

Detection of Toxic Compounds by Cavity Ring-Down Spectroscopy

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Sensitive detection of gaseous toxic compounds of environmental concern by cavity ring-down spectroscopy (CRDS) is demonstrated. In particular, CRDS is applied to the detection of nitrogen dioxide and four chlorinated aromatic volatile organic compounds. Detection limits in this feasibility study are in the parts-per-million range, but experimental improvements will enhance the sensitivity to the parts-per-billion range or better. For chlorinated aromatics, the sensitivity is found to be independent of the degree/site of chlorination. In this respect, it is superior to other laser-based methods such as laser-induced fluorescence and resonance-enhanced multiphoton ionization that are quite strongly influenced by excited-state nonradiative decay induced by the presence of chlorine substituent(s). In addition, since CRDS is self-calibrating, fairly simple to implement and perfectly general, it promises to be a universal environmental toxic gas detector.

Introduction

There exists a need for a general, sensitive, real-time detector for toxic compounds of environmental concern. Although there are many conventional laser techniques in use for real-time detection of specific molecules, none of them is perfectly general in the sense that each is applicable to a somewhat narrow class of molecules. Laser-induced fluorescence (LIF), for example, is excellent for molecules that fluoresce but is obviously inapplicable to molecules with low fluorescence quantum-yield. This is especially true for chlorinated aromatic molecules because of fast intersystem crossing (ISC) that dramatically reduces the fluorescence quantum-yield (the so-called "heavy atom effect" due to the presence of chlorine, see ref 1). ISC also influences detection schemes (2, 3) based on resonance-enhanced multiphoton ionization (REMPI). ISC depletes the excited state on a time-scale faster than the nanosecond-duration of the lasers usually employed in such experiments, thus lowering the photoionization efficiency. Use of ultrafast (femtosecond duration) lasers may alleviate this problem, but the cost and complexity of such systems would render the method unsuitable for field-deployment. By contrast, the relatively new technique used here, cavity ring-down spectroscopy (CRDS), is not plagued by such photophysical complications and is perfectly general because it is solely absorption-based (4–11). It is also superior to other conventional popular techniques such as FTIR spectroscopy because it is much more sensitive and optoacoustic spectroscopy because it can provide absolute ab-

sorption cross-section and is thus self-calibrating (11, 12). It is thus a very promising universal toxic gas detector. In the exploratory experiments described here, we show that CRDS is eminently suitable for detecting simple, small toxic compounds such as NO₂ as well as the much larger chlorinated aromatic volatile organic compounds (VOCs). In CRDS, the absorption path length of a pulsed laser through an absorbing sample is made very long by trapping the pulse between the mirrors of a high-finesse (low-loss) optical cavity containing the sample. The effective absorption path length can be several kilometers, so very small concentrations of chemical species can be detected, being limited mainly by the cavity mirror reflectivity and scattering losses. CRDS is more suitable for environmental work than conventional multipass absorption spectroscopy (with a white cell) because long optical path lengths are more easily achieved. In addition, since the diameter of the CRDS cell needs to be only large enough (few millimeters) to accommodate the laser beam, the necessary gas-volume for CRDS is much smaller than in the case of a typical white cell.

Experimental

The CRDS experimental setup has been described previously (4–10). Briefly, a laser pulse (few ns duration) is injected into a high-finesse optical cavity containing the absorbing species, and the pulse decay is monitored by measuring the light transmitted by the cavity. The cavity is formed by two mirrors of very high reflectivity (preferably $R \geq 0.999$). In an empty cavity (without the sample), the only loss mechanism is the very small transmission of the mirrors, and the pulse can be trapped in the cavity for microseconds, making a very large number of round trips. The intensity of the light transmitted by the cavity decays exponentially, with a characteristic $1/e$ decay-constant (the "ring-down" time) which is a function of the mirror reflectivity and the cavity length only. If an absorbing species is present in the cavity, an additional loss mechanism is introduced, the ring-down time τ decreases, and the transient CRD signal decays faster

$$I_{\text{CRD}}(t) \propto \int I(\nu) \exp[-t/(\tau(\nu))] d\nu \quad (1)$$

where ν = laser frequency, $I(\nu)$ = intensity distribution of incident light, $\tau(\nu) = d/\{c[\ln(R(\nu)) + \sigma(\nu)N]\}$, d = separation between the cavity mirrors, c = speed of light, $R(\nu)$ = cavity mirror reflectivity at frequency ν , $\sigma(\nu)$ = absorption cross-section, and N = species number density. The ring-down time and CRD spectrum (absorption/pass vs wavelength) can be obtained from the transient signal with a fast digitizing oscilloscope or a boxcar averager interfaced to a microcomputer, as described elsewhere (4, 5). For more details on CRDS theory and calculations, the reader is referred to refs 4, 5, and 9.

In our current experimental setup, the tunable laser is a Moletron DL18 dye laser, pumped by a Quantel YG581-10 Nd:YAG laser. The cavity transmission is monitored either by a photodiode (EG&G FND100Q) or an EMI 9871KA photomultiplier. The data are acquired with a Tektronix 420A digitizing oscilloscope or with a boxcar averager (Stanford Research Systems) interfaced to a microcomputer. The CRDS cavity is formed by two relatively inexpensive high reflectors fabricated by CVI Corp or VLOC. The cavity is enclosed in a stainless steel cell the ends of which are made vacuum-tight by two quartz windows. The mirrors and the windows are mounted in flanges that are connected to the rest of the cell by flexible bellows and are held in precision adjustable

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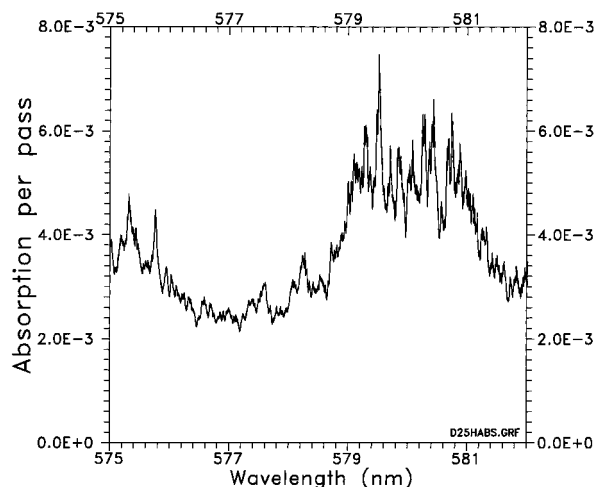


FIGURE 1. Survey CRD spectrum of NO_2 (~ 150 mTorr) in the 575–582 nm region, recorded with $R = 0.9971$, $d = 23.8$ cm. In this spectrum and the one in Figure 2, the spikes do not constitute “noise” and are genuine, reproducible, spectroscopic features. The visible absorption spectrum of NO_2 is notorious for very high density of transitions (see, for example, ref 13).

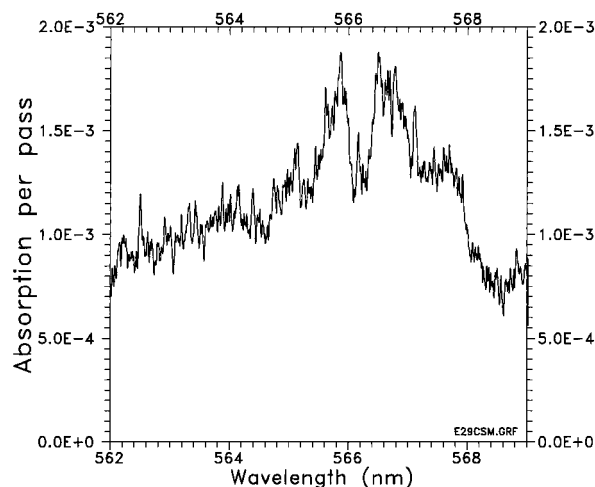


FIGURE 2. Survey CRD spectrum of NO_2 (~ 48 mTorr) in the 562–569 nm region.

mounts for optical alignment. Although the cheap CVI and VLOC mirrors in our current setup are somewhat substandard for this type of work (typical $R \sim 0.980$ – 0.997), they are just about adequate for the initial preliminary exploratory experiments described here.

Results and Discussion

(a) Nitrogen Dioxide. The capabilities of our current CRDS system are illustrated for NO_2 in Figures 1–4. Parts of the visible spectrum of NO_2 have been recorded (Figures 1 and 2). Figure 3 shows the variation of the ring-down waveform as a function of NO_2 pressure at a wavelength of 566.5 nm, corresponding to a peak in the absorption spectrum shown in Figure 2. In Figure 4, we show a plot of $1/\tau$, which is proportional to absorption, as a function of NO_2 pressure. The variation is linear, and we find that the lowest detectable NO_2 pressure is a few mTorr, corresponding to a limit of detection (LOD) of a few parts-per-million (ppm) by volume. This can be improved to parts-per-billion (ppb) range with superior (higher R) CRDS mirrors (5), a longer cavity, and detection in the blue region of the NO_2 spectrum where the absorption coefficient is higher (13).

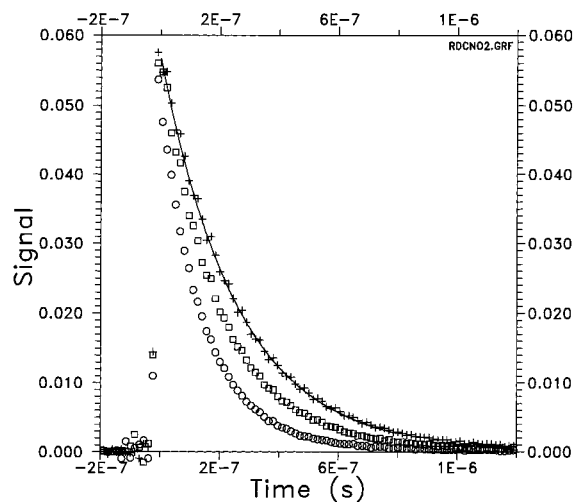


FIGURE 3. RD curves as a function of NO_2 pressure: $\lambda = 566.5$ nm, $R = 0.9971$, $d = 23.8$ cm. The symbols used are (+) 0 mTorr; (\square) 18 mTorr; and (\circ) 38 mTorr. For clarity, only one-third of the data points are shown. The solid curve represents an exponential fit of the 0 mTorr data points.

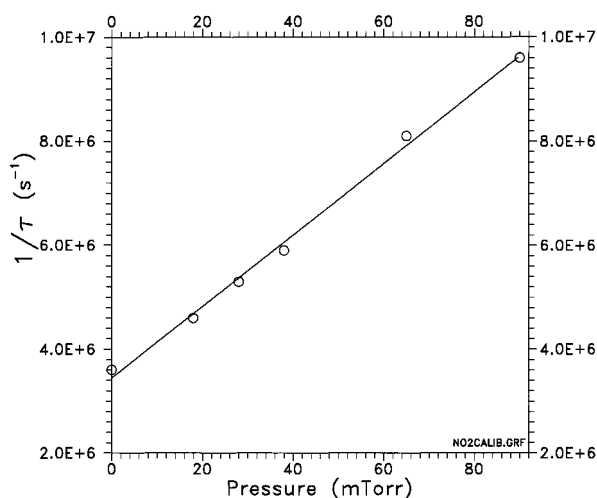


FIGURE 4. $1/\tau$ vs NO_2 pressure. The error in the pressure measurements here and in the following figures is 2–3 mTorr.

(b) Chlorinated Aromatic Volatile Organic Compounds.

For demonstrating detection of chlorinated aromatic VOCs, we have applied CRDS to chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene. In these feasibility studies, we have exploited the accidental coincidence of the fourth harmonic (266 nm, $37\,579\text{ cm}^{-1}$) of a Nd:YAG laser and an absorption feature of the $S_1 \leftarrow S_0$ transition for each of the chlorinated aromatic (14). Results for chlorobenzene and 1,3-dichlorobenzene are shown in Figures 5 and 6, respectively. Similar results have been obtained for 1,2- and 1,4-dichlorobenzenes. The LOD for each compound is in the ppm range and can be improved upon because the fixed wavelength (266 nm) used here coincides with rather weak absorption features in the spectra of these molecules (see, for example, ref 14c). With the use of a tunable laser operating at the wavelength of a strong absorption peak and with other planned improvements in our experimental setup described below, the LOD will be in the sub-ppb range. Additional sensitivity can be gained by preconcentration (for a few minutes) of environmental samples prior to analysis.

The most significant aspect of this work is the ease with which chlorinated aromatics can be detected by CRDS. In addition, the LOD is unaffected by the extent and site of

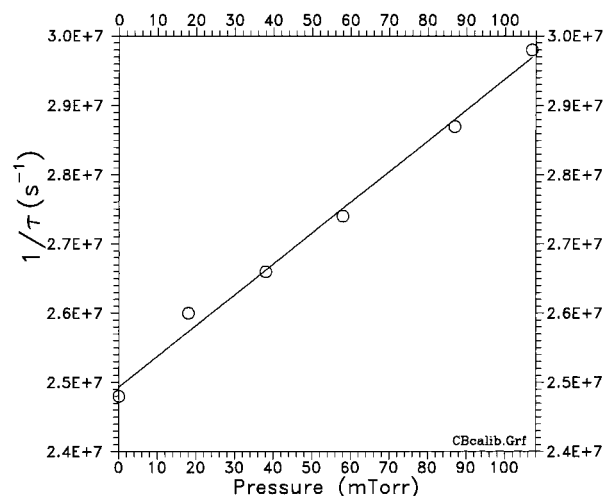


FIGURE 5. $1/\tau$ vs pressure of chlorobenzene at $\lambda = 266$ nm, with $d = 23.8$ cm and $R = 0.9803$.

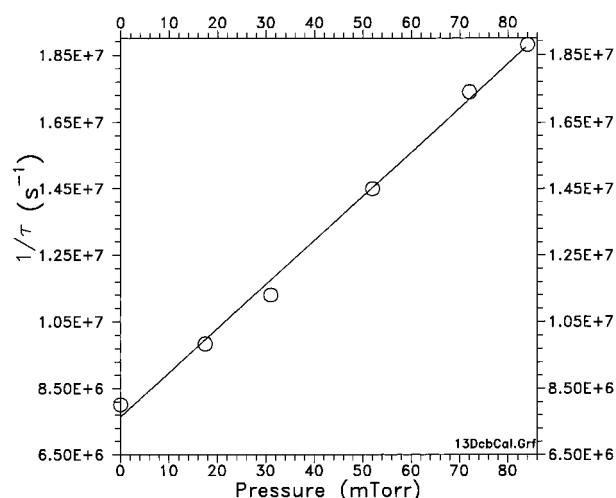


FIGURE 6. $1/\tau$ vs pressure of 1,3-dichlorobenzene at $\lambda = 266$ nm, with $d = 23.8$ cm and $R = 0.9936$.

chlorination. In this respect, CRDS is superior to other laser-based methods that are influenced by excited-state photophysical properties. Techniques such as LIF and REMPI are not very suitable for chlorinated aromatics because the excited states undergo fast nonradiative decay due to ISC, as mentioned previously. In addition, the influence of ISC increases with increasing chlorine content, thus requiring extensive calibration even in cases where these techniques "work".

It is possible to improve upon the LODs achieved here by incorporating changes to the experimental setup (15). However, even the detection limits demonstrated in this feasibility study should be good enough for monitoring aromatic VOCs in concentrations found in, for example, solid-waste landfills (16). The present LODs for VOCs have been obtained with substandard cavity mirrors with R of only 0.9803–0.9945, corresponding to effective absorption path lengths of only 0.024–0.086 km (for $t = \tau$). With better ultraviolet mirrors currently available or which may be available in the future (17) and with a cavity length of ~ 50 cm, an effective absorption path length ≥ 2.5 km is possible. Coupled with the use of a tunable UV laser, the detection limit can be improved significantly. We also note that it is possible to spectroscopically distinguish between different aromatic VOCs (15) because the location of the electronic origin band and the vibrational frequencies are sensitive to the number/type of substituents and their positions on the

phenyl ring, i.e., the molecular structure (14). Consequently, it is possible to readily characterize a mixture of VOCs, provided their spectroscopy is understood (15). CRDS will thus be an ideal monitor for these molecules.

CRDS will also be suitable for detection of larger chlorinated aromatics of environmental concern such as dioxins. These compounds are generated as unwanted byproducts of high-temperature processes such as waste incineration and are a major threat to public health, being among the most toxic man-made chemicals (18). The need for a sensitive, real-time monitor for these compounds is thus quite obvious. Unfortunately, there are currently no general, real-time, sensitive detectors available for this class of molecules, and existing monitors are time-consuming or lack sensitivity/accuracy. Successful application of CRDS to sensitive environmental dioxin detection, however, will be challenging because the vapor pressures of these semivolatile compounds are rather low, and, in addition, the detection limits specified by the EPA for verifying compliance by incinerators are quite stringent (ppt range). Preconcentration (for a few minutes) of environmental samples prior to analysis can help alleviate this problem. We also note that related simpler (monocyclic) chlorinated volatile aromatics, such as the chlorobenzenes studied here and chlorophenols, have been previously suggested as environmental "surrogates" for dioxins (2, 3) because they are easier to detect as they are present in larger concentrations, and there is some correlation between their concentration and dioxins in incinerator emission. Thus, their detection will provide an "early warning" for the presence of chlorinated dioxins. Be it as it may, we feel that a useful dioxin monitor based either on direct dioxin-detection or detection of dioxin-surrogates is within reach.

An issue that may be raised regarding environmental application of CRDS concerns species-specificity in view of congestion in polyatomic molecular spectra. We note that this may be overcome by enhancing spectral resolution by using a moderately high-resolution tunable laser (15) and/or using supersonic expansion to generate rotationally cold samples (the reader is referred to ref 9 for CRDS of supersonically cooled molecules). In fact, for simple (monocyclic) chlorinated aromatics at room temperature, we find that a modest resolution of ~ 0.6 cm^{-1} is sufficient to unambiguously characterize the absorbing species through their ultraviolet spectral signatures (15).

Acknowledgments

We have benefited from the comments of an anonymous referee. This feasibility study was supported by seed money from Mississippi State University's Diagnostic Instrumentation & Analysis Laboratory (DIAL). DIAL is supported by the Department of Energy.

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Received for review September 28, 1998. Revised manuscript received January 19, 1999. Accepted February 16, 1999.

ES981004V