Double Modulation Technique in Pulsed Jet Experiments with Tunable Diode Lasers

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A double modulation technique was used to achieve higher sensitivity in absorption measurements with a pulsed supersonic jet. The wavelength of a lead-salt diode laser was modulated at a frequency of 10 kHz and detected at twice the frequency by a lock-in amplifier, reducing significantly the influence of the low frequency excess laser noise. The output of this lock-in amplifier was measured by a boxcar integrator, driven at 80 Hz, the frequency of the pulsed jet. In case the duration of the jet pulse is long enough, a second lock-in amplifier can also be used instead of the boxcar integrator. The optical path of the diode laser radiation through the jet was increased 16 times by using White type multireflection optics. The achieved value for the minimum detectable absorption of Ar–CO complexes in the jet was 2×10^{-5} in relative absorption, limited by the excess noise of the diode laser.

1. Introduction

In this paper we first show the essentials of the double modulation technique by using a hot band spectrum of C_2H_2. Then we apply this double modulation technique to the detection of the $K = 0–1$ Q-branch transition of the CO-stretching mode of the Van-der-Waals molecule Ar–CO.

One important goal in any application of tunable diode laser (TDL) spectroscopy constitutes the increase in sensitivity; especially in supersonic jet measurements, the absorption to be measured often ranges in the order of 10^{-3}–10^{-4} of the incident radiation. Aside from increasing the optical path by multireflection optics, various modulation schemes are in use. In our laboratory, pulsed molecular jets are employed in experiments concerning cluster formation and the determination of population distributions in expanding gases. At the same capacity of the pumping unit, the pulsed mode of the nozzle operation provides higher densities of molecules in comparison with a continuous flow of the jet. A periodical modulation of the absorption signal in the pulsed jet is commonly used in the detection procedure. The absorption signal can be monitored either by phase sensitive detection with a lock-in amplifier or by a gated detection with a boxcar integrator, synchronized to the jet repetition frequency. The sensitivity of this method of registration does not exceed the level of 10^{-4} in absorption [1–3], which is determined by the low frequency excess laser noise. This noise (alternatively termed $1/f$ noise) mainly appears in TDLs due to the influence of the closed cycle refrigerator, compressors, pumps and other sources of mechanical vibrations. The maximum repetition rates of electromagnetic valves are usually of the order of one hundred Hz, limited towards higher frequencies by mechanical properties of the valve. If a lock-in amplifier, driven at the repetition frequency of the pulsed jet, is used for the detection of the signal, the influence of the excess laser noise at such low frequencies ($\sim$100 Hz) becomes significant. A considerable reduction of this excess noise could be achieved by using valves which are able to produce shorter jet pulses with a duration of a few 100 μs. The appropriate detection with a boxcar integrator corresponds to detection frequencies of the order of several kHz. These frequencies, however, are still not high enough to suppress the excess laser noise below the thermal noise of the detector-preamplifier system or the shot noise. The advantage of the valve modulation method is that the registered spectrum is not influenced by the interference fringes, which appear usually in the baseline of the TDL spectrum on the level 10^{-3}–10^{-4}. The fringes do not affect the absorption spectrum recorded by the jet modulation technique because only the periodically time dependent component of

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the signal from the detector is registered. If the lock-in amplifier or boxcar integrator is operated in the $1f$ mode, the registered lines display a regular line shape, which is convenient for accurate measurements of the line profile and the line intensity.

Although the jet modulation technique is sensitive enough, the influence of the excess laser noise can further be decreased by TDL wavelength modulation at modulation frequencies in the 10–100 kHz range. It is simply accomplished by modulating the laser current, followed by an appropriate phase sensitive demodulation of the detector signal by a lock-in amplifier. This method reduces the excess noise to a level lower thn 10^{-5} [4, 5]. In practice, however, it is not easy to realize such a low absorption limit with TDLs. One of the reasons is that interference fringes appear with a period close to the width of absorption lines, especially, when multireflection optics of Herriott or White type are used to increase the absorption path for the TDL radiation. Even with careful adjustment, the amplitude of these fringes can hardly be reduced to a level much lower than 10^{-4} [5], because the optical scheme of the spectroscopical measurements requires a monochromator, a vacuum chamber, beam splitters, cells and other potential sources of interference fringes.

An effective way to reduce the influence of the excess laser noise and to remove the interference fringes is a fast scanning technique, which is in fact a sort of TDL wavelength modulation. In this method, the wavelength of the TDL is scanned rapidly, allowing an effective modulation of the detected absorption signal in the range of frequencies of several 10 kHz. The whole spectrum is measured during each pulse of the jet with an appropriate subtraction of the TDL baseline, registered shortly before the jet pulse, i.e. in the absence of the absorption. The application of this method for absorption measurements in pulsed jets was demonstrated by De Piante et al. [6]. A minimum absorption signal as small as 3×10^{-5} could be detected if the spectra data are averaged over 2000 pulses [6]. This method is commonly used to detect weak absorption of complexes in slit jets with low repetition rates.

Sharpe et al. used in their work a 10 kHz triangular waveform modulation of the TDL wavelength for pulsed jet measurements of the $Ar-CO_2$ absorption spectrum [7]. Later, however, they did choose the fast scanning technique [8, 9], which is more effective in the case of slit jets with repetition frequencies of the order of one Hz.

The aim of the present work is to present a double modulation technique which is capable to achieve a sensitivity close to 10^{-5}. In its technical realisation, the double modulation technique is similar to the usual jet modulation technique. Commercially available pulsed valves operated at repetition rates of the order of 100 Hz were employed. A second 10 kHz modulation of the TDL wavelength was used to reduce the excess laser noise; a demodulation of the signal at the repetition frequency of the jet removed the influence of the TDL baseline structures, including unwanted interference fringes.

2. Experimental

The experimental set-up partly described in our earlier paper [10] is shown in Figure 1. A mixture of gas seeded in argon was injected through a pulsed nozzle at a repetition rate of 80 Hz. A 2000 l/s oil diffusion pump was used to evacuate the chamber and to maintain the background pressure at 10^{-3} mbar. When the multireflection optics were used, the TDL beams crossed the jet in a plane perpendicular to the jet axis.

For the double modulation measurements the laser frequency was modulated at a 10 kHz sinewave. The signal was registered by a HgCdTe detector with 1×1 mm^2 sensitive area. During the registration of an absorption line in the jet, the detector signal contained two types of frequency components, the 10 kHz modulation of the TDL wavelength, and the 80 Hz modulation of the jet. Accordingly, two steps of demodulation were used. The signal after preamplification was demodulated by a lock-in amplifier (Princeton Model 128 A), synchronized with the 10 kHz modulation frequency. The lock-in amplifier was operating in the $2f$ mode with a time constant of less than 1 ms. The time constant was small enough to retain the 80 Hz component in the output signal, which was then measured by the boxcar integrator (Princeton Model 162, with two Model 164 gated integrators) or demodulated by a second lock-in amplifier, depending on the type of the pulsed valve. An IBM compatible PC together with an AD converter board served to collect the data and to record the spectra.

Two different types of the pulsed valves were used in these measurements, representing two possible situations. In the first case the duration of the pulsed jet was comparable with the time interval between two

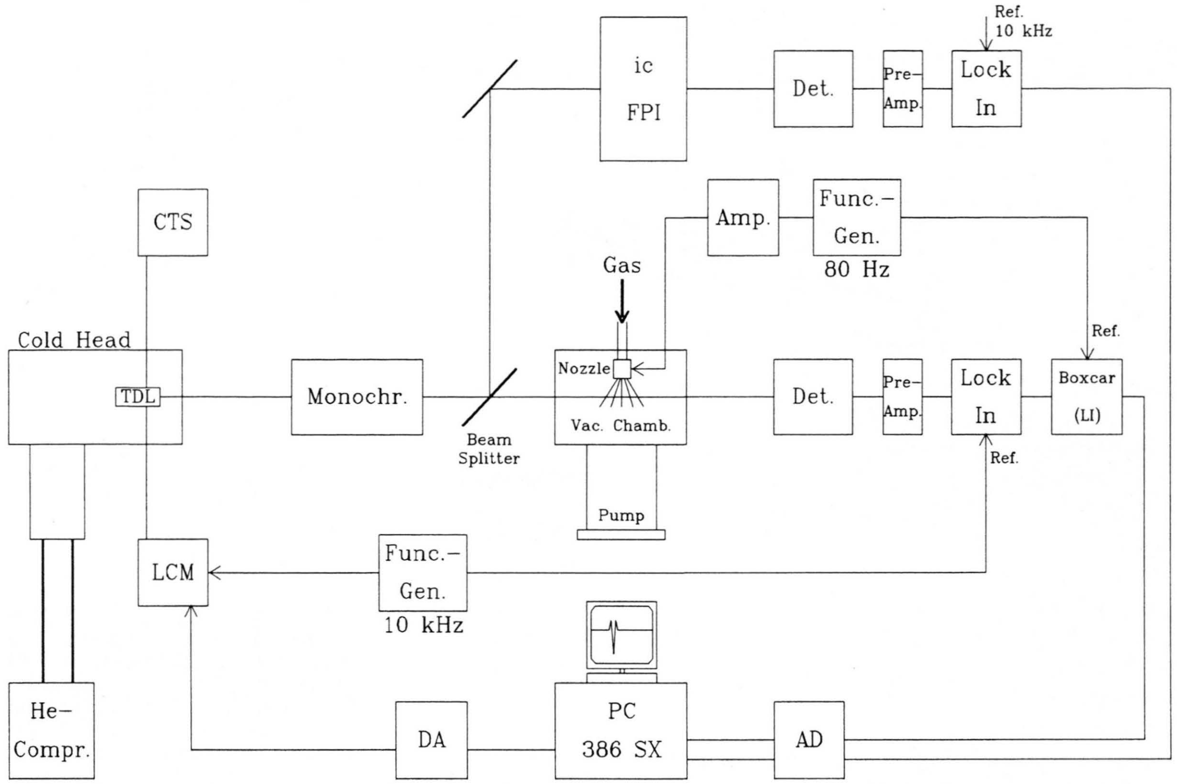


Fig. 1. Block diagram of the diode laser-supersonic jet spectrometer. The molecular jet is modulated with 80 Hz, the diode laser with 10 kHz.

pulses. In the second case the pulses were considerably shorter than the interval between successive pulses.

The first valve was a modified automobile fuel injector valve (Bosch) with a pinhole of 0.1 mm diameter. The duration of the jet pulse for this valve was approximately 3 ms. A mixture of 20% acetylene in argon at a pressure of 1 atm was injected through this nozzle into the vacuum chamber to observe several weak hot-band transitions of acetylene in the jet. The beam of the TDL, operating in the 14 μm region, crossed the jet in a distance of 1 mm from the nozzle. No multireflection optics were used in this part of measurements. For the double modulation procedure two lock-in amplifiers were used successively to demodulate the detector signal at the TDL modulation frequency of 10 kHz and at the valve frequency of 80 Hz.

The second valve (General Valve Corp.) with a pinhole of 0.2 mm diameter was used to produce jet pulses fo 300 μs duration at half intensity of the pulse. In this case the duration of the pulse was considerably shorter than the interval between the pulses. A gated detection by a boxcar integrator was used instead of the phase sensitive detection via the second lock-in amplifier. To measure the output of the first lock-in amplifier, the timing of the two gates of the boxcar integrator were set shortly before the jet pulse and during the pulse, followed by an appropriate subtraction of two registered signals performed within the boxcar. A mixture of 25% CO in argon at a pressure of 5 atm was used to produce Ar–CO complexes in the free jet expansion. The absorption of Ar–CO complexes was detected with a TDL, operated in the 5 μm region. The White type multireflection optics shown in Fig. 2a were mounted in the vacuum chamber to allow 16 passes of TDL radiation through the expanding gas at a distance of 4 mm from the nozzle. The distance between the mirrors was 120 mm. The diameter of the probing IR beams did not exceed 1.5 mm along the jet (Figure 2b). Therefore the spatial resolution along the jet was almost the same as for a single pass measurement, allowing to keep the high spatial resolution of a single IR traverse of the jet.

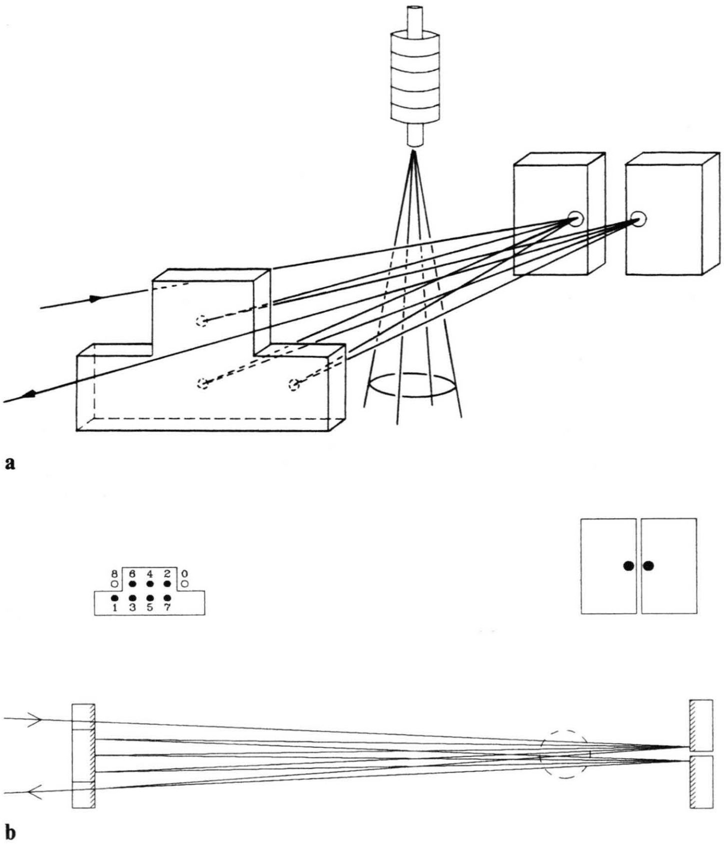


Fig. 2. White type multireflection optics. (a) Optical arrangement. For simplicity only eight instead of 16 reflections of the laser beam are shown. (b) Top view. The position of the supersonic jet is shown by the dashed circle relative to the reflected laser beams. The distance between mirrors is 120 mm.

3. Results

As a typical example for the measurements with the fuel injector valve we present in Figs. 3a–c several weak absorption lines of C_2H_2 near 731 cm,$^{-1}$, which are part of our ongoing investigations to determine the population distribution in jet conditions of several molecular species, i.e. CH_4 [11], NH_3 [12] and CH_3OH [13]. They belong to the head of a hot band Q-branch, accompanying the ν_5 fundamental band of C_2H_2.

To allow a comparison, a recording with the jet modulation only, i.e. without TDL wavelength modulation, was made at first (Figure 3a). The detector signal was demodulated by a single lock-in amplifier driven at the 80 Hz frequency of the jet. The time constant of the lock-in amplifier was 1 s. The relative absorption of the strongest line in Fig. 3a was 2×10^{-3}. A minimum detectable absorption close to 10^{-4} was estimated from the observed signal-to-noise ratio in the spectrum. As has been mentioned earlier, this value is close to the limit of sensitivity for this type of registration and is determined by the excess noise of the TDL.

The same part of the absorption spectrum was then measured with the double modulation technique by adding TDL wavelength modulation at 10 kHz (Figure 3b). The amplitude of the sinewave modulation was equivalent to half of the Doppler width (HWHM) of the acetylene lines in the reference cell at room temperature. The time constant of the second lock-in amplifier was 1 s. The noise was reduced by shifting the frequency of registration to 20 kHz ($2f$ mode of the lock-in amplifier) and was mainly determined in this case by the detector-preamplifier noise. The signal-to-noise ratio for the strongest line was 200, showing a minimum detectable absorption close to 10^{-5}.

A decrease in the 10 kHz modulation amplitude resulted in an improved spectral resolution: the spectrum in Fig. 3c was recorded with half the previous modulation amplitude of the TDL wavelength. The

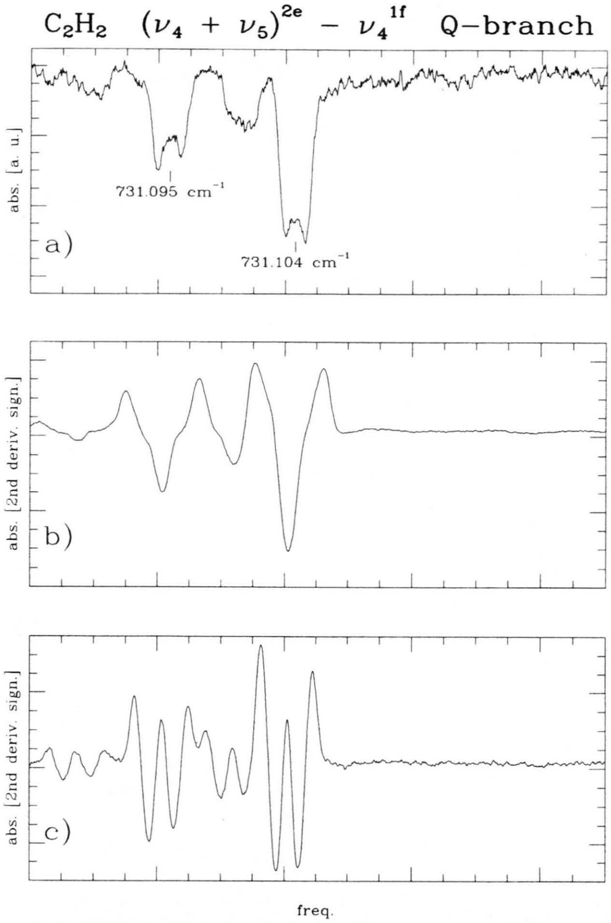


Fig. 3. The head of a hot-band $(\nu_4+\nu_5)^{2e}-\nu_4^{1f}$ Q-branch of acetylene near 731 cm^{-1}. The fuel injector valve was used for the pulsed jet. (a) Spectrum taken with the jet modulation technique. The detector signal was demodulated at 80 Hz frequency of the pulsed jet. (b) The same part of the absorptionb spectrum, measured by double modulation technique. The minimum detectable absorption is close to 10^{-5}. (c) To achieve better spectral resolution, the amplitude of the TDL wavelength modulation was reduced by a factor of two in comparison with the previous case. Each line exhibits a dip at the center due to the lower on axis temperature of the jet.

second derivative lines shown in Fig. 3c appear less over-lapped than in Figure 3b. Each line displays a prominent dip at the center. According to our opinion, this dip is mainly due to the lower temperature on the axis of the jet.

In the second part of this work the double modulation technique is used together with White type multireflection optics for absorption measurements of molecular complexes in a supersonic jet. The absorption spectra of Ar–CO complexes in the region of the CO stretching mode were already investigated by Fourier transform and diode laser spectroscopy [6, 14, 15] and appeared to be convenient for a comparison of the sensitivity of our spectrometer with other methods.

Figure 4 presents the Q-branch of the $K=0-1$ band of the CO-stretch of the Ar–CO complex. As in the previous case, the spectrum in Fig. 4a was taken with the jet modulation only, i.e. without a TDL wavelength modulation. A boxcar integrator, driven at the 80 Hz frequency of the jet, was used to record the spectrum. The duration of the two gates of the boxcar integrator was 400 µs with one gate set before the jet pulse and with the other gate being set to measure the signal during the pulse. The relative absorption of the strongest features of the Q-branch in Fig. 4a was 2×10^{-3}. The excess laser noise limited the minimum detectable absorption on the 10^{-4} level.

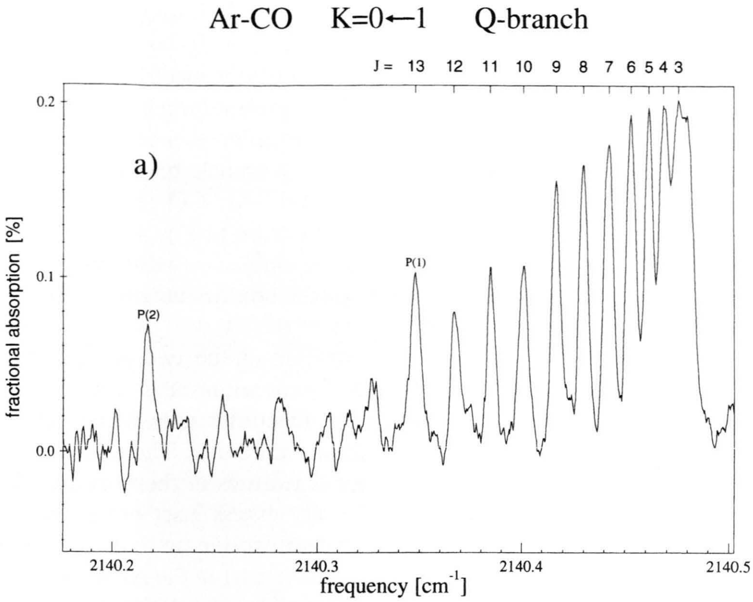
Figure 4b shows the same part of the Ar–CO spectrum recorded with the double modulation technique by using the 10 kHz modulation of the TDL wavelength. The excess laser noise was reduced nearly to the level of the detector-preamplifier noise, exceeding now the detector-preamplifier noise only by a factor of two. The minimum detectable absorption signal was estimated as 2×10^{-5}.

4. Discussion

The double modulation technique used in the present measurements provides improved sensitivity with several useful features, which can be summarized as follows:

1. Commercially available pulsed jet valves can be used to achieve a sensitivity which is sufficient for absorption measurements of molecular complexes in a jet. The value of 2×10^{-5} for the minimum detectable absorption of Ar–CO demonstrated in the second part of this work is close to the best results reported for the fast scanning technique.

2. In many respects the technical realization of the double modulation technique is similar to the usual jet modulation technique, as can be seen in Figure 1. During a recording of the spectrum, the frequency of the TDL was scanned slowly over the spectral range of interest. The signal was detected with the time constant of the order of one second, reducing appropriately the level of the noise because of the narrow detection bandwidth.



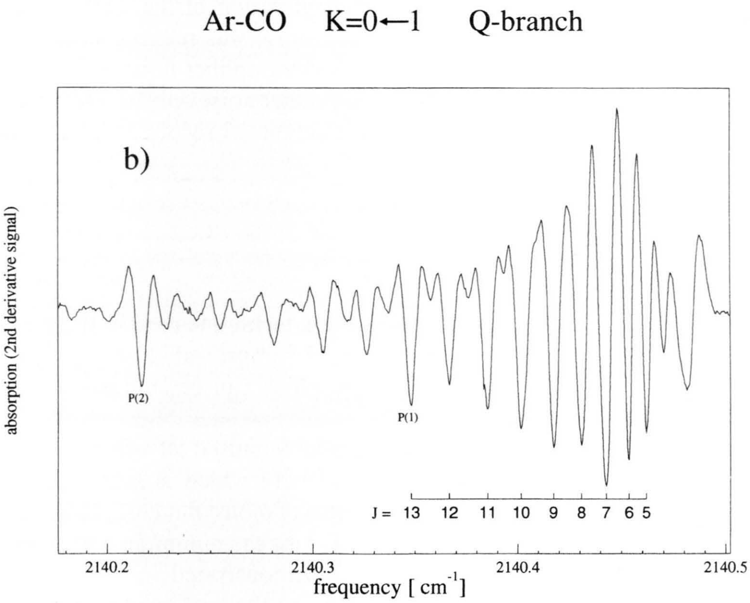


Fig. 4. Q-branch of the $K = 0-1$ transition of Ar–CO (CO-stretch) near 2140 cm^{-1}. The valve from the General Valve Corporation was used for the pulsed jet. The time constants of the boxcar integrator were 3 s in both cases shown in Figure 4. (a) Spectrum taken with the jet modulation technique. The absorption in the band head of the Q-branch was 2×10^{-3}. (b) The same spectrum measured with the double modulation technique. The minimum detectable absorption was 2×10^{-5}.

3. The detected spectrum is not affected by interference fringes. In our case, the main source of the fringes were multireflection optics, which produced interference fringes on the 10^{-3} level. The period of interference was 2×10^{-2} cm^{-1}, determined by the distance between the spherical mirrors of the multireflection optics.

4. The spectra of Ar–CO complexes were measured at a relatively low mean flow of the gas mixture through the nozzle. The capacity of our diffusion pump was in fact not higher than 1000 l/s, reduced from maximum value by a factor two by the cooled baffle. The reduced pump capacity, however, was sufficient to keep the background pressure in the vacuum chamber at a level of 10^{-3} mbar.

There are several possibilities to reduce the excess laser noise further and to increase the sensitivity of the described method. One way is to use higher frequencies of TDL wavelength modulation. In our case, the limit of 10 kHz modulation frequency was connected with the properties of the TDL's power supply (LCM in Figure 1).

A significant contribution to the low frequency noise of the TDL arises from the closed cycle refrigerator, rotary pumps, compressors and other sources of mechanical vibrations. In the present work no special efforts were made to suppress these sources. It is planned to use in the future a shock isolated cold head for the TDL, which was recently developed in our laboratory [16].

The detected power of the two TDL's in our measurements was 20 μW and 80 μW for the 14 μm and 5 μm TDL's, respectively. With this power we estimated the limit of the sensitivity in absorption determined by the TDL shot noise in 1 Hz bandwidth as 2×10^{-7}, i.e. nearly two orders of magnitude lower than the detector noise.

The spectral width of the absorption lines in Fig. 4 was 6×10^{-3} cm^{-1}. The observed linewidth is a result of the Doppler effect combined with the large divergency of the jet from the pinhole nozzle. A modification from the pinhole to the slit geometry of the nozzle is planned. The reduction of the linewidth by a factor of two or three is expected, with an appropriate increase in the peak absorption.

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[1] J. Hodge, G. D. Hayman, T. R. Dyke, and B. J. Howard, J. Chem. Soc. Faraday Trans. II **82,** 1137 (1986).
[2] M. Takami, Ya. Ohshima, S. Yamamoto, and Yo. Matsumoto, Faraday Discuss. Chem. Soc. **84,** 1 (1988).
[3] M. Snels and W. L. Meerts, Appl. Phys. **45,** 27 (1988).
[4] J. A. Silver, Applied Optics **31,** 707 (1992).
[5] D. S. Bomse, A. C. Stanton, and J. A. Silver, Applied Optics **31,** 718 (1992).
[6] A. DePiante, E. J. Campbell, and S. J. Buclow, Rev. Sci. Instrum. **60,** 858 (1989).
[7] S. W. Sharpe, R. Sheeks, C. Wittig, and R. A. Beaudet, Chem. Phys. Lett. **151,** 267 (1988).
[8] S. W. Sharpe, Y. P. Zeng, C. Wittig, and R. A. Beaudet, J. Chem. Phys. **92,** 943 (1990).
[9] S. W. Sharpe, D. Reifschneider, C. Wittig, and R. A. Beaudet, J. Chem. Phys. **94,** 233 (1991).
[10] P. Wallraff, K. M. T. Yamada, and G. Winnewisser, Z. Naturforsch. **42a,** 246 (1987).
[11] M. Hepp, G. Winnewisser, and K. M. T. Yamada, J. Mol. Spectrosc. **146,** 181 (1991); J. Mol. Spectrosc. **164,** 311 (1994).
[12] M. Hepp, G. Winnewisser, and K. M. T. Yamada, J. Mol. Spectrosc. **153,** 376 (1992).
[13] M. Hepp, I. Pak, K. M. T. Yamada, and G. Winnewisser, J. Mol. Spectrosc. **166,** 66 (1994).
[14] A. R. W. McKellar, Y. P. Zeng, S. W. Sharpe, C. Wittig, and R. A. Beaudet, J. Mol. Spectrosc. **153,** 475 (1992).
[15] M. Havenith, G. Hilpert, M. Petry, and W. Urban, Mol. Phys. 81, 1003 (1994).
[16] N. Anselm, K. M. T. Yamada, R. Schieder, and G. Winnewisser, J. Mol. Spectrosc. **161,** 284 (1993).