3 Experimental Setup

It is imperative to explain the different experimental designs used during this thesis to obtain the jet spectra. The concept is similar for every case but essential differences among the experimental setups are reflected in the acronyms which are used. In all cases a commercially available FTIR spectrometer is coupled to a pulsed free jet expansion. In the following chapter, the *ragout*-, *popcorn*- and *filet*-jet will be explained in more detail.

3.1 *Ragout*-Jet FTIR Spectrometer

The *ragout*-jet (*r*apid *a*quisition *g*iant *out*let) setup has been explained in detail elsewhere [1,2] and will only be summarized briefly. The *ragout*-jet couples an IFS 66v/S Bruker vacuum spectrometer with a slit nozzle through which the gas is expanded into a vacuum chamber. This vacuum chamber ($11\,\mathrm{m}^3$ or $23\,\mathrm{m}^3$) serves as a buffer volume for the gas pulse and is pumped by a series of roots blowers consisting of one WKP2000, one WKP250 and one UniDry ($50\,\mathrm{m}^3\,\mathrm{h}^{-1}$), which are linked together in a series. The mechanical pumps allow for a pulse repetition rate of about $0.03\,\mathrm{s}^{-1}$ and a He pulse duration of up to 240 ms, whereas the vacuum chamber keeps the background pressure below 1 mbar at all times. The gas pulse is fed from a glass reservoir (65 L). The nozzle (General Valve Series 97), which corresponds to a typical gas flow of one $\mathrm{mol\,s}^{-1}$, is 120 mm long with a variable width between $0-1\,\mathrm{mm}$ (typically 0.5 mm) and is pneumatically controlled by a pulse generator (General Valve Multichannel IOTA ONE) through which the spectrometer is synchronized.

The IR beam from the FTIR spectrometer probes the expansion along the nozzle. The distance of the slit nozzle to the center of the IR beam is 15 mm. For the detection of the IR light, an externally evacuated detector chamber is used in which an InSb or MCT detector is placed.

3.2 Heatable Nozzle (*popcorn*-jet)

The heatable-nozzle setup uses the same spectrometer and mostly the same components as the *ragout*-jet FTIR spectrometer with some modifications, which will be stated in section 3.2.2.

3.2.1 Introduction to Heatable Nozzles

Pulsed slit jets are of interest because of the large cluster number densities ($\geq 10^{12}$ molecules cm^{-3}), which can be obtained in a 2-dimensional expansion over that in a 3-dimensional pinhole expansion. The spectral linewidth is also reduced below the room temperature Doppler limit, which is not relevant for the low resolution work presented here.

Resistive heating is the simplest method to study low-volatility compounds in a supersonic jet. A wide range of concentrations in the carrier gas can be realized and the nozzle exit temperature can further influence the cluster distribution. A common alternative to resistive heating is laser ablation [3,4]. This is more suitable for thermally unstable compounds but it is less compatible with the long gas pulses and high number density requirements of jet-FTIR spectroscopy. Laser ablation on a timescale of several 100 ms becomes rather similar to common heating processes.

Many heatable nozzles are based on the fast General Valve Series 9 solenoid valve. By combining several such valves, a rather high throughput can be attained. This is impressively demonstrated in the Berkeley design [5] of a slit nozzle, which is supplied by three General Valve solenoid valves. For the purpose of FTIR detection, this throughput is not sufficient, whereas fast repetition is less essential; therefore, a new heatable nozzle was designed and will be discussed below.

3.2.2 Experimental Design

The basic concept is to pass a flow of carrier gas through a heatable segment which contains the compound and is sealed whenever the carrier gas flow is interrupted. Its dimensions are shown in Figure 3.1. The jet expansion from this recently developed *pop*pet-*co*ntrolled, *r*esistively heated *n*ozzle (*popcorn*-jet) still needs to be characterized in detail. The differential pressure drops in the three valves and the supporting frit may lead to pre-expansion phenomena prior to the final expansion through the slit orifice. A systematic probing of these pressure drops and characterization of the Mach disk will be required and is planned for a subsequent thesis [6]. The present approach involves a phenomenological characterization via the jet expansion spectra.

The experimental idea is to synchronize an IR scan with one pulse of the nozzle. This means that there must be enough substance in the gas phase to sustain a long pulse. For a spectral resolution of $2\,\mathrm{cm}^{-1}$ with the speed of the mirror up to $0.2\,\mathrm{m\,s}^{-1}$, the duration is on the order of several 100 ms and the volume of gas flowing through the nozzle is on the order of several 100 ml, depending of course on the area of the nozzle. Therefore, the volume of the region where the gas picks up the heated compound (called pick-up cell in the following) must be relatively large. The experimental realization will now be briefly described (Figure 3.1).

The carrier gas from the reservoir is supplied to the nozzle cavity through a 8 mm nominal width magnetic valve (Parker Lucifer, 221J3301E-299560-483816C2), which is controlled by a pulse generator (General Valve Multichannel IOTA ONE). The vertical nozzle body is resistively heated by an external heating supply ($\simeq 700\,\mathrm{W}$) and the temperature is held constant by using a thermocouple. After passing through a stainless steel neck, the flow of the carrier gas opens a check valve (Swagelok, SS-8CP2-1), which has a differential opening pressure of 70 mbar and circumvents the heated substance from diffusing back into the neck between two pulses. The gas flow picks up the heated vapor, passes through a stainless steel frit and opens the next check valve (Swagelok, SS-8CP2-10), which has a differential opening pressure of 680 mbar and prevents leaking of the heated com-

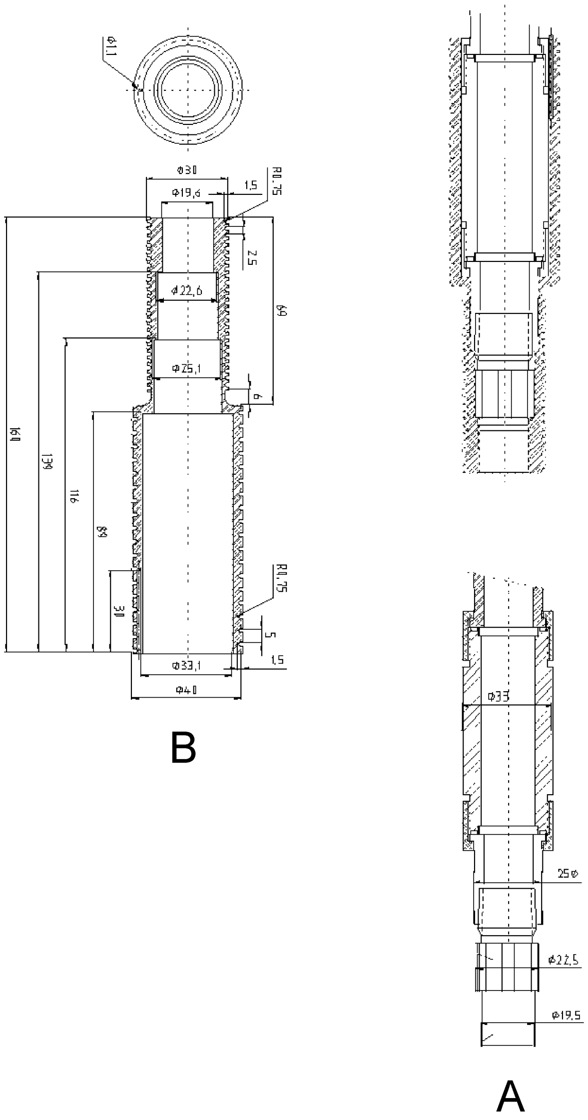

Figure 3.1: Technical details of the *popcorn*-jet (A) and the heatable jacket (B).

pound into the vacuum chamber during breaks between pulses. The gas expands into the vacuum through a slit nozzle of variable dimensions, here 5×1 mm^2. A CaF_2 or KBr lens focuses the IR light from the spectrometer (Bruker, IFS 66v/S), which is equipped with a tungsten or globar light source and CaF_2 or KBr beamsplitter, onto the expansion. A second CaF_2 or KBr lens forms a collimated beam of light which is focused with a parabolic mirror ($f = 43\,\mathrm{mm}$) onto a large area 2 mm InSb or MCT detector. The detector is located in an externally evacuated chamber. In all cases the magnetic valve controlling the gas flow has an opening time of 175 ms and a delay of 54 ms. The magnetic valve is opened slightly longer than the normal 140 ms of the *ragout*-jet [2] in order to allow for a pressure build up in front of the mechanical valves and in the pick-up compartment.

3.3 *Filet*-Jet FTIR Spectrometer

The *filet*-jet, which stands for the *fi*ne-but-*le*ng*t*hy nozzle, is described in detail in References [7–14]. Its standard dimensions are $600 \times 0.2\,\mathrm{mm}^2$, which optimizes monomer and dimer number densities compared to the wider *ragout*-jet slit [1, 2]. The cluster distribution can be modulated by stagnation pressure and sample concentration.

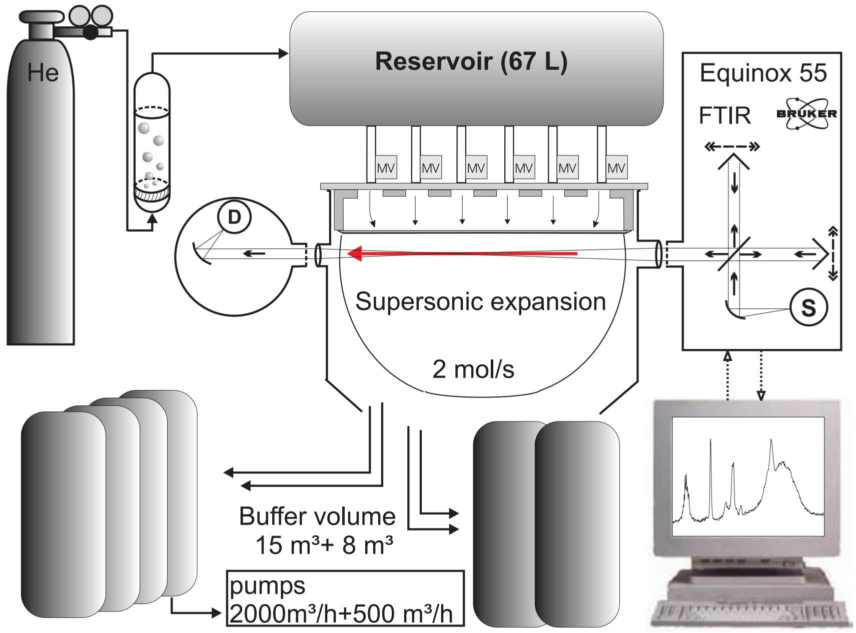

Figure 3.2: A schematical representation of the *filet*-jet setup.

The *filet*-jet has the advantage over the *ragout*-jet that the IR beam passes through a 600 mm zone-of-silence. This long path length allows for the observation of small cluster concentrations of trace gases expanded in He or Ar. The experimental setup is similar to the *ragout*-jet presented earlier but the IR beam is focused by CaF_2 or KBr lenses for a better overlap with the expansion zone. The two lenses, which are used, have $f = 500\,\text{mm}$ and 250 mm, respectively, and applied in this sequence, they act as a mild beam condenser.

The gas expansion of 135 ms duration is controlled via six fast responding magnetic valves of 8 mm nominal width (Parker Lucifer, 221J3301E-299560-483816C2) in combination with a pulse generator (BNC, Model 400). The vacuum buffer is pumped by a series of roots blowers at $2000\,\text{m}^3\,\text{h}^{-1}$. After a recovery period of up to 120 s, the process is repeated and the resulting spectra are coadded.

After each probe scan, there is a post-probe scan, which monitors the background gas $\approx 0.1\,\text{s}$ after the breakdown of the expansion. Initially, the local pressure in the jet chamber is significantly higher than that in the total buffer volume and adsorption processes are also minimized. The post-probe scan allows for a quick comparison of the gas phase and jet expansion spectra.

3.3.1 1-Octanol and Methanol/1-Octanol

The limits of the *filet*-jet setup were tested using a relatively low-volatile alcohol, 1-octanol.

Table 3.1: Observed $\tilde{\nu}_{\text{OH}}$ of 1-octanol and the mixture with methanol.

	monomer	dimer
	$\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}/\text{cm}^{-1}$
1-octanol	3680	~3554
methanol	3686 [1, 11, 15]	3575 [1, 11]
mixed complex	—	3561

Although long chain alcohols potentially show rich conformational isomerism, Figure 3.3 (a) shows a single sharp monomer peak (M_O), which is located at the

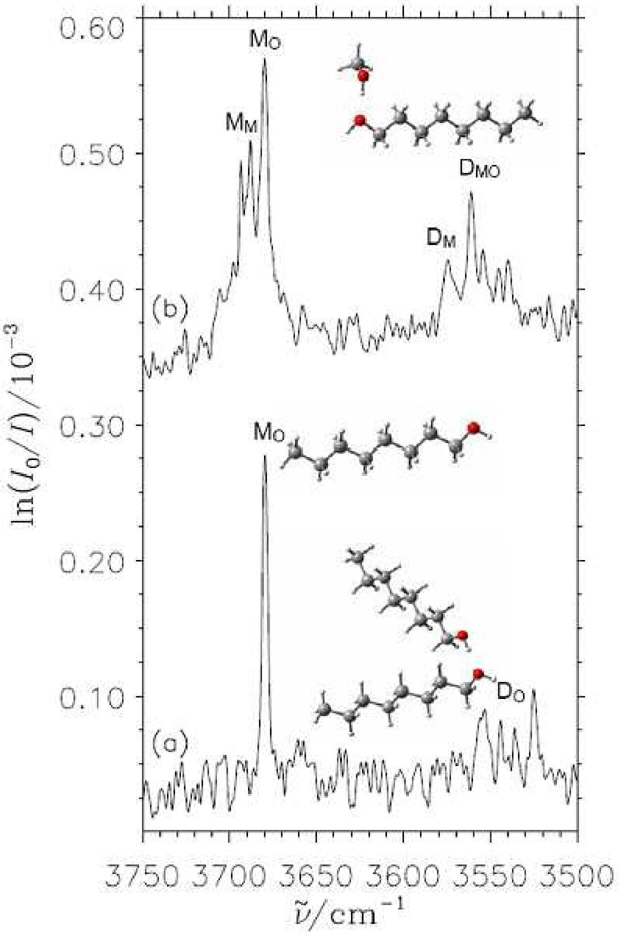

Figure 3.3: Donor O−H stretch spectra of jet expansions of pure 1-octanol (a) and of a mixture of 1-octanol with methanol (b). Monomer and dimer peaks are marked M and D, respectively. Taken from Reference [10]

high frequency end of a number of gas phase absorptions due to different thermally populated conformers. Exploratory calculations up to the MP2/6-311+G(d) level [10] indicate that it corresponds to a *trans* conformation of the −O−H group relative to the first backbone C−C bond. While the energy difference to the *gauche* conformation is small and not uniform in sign, the *trans* conformation is consistently predicted to be more blueshifted. However, there are now indications that the neighboring C−C bond is not *trans* configured [16, 17], as implied in