of dogs for the liquid explosive nitroglycerine is in the or just below the ppb-level (parts per billion i.e. one among 10^9) [6]. However, notice that dog are believed to detect not only gaseous explosive molecules but also explosive particles and particles with adsorbed explosives.

At present, ion mobility spectroscopy (IMS), the system commonly in use, is able to detect pg of DNT. The advantage of the jet-REMPI method compared to IMS is, apart from the lower detection level, its capability to extend the method to a large number of substances without increasing the false alarm rate. A comprehensive database allows scanning a sample for many different compounds at the same time. The database can be easily extended when new threats emerge.

The system can be made mobile and should fit into the boot of an estate car. We expect further size reductions due to the ongoing miniaturisation of both mass spectrometer and laser system.

The sample for jet-REMPI analysis can be taken directly from air without additional preparation and gives a quick result (seconds to minutes). Only those explosives having a sufficiently high vapour pressure so that their concentration exceeds the detection limit can be detected through direct air sampling. TNT, Hexogen, Pentyl, TATP, Ammonium nitrate, and nitro glycerine have a high enough vapour pressure to yield concentrations in or above the ppt-level [7]. For compounds with a very low vapour pressure, sampling and desorption of particles will be necessary. Figure 6 displays the mass and vapour pressure for a number of common explosives and the detection limits for dogs and jet-REMPI.

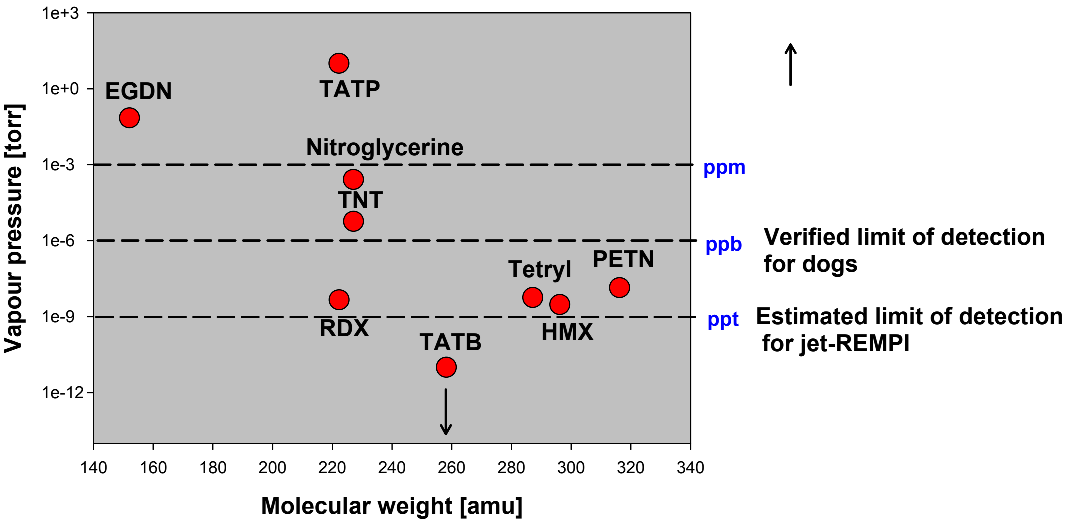

Figure 6 *Vapour pressure for a number of common explosives [8, 9]. TATB is used only in very special applications and complicated to synthesise without advanced equipment, so its detection does not have high priority.*

3.1.4 The challenges for jet-REMPI

There are a few possible problems which may emerge when ionising molecules by means of REMPI. Those are illustrated in Figure 7. If the excited state has less energy than half of the ionisation potential it is not possible to ionise the molecule by using only one laser (A). In that case, two lasers with different wavelengths must be used. The excited state must not lie higher than 6 eV (equivalent to a wavelength of 200 nm) above the ground state, because this is the highest energy of photons from common lasers (B). Low transition probability of the ionisation step (C) can be solved by using another vibrational state. A fourth imaginable problem is a too fast relaxation of the excited state (D), i.e. that the molecule decomposes.

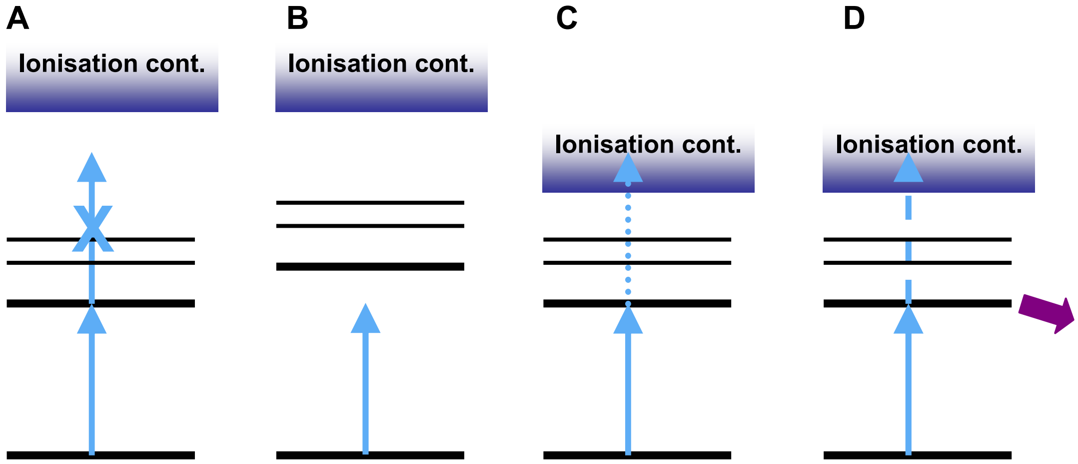

Figure 7 *Possible problems with ionisation by REMPI. More information in the text.*

According to SRI [10], the lowest excited state of the nitro aromatics TNT and DNT is dissociative with a life time so short that the second photon does not manage to ionise the molecule before it fragments (compare case D in Figure 7). It is necessary to study the decomposition of explosives and their excited states in order to find a suitable modification to the ionisation and / or detection scheme to be applicable also in those cases. One possibility is to monitor the emerging fragments and draw conclusions from them to the parent molecule. TNT releases NO_2 upon laser ionisation which then undergoes rapid predissociation to form NO + O. Pond *et al*. [10] monitored the NO fragment via the subsequent REMPI process that occurs during the same laser pulse. Measurements of NO from fragmentation resulted in a limit of detection of 50 ppt.

3.2 The equipment of the experimental setup

To perform initial experiments with jet-REMPI, a laser with variable frequency, a time-of-flight mass spectrometer, a pulsed valve and a pulse generator are needed. Those pieces of equipment were already present at FOI Grindsjön at the beginning of the project but needed some adaptation. The single parts of the setup are described in the following sections.

3.2.1 Laser

The tuneable laser is a dye laser (Lambda Physik LPX300) which is pumped by an excimer laser (Lambda Physik LPD3000). Using adequate dyes, the wavelength of the laser can be varied between 340 and 850 nm. Shorter wavelengths are achieved by doubling the frequency with a BBO crystal (see figure 1). The emitting wavelength within the dye's range (~ 40 nm depending on wavelength range and half of that in the doubling mode) is tuned by adjusting a grating. Tuning it over a longer range requires frequent dye changing. The laser's wavelength cannot be scanned continuously but only in discrete, even though very small steps. At present scanning the laser and recording of the mass spectrum is not automated. Therefore recording a spectrum signal versus wavelength has to be done so that first the wavelength has to be adjusted then the signal has to be measured before the wavelength is changed again. This procedure is very time-consuming.

The optimal laser for our experiments would be an **o**ptical **p**arametric **o**scillator (OPO) with which the wavelength can be changed quickly over a wide range. Currently we do not have access to an OPO but we plan to get one during 2007.

3.2.2 Mass spectrometer

A time-of-flight mass spectrometer from Comstock Inc. (RTOF-210/EII) with two multiple channel plate detectors (MCP) were available for the experiments. During the first year of the project we changed its commercial electron impact ion source to a laser ionisation source which has enough space for a jet expansion between the electrodes. The bigger source requires a higher acceleration potential applied to the repeller electrode to allow the ions to reach the detector after reflexion from the ion mirror. Using the reflected mode results in better resolution, mainly due to the ions' longer flight path than detection of the ions in linear mode. Unfortunately, the existent power supply cannot deliver the required voltage so the ions were detected by the MCP at the end of the flight tube. The spectra taken with the TOF are recorded by means of an oscilloscope (LeCroy, LC 684 DL).

Beside the TOF-MS, the vacuum chamber was equipped with a conventional quadrupole mass spectrometer (Stanford, SRS RGA 200) to analyse the composition of the background gas.

Each of the two vacuum chambers containing the sample inlet plus the ion source and the flight tube, respectively, are pumped by a turbo molecular pump which is backed by a mechanical fore pump. The base pressure in the system is $8x10^{-8}$ torr.

3.2.3 Pulsed valve

The pulsed valve (Parker Hannifin Corporation, General Valve Series 9, opening diameter is 0.5 mm) is mounted perpendicular above the ion source of the ToF with the opening in the middle between the electrodes and a distance of approximately 40 mm above the extraction hole of the ion source (Figure 8). Coggiola *et al*. have experimentally shown, that ions can be detected if that distance is between 23 and 75 mm [11]. Due to the fact that the vacuum chamber did not have a flange on which the valve could be mounted to give this distance to the ionisation region, it was mounted via a Swagelok connection on a stainless steel tube inside the vacuum chamber. The whole tube is about 50 cm long of which one half is inside and one half outside the chamber, respectively. Both ends are bent conveniently so that the valve sits in the above described position and the outer end points downwards. A small glass vial which houses the sample was taped to the tube's outer end. Since this connection is not air tight, there is atmospheric pressure in the tube behind the valve. The air works as carrier gas for the sample molecules, a necessary part for efficient cooling. The power connections to control the valve enter the vacuum chamber via an electrical feedthrough mounted on different flange than the tube.

The valve is operated by a power supply (Parker Hannifin Corporation, Iota One) which can be triggered remotely. The valve's shortest opening time is 140 μs and its closed time must be longer than the selected opening time.

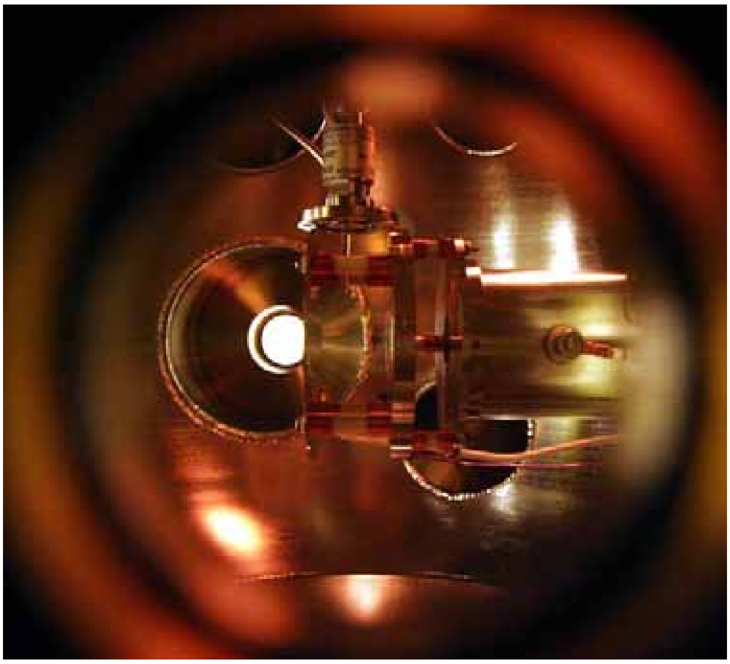

Figure 8 *The valve mounted above the ionisation region with opening in the middle between the two electrodes: repeller (left) and extraction electrode (right). On the very right, the beginning of the flight tube can be seen.*

3.3 Results

Before getting started with real laser ionisation measurements, some small, but important details had to be considered and adjusted.

3.3.1 Partial pressure measurements

Tests of the pulsed gas inlet were performed by letting a sample gas into the system and mass spectra of up to 200 amu were recorded with the RGA. The valve was pulsed with a frequency of 3 Hz using an open time of 200 μs. These tests were done to make sure that the sample reaches the chamber. It was observed that the amount of detected sample increases with time during the first hours then reaches saturation and decreases very slowly after the sample has been removed. These observations refer to absorption of sample molecules inside the stainless steel tube. This means that the tube has to be heated to detect traces of molecules and molecules with a low vapour pressure. However, for showing the suitability of LI-MS as an explosives detector, it is sufficient at the moment to focus on explosives with an adequate vapour pressure and leave improving of the inlet for later.

3.3.2 Pulse sequence

Another very important part of setting up a laser ionisation experiment is to determine the best pulse sequence of the system. Since the optimal starting time for every single pulse depends on the real laboratory dimensions like the distance between laser and mass spectrometer or the lengths of the cables they have to be determined individually and experimentally for every setup. The reasons for this individuality are the times required for the pulses to reach the laser and the valve and the travelling time of the light through the laboratory and into the vacuum chamber. Further reasons for the specific times are the dimensions inside the vacuum system like the position of the inlet relative to the ionisation region.

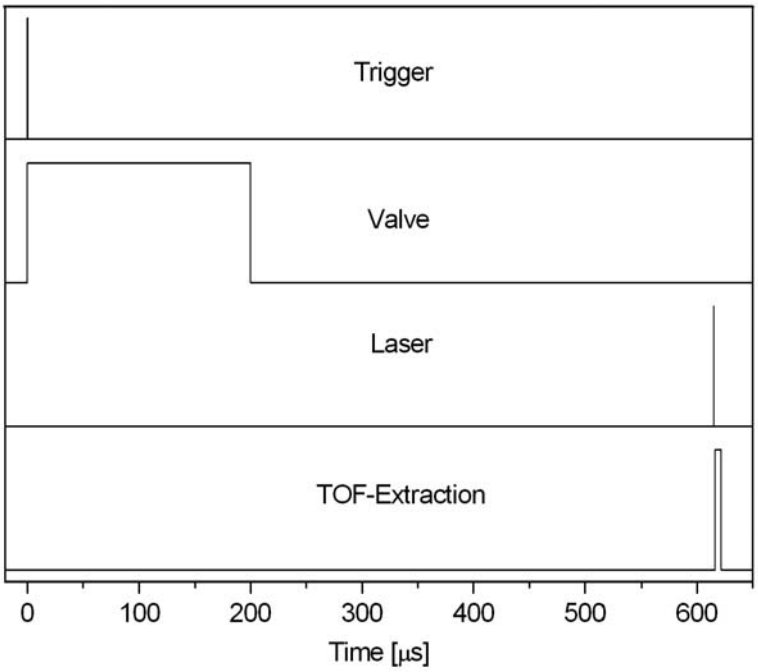

Figure 9 *Pulse sequence of the jet-REMPI system. For detailed information see text.*

In our laboratory, a delay generator (Stanford, DG 535) triggers opening of the valve, emission of a laser pulse and ion extraction in the mass spectrometer at certain time intervals relative to its internally created trigger pulse. Toluene was used as test sample to optimize time delays for each trigger pulse and the laser wavelength was the optimum resonance wavelength, 267 nm. The TOF-signal of toluene was then maximized by adjusting the starting time of the pulses. The optimal pulse sequence for our system is shown in Figure 9. At the time t = 0 the pulse generator creates a trigger signal and sends simultaneously a pulse to the valve which opens immediately and stays open for the next 200 µs to let in the sample. 615 µs after the trigger signal, that means that the valve is already closed for 415 µs, a 10 ns pulse from the laser ionises the cooled sample gas. 160 ns after the laser pulse, the ions are extracted into the flight tube with a 5 µs long pulse. The delay of the extraction as to the laser pulse and the extraction duration were already determined with the previous capillary inlet. The whole sequence is repeated with a frequency of 3 Hz. This is the highest repetition frequency maintaining a pressure better that 1×10^{-6} torr in the flight tube which is the highest operating pressure of the MCP detector. The repetition frequency could be increased with a valve having a smaller orifice or a shorter open time.

3.3.3 Positioning the laser beam in the molecular jet

The jet expansion through the pulsed valve leads to cooling of the sample gas. Since the cooling is not homogeneous the optimal position where the laser ionises the sample has to be found. To maximize the throughput of ions in the mass spectrometer this point should be slightly above the central axis of the flight tube.

Ionising only the coldest ions will result in a narrow full width at half maximum giving good resolution and high selectivity. Therefore different positions where the laser enters the ion source were tested and the ratio of two signals, one corresponding to the resonance wavelength and the other to an off-resonance wavelength, was determined. The higher the ratio, the better resolution will be achieved. For those measurements toluene was used as sample and the ratio of the signals corresponding 266,95 nm and 267,5 nm were determined. A maximum ratio of 35,5 was obtained. To be able to readjust the laser quickly after a dye change or other changes in the laser beam a mask with a mark of the optimal position was placed over the window through which the laser enters the vacuum chamber. This mask will be taken off for measurements and put back for adjusting and controlling the laser beam's position.

It is very likely that the laser beam's position in the ion source is not fully optimised and that adjusting it more precisely will result in a better sensitivity. However, for initial experiments the best sensitivity is not needed.

3.3.4 Calibration

The installation of the pulsed valve directly above the TOF's ion source made it necessary to remove the microwave discharge assembly which was mounted there and used for calibration of the TOF. Calibration of the instrument is necessary for the later calculation of the masses which correspond to the measured flight times.

Calibration of a mass spectrometer is normally performed by use of a special calibration mixture giving a known fragmentation pattern. This will be attempted at a later stage and will require a calibration mixture that can be used with laser ionisation.

A rudimentary calibration which sufficient for our needs at this stage can be made in the following way: Ionising a mixture of toluene and air a wavelength of 267 nm results in only one signal which corresponds to mass 92 according to our measurements from last year when the system was calibrated. Therefore this signal was used to calculate the specific dimensions of our TOF with the following formula for TOF mass spectrometry:

$$\tfrac{1}{2}\,\mathrm{m}\,(l/t)^2 = \mathrm{e}\,U_{\mathrm{Rep}}$$

with: m: ion mass
l : length of flight tube
t : flight time
e : elementary charge
U_{Rep} : repeller voltage, 190 V

For convenience the formula was transferred into where the constants are merged together to k:

$$\mathrm{m} = (2\mathrm{e}U_{\mathrm{Rep}})/(\mathrm{l}^2)\; t^2 := k\, \mathrm{t}^2$$

k was determined from the toluene signal which appears with the present settings 25,93 µs after the ion extraction to 7.31. This was deployed to calculate the masses corresponding to the measured flight times when ionising air at 445 nm, shown in table 1.

Flight time [µs]	Calculated mass [amu]	Molecule, mass [amu]
10,02	13,73	N, 14
11,17	17,07	OH, 17 or H_2O, 18
14,20	27,58	N_2, 28
15,19	31,56	O_2, 32

Table 1: *Measured flight times for air components, calculated masses and allocated molecules.*

The fact that typical air components can be unambiguously assigned to the measured flight times shows, that a molecules mass can be deduced with simple mathematics. This way of calibration is sufficient as long as it is only needed to confirm the mass of the samples molecules.

3.3.5 Jet-REMPI spectra

After determining and adjusting the best pulse sequence and the optimal position of the laser beam, jet-REMPI spectra for toluene and chlorobenzene were recorded. To make the advantage of the cooling by jet expansion obvious, comparisons of spectra taken with both the continuous (capillary) and the pulsed sample inlet are shown (Figure 10 and Figure 11). Both times, spectra with the same inlet but different molecules were taken simultaneously and a mixture of the two liquids was used. The sample used with the pulsed inlet contained mainly chlorobenzene and only traces of toluene. The received signal for toluene was therefore multiplied by a factor of 6 so that the maxima have the same height. The mixture of the samples for the capillary inlet was approximately 1:1, and the corresponding spectra were multiplied by 3 (toluene) and 10 (chlorobenzene) respectively. Since the aim of our jet-REMPI system is not quantification the spectra can be mathematically amplified for better visualisation.

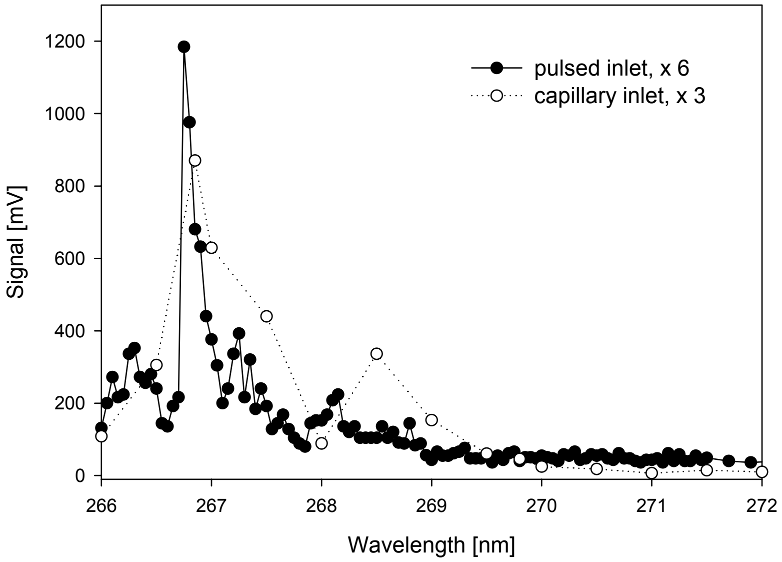

Figure 10 *Comparison of the measured spectra for toluene with pulsed (filled circles) and continuous (open circles) inlet.*

As for toluene, both spectra show a similar wavelength dependency and the maxima overlap each other (Figure 10). The spectra with the capillary inlet were recorded in wavelength steps of only 0,5 nm while the other spectra was taken with steps of 0,05 nm. Since the value for the resonance found in literature is 266.95 nm [3] it is possible that the maximum with the continuous inlet was missed and that a better agreement would have been achieved if this value would have been measured as well. The gas cooling reduces the full width at half maximum to 0,2 nm compared to 1 nm for the capillary inlet and the spectrum shows a fine structure which could not be resolved without jet. The best toluene spectra measured with our system shows a full width at half maximum of 0,1 nm despite having 0,1 nm between two points (not shown), so it is very likely that this value could be reduced further.

The spectra for chlorobenzene are more difficult to interpret (Figure 11). The wavelength dependencies are not that similar as in the case for toluene and the main maxima differ by a nanometre. In the case of the spectrum with the continuous inlet, the maximum signal has a height of only 0.7 mV and the signal is only about a factor of 5 above the noise level. This means that the main maximum of the spectrum is not that prominent compared to the other maxima. Since the mixture of both liquids for that experiment was 1:1, toluene may have clogged the capillary (0,1 mm inner diameter, 25 m length) so that only few chlorobenzene molecules could travel through the capillary. In our first experiments while using the capillary inlet with a pure toluene sample, we experienced that toluene can clogg the capillary fully so that no molecules could be detected any more.

Nevertheless, the cooled spectrum shows the same advantages as the one for toluene: a sharp maximum at 269,35 nm which is in good agreement with the value from literature 269,81 nm [3] and a resolved fine structure. The enhancement of spectral resolution and signal to noise ratio clearly shows the advantages of jet cooling as obtained with the pulsed valve.

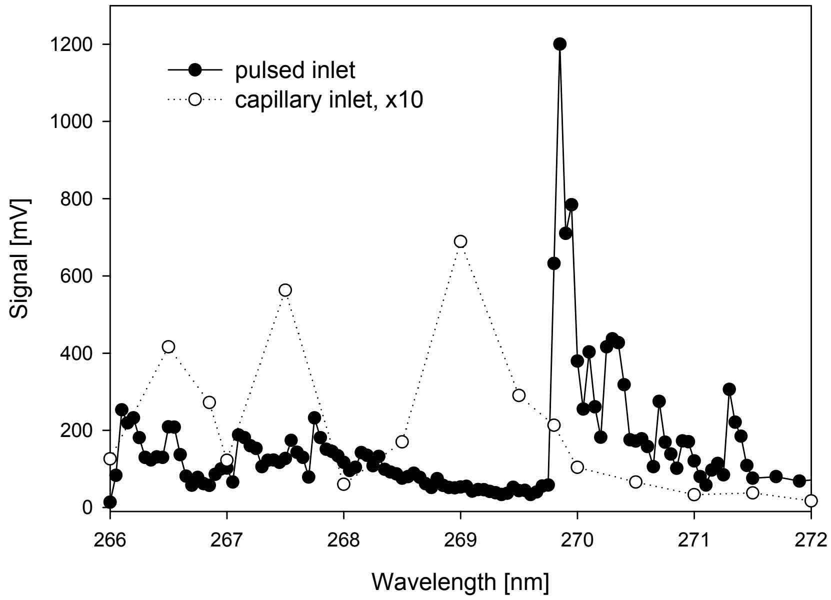

Figure 11 *Comparison of the measured spectra for chlorobenzene with pulsed (filled circles) and continuous (open circles) inlet.*

In summary, pulsing the sample inlet results in a higher and narrower signal due to the fact that so many molecules are gathered in the same molecular level, the ground state.

3.3.6 Measurements on nitromethane

Beside toluene and chlorobenzene we have also done measurements on nitromethane. According to UV absorption spectra taken last year [12] gaseous nitromethane has an absorption peak at 225 nm, a wavelength which is accessible with the existing laser.

When performing the same measurement with the pulsed valve three peaks were obtained which turned out to be air but no nitromethane was detected. By means of RGA, nitromethane was detected inside the vacuum chamber. According to the literature [13] the molecule's ionisation potential is (11.08 ± 0.04) eV which corresponds to a wavelength of 223,6 nm for two photons. Since this wavelength is shorter than the one of the absorption peak, the energy of the incident light was too low to ionise nitromethane. For successful REMPI, the absorption wavelength must be low enough so that the energy in two photons is sufficient to reach the ionisation potential. Otherwise, the problematic circumstance depicted in figure 7 A will arise.

Questions about the reliability of this particular UV spectrometer have been raised. In addition to the suspicion that the spectra obtained are not always reliable, the resolution of the spectrometer, especially for short wavelengths, is decreased due to its old age. This means that it is not possible to achieve good gas phase spectra in that range.

Another spectrum of liquid nitromethane in acetonitril was recorded (Figure 12). This is in good accordance with the literature [14]. The spectrum shows an absorption peak at around 202 nm where it should be possible to ionise the molecule. This wavelength is currently out of reach with the used dye laser, but will eventually be reached using a sum frequency crystal (summing the fundamental and doubled frequencies). This ionisation scheme will be tried out but is pending, awaiting the repair of a motor driver unit for dye laser crystals. Using the sum frequency mixing crystal will allow us reach to 198 nm.

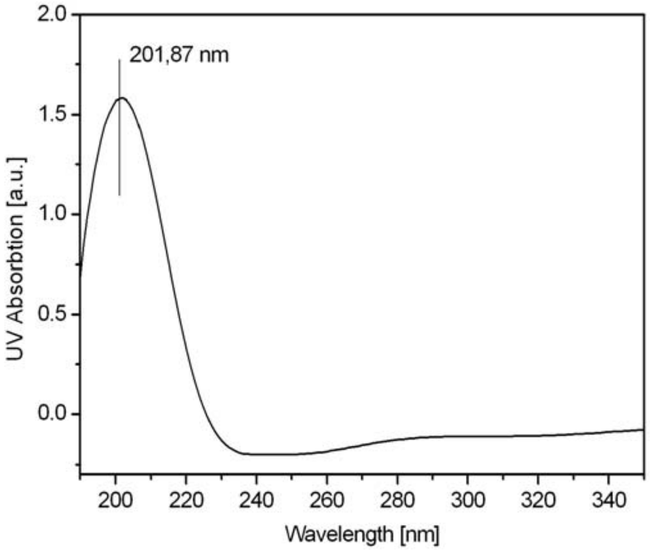

Figure 12 *UV sprectrum of liquid nitromethane diluted with acetonitril*

Wavelengths shorter than 198 nm are not readily accessible with a dye laser, so another solution has to be found. In [15], the use of two-photon resonant four-wave mixing for creating tunable, coherent light in the wavelength region of 200-115 nm is presented. The authors use this method for studying excited state dynamics of jet-cooled molecules. This method requires two dye lasers pumped by the same source, and a frequency conversion cell. Although experimentally challenging, the equipment needed is available in our laser lab, save the conversion cell. This allows for the possibility to try resonant laser ionisation at VUV (vacuum UV) wavelengths if this proves to be necessary.

4 Standoff Raman detection of explosives

For standoff detection of explosives, Resonance Raman spectroscopy is one of the most promising techniques. It offers good selectivity and is well suited for measurement over distances since the laser beam is collimated and does not diverge notably.

4.1 Introduction

Spontaneous (i.e. ordinary non-resonant) Raman spectroscopy has moderate selectivity and poor sensitivity; still it has been brought up lately for explosives detection and been proved to work in initial experiments. With this technique, standoff detection of explosives has been demonstrated on bulk samples of explosives at 50 meters and 500 meters on some solvents and polymeric materials [16].

The use of Resonance Raman spectroscopy instead provides a significant improvement of sensitivity and selectivity compared to spontaneous Raman spectroscopy. We believe that it will show the sensitivity required at standoff distances

An experiment for pulsed Raman spectroscopy on explosives has been set up at FOI as a step on the way to pulsed Resonance Raman experiments. Filters and optical setup were not optimized but rather chosen from what was readily available in our laboratory.

4.2 Raman spectroscopy

Raman spectroscopy is a technique used to study vibrational, rotational, and other low-frequency modes in a molecule. These modes depend on the structure of the molecule and determine how the light that is inelastically scattered by the molecule change energy. Only a small portion of the light incident on the molecule is scattered inelastically, or Raman scattered (Figure 13). The method relies on monochromatic light, usually from a laser. Vibrational energy or other excitations in the system are absorbed or emitted by the laser light, resulting in the energy of the laser photons being shifted up or down. The scattered light of longer wavelengths is called Stokes Raman scattering and the light of shorter wavelengths is called Anti-Stokes Raman scattering. This is equal to a shift in wavelength of the scattered light. The shift gives information about the structure of the molecule and is constant no matter the wavelength of the incident light that caused it. By detecting the shift and comparing it with reference measurements or theoretical calculations it is possible to determine the species.

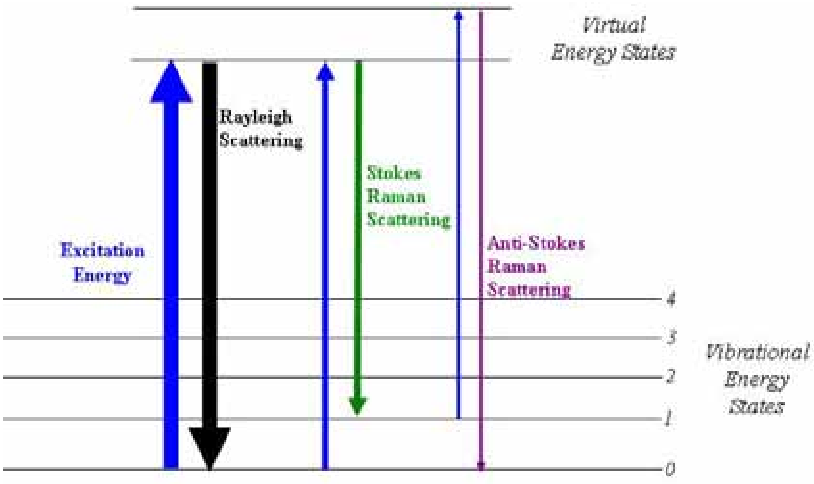

Figure 13*: Most of the exciting energy from the laser (blue) is Rayleigh scattered with no wavelength shift (black). A much smaller part of the scattered light is being shifted towards longer wavelengths, called Stokes Raman scattering (green). An even smaller part is shifted towards shorter wavelengths, called Anti-Stokes Raman scattering (violet). Our setup detects the Stokes Raman scattering.*

In a typical setup, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and spectrally resolved in a monochromator. The Rayleigh scattered light is filtered away before the monochromator since it contains no information and is intense enough to potentially damage the detector, while the light shifted away from the laser line are dispersed onto a detector.

4.3 Resonance Raman Spectroscopy

The low sensitivity of Raman spectroscopy is due to its non-resonant nature. Resonance Raman scattering occurs when the excitation wavelength is matched to an electronic transition of the molecule, so that vibrational modes associated with the excited electronic state are greatly enhanced. With a tuneable laser the wavelength can be chosen to match or nearly match a resonant absorption in the investigated species leading to an intensity enhancement of 100 to 10^6, hence significantly lowering detection limits and simplifying spectra since they will be dominated by the resonantly enhanced peaks. A careful choice of excitation wavelength will enhance the Raman spectrum from the target molecules relative other molecules present. Several problems with Raman spectroscopy are solved with UV Pulsed Resonance Raman spectroscopy. The pulsing reduces stray light from the background and fluorescence induced by the laser light in the sample. UV is preferred because the intensity of Raman scattered light is proportional to $1/\lambda^4$ and the background emission of UV is low. Real samples are very likely to contain impurities that fluoresce when illuminated by visible light. The use of UV light will cause fluorescence in the visible – well out of the region where the Raman signal is detected.

4.4 Experimental setup

As all our optical equipment, e.g. the telescope, is not adopted for UV spectroscopy, we conducted experiments mainly in the visible range (532 nm). The signals from the UV setup (355 nm) were almost equally good, while with appropriate equipment they should have been considerably better.

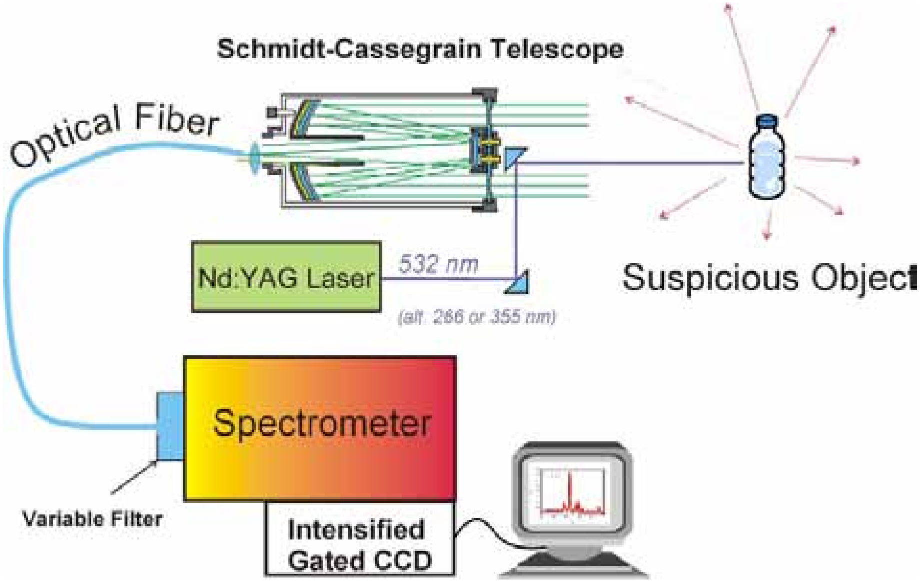

Figure 14: *Standoff Raman spectroscopic setup.*

A schematic setup can be seen above (Figure 14). To better simulate a situation where an ideal testing setup is unattainable, outdoors testing was chosen from start. This means that natural circumstances such as interfering substances from the background, rain and dew were present. Two liquid explosive precursors were poured into clear glass bottles: isopropyl nitrate and nitrobenzene. Nitromethane, a liquid “explosive”, was also put into a used standard soft drink bottle. Later a solid piece of TNT was used too. The object to be sampled was placed in the grass outside the lab and the pulsed laser beam was directed to illuminate right through the liquid with a coated mirror adapted for the laser wavelength (Figure 15). The scattered Raman signal was collected from a 12 m distance with a standard astronomical telescope with a homemade fiber interface. The light was directed into the spectrometer via the optical fiber. An intensified CCD camera was used as detector, its short gating being adapted to capture the instant Raman signal but to discriminate most of the fluorescence that typically has a lifetime of hundreds of ns. To block the Rayleigh scattered light from the laser beam from reaching the detector, a sharp long-wave-pass filter was used.

Figure 15*: Outdoors experiment on nitromethane in a standard 33 cl soft drink bottle. The telescope can be seen to the left of the mirror directing the laser beam. The bottle used for nitromethane and the smaller bottle of Pyran used for nitrobenzene and isopropyl nitrate is seen to the right.*

4.4.1 Technical details of the equipment

- The laser is a pulsed Q-switched Quantel YG580 Nd:YAG (pulse length 12 ns, pulse energy 415 mJ at 532 nm). The output of 1064 nm can be frequency tripled to 355 nm or frequency quadrupled to 266 nm, but with lowered intensity. Pulse frequency 10 Hz at 532 nm was used.
- As spectrometer a Jobin-Yvon monochromator SPEX 500M was used. The grating has 600 grooves/mm (blazed at 300 nm) allowing depiction of the interval 532 – 610 nm (2400 wavenumbers) on the detector.
- The filter was a Long-Wave-Pass LP03-532RU-25 from Semrock with OD 6 at the laser wavelength but transmitting over 99% for longer wavelengths.
- The telescope was a C6-S Celestron, 1250 mm wide of Schmidt-Cassegrain construction.
- The detector was a Jobin Yvon CCD-3000i (1024 x 256 pixels), max gain 18000, minimal gate time for linear effect 100 ns. Gate time of 50 ns was used.

4.4.2 Results

Even though we had rather difficult weather with rain or slight fog, the signals were well above the noise. The Raman signals could easily be detected from nitromethane, nitrobenzene and isopropyl nitrate in clear glass bottles at 12 meters distance (Figure 16).

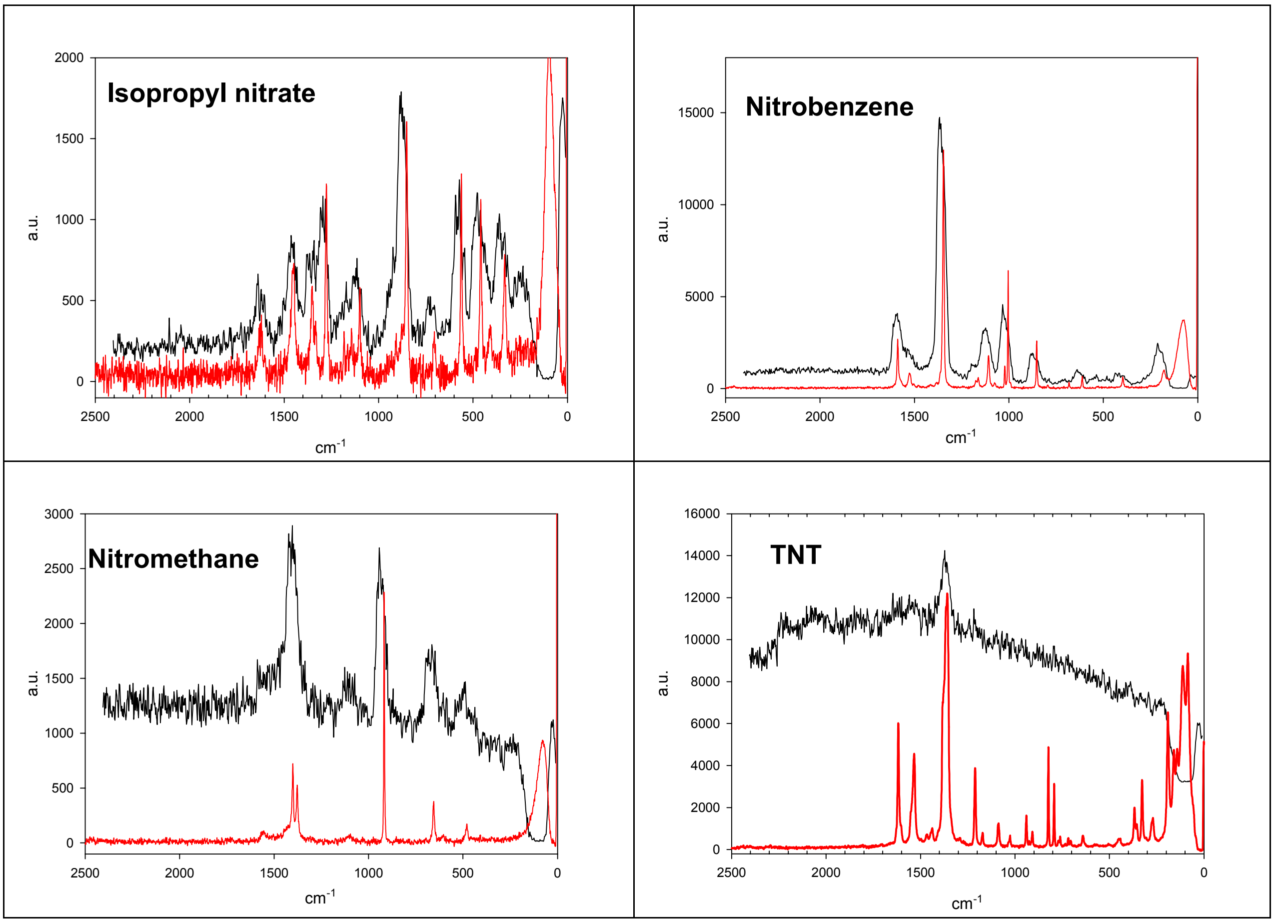

Figure 16: *Raman spectra measured with 10Hz pulsing of 50 ns during 20 s (black). Scaled reference spectra (red) measured on a Bruker FT-IR/Raman spectrometer inlaid in red.*

For the liquids the matching to reference spectra is very good, except from a small drift of calibration that increases for lower wavenumbers. It could probably be significantly improved with a better calibration routine than the linearisation to a Ne- and an Ar-lamp that we performed. The nitromethane had the most worn bottle and therefore the signal is not as good as that of the other two. TNT was more difficult to get a good signal from; as the sample does not transmit the laser light, only molecules on the surface rather than in the volume contribute to the signal. It was noted by Carter *et al.* [17] that with intensities over $3 \cdot 10^6$ W/cm^2 the intensity response was no longer linearly increasing but started to level off, even if no obvious degradation of the sample could be seen. As the intensity used in our experiments is around $25 \cdot 10^6$ W/cm^2 it is likely that the weak signal we get is a worsened effect of that.

5 Conclusions and outlook

Testing of the two different techniques for explosive detection, the jet-REMPI based ESSEX and Resonance Raman spectroscopy for stand-off detection have proven their applicability. In the following, the results from this year are summarised and an outlook for the next year is given.

5.1 Jet-REMPI technique

ESSEX' most important advancement made in 2006 was the insertion of the pulsed valve to perform cooling of the sample gas. This resulted in a significant improvement in both resolution and signal to noise ratio, with a reduction in full width at half maximum of 5 times and the appearance of additional absorption peaks in the spectra of molecular ion signal versus wavelength. Application of the pulsed sample inlet made the deployment of a pulse sequence to steer the individual devices of the experimental set-up. The positioning of the laser beam relative to the valve was investigated and optimised. To be able to assign the measured flight times to the corresponding masses, a mathematical calibration was used.

The further development of the ESSEX explosives detector will focus on exploring excitation and ionisation paths for energetic compounds. The first step will be to investigate nitro compounds having absorption lines that are easily accessible with the current laser system and that have an ionisation potential that is accessible with one colour (two photons of the same wavelength).

With the currently used unheated inlet, low vapour pressure compounds will not be conveyed into the MS. This means that the first choice of energetic compounds for detection scheme mapping will be those of high vapour pressure. Even so, this will constitute a good selection for verifying the usefulness of this resonant laser ionisation MS technique.

To further increase the number of energetic molecules that can be targeted, the sample inlet should be modified by introducing the possibility of heating it. This will reduce the required level of vapour pressure, allowing detection scheme mapping also for energetic molecules with lower vapour pressures.

Preparations should also be made to expand the experimental setup to include a second laser source. This will enable the use of two colour excitation and ionisation schemes, which will target molecules that have too high an ionisation potential to allow for ionisation with a second photon of the excitation colour (as described in figure 7A). The modification of the setup can be made using existing equipment and will involve the use of two dye lasers pumped with the same excimer source. In the long term, this is also the equipment needed for looking into the possibility of tuning to wavelengths below 198 nm, should this be required.

5.2 Resonance Raman spectroscopy

Using Raman spectroscopy with a pulsed laser at 532 nm, successful detection of isopropyl nitrate, nitrobenzene and nitromethane in bottles was achieved. The distance was 12 m and the signals were strong even if the setup was provisional.

The initial experiments have proved promising enough to encourage further work. The exact form of the continuation is somewhat uncertain as it depends on what funds will be available next year. The focus of this project will remain jet-REMPI, but there is a natural connection between the technologies since they both require that the high absorbing or resonant wavelengths of the investigated substances are found. For stand-off Raman spectroscopy the obvious next step is to find the resonant wavelengths for a few substances, preferably explosives or related to compounds, to be able to assert how much stronger that will make the scattered signal. This is also needed for the efficient laser excitation and ionization used in jet-REMPI. Therefore, work on Resonance Raman spectroscopy will at least continue as a spin-off from this project.

Other interesting developments are also possible, even if of less principal character. The present setup could likely be improved by changing to 355 nm for less background and increased Raman scattering. This would make it possible to attain good spectra from solid explosives, which we so far have not achieved since our laser pulse is of such high intensity to cause decomposition.

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