

Other applications can be the extraction of lithium from sea water and waste brines.

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Gas Phase Optoacoustic Spectra and Raman Spectra of Some Chlorinated Pollutants

Joong-Gill Choi*, Jin-Soo Hwang, Ki-Jung Paeng[†], and Gerald J. Diebold[‡]

Department of Chemistry, Yonsei University, Seoul 120-749

[†]*Department of Chemistry, Yonsei University, Wonju 222-701*

[‡]*Department of Chemistry, Brown University, Providence, RI 02912 U.S.A*

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Laser optoacoustic technique has been employed to obtain the gas phase absorption spectra of 1-chloronaphthalene, 3-chlorobiphenyl, and 2,5,2'-trichlorobiphenyl in conjunction with a gas chromatograph and a Helmholtz resonator at the various CO₂ laser wavelengths. Raman spectra of 1-chloronaphthalene, 4-chlorobiphenyl, and 4,4'-dichlorobiphenyl in condensed phase have been also obtained. The optoacoustic measurement of the infrared absorption in gas phase has been shown to be of value in monitoring the environmental pollutants.

Introduction

In recent years the development of ultra-high sensitivity detection techniques has taken on an increased importance as the environmental contamination from industrial and agricultural chemicals increases. One particular health and environmental concern is halogenated organic hydrocarbons, due to their ubiquity, stability, potential for biomagnification, and highly toxic nature. The most striking examples of such chemicals include halogenated dibenzo-*p*-dioxins (*e.g.*, TCDD), dibenzofurans, polychlorinated and polybrominated biphenyls (known as PCB and PBB), and chlorinated naphthalenes. These chemicals may be industrially useful (biphenyls and

naphthalenes) or unwanted contaminants (dioxins and furans) of other useful compounds¹. However, interest in their environmental effects has greatly increased as a result of their notorious toxicity; even in extremely small concentrations public health can be threatened.

Since almost all pollutants have their fundamental absorption bands in the infrared region, IR and Raman spectroscopic techniques have been found to be useful for these studies. However, from the fact that molecular vibrational absorption cross sections in this spectral region are not large in general, for extremely sensitive trace detection, the development of new techniques have been required. The combination of infrared detectors with gas chromatography (GC-

IR)^{2,3} has increased the utility of spectroscopic techniques and made possible for the identification of trace analytes based on the spectral information as well as retention time. Since conventional absorption techniques require precise measurement of the difference between incident and transmitted intensities of the radiation, when used for very weak absorbing species their sensitivity is diminished because the two signals are nearly equal. Furthermore, conventional IR instruments have difficulties detecting the very limited amount of sample available at the output end of the GC separation column (*i.e.*, they are unable to work with samples smaller than about 1 μg).

The optoacoustic detection directly measures the absorption of the sample of interest by the use of a microphone, whose signal is directly proportional to the absorptivity of the sample. It is not necessary to do any subtraction of two nearly identical signals, so that the problems inherent in conventional absorption techniques are eliminated. The application of optoacoustic detection for trace analysis has become particularly attractive with the availability of laser sources⁴⁻⁶. Recently, Kreuzer⁷ developed a new GC-IR system to achieve greater sensitivity than the conventional GC-IR systems (by more than 3 orders of magnitude) by using an IR radiation source and an optoacoustic detector with a gas chromatographic technique. This new system allows the IR absorption measured by the optoacoustic detector to be used in conjunction with the retention time to identify peaks. Furthermore, compounds with similar retention times are distinguished by different absorption properties. The ratio of absorption at one wavelength to that at another wavelength depends on the absorption properties of the compound⁷ and provides a criterion for the identification. Although an optoacoustic detector, generally in gas phase, is not as sensitive as a GC-mass spectrometer (GC-MS) system, it is advantageous in distinguishing compounds that have similar mass spectra but different IR absorptions, *i.e.*, isomer identification.

Rapid, sensitive, selective, and reliable methods to detect extremely low levels of molecular gases including various toxic vapors in ambient air have been studied with CO₂ laser-based optoacoustic spectroscopy⁵⁻¹⁷. There is a need for detailed infrared absorption information at CO₂ laser wavelengths for such applications as trace gas or pollutant monitoring, laser-induced chemistry, and energy transfer studies¹³. The wide availability and high output power of the CO₂ laser have proven to be of utmost importance for these applications, particularly for condensed matter whose gas phase absorption data have been unavailable. In order to select appropriate wavelengths in each measurement, a detailed knowledge of the absorption spectra of the species of interest and of possible interfering species regardless of their phases are necessary. Unfortunately, infrared absorption spectra of compounds exemplified above have been reported only for the condensed phase^{2,18}.

Here we report the gas phase absorption spectra of several environmental pollutants such as 1-chloronaphthalene (CINT), 3-chlorobiphenyl (CIBP), and 2,5,2'-trichlorobiphenyl (TCIBP) by the use of the optoacoustic detection technique in conjunction with a gas chromatography. In addition, the Raman spectra of PCB related compounds such as 1-chloronaphthalene, 4-chlorobiphenyl, and 4,4'-dichlorobiphenyl in condensed phase are obtained.

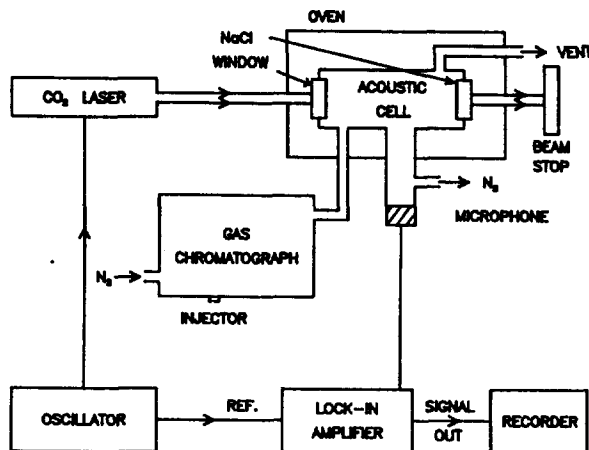


Figure 1. Experimental arrangement for GC-optoacoustic detection.

Experimental

Figure 1 shows a experimental arrangement for GC-optoacoustic detection of environmental pollutants used in this experiment. The optoacoustic cell was a Helmholtz resonator which was 1.9 cm in diameter and 3.3 cm in length with an adjoining tube of 1.0 cm in diameter and 10 cm in length, providing the detection chamber volume of approximately 10 cm³. A CO₂ laser (Advanced Kinetics, Inc., model MIRL 50-SL) was internally amplitude modulated at audio frequencies by an oscillator. The laser modulation frequency was tuned to the Helmholtz resonance of the cell, which was about 1.1 KHz. The output laser wavelength was determined by the diffraction grating angle controlled by a stepping motor.

Liquid or solid samples (all 99% purity) of 1-chloronaphthalene, 3-chlorobiphenyl, 2,5,2'-trichlorobiphenyl, 4-chlorophenyl, and 4,4'-dichlorobiphenyl were purchased from Analab Inc.. Several concentrations of each compound were made by the dilution with methylene chloride (Fisher Scientific Co., Certified A.C.S.). Several microliters of each sample were injected into a gas chromatograph (Varian, Inc., model Aerograph 90-A-P) by a microsyringe. Separation of the sample was carried out with a stainless steel column (Analab, Inc.) with a length of 1.8 m and a diameter of 3 mm packed with 5% SE-30 on 80/100 mesh Chromosorp W HP. N₂ was used as a carrier gas and its flow rate was set at about 25 cm³/min where the column temperature was varied from 50 to 250°C.

The acoustic cell was heated to prevent the condensation of the sample in the cell. The effluent from the gas chromatograph was admitted to the cell through a narrow bore tube. NaCl windows formed the ends of the cell and an electret microphone with a built-in field effect transistor preamplifier (Radio Shack, Inc., model 270-092A) was placed at the end of the adjoining tube. To prevent the damage to the preamplifier at high temperatures, the adjoining tube near the microphone was water-cooled; additionally, a coolant gas of N₂ was slowly passed over the microphone. Signals from the microphone were detected by a lock-in amplifier (EG & G-PAR, model 5204) with the time constant set to 1 s. The magnitude of the in-phase lock-in signal was then displayed

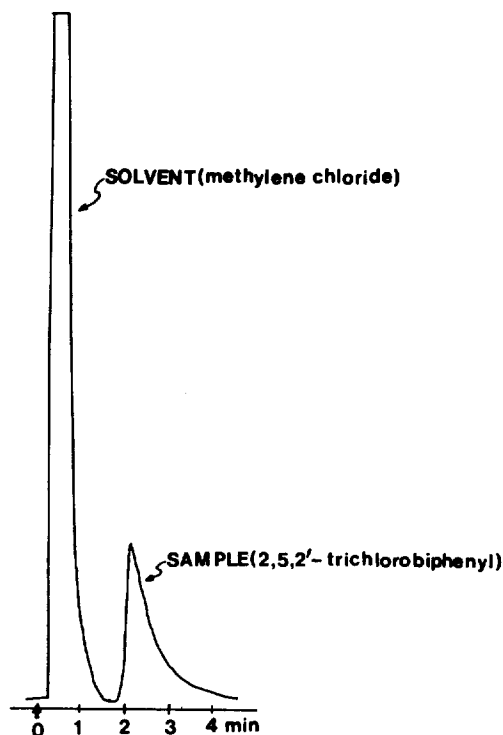


Figure 2. Typical chromatography of 10 μg of 2,5,2'-trichlorobiphenyl injected onto the chromatograph to give an optoacoustic signal. The sample was dissolved in methylene chloride and the solvent peak (first peak) was truncated.

on a stripchart recorder.

In order to compare the absorption characteristics of these compounds in the gas phase with those in condensed matter, conventional Raman spectra for the solid samples of 1-chloronaphthalene, 4-chlorophenyl, and 4,4'-dichlorobiphenyl were also obtained. The Raman spectrometer was consisted of an Ar ion laser (Coherent Inc., model 90) and a 1-m focal length monochromator (Jobin Yvon U-1000) in conjunction with a photomultiplier tube (Hamamatsu, C-2761).

Results and Discussion

The response of the gas chromatograph detector to several condensed phase pollutants was found that the optoacoustic signal of the detector was linearly proportional to the concentration of sample injected into the GC. A typical output from the lock-in amplifier is shown in Figure 2 where the sample was dissolved in methylene chloride and diluted prior to the injection. The laser power was 4 W at 9.6 μm and the time constant of the lock-in amplifier was set to 1 s. In this chromatogram, the separation of the analyte of interest from the solvent can be easily observable. The intensity of peaks is dependent upon the absorption strength at the given laser wavelength as well as the concentration of the sample injected.

The CO_2 laser was then scanned throughout its entire working region from 9 to 11 μm and samples were injected into the gas chromatograph at each CO_2 laser transition line. The relative optoacoustic signal amplitudes from the lock-in amplifier were recorded at every accessible wavelength. Fig-

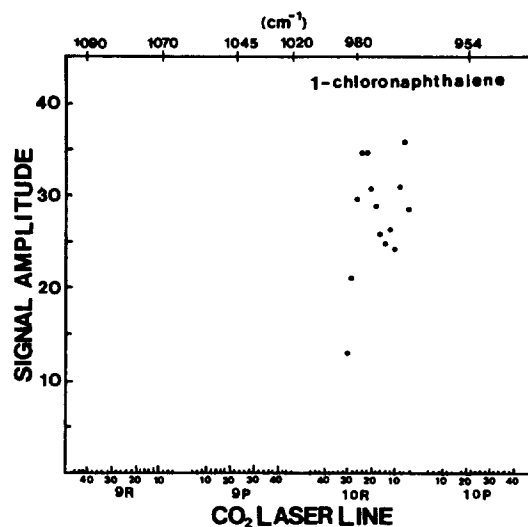


Figure 3. Gas phase optoacoustic spectrum of 1-chloronaphthalene as a function of CO_2 laser wavelength.

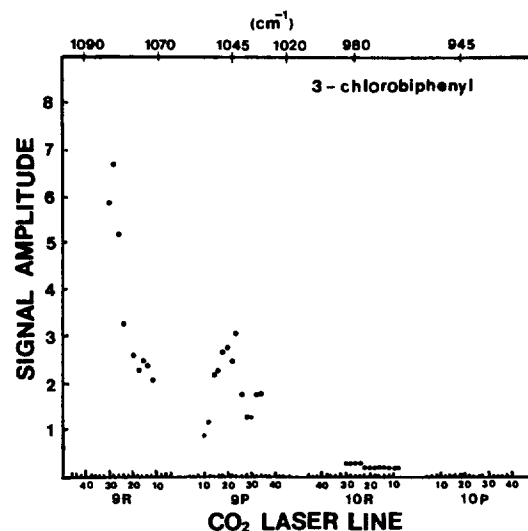


Figure 4. Gas phase optoacoustic spectrum of 3-chlorobiphenyl as a function of CO_2 laser wavelength.

ures 3, 4, 5 show the optoacoustic absorption spectra at CO_2 laser wavelengths for gases of 1-CINT 3-CIBP, and 2,5,2'-TC-IBP, respectively. The 9R and 10P in the figures stand for the R branch lines at the wavelengths region of 9 μm and P branch lines at 10 μm region, respectively. The signal amplitude of each spectrum was normalized to experimental conditions of 4 W laser power and 1.2 μg sample injection. Although the vertical scale is arbitrary, the numbers reflect the relative absorption strengths. The lack of continuous lines in these figures is a result of the discrete-tunability of the CO_2 laser. The absent of data points is mainly due to the fact that the absorption strength of the sample in the gas phase is so small that the optoacoustic signal can not be measured at these wavelength regions. Moreover, it is also a consequence that the peak of the absorption line is often offset from the peak of the CO_2 laser emission as the laser is tuned. As easily seen in these figures, it is apparent that absorption profiles of these species in the gas phase

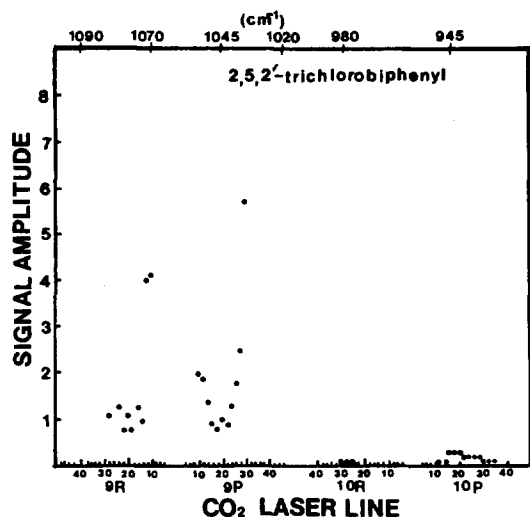


Figure 5. Gas phase optoacoustic spectrum of 2,5,2'-trichlorobiphenyl as a function of CO₂ laser wavelength.

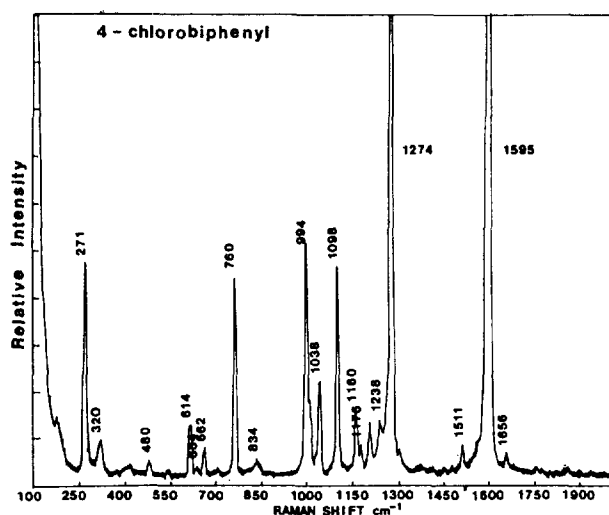


Figure 6. Raman spectrum of 4-chlorobiphenyl.

are in contrast with those reported for liquid or solid phases^{2,8}. Unfortunately, since the actual pressure of the samples in the acoustic cell was not able to be measured, the molar absorption coefficient data of these species in the gas phase could not be determined.

Figure 6 and 7 display the Raman spectra obtained with 4-CIBP and 4,4'-DCIBP, respectively. The characteristic peaks observed are summarized and compared with those reported for the biphenyl related species in Table 1. Three strongest peaks of Raman Spectra of BPs are probably correlated with the ν_4 , ν_5 and ν_6 fundamentals in totally symmetric modes (A_g in D_{2h}) of BP^{19,20}. Those bands are frequently used to postulate the electron configuration and geometry of BP molecules. The strong bands at 1596 cm⁻¹ for 4-CIBP and 1594 cm⁻¹ for 4,4'-DCIBP in the Raman spectra, which are assigned to ν_4 for BP, show the decrease in frequency by approximately 10 cm⁻¹ from that of normal BP. That is a consequence of the change of π electron density in the molecule due to the chlorine substitution. Note that ν_4 is strongly influenced by the vibration of π electron density

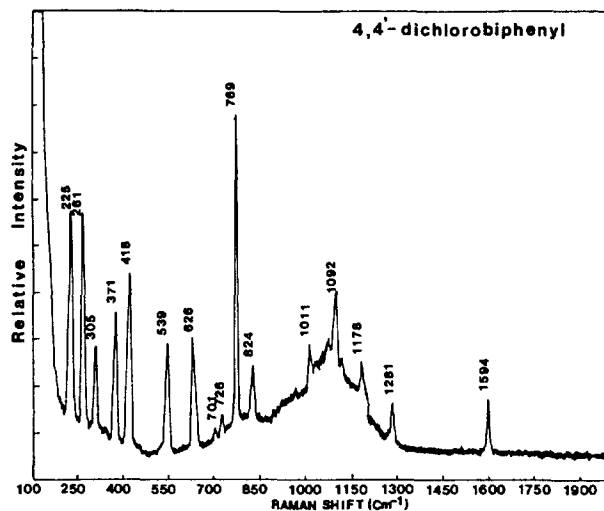


Figure 7. Raman spectrum of 4,4'-dichlorobiphenyl.

Table 1. Raman Frequencies of Biphenyl Related Species in Crystal Forms. The Data in Parentheses Indicate the Vibrational Frequencies in Solution Media

	BP ^a	CIBP ^b	DCIBP ^b	BP ^{+a}	BP ^{-a}
ν_4	1605(1612)	1595	1594	1616	1587
ν_5	1512(1510)	1511		1502	1493
ν_6	1277(1287)	1274	1282	1343	1326

^areference 22, ^bthis work.

in the phenyl ring, giving rise to the upshift by about 10 cm⁻¹ for less electron density such as in BP cation radical and downshift by about 20 cm⁻¹ for anion radical (see Table 1).

It should be noted that, however, the very weak intensity or the absence of ν_5 in CIBP and DCIBP is attributed to the weakness of the resonance enhancement for this band where it is excited with the radiation of 514.5 nm used in this measurements. The enhancement of this band has been found only a medium strength even with the excitation wavelength closely tuned to the resonant absorption maximum²². The character of ν_6 band has been found to be very sensitive to the π -bond order of the inter-ring C-C bond²¹. A considerable positive frequency shift has been reported for both cation and anion radicals of BP as shown in Table 1. This confirms that it gives a marked positive contribution to the inter-ring C-C bond order by an additional electron in LUMO of anion radical or electron density decrease as a hole in HOMO of the cation radical²². However, relatively small frequency shift of ν_6 observed for both CIBP and DCIBP are believed due to the fact that the electronic configuration in the inter-ring is not strongly affected by the Cl substitution.

In addition, the variations of vibration frequencies for differing phases in BPs can be explained on the basis of molecular geometry, in which a planar conformation (D_{2h}) in the crystal is changed to the twisted form (D_2) in vapor and solution²⁰. The vibrational characteristics in these BPs can be summarized that they are not strongly affected by the change in symmetry and electronic configuration, but by the

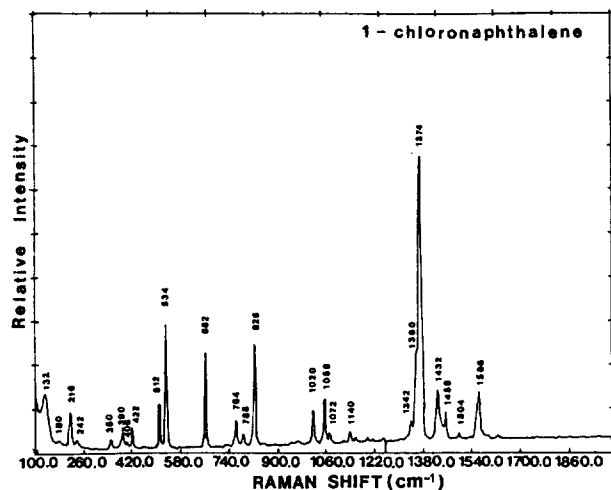


Figure 8. Raman spectrum of 1-chloronaphthalene.

difference of the electron density due to the substitution of chlorine in the phenyl rings. The Raman spectrum of 1-CINT in Figure 8 shows great difference in characteristic band from those of BPs. It is indicative of totally distinct electronic configuration and molecular geometry. Note that naphthalene is consisted of two conjugated aromatic rings with a flat geometry, while in biphenyls two phenyl rings are connected through the C-C single bond with a twisted geometry especially in solution medium so that the characteristics of the conjugation is lost.

The sensitivity of the optoacoustic detector and the detection limits for species investigated here can be found elsewhere¹⁷. The relatively low detectability of chlorinated pollutants by using the optoacoustic technique is attributed to their low absorption coefficients in the CO₂ laser wavelength region. Other difficulties includes the lack of absorption spectra for these compounds in the gas phase and the general lack of exact coincidences between absorption lines of the pollutants and the discrete laser emission lines. By the use of various CO₂ isotopes, the working region of the CO₂ laser can be extended, possibly yielding the overlap with stronger molecular transition bands.

Conclusion

The absorption characteristics of some environmental pollutants in gas phase have been reported in this paper by using the optoacoustic detection. The experimental demonstration and the absorption data obtained here indicate that the CO₂ laser optoacoustic technique possesses a convenient and sensitive method of investigating the absorption characteristics of environmental pollutants. It should be pointed out that, although the vapor pressure of the compounds investigated above are relatively low at the room temperature, a detailed information on gas phase is essentially required

in many purposes such as industrial applications and environmental pollutant monitoring, in general. The comparison of the characteristics between optoacoustic and Raman spectra could not be easily made since optoacoustic signals have been measured at only limited wavelength region of CO₂ laser. The compounds used here are only a few among many chlorinated hydrocarbons and their isotopes, however, the absorption and Raman profiles of these pollutants based on the detection technique described in this work will provide a useful information in the environmental point of view. In addition, the optoacoustic technique itself is general in nature so that it can be applied to a number of trace detection problems.

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