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Highsensitivity, interferencefree, Starktuned CO2 laser photoacoustic sensing of urban ammonia

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we find a maximum f_c of 240 GHz for a doping level of 10^{17} cm^{-3} and 350 GHz at 10^{18} cm^{-3}. It should be noted that in real structures, the presence of parasitic resistances and capacitances will further reduce this figure. Although these figures do not define an absolute limit, they do suggest that, for very high-speed operation, Schottky diodes (where f_c is generally > 1000 GHz) may still be more suitable.

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High-sensitivity, interference-free, Stark-tuned CO_2 laser photoacoustic sensing of urban ammonia

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Low-concentration (few ppbv), interference-free, on-line photoacoustic detection of ambient ammonia (NH_3) is reported by Stark tuning the $Q(J=5, K=5, M=5)$ NH_3 absorption line into resonance with the CO_2 laser. Measurements were made over a range of total pressure between 600 and 50 mbar.

Photoacoustic spectroscopy (PAS), in particular when combined with strong lasers as radiation sources, has been recognized for its capacity to measure weak absorptions in gases, liquids, and solids.[1] Since the majority of pollutants absorb in the infrared between the 2- and 20-μm region, also characterized by the availability of several strong lasers, there have been considerable amounts of laboratory and field work performed towards a practical instrument for on-line analysis of atmospheric gases in the low-concentration range (several ppbv).[2]

Among those, ammonia, due to its role in the soil acidification, has received ample attention from worldwide scientific communities, and its control through the concentration of measurements has become a necessity. Fortunately there is a good degree of spectral overlap between ammonia absorption frequencies and the frequencies of the CO_2 laser, the strongest one being that coinciding with the $9R(30)$ laser transition.

In situ, conventional chopped radiation mode photoacoustic studies of ammonia carried out so far, encompass both low- and high-concentration ranges. Examples involve trace detection in ambient air by preconcentrating the sample on the selective absorber[3] and flux measurement of NH_3 emitted from the fertilized fields.[4] Gandurin *et al.* constructed a modular (three lasers) laboratory setup for photoacoustic analysis of mixtures containing NO, NO_2, NH_3, C_2H_4, and saturated hydrocarbons, by making use of a two-channel differential scheme and a wavelength-modulation technique.[5] Above ppmv level, ammonia emission rate measurements in a power plant using a CO_2 laser[6] and diode laser studies of ammonia concentration, diurnal variation[7] have been reported.

Due to the additive character of the photoacoustic signal under normal atmospheric conditions, the presence of a large amount of water vapor and carbon dioxide impedes NH_3 detection in the low-concentration range (ppbv). Consequently, some means of selective spectral discrimination is required if ammonia is to be detected interference free in the matrix of absorbing gases.

An interesting methodology that enables the experi-

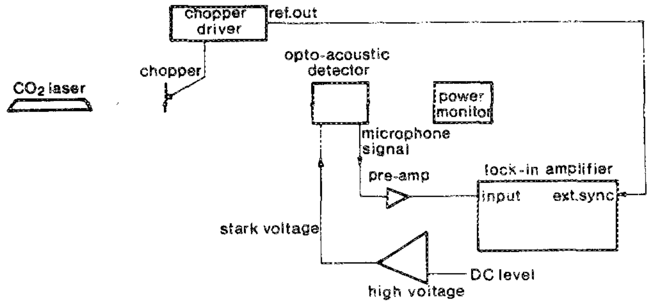

FIG. 1. Experimental setup used in this study.

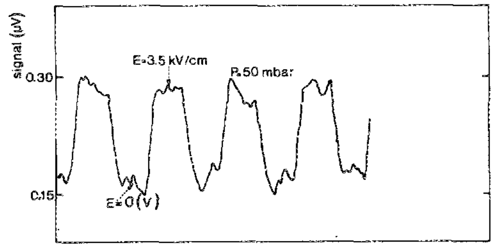

FIG. 2. Stark signal of NH_3 obtained at $10R(6)$ CO_2 laser line at the total pressure of 50 mbar and the electric field strength of 3.5 kV/cm.

mentalist to deduce the NH_3 concentration through the proper interpretation of phases and signal strengths obtained by measurements at selected CO_2 laser wavelengths has recently been suggested.[8] The effectiveness of ammonia, present in a mixture of four gases, on the photoacoustic signal has been studied in the laboratory.[9] Tuning the NH_3 absorption into resonance with a proper CO_2 laser line by means of the Stark effect, thereby greatly enhancing the specificity, has been demonstrated in laboratory studies.[10–13] In this communication we report on the design and use of a Stark-tuned spectrometer (see Fig. 1) that has permitted, what is believed, the first PA measurements of ammonia ever conducted in the outside air.

A home-made, stable CO_2 line-tunable waveguide laser was used in this experiment. The resonant photoacoustic cell made of high-quality polytetrafluorethylene (PTFE) Teflon was designed for the operation in the flow-through mode and can be driven either in the conventional chopper mode or the Stark-tuned mode. It is equipped with carefully designed baffle volume[14]: its resonance frequency corresponded to the first longitudinal mode is 1608 Hz (293 K). The cell incorporates three identical rectangular channels of 5.0×5.0 mm^2 cross section and of 100 mm length. Only the middle channel is illuminated by the unfocused laser radiation. Each channel is equipped with a miniature Microtel M37 microphone (10 mV/Pa at 1608 Hz); those in the side channels serve for averaging of the background signals prior to the subtraction from the signal recorded in the main channel. An ultralow noise amplifier was used before feeding the signals into the Ithaco 3961-A two-phase lock-in amplifier. A detailed description of cell construction and accompanying electronics will be given elsewhere.[15] Two identical rectangular, polished aluminum plates, forming a 5-mm gap, are separated by two PTFE-Teflon spacers. High dc voltage generated by power supply (FUG HCN 7E-12500) is applied to the bottom plate; the upper plate carrying the three microphones is grounded.

Figure 2 displays results of the measurement taken at $10R(6)$ laser line in the flowing regime (0.4 ℓ/min). The outside air was drawn through tetrafluorethylene-perfluorpropylene (FEP)-Teflon tubing by a vacuum pump. With an electric field strength of 5 kV/cm, without causing electric breakdown, $Q(J=5, K=5, M=5)$ of the multiplet transitions with $\Delta M=0$ was Stark tuned at 50 mbar and room temperature. The cell with the laser beam mechanically chopped at 1608 Hz is operated in the first longitudinal mode. The Stark field which is modulated by a square wave at 0.1 Hz is provided by the FUG HV power supply driven by a Wavetek generator. Measurements performed at different pressures, while maintaining the experimental conditions unaltered, show the same trend as illustrated in Fig. 2 above. With increasing pressure the modulation depth decreases. No Stark shift is observed at pressures exceeding 600 mbar, with a field strength of 5 kV/cm. In order to check the identity of the measured signals, several control tests have been run. At first, a small vessel containing a few droplets of 32% aqueous solution of ammonia (Merck) was placed in the immediate vicinity of the feed-line tubing. Accordingly, a rapid and large increase of the photoacoustic signal (lock-in signal 10 mV) at $10R(6)$ laser line was observed under normal operating conditions.

As a final test, the cell was coupled to a bubbler containing only distilled water at 293 K, through which very pure (class 5.0) nitrogen is flowed. No Stark shift was observed when the mixture of saturated water vapor $\approx 10^4$ ppmv and nitrogen at pressures between 50 and 600 mbar in the cell.

With the CO_2 laser mechanically chopped and tuned to the $10P(14)$ transition, the cell was calibrated using a certified precision mixture of 101.6 ppm C_2H_4 [absorption cross section[16] of ethylene is about 35 $atm^{-1}\,cm^{-1}$ at $10\,P(14)$] at the first longitudinal resonance mode (1608 Hz, 293 K), yielding a cell constant of $(3.9\pm0.1)\times10^3$ Pa cm/W for one microphone. Using this value, the observed signal (Fig. 2) is found to correspond to 7.5 pppbv of ammonia. The ultimate $(S/N=1)$ detection limit of 0.4 ppbv for a given set is derived by considering the noise atop the signal shown in Fig. 2.

In conclusion, on-stream and interference-free detection of ammonia present in the urban air has been demonstrated. The cell is potentially susceptible to further optimization, such as the reduction of baffle volume dimensions and modulation of the Stark field at resonant frequency.

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Synthesis of electrostatic lenses by simulated annealing

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The use of simulated annealing is proposed for automatic design of electrostatic lenses with given first-order properties and minimum aberrations. The synthesis of a high-quality lens for focusing an ion beam produced by a liquid-metal source is shown as an example.

The performance of electron and ion lenses is limited by their aberrations. We have shown[1] that the automatic design of electrostatic lenses with given first-order properties and minimum aberrations is possible, and a very substantial improvement in the practical design of superior quality lenses can be achieved[2] by our approach of lens synthesis.

The synthesis procedure is aimed at the reduction of the lens aberrations with the simultaneous satisfaction of numerous constraints resulting from practical requirements, such as source parameters, working distances, electric breakdown, etc. We are searching for such electrode or pole piece configurations whose axial potential distributions (APD) satisfy all the constraints, and simultaneously minimize a certain objective function. Our procedures search for these APDs in the form of sets of specific variables that are related to the corresponding APDs in a simple way. One possibility is to express the APDs in the form of cubic splines,[3] in which case the variables are the values of the potential or its derivatives at the boundaries of the spline intervals. The subsequent construction of the electrodes is then a very simple task.[4]

The selection of the objective function is based on practical requirements. The total spot diameter at the target can serve as a realistic figure of merit, and this quantity is used as the objective function. Penalties are added to it for violation of the constraints. The sum of the objective function and the penalties is the target function W that should be minimized.

Minimization of the target function is an essential element of lens synthesis. Generally, however, it is impossible to find a global optimum. An optimum solution can only be defined by its relationship to neighboring solutions (local optimum). The success of optimization is, therefore, strongly dependent on the proper selection of the initial values of the variables and on our ability to avoid shallow local optima.

There are many well-known methods of optimization. We have used dynamic programming[5] and various nonlinear constrained optimization techniques.[2,6] In order to avoid shallow local optima, we tighten and loosen the constraints periodically with the simultaneous swapping between different optimization methods.[7] This is a sophisticated technique that works quite well but requires considerable skills.

In this communication we propose the use of simulated annealing[8] as a simple and effective alternative to the solution of this problem. Simulated annealing is based on a deep connection between statistical mechanics and multivariate or combinatorial optimization. However, so far it has been mostly used for the latter case only (graph partitioning, component placement, wiring, and the omnipresent traveling salesman problem).[8,9] Combinatorial optimization is characterized by a very large number of independent vari-

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