

## Urban air pollution monitoring: laser-based procedure for the detection of carbon monoxide gas

W. X. Peng<sup>†</sup>, K. W. D. Ledingham\*, R. P. Singhal and T. McCanny

Department of Physics and Astronomy, University of Glasgow, Glasgow, UK G12 8QQ.

E-mail: k.ledingham@physics.gla.ac.uk

Urban air quality is of considerable importance in many cities throughout Europe and the USA. In particular, current EU legislation has driven an expansion of monitoring of more pollutants at more sites. At present in the UK, real time readings are now available for benzene, buta-1,3-diene and other volatile organic compounds, airborne fine dust (PM<sub>10</sub>), CO, O<sub>3</sub>, SO<sub>2</sub> and NO<sub>x</sub>. Carbon monoxide is produced to varying degrees in all combustion processes but more than 90% is caused by emissions from petrol vehicle exhausts. The World Health Organisation guidelines for exposure to the gas is <10 ppm for 8 h and 85 ppm for periods not exceeding 15 min. All of the pollutants mentioned above are monitored by different detection techniques and it has been the authors' philosophy to develop instrumentation which can monitor all the different pollutants using a single detector. To this end, a multiphoton laser based procedure, using simple ionization chambers, has been developed to detect the different pollutants with different wavelengths. For CO, a 2 + 1 resonance enhanced multiphoton ionization (REMPI) scheme at 230 nm can be used with detection limits of about 1 ppm.

**Keywords:** Laser ionization; resonance-enhanced multiphoton ionization; trace detection; carbon monoxide; urban monitoring; ion chamber; air quality

In the 1950s and 1960s, the problems of urban pollution in the UK and other industrialised countries were obvious with the regular occurrence of severe winter smogs. The UK Clean Air Acts of 1956 and 1968 and similar legislation in mainland Europe and the USA resulted in the drastic reduction of SO<sub>2</sub> and smoke within urban areas, improving air quality dramatically. There was a tendency in the 1970s and 1980s to imagine that these problems had been eliminated permanently. However, a lowering of air quality has reappeared owing to the massive growth in car ownership. Car emissions now dominate urban air pollution with the concomitant fear that they may be linked to respiratory diseases, and this has led to a recent resurgence of public awareness of and concern with urban air quality. The implications for public health that private car ownership will double in the next 20 years are clearly serious.

In order to allay public disquiet, recent EU legislation has driven a rapid expansion of urban pollution monitoring of more pollutants at more sites. In order to comply with EU Directives, the UK has established several expert committees that have produced a number of publications<sup>1–8</sup> concerned with various aspects of urban pollution including carbon monoxide.

Carbon monoxide is produced to varying degrees in all combustion processes but most emissions to ambient air come from petrol exhausts. In the combustion process it is formed by the incomplete oxidation of the fuel, although it is also produced in the atmosphere by the oxidation of methane and higher

hydrocarbons. It is a toxic gas that combines with haemoglobin more readily than oxygen and hence restricts the blood's ability to transport oxygen. World Health Organization guidelines have recommended a concentration limit of 10 ppm CO in urban air as a running 8 h average and with a maximum 85 ppm for periods not exceeding 15 min. In the UK, along with benzene, buta-1,3-diene and other volatile compounds, airborne fine dust (PM<sub>10</sub>), O<sub>3</sub>, SO<sub>2</sub> and NO<sub>x</sub>, CO is one of the pollutants for which real-time readings are available. There are about 30 urban sites in the UK which are permanently monitored giving average street level concentration readings typically between 1 and 3 ppm.

Sensitive detection of CO in the atmosphere has been carried out by photoacoustic spectroscopy,<sup>9</sup> long path monitoring by infrared resonant absorption spectroscopy,<sup>10</sup> differential infrared tunable diode laser absorption spectroscopy<sup>11</sup> and gas filter correlation spectroscopy.<sup>12,13</sup>

More recently, lasers have begun to be used extensively in methods for monitoring atmospheric pollutants.<sup>14–25</sup> A number of studies have employed laser induced fluorescence and others have used resonance enhanced multiphoton ionization (REMPI). Our approach has been to couple REMPI with simple ionization chambers at atmospheric pressure using normal air samples, as in this work. Alternatively, one can use high vacuum time-of-flight mass spectrometers, which have the advantage of giving additional mass information but have the disadvantage of requiring an atmospheric to high vacuum interface. The philosophy behind the present system is that a number of different pollutants can be detected by the same apparatus just by changing the wavelength of the laser. The REMPI approach has the necessary requirements for an advanced atmospheric pollutant monitoring technique of high sensitivity, multicomponent and real time monitoring. The object of this present paper is to show how the technique can be extended from monitoring NO<sub>x</sub><sup>21</sup> and benzene<sup>19</sup> to the detection of CO.

### Molecular spectroscopy involved in REMPI of CO

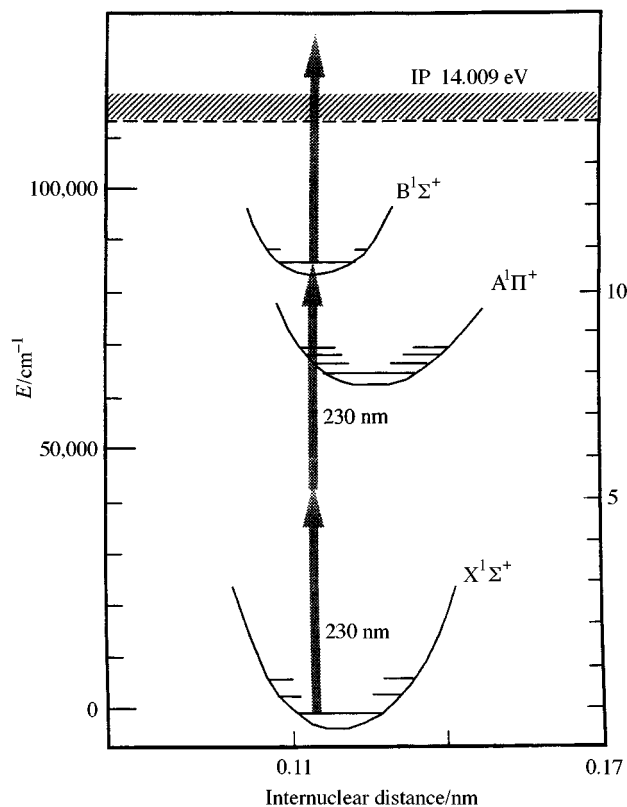
A number of papers describing REMPI spectroscopy of CO have been published.<sup>23–35</sup> A partial energy level diagram for CO is shown in Fig. 1.<sup>36</sup> The multiphoton absorption technique *via* the A and B states has found application in detecting CO in both cells and hydrogen flames. In particular, the strong B<sup>1</sup>Σ<sup>+</sup> ← <sup>1</sup>X<sup>+</sup>Σ<sup>+</sup> two photon absorption has generated considerable attention as a probe of photodissociation dynamics<sup>30</sup> for the production of CO<sup>+</sup> and for imaging CO produced in hydrogen flames.<sup>37,38</sup> A preliminary study dealing with the REMPI of CO has already been carried out by the present authors.<sup>39</sup>

In general, for the two photon absorption from <sup>1</sup>Σ<sup>+</sup> ← <sup>1</sup>Σ<sup>+</sup> states, three branches, O, Q and S (ΔJ = −2, 0, +2), are allowed whereas the P and R branches (ΔJ = ±1) are forbidden. For the B ← X branch, however, two studies show that the O and S branches are missing.<sup>40,41</sup> The difference in rotational constants of the B state (1.96 cm<sup>−1</sup>) and the ground state (1.93 cm<sup>−1</sup>) is very small and, as a consequence, the Q branch, at least for low J, cannot be resolved, resulting in a single peak.

<sup>†</sup> Permanent address: Department of Physics, Jilin University, Changchun 130023, China.

## Experimental

The experimental set-up is shown in Fig. 2. A Lumonics (Rugby, UK) excimer pumped dye laser system (TEM 860-M and EPD 330 models) was operated usually at frequencies



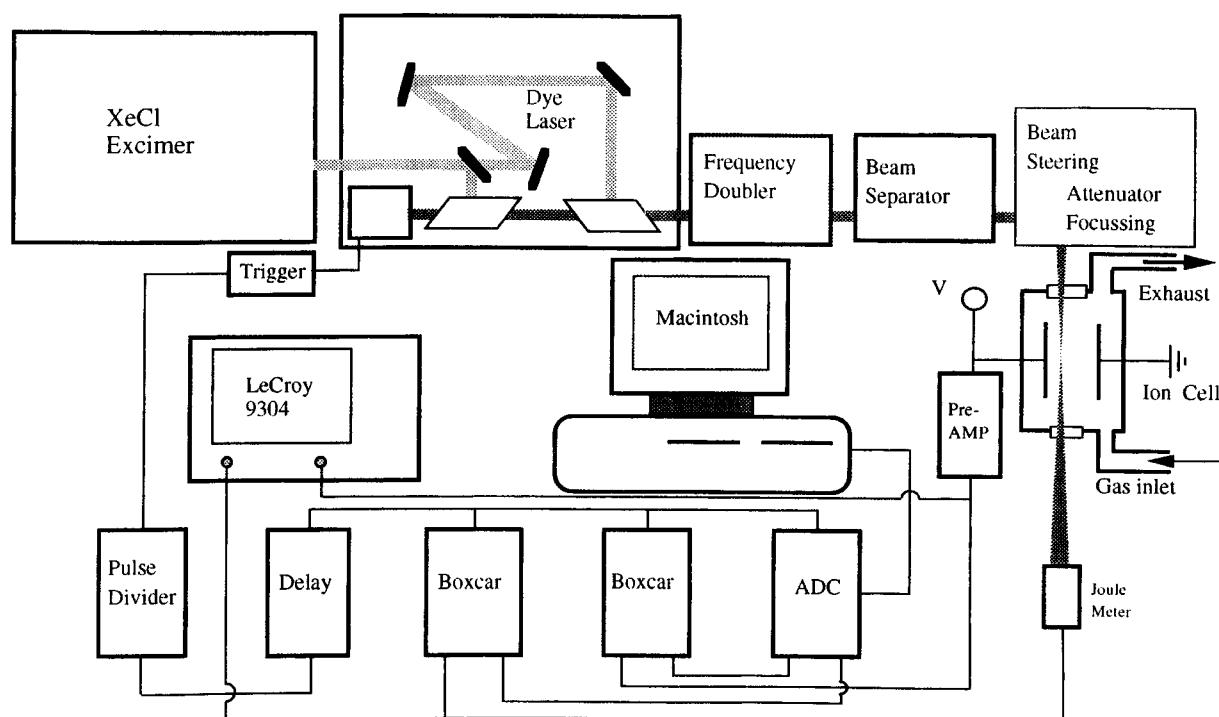
**Fig. 1** A partial energy level diagram for the CO molecule (adapted from Ref. 36).

between 10 and 15 Hz. Coumarin 47 laser dye was used to span the wavelength range 448–460 nm. UV radiation in the range 224–230 nm was obtained by frequency doubling the dye output using a BBO B cut crystal. This was mounted on an Inrad (Northvale, NJ, USA) Model II autotracker unit. The laser beam was focused at the centre of the ionization chamber using a 30 cm lens.

A diecast box with two 15 × 25 mm parallel plates with a separation of 15 mm and fitted with quartz windows for laser access constituted the ionization detector. Ports for vacuum pumping and gas flow were added to allow dilution experiments to be performed. A charge sensitive pre-amplifier was used to bias the detector plates, typically a few hundred volts, and record the ionization signal.

The data acquisition system is based on a Stanford Research Systems (Sunnyvale, CA, USA) gated integrator and boxcar averagers (SR 250) with LabView data acquisition software and controlled by a Macintosh IIFX computer *via* an SR 245 computer interface. The system is powered using an SR 280 crate and power supply and records the ionization yield and the pulse to pulse laser energy. Data can be recorded in either single shot or averaged modes.

Two types of experiment were carried on the CO molecules. First, the tunable, frequency doubled output of the dye Coumarin 47 was directed between the plates of an ionization chamber which contained gases with trace concentrations of CO. A strong peak was observed at the wavelength 230 nm corresponding to the (2 + 1) REMPI process for the transition  $B^1\Sigma^+ (v = 0) \leftarrow X^1\Sigma^+ (v = 0)$ . The gases used in the ionization chamber were calibrated samples of 20 ppm CO in air and 200 ppm CO in nitrogen, supplied by Linde Gas UK. To obtain lower concentrations of CO, the standard gases can be diluted by a factor of as much as 1000:1 with pure air or nitrogen using the flow system described elsewhere.<sup>21</sup> Typical experimental operating conditions for the 20 ppm CO in air sample were 250 μJ laser pulse energy and a chamber bias voltage of 200 V and those for the 200 ppm CO in nitrogen sample were 50 μJ laser energy and 500 V chamber bias.



**Fig. 2** Experimental set-up for the detection of CO in air or nitrogen using an ionization chamber. For the analysis of the gas samples the ionization chamber was replaced with a linear TOF mass spectrometer.

The second part of the experiment was to irradiate the gas with the laser and to analyse the ions produced with a time-of-flight (TOF) mass spectrometer. The TOF system is a conventional linear system of 1.2 m length, pumped by a turbo pump to a base pressure of  $10^{-8}$  Torr. The operational parameters of the extract optics are based on a Wiley–McLaren design and the ions were detected with a Thorn EMI (Ruislip, UK) electron multiplier. An Einzel lens placed immediately after the extract optics increased the ion transmission through the system. The mass resolution was typically 200 at 100 Da.

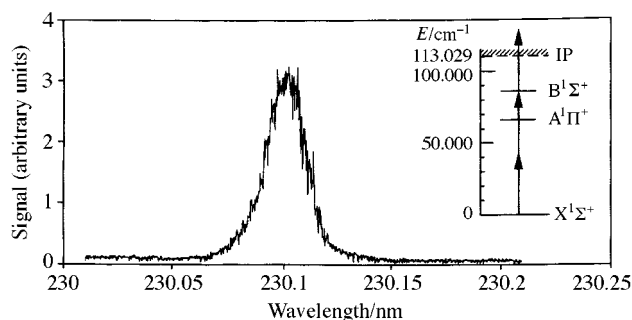
The CO sample was admitted effusively from the inlet system to the high vacuum system through a needle valve. The gas was admitted through a tiny hole in the pusher electrode of the TOF unit and the positioning of the ionizing laser beam with respect to this hole was critical. The sample inlet system could be heated and pumped by a roughing pump to a pressure of  $10^{-3}$  Torr. The inlet line to the high vacuum chamber could be heated independently as well as the entire TOF system. Normally the inlet line was operated at about 120 °C to prevent the samples from sticking to the walls. Sample pressures during data acquisition were typically  $10^{-5}$ – $10^{-6}$  Torr.

The TOF mass spectra were recorded by taking the electron multiplier output directly into a LeCroy (Chestnut Ridge, NY, USA) 9304 digital oscilloscope and averaging over hundreds or thousands of shots.

## Results

A typical CO spectrum corresponding to the  $B^1\Sigma^+(0) \leftarrow X^1\Sigma^+(0)$  (two photon absorption, one photon ionization) REMPI process at 230 nm using the ionization chamber is shown in Fig. 3. It can be seen that only one sharp peak appears in the spectrum corresponding to the Q branch of the transition. The O and S branches are completely absent and all the rotational lines are located in a single bandhead with a width of  $\Delta\lambda = 0.02$  nm. The individual rotational lines could not be resolved using our laser system, which has a bandwidth of about 0.01 nm.

The Q head of the CO transition [ $B^1\Sigma^+(0) \leftarrow X^1\Sigma^+(0)$ ] was used as the fingerprint to conduct sensitivity measurements for the system. However, since the Q head is a very congested single peak, one cannot verify it without a wavelength calibration. Fortunately, the characteristic double headed spectrum of NO [ $A^2\Sigma^+(0) \leftarrow X^2\Pi_{1/2,3/2}(0)$ ] around 226 nm shares the same wavelength region as that of CO [ $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ ] when using the dye Coumarin 47. Therefore one can conveniently use NO or NO<sub>2</sub> as the wavelength calibrants. The wavelengths of the two heads of NO are known to be 226.9 and 226.3 nm.<sup>36</sup> Fig. 4 shows a spectrum of a mixture of 20 ppm of CO in air and 1 ppm of NO<sub>2</sub> in air and from this spectrum the position of the CO peak was verified to be at 230.1 nm. The peaks between 228 and 230 nm belong to molecular oxygen and have been the subject of a previous paper.<sup>42</sup> It should be pointed out that from

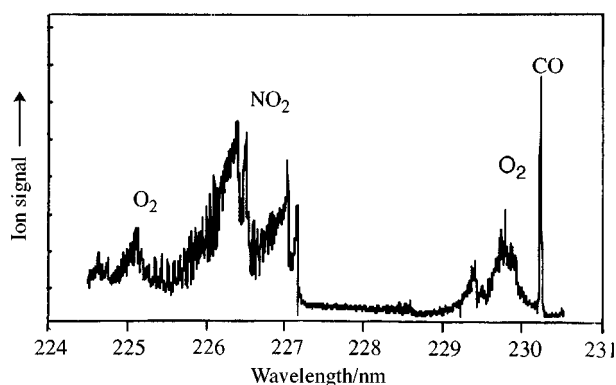


**Fig. 3** A typical 20 ppm CO in air spectrum recorded in the ionization chamber. The single unresolved peak at 230.1 nm is the Q head of the  $(2 + 1)$  transition  $B^1\Sigma^+(0) \leftarrow X^1\Sigma^+(0)$ .

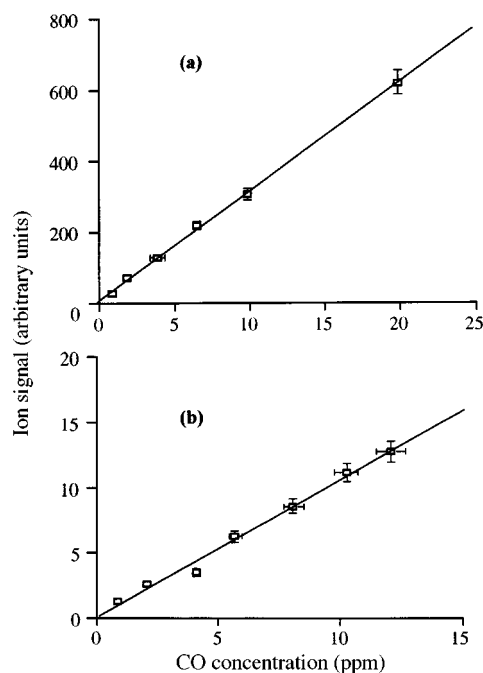
the one graph, *i.e.*, a wavelength scan of about 6 nm, three important gas concentrations can be measured.

Two series of sensitivity measurements were conducted using the two standard gases of 20 ppm of CO seeded into air and 200 ppm of CO seeded in nitrogen. Graphs of the ion signal size as a function of concentration of CO for the two gases are shown Fig. 5(a) and (b). Dilutions were made by adding air and nitrogen to the two standard gases. It can be seen that good linear plots were obtained for the two concentration ranges and with a limit of detection (LOD) about 1 ppm. The CO LOD level was defined to be for a peak with a signal to noise ratio of 2 : 1. This LOD can be reduced by a factor of at least 10 using signal averaging techniques.

It was important to verify that the peak at 230 nm was indeed from CO and not N<sub>2</sub>, which has a very similar atomic mass. Two



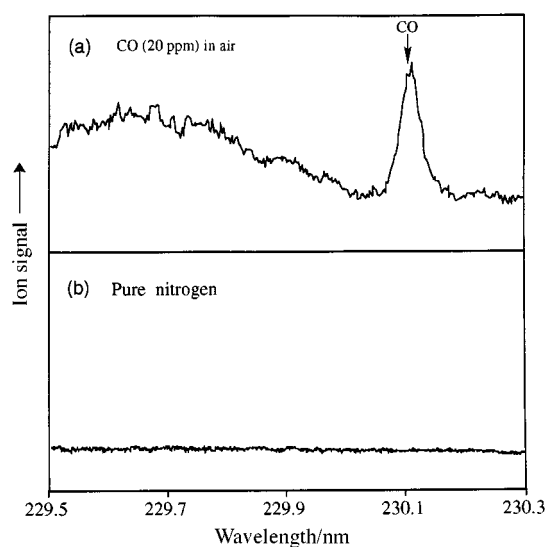
**Fig. 4** A spectrum taken in the ionization chamber of a mixture of 20 ppm of CO in air and 1 ppm of NO<sub>2</sub> in air. The O<sub>2</sub> bands marked in the spectrum have been described in detail in Ref. 42.



**Fig. 5** (a) Ion signal size as a function of concentration for the sample 20 ppm CO in air using air to dilute the sample after the method described in Ref. 21. The limit of detection was about 1 ppm as described in the text. (b) Ion signal size as a function of concentration for the sample of 200 ppm CO in N<sub>2</sub>. The sample was diluted with pure nitrogen down to values less than 15 ppm. This graph was included to show that accurate low concentration samples can be obtained from high concentration samples with large dilutions.

spectra were taken in the ion chamber with 20 ppm of CO in air and a spectrum of pure nitrogen. These are shown in Fig. 6 and it is clear from the flat nitrogen spectrum that there is no contribution to the peak at 230 nm from nitrogen.

It was also important to check that there were no other ions of any mass generated by the laser at 230 nm apart from CO. For this experiment the standard gases (20 ppm of CO in air and 200 ppm of CO in nitrogen) were admitted effusively from the inlet to the high vacuum of the TOF via a needle valve and the laser, operating at 230 nm, irradiated the gases at a pressure between  $10^{-5}$  and  $10^{-6}$  Torr. The TOF was mass calibrated using nitrobenzene (NB) under irradiation with a 266 nm laser beam, which provides a well known mass spectrum.<sup>43</sup> The mass spectra on resonance at 230.1 nm and off-resonance at 229.87 are shown in Fig. 7(a) and (b), respectively. Mass 28 (CO) is the only strong peak and all other small peaks are associated with NB. It should be pointed out that the air samples used in these laboratory experiments were in no way purified and hence are typical of urban air.

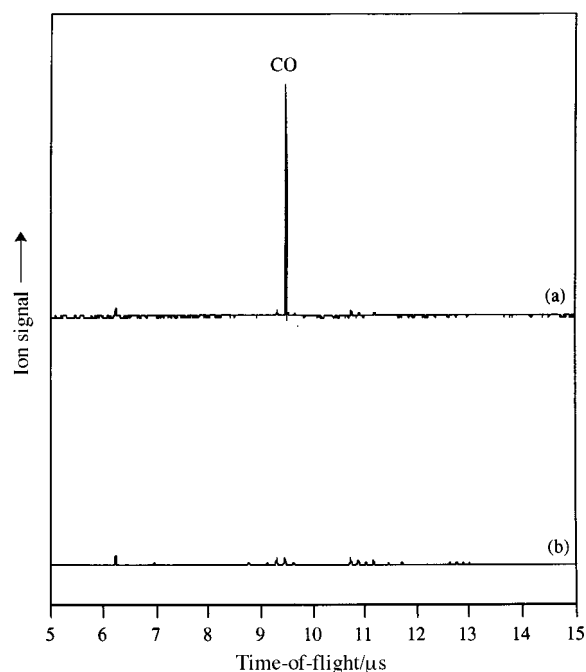


**Fig. 6** Comparison of two spectra in the ionization chamber taken at 230.1 nm for (a) the sample gas 20 ppm CO in air and (b) pure nitrogen, showing that there is no contribution to the ion signal from nitrogen gas.

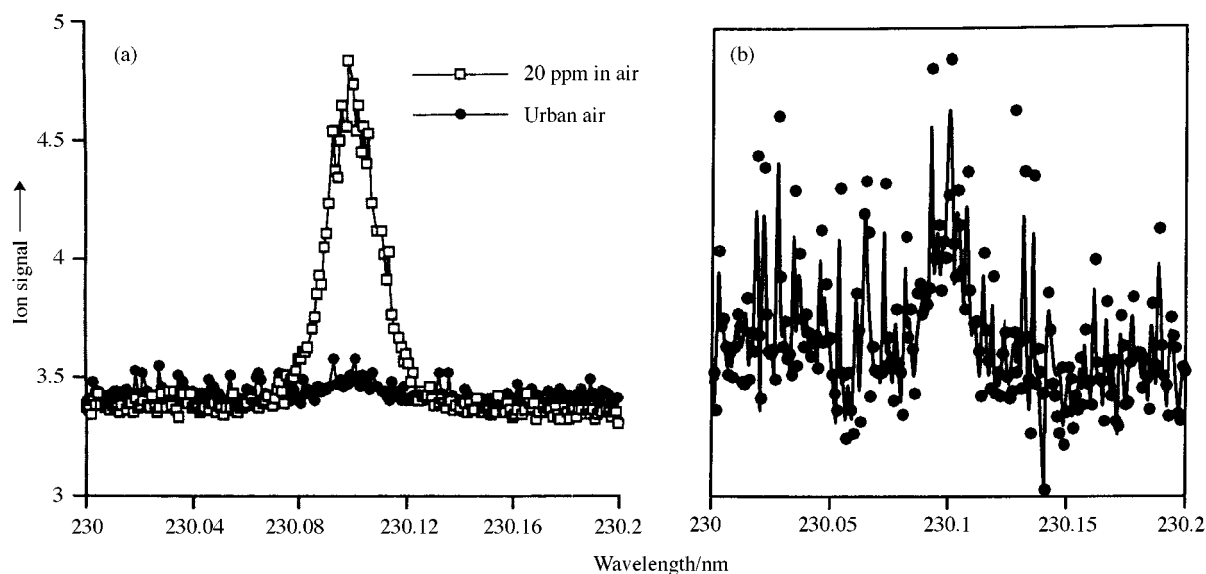
The CO level in urban air was measured in a busy street in Glasgow at 1 pm on a January day. The ion chamber was evacuated in the laboratory and transported to the measurement site under vacuum and the valve of the chamber was opened to admit the urban air sample. The sample was irradiated with laser light tuned to 230.1 nm and compared with a 20 ppm CO in air sample. These two spectra are shown in Fig. 8. The CO concentration in the urban air sample was measured to be about 2.5 ppm, well below the 10 ppm WHO recommended lower level, and is typical of the CO pollution in Glasgow.

## Conclusions

It has been shown that CO in air and nitrogen can be detected with a laser based procedure using a simple ionization chamber



**Fig. 7** Spectra taken in a TOF mass spectrometer using the 200 ppm CO in nitrogen sample. On-resonance at 230.1 nm there is a strong peak at mass 28 corresponding to CO. Off-resonance at 229.87 there is no contribution at mass 28.



**Fig. 8** (a) Spectra of calibrated 20 ppm CO in air sample and (b) an enlarged diagram for the urban air sample. The solid line represents a three point smoothing procedure applied to the data points. From this spectrum, the CO concentration in the air sample was measured to be 2.5 ppm.



system with a three photon absorption process at 230.1 nm down to sensitivities of about 1 ppm using a single laser pulse wavelength scan. This level is a factor of 10 lower than the WHO recommended lower level and when the pulses are averaged much lower sensitivities may be reached. A 10 pulse average scan would produce an LOD a factor of three lower. The linearity of the laser system up to 200 ppm is very good.

It was explained earlier that the analysis of air samples was typically carried out using a laser pulse energy of about 250  $\mu$ J (close to the maximum performance of our system). At this value, the signal was increasing as a function of pulse energy with a cubic dependence [characteristic of a (2 + 1) REMPI process far from saturation] whereas the background below the peak had a linear dependence. Hence increasing the pulse energy further would have resulted in an increased signal-to-noise ratio and a reduced LOD. The background ion signal in a proportional counter comes from the sum of a variety of trace impurities which were separately below the detection limit of our mass spectrometer and hence could not be identified. This causes few problems for CO quantification provided that the background is flat and hence can be subtracted easily from the source signal.

The perceived advantages of the laser based procedure over other methods for analysing urban air pollutants are ease of use, the possibility of computer control and the extension to other automobile produced pollutants which are likely to be monitored under new legislation. With a single laser system tunable between 200 and 400 nm, a number of organic and inorganic pollutants can be detected with great sensitivity and selectivity, without recourse to purchasing a number of different monitors.

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