Fluorescence lifetime measurement of dibenzofuran and monochlorodibenzofuran

Do Quang Hoa, Tomohiro Uchimura, Totaro Imasaka, Nguyen Dai Hung

Abstract

The fluorescence lifetime of dibenzofuran and monochlorodibenzofuran was measured directly using a picosecond distributed-feedback dye laser and a fast-response microchannel-plate photomultiplier. The fluorescence lifetimes for dibenzofuran and monochlorodibenzofuran were determined to be 10.8 ± 0.5 ns and ca. 1 ns, respectively, suggesting that the fluorescence quantum yield is reduced 10-fold by intersystem crossing induced by a chlorine atom in a dibenzofuran molecule. These findings highlight the advantages of a picosecond laser for the efficient multiphoton ionization of polychlorinated dibenzofurans.

1. Introduction

Chlorinated polycyclic aromatic hydrocarbons such as polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran are formed during incomplete combustion and are released from incinerators into the atmosphere. They are extremely toxic and are present at ultratrace levels in the environment. In addition, their toxicities are strongly dependent on the number of chlorine atoms and the positions of these atoms on the benzene rings. Therefore, to quantitate such compounds, it is necessary to use an analytical instrument that has both a high sensitivity and selectivity. Gas chromatography combined with mass spectrometry is currently utilized after a lengthy pretreatment procedure. Because of this, a new analytical tool that allows on-line real-time monitoring of dioxin emitted from an incinerator would be highly desirable. Supersonic jet spectrometry (SSJ) combined with multiphoton ionization mass spectrometry (MPI/MS) is a promising candidate for this purpose. A few mass and MPI spectra for polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran have been reported [1,2]. The ionization efficiency is, however, rather small for dioxin molecules, resulting in poor sensitivity in mass analysis, which makes the trace analysis of dioxins difficult.

Toxic dioxin contains several chlorine atoms in the molecule, which substantially increase spin–orbit interactions. The energy in the singlet-excited state is then efficiently relaxed to triplet levels, providing a short excited-state lifetime. This is the reason for why the ionization efficiency is rather small when a nanosecond laser is utilized. It has been reported that the maximal ionization efficiency is obtained when the pulsewidth of the laser is identical to or similar to the excited-state lifetime of the analyte molecule [3,4]. The lifetimes of a few chlorophenols have been reported elsewhere [5,6]. It is, however, well known that the toxicity equivalent (TEQ) is proportional to the concentration of chlorinated dibenzofuran, especially to that of pentachlorodibenzofuran; the correlation factor is reported to be much higher than 0.9, sometimes approaching 0.99 for a sample in the flue gas [7,8]. However, no published data on the lifetime of chlorinated dibenzofuran are available.
Two approaches are possible for the measurement of a lifetime of such a molecule i.e., a pump–probe method based on two-photon ionization and a direct measurement of fluorescence decay. The former has already been used in the picosecond lifetime measurement of chlorophenols in a jet because of its high sensitivity [5,6]. This technique is, however, difficult to apply to a molecule having a long lifetime, since the probe pulse must be delayed by a factor several times longer than the lifetime of the molecule to be measured. For example, the mirror for a delay of the probe pulse must be translated more than 1 m for the measurement of nanosecond decay. In addition, the 0–0 transition is located around 300–320 nm for chlorinated dibenzofuran, and, as a result, a two-color ionization scheme is necessary in MPI. This makes the spectroscopic measurement more complicated; i.e., two lasers are required in the experiment. For this reason, the use of a technique based on fluorescence spectrometry is recommended. For example, a picosecond as well as a nanosecond decay curve may be measured using a streak camera at the photon counting levels. Such a technique was examined in this study but was unsuccessful, due to a very small signal intensity arising from the extremely low density of the analyte molecule in the jet. It should be noted that the sensitivity of the streak camera is limited, since the fluorescence must be tightly focused into a spot on the slit of a monochromator for two-dimensional measurements against the time and wavelength scales.

In this study, we report on the use of a picosecond narrow-band distributed-feedback dye laser and a fast-response microchannel-plate photomultiplier for the direct measurement of the fluorescence decay of dibenzofuran (DF) and 2-monochlorodibenzofuran (MCDF), the lifetimes of which are suspected to be in the nanosecond or sub-nanosecond range. The observed long lifetimes suggest sufficiently high efficiencies in MPI for these molecules even when a nanosecond laser is used. In other words, a picosecond laser is essential for the efficient ionization of a dibenzofuran containing a larger number of chlorine atoms, e.g., pentachlorodibenzofuran, for the evaluation of the TEQ value of the sample emitted from the incinerator.

2. Experimental

A schematic diagram of the supersonic jet fluorescence spectrometer used in this study is shown in Fig. 1. The sample was heated and the temperature was monitored by a thermostat (Shimaden, SR74) attached to the reservoir. The vaporized sample is introduced into a pulsed nozzle for supersonic jet expansion into a vacuum chamber maintained at <10⁻⁴ Torr. The temperature at the nozzle was maintained at 175 °C. Details of the vacuum system used in this study have been described elsewhere [9,10]. The analyte molecule in the supersonic jet is excited by the second harmonic emission of a distributed-feedback dye laser constructed in this laboratory [4,5,11–13]. In this laser, the third-harmonic emission of a Nd:YAG laser was separated to two parts and they are combined on the surface of the dye cell to form an interference pattern, the spacing of which determines the wavelength of the laser emission. Using a C 153 laser dye (concentration, 3 × 10⁻³ mol/l), the wavelength was tuned in the range of 540–590 nm. After pre- and post-amplification, the pulse width and pulse energy obtained were 80 ps and 1.2 mJ, respectively. As reported in the previous study [13], the linewidth of this dye laser was typically 5 pm. The fundamental beam was then frequency-doubled using a β-barium borate (BBO) crystal, producing a 0.12-mJ UV pulse. Two wavelengths, i.e., 289.5 and 276.8 nm, were used for the excitation of DF and MCDF, respectively. The fluorescence is collected by two lenses onto the entrance slit of a monochromator (JASCO CT-25CP, dispersion 0.6 nm/mm) equipped with a photomultiplier (Hamamatsu, 1P28 and R1294); the former photomultiplier was used for recording a fluorescence spectrum and the latter, which is a
fast-response microchannel-plate photomultiplier (rise time 0.3 ns, transit time spread 0.14 ns), for a lifetime measurement. All the samples used in this study, i.e., dibenzofuran (Tokyo Kasei Co.) and monochlorodibenzofuran (Cambridge Isotope Laboratory) are commercially available, the purities being specified to be 99.9% by the manufacturers. The sample was mixed with a carrier gas of argon (typical flow rate, 1 ml/min) using a T-shape connector and was subsequently entrained into a supersonic jet. The data were recorded and averaged 500–1000 times by means of a digital oscilloscope (LeCroy, Model 9360, 600 MHz).

3. Results and discussion

Before the measurement of a fluorescence decay curve, it is necessary to determine the wavelengths that correspond to analyte excitation and fluorescence detection. Unfortunately, it is difficult in practice to change the dye laser wavelength in a wide spectral region. Owing to this, we first measured the conventional absorption spectrum for DF and MCDF in the condensed phase. These molecules were found to have maxima at around 290 and 275 nm, respectively. The wavelength of the laser was then tuned and precisely adjusted to one of the peaks, i.e., at 289.5 and 276.8 nm for the excitation of DF and MCDF, respectively, in the supersonic jet. Alternatively, we measured the fluorescence spectrum in the range of 300–340 nm for DF and from 280 to 310 nm for MCDF. The spectral linewidth was substantially reduced for these molecules in the jet by rotational cooling, even for excitations at 1200 cm\(^{-1}\) from the 0–0 transition. Accordingly, we adjusted the wavelength of the fluorescence monochromator to one of the peaks, i.e., at 315 nm for DF and at 286 nm for MCDF, as was observed in the fluorescence spectrum.

A fluorescence lifetime of the sample can be measured by observing the fluorescence decay curve. The fluorescence intensity, \(I(t)\), at time, \(t\), after impulse excitation can be written by

\[
I(t) = I_0 \exp \left(-\frac{t}{\tau}\right),
\]

where \(I_0\) is a pre-exponential factor, \(\tau\) is referred to as the lifetime and is equal to the time at which \(I = I_0/e\). The raw data for the fluorescence decay curves measured for DF and MCDF are shown in Fig. 2. The lifetime of DF can be readily calculated from the data and is \(10.8 \pm 0.5\) ns. This result is in reasonably good agreement with the reported lifetime of \(14.8 \pm 0.3\) ns at the band origin and \(11.8 \pm 0.3\) ns at \(444\) cm\(^{-1}\) from the origin of DF [14]. However, due to the low density of MCDF in the jet, which may arise from a low vapor pressure, even at the elevated temperature in the nozzle, the fluorescence signal was weak and the background signal originating from scattered light was not completely negligible. The background signal was then carefully subtracted from the fluorescence decay data. As shown in Fig. 3, the lifetime of MCDF is estimated to be ca. 1 ns. It should be noted that the rise time of the photomultiplier (R1294) is 300 ps, which is faster than the response time of the oscilloscope (bandwidth 600 MHz, rise time 700 ps). As a result, the time resolution is currently limited by the bandwidth of the oscilloscope. A faster oscilloscope (e.g., 6 GHz, rise time 60 ps) and a faster photomultiplier (e.g., R2809U, rise time 150 ps) may be useful for the direct and more reliable measurement of the fluorescence decay curve, since the pulsewidth of the dye laser is in the picosecond range (80 ps). This observed value (ca. 1 ns) suggests that the fluorescence quantum yield is reduced 10-fold by intersystem crossing induced by a chlorine atom in a dibenzofuran molecule. When DF is substituted with a larger number of chlorine atoms, the lifetime will become a few tens of picoseconds (e.g., for...
trichloro-, tetrachloro-, pentachloro-) and the fluorescence quantum yield is reduced due to the more efficient intersystem crossing induced by the spin–orbit interactions. Another possibility for measuring picosecond decay with a better time resolution and sensitivity may be the use of a time-correlated photon counting system, since the time resolution is not determined by the response time but, rather, by the transient time spread of the photomultiplier.

Acknowledgments

This work was supported by the RONPAKU program of the Japan Society for the Promotion of Science and by a cooperative effort between the Centre for Quantum Electronics, Institute of Physics, Vietnam Academy of Science and Technology (Vietnam) and the Department of Applied Chemistry of Kyushu University (Japan). This work is also supported by Grants-in-Aids for Scientific Research and for the 21st Century COE Program, “Functional Innovation of Molecular Informatics” from the Ministry of Education, Culture, Science, Sports and Technology of Japan.

References

[1] T. Uchimura, T. Ito, T. Uchida, T. Imasaka, Organohalogen Compounds 67 (2005) 318.
[2] N. Kirihara, H. Yoshida, M. Tanaka, K. Takahashi, N. Kitada, T. Shiomitsu, Y. Suzuki, Organohalogen Compounds 66 (2004) 731.
[3] J. Matsumoto, T. Imasaka, Anal. Chem. 71 (1999) 3763.
[4] N. Yoshida, Y. Hirakawa, T. Imasaka, Anal. Chem. 73 (2001) 4417.
[5] T. Deguchi, N. Takeyasu, T. Imasaka, Appl. Spectrosc. 56 (2002) 1241.
[6] T. Uchimura, T. Deguchi, T. Imasaka, Anal. Sci. 21 (2005) 693.
[7] M. Blumenstock, R. Zimmermann, K.-W. Schramm, A. Kettrup, Chemosphere 42 (2001) 507.
[8] M. Kato, K. Urano, Waste Manage. 21 (2001) 55.
[9] T. Urabe, T. Imasaka, Talanta 52 (2000) 703.
[10] T. Onoda, G. Saito, T. Imasaka, Anal. Chim. Acta 412 (2000) 213.
[11] T. Deguchi, N. Takeyasu, T. Imasaka, Rev. Sci. Instrum. 73 (2002) 2203.
[12] N. Takeyasu, T. Deguchi, M. Tsutsumikawa, J. Matsumoto, T. Imasaka, Anal. Sci. 18 (2002) 243.
[13] D.Q. Hoa, N. Takeyasu, T. Imasaka, N.D. Hung, Rev. Sci. Instrum. 74 (2003) 28.
[14] A.R. Auty, A.C. Jones, D. Phillips, Chem. Phys. Lett. 112 (1984) 529.