Photothermal deflection spectroscopy in cryogenic liquids and its application to quantitative atmospheric trace analysis

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An evaluation is presented of quantitative trace concentration measurement using liquefied samples of gas. The trace molecule of interest in a mixture of molecules is excited using a tunable IR laser. Following excitation, the vibrationally excited molecules are deactivated rapidly in collisions with the solvent. This leads to local solvent heating and a local density gradient. These are detected using the photothermal deflection of a He–Ne probe laser beam. Tests have been made using SF_6, which has been quantitatively detected down to 10 parts per trillion in liquid argon. The application of this technique to the analysis of atmospheric samples is discussed.

Introduction

In this paper, a preliminary report on the detection of molecules at the parts per trillion (10^{12}) (ppt) and parts per billion (10^9) (ppb) levels in cryogenic liquids is presented. The method used is selective IR excitation of the trace molecule in a liquefied sample followed by photothermal deflection detection of the heat released from the trace molecule into the solvent using a He–Ne laser beam.

Although trace detection is very well established in many laboratories it is still desirable to develop a relatively inexpensive and versatile method which can be used to detect several different trace molecules in the same sample, making use of their characteristic IR absorption spectra.

The idea of using liquefied samples for trace detection is not new. Freund *et al.* measured the IR spectra of impurities in liquefied gases,[1] Brueck *et al.* also used liquefied samples to detect CCl_2F_2 in N_2, predicting a limit of *ca.* 1 ppb for thermal lensing detection,[2] although this was not pursued. Previously concentrations of CO in liquid Ar down to 500 ppt have been determined by two of the authors using IR fluorescence detection.[3] Whilst it was realised that this could not be used as a general technique, the results demonstrated the potential of the use of cryogenic solutions for trace detection and quantitative analysis.

In the method described in this paper, a strong IR-active vibration of the trace molecule is excited using a line-tunable CO_2 laser. In the liquid, the high collision frequency (*ca.* 1×10^{13} s^{-1}) results in the vibrational deactivation of the excited trace molecules causing heat to be released into the solvent. Since this heating occurs rapidly relative to thermal diffusion, it is localised in the volume of the focused excitation laser beam, resulting in a local density gradient. This gradient may be probed by a stable He–Ne laser with great sensitivity. In the work presented here, the He–Ne laser beam is deflected from its equilibrium position.

One of the major advantages of working in cryogenic liquids is the great simplification in molecular spectra since the P-, Q- and R-branch structure of gas-phase absorption lines is replaced by a strong line, which lies near the band centre and has approximately the same integrated intensity as the entire gas-phase band.[4,5] The lines of many solute molecules are *ca.* 1–2 cm^{-1} wide, giving a high probability of a coincidence with a line of a laser operating on the regular and non-regular bands of CO_2. Finally, line positions in solution depend upon the solvent and the temperature. The shift from

the gas-phase band centre depends on the relative permittivity of the liquid;[6] this allows the tuning of the absorption in the liquid into resonance with the nearest laser line by altering the liquid-mixture composition or temperature should this be necessary.

The greater the IR band intensity in the liquid and the narrower the line, the greater the sensitivity of the detection. Amongst the molecules best suited for this method are SF_6, CF_4, CCl_3F and N_2O and their isotopic derivatives, OCS and volatile carbonyl molecules, including acetone and formaldehyde. Molecules with somewhat weaker IR line strengths include SO_2, NO_2 and CH_4, CO and NO and their isotopic derivatives.

The isotopes of N_2O, CH_4 and CO are present in the atmosphere at the ppb level, while SF_6 is present at *ca.* 4 ppt, CF_4 at nearly 80 ppt and OCS at 500 ppt.

Clearly, the simplification of the molecular spectra greatly reduces the spectral interference between the bands of related trace molecules. An example for small halomethanes is given by Freund *et al.*[1] Another important example of molecules which have overlapping gas-phase spectra is in the C=O vibrations of formaldehyde and other carbonyl compounds. Again, these spectral features should be separated in cryogenic solution. Equally important for atmospheric samples is the elimination of interference by water vapour which has a very extensive IR spectrum which overlaps with many trace molecules of interest, including SO_2.

The greatest gain in sensitivity over gas-phase detection is due to the increase in the number density by a factor of 800 from gas at atmospheric pressure and 295 K to the liquid. Set against this gain is the disadvantage of the requirement of large volumes of test gas unless the internal volume of the liquids cell is very small.

SF_6 is believed to have no natural abundance in the atmosphere; however, as a man-made pollutant it is rapidly increasing in concentration and in contribution to the global greenhouse effect. As long ago as 1968, the specialist technique of gas chromatography (GC) coupled with electron capture was used to detect SF_6 down to 0.01 ppt.[7] However, since the global atmospheric level of SF_6 has now risen to 4 ppt, the simpler GC–mass spectrometry (MS) technique is now sufficiently sensitive for ongoing monitoring of this level.

Against this background, we have first tested trace detection with SF_6. This absorbs strongly and can be excited readily using a CO_2 laser. Very many other molecules can be excited using either a CO_2 or a CO laser. The sensitivity of this tech-

nique for the detection of these other molecules can be estimated from their known integrated band intensities and known, or predicted, band widths in solution.

Experimental

A schematic diagram of the photothermal deflection apparatus is shown in Fig. 1.

The excitation laser is a 2 m longitudinal discharge CW CO_2 laser. The output is coupled from the 1500 lines mm^{-1} diffraction grating via two mirrors and through an AR/AR-coated ZnSe window. The mirror arrangement ensures the directional stability of the output as the laser is grating tuned. The other end of the cavity is a 5 m focal length gold-coated mirror. The laser produces powers of up to 15 W on the regular band lines and up to 7 W on the sequence band lines used for this study. The laser may also be operated as a CO laser by exchanging the laser tube and grating assembly.

A variable attenuator consisting of two ZnSe flats set at the Brewster angle on a rotatable mount allows the adjustment of the laser power between 5 and 80% of the incident power. A slow chopper is used to produce pulses of 50 ms duration. An AR/AR-coated ZnSe lens focuses the laser beam through the cell.

The He–Ne probe laser is a SpectraPhysics 1 mW output laser stabilised for intensity. This is fitted with a $10 \times$ beam expander. The beam is focused through the cell using an AR/AR-coated BK7 glass lens. Vertical movements of the beam caused by thermal deflection are detected using a split diode detector supplied by Hamamatzu.

The cell is constructed from Hidurel 5, a copper–nickel alloy. A pair of AR/AR-coated ZnSe windows and a pair of AR/AR-coated BK7 optical glass windows are sealed using a side-sealing indium arrangement based on that of Lim.[8] The cell is connected to a cold copper finger which descends into a liquid-N_2 dewar upon which the cell stands. The cell and dewar are contained in a vacuum cryostat. The cryostat also has a pair of AR/AR-coated BK7 windows sealed with O-rings and a pair of Brewster angle ZnSe windows to allow the laser beams through the cell. The temperature of the cell is determined by means of a Rh–Fe sensor, and controlled using eight ceramic heaters inserted in holes in the cell body.

The diode elements are connected to the two inputs of a differential amplifier. The output is fed via a digital oscilloscope card to a computer where traces are averaged, stored and analysed.

Gas mixtures are prepared in glass bulbs at room temperature by means of successive dilutions. After a period of several hours has been allowed for mixing, the mixtures are introduced to the cold cell. Liquefaction occurs over approximately one minute, after which the cell is isolated from the vacuum line.

It is well known that ice crystallites formed in liquefied moist air samples give absorption in the 3 μm region.[9] In the experiments presented here, large signals over the full tuning range of the laser were observed after liquefaction, which reduced with time, completely disappearing after two hours. These signals have been attributed to water crystals forming and settling out of solution as has been observed in other work.[9] Subsequently, this waiting period has been avoided by drying the buffer gas by cooling to 120 K prior to mixture preparation, yielding gas with a negligible water content. Due to the extremely low vapour pressure of water relative to other small trace molecules of interest at this temperature, the same drying process could be used for atmospheric samples.

Results

Experiments were carried out with concentrations of between 6 ppb and 10 ppt of SF_6 in liquid Ar at 85 K.

The He–Ne laser beam position may be altered by adjusting the height of the focusing lens. In this way the vertical separation of the laser beams in the interaction region within the sample may be changed. An example plot of signal against lens position is shown in Fig. 2 for 5.5 ppb SF_6 in liquid Ar excited using the sequence band line: 10SP(23). As would be expected the maximum signal is obtained on either side of the IR beam position, where the density gradient is steepest. The probe beam is deflected away from the low-density region formed by the pump laser. The asymmetry of the plot shown in Fig. 2 is attributed to convectional effects, which tend to cause the low-density region to rise, extending the 'tail' on the positive displacement side of the graph.

The ZnSe lens in the cryostat may be displaced along the pump laser beam in order to move the focus through the cell. By carrying out a He–Ne laser scan as described above at each different ZnSe lens position, the focus of the pump beam may be moved into the interaction region of the two laser beams. This gives the smallest displacement between positive and negative maxima for the He–Ne beam scan and the maximum signal. The reason for this latter effect is that the heating increases as the inverse square of the beam width, while the interaction distance decreases linearly with decreasing beam width; therefore the signal increases as the pump laser is focused more tightly.

The variation of signal with pump laser power is linear. Similar linear plots have been obtained for different concentrations of SF_6 and on both the 10P(26) and 10SP(23) laser lines.

By tuning the laser from line to line, a spectrum can be obtained, the signal is normalised by dividing by the laser power on each line. An example of a spectrum is given in Fig.
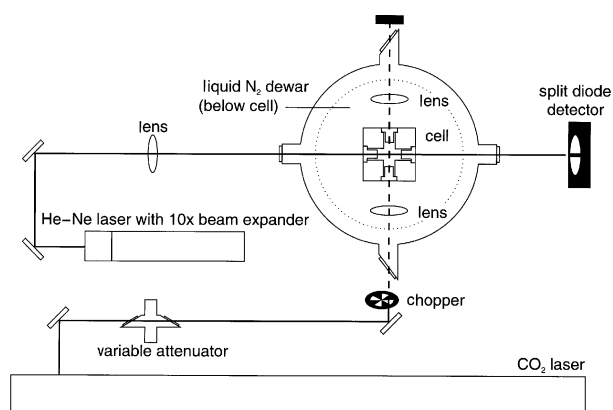

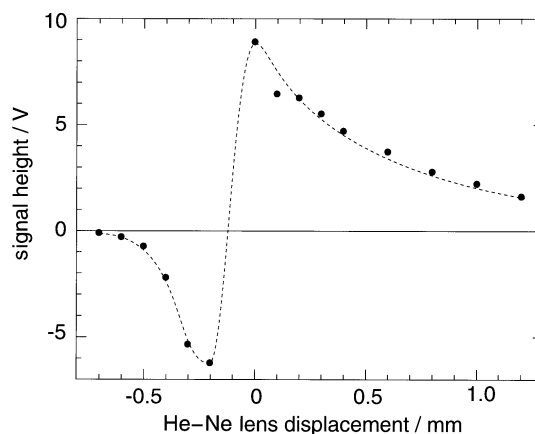**Fig. 1** Schematic diagram of photothermal deflection apparatus

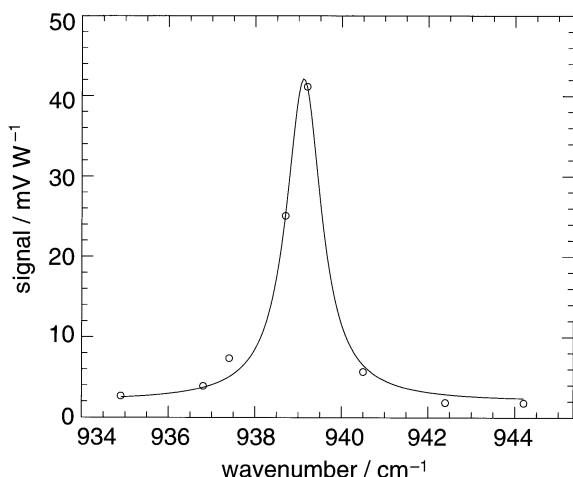**Fig. 2** Variation of signal with probe laser beam position

Fig. 3 Variation of normalised signal with wavenumber

3 for 145 ppt of SF_6. The data are fitted well by a Lorentzian curve centred at 939 cm^{-1} with FWHM 1 cm^{-1}.

Bulanin reports a frequency of 939.6 cm^{-1} in liquid Ar and O_2 solutions with a half width of <0.5 cm^{-1}.[4] This is in agreement with the spectrum measured by Brueck *et al.* in liquid O_2 solution.[10]

Finally, by carrying out a Lorentzian fit of spectral data for different concentrations of SF_6, a calibration curve was determined. The use of height of the Lorentz fit, rather than the magnitude of the signal on either the 10P(26) or 10SP(23) laser line was chosen, as this acts to smooth random fluctuations in the signals. The calibration is shown in Fig. 4.

This calibration, which is derived from the first results with the new apparatus, could be used for determinations of 10–100 ppt of SF_6 to $\pm 40\%$, 0.1–1 ppb to $\pm 20\%$ and concentrations in excess of 1 ppb with accuracies greater than $\pm 10\%$. Further experiments and refinements of experimental technique and apparatus would be expected to improve the accuracy of quantitative results.

Prospects for atmospheric sample analysis

Any new method of ultra-trace detection requires considerable development time. The results presented in this paper have only been obtained in the last few months and it is time to consider what has been achieved and what improvements can be made. Strongly absorbing species can be detected down to the 10–20 ppt range, and less strongly absorbing species to about 1 ppb. It is considered that improvements to the detection technique should lower these limits by a factor of 40 by
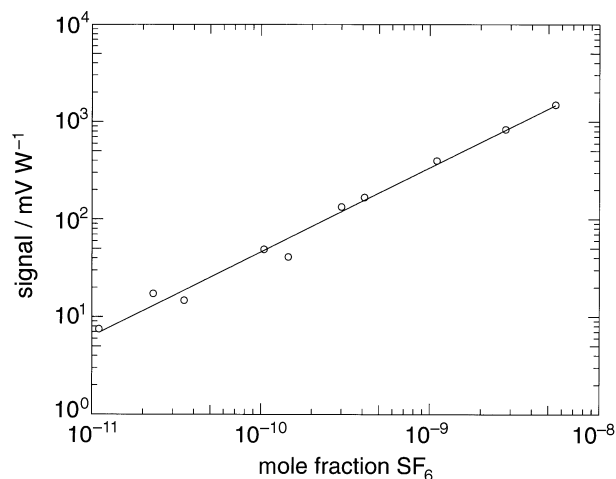
concentrating the trace content of a 0.5 l gas sample, or even in excess of 100 for a multi-pass detection system. This would not place the method in the same category as electron capture for SF_6, but it would make it comparable with GC–MS, and thus a practical method for trace analysis.

Atmospheric samples could be studied using two different approaches. The first is to liquefy the air sample in the cryogenic cell. This should be possible, although the broad collisionally induced IR spectra of liquid N_2 and liquid O_2 may obscure some trace spectral features. The other approach is to freeze-out trace molecules in a cryogenically cooled copper vessel, allowing the removal of the bulk N_2 and O_2 which could then be replaced by another buffer gas such as argon. This latter method has the advantage of allowing a concentration stage in which the trace species from relatively large atmospheric samples are transferred into a smaller sample of inert gas. It also allows the selection of solvent permitting the tuning of molecular absorptions, *e.g.* the absorption line of SF_6 used in this study is shifted to 940.5 cm^{-1} in liquid N_2 solution. The shift may be estimated from the dielectric constant using the Kirkwood–Bauer–Magat formula.

It would be beneficial to partially dry samples by cooling them to freeze-out the water, to prevent ice crystals interfering with detection. Fortunately, the vapour pressure of ice falls very rapidly with decreasing temperature, so drying would be possible even in the case of measurement of SO_2 concentrations in atmospheric samples taken over sea water by precooling the gas mixture to 120 K as outlined above.

One of the most significant applications may be in the measurement of isotopic ratios; *e.g.* ^{15}N and ^{18}O in N_2O, ^{13}C and ^{18}O in CO and CH_3D in methane. All these isotopic species are present in the high ppt to ppb range. The detection of $^{12}CH_3D$ by MS is complicated by the equal mass species $^{13}CH_4$, which is twenty times more abundant.

Sometimes it is important to measure small differences in isotopic ratios for different samples. In these cases we suggest that a differential method similar to that used in dual-beam spectrometers could be used, rather than striving for extreme precision in sequential measurements.

Other cases of importance include the detection of OCS at the level of 500 ppt. It should be possible to measure volatile fluorocarbons at levels of about 50 ppt as well as carbonyl compounds such as acetone and formaldehyde. Indeed, one of the attractions of this technique is its versatility and ability to detect several species in a mixture simply by tuning the laser frequency.

The reliability of this new technique will be checked by calibration with mixtures of known composition and by comparison with well established techniques.

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Fig. 4 Variation of normalised signal with SF_6 concentration