

Photoacoustic Detection of Multiphoton Dissociation of Molecular Chlorine by Probe Beam Deflection

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Photodissociation of diatomic molecules has been extensively studied as a research topic of fundamental importance.¹ The products of photodissociation, or photofragments, have been in general detected by ionization,² fluorescence,³ or absorption spectroscopy.⁴ To detect ions, a quadrupole mass spectrometer with ionizer or an additional laser is necessary for the ionization of neutral photofragments. Fluorescence and absorption spectroscopy require tunable probe lasers or lamps to excite them to an upper state.

As an alternative, an electret microphone has been introduced as a sensitive detector of neutral species. Choi *et al.*⁵ have proven that the electret microphone can be used to detect molecular jet from a pulsed nozzle in high vacuum. Later, Park *et al.*⁶ have successfully applied microphone technique to detect photofragments. In their experiment, chlorine molecules were photodissociated by absorption of 355 nm radiation (¹Π←³Σ transition). The collective momenta of photofragments, or chlorine atoms, were detected by microphone. By rotating the incident polarization of 355 nm laser light, anisotropic distribution of chlorine atoms were clearly demonstrated, which is basically the reincarnation of the well-known work of Wilson,² the quadrupole mass spectrometer being replaced with a microphone.

The microphone, however, has short lifetime in the corrosive medium since the diaphragm is severely damaged in such harsh condition.⁶ Therefore, it can not be used at high partial pressures of corrosive gas such as chlorine in spite of its simplicity and high sensitivity in detection of non-radiative relaxation. Another drawback of microphone is its narrow bandwidth. The bandwidths of microphones are on the order of just tens of kHz due to its mechanical limitations caused by ringing of the diaphragm. Thus, microphones have difficulties in time-resolved studies of chemical phenomena on μs time scale or shorter.

Here, we present an experimental method regarding the detection of photofragments by probe beam deflection (PBD).⁷ In PBD experiment, the change of index of refraction caused by either generation of acoustic wave or heat release by absorption of pulsed laser radiation is monitored by a cw probe laser which propagates perpendicular to the pump laser.⁸ Since PBD is a noncontact technique, it can be applied to the corrosive media as long as the medium is optically transparent at the probe wavelength. Also, time-resolved information is available from the acoustic or thermal wave obtained in real time. In PBD, the time resolution is determined by the spot size of the focused laser beam, making possible the fast relaxation processes oc-

curing in submicrosecond thereby. In applications where the selectivity of chemical species is not crucial, PBD would be a powerful technique in the study of physical or chemical phenomena in gas, liquid, or solid phase with relatively high time resolution.⁹⁻¹¹

In this note, we show that PBD can be applied to detect acoustic wave generated by multiphoton dissociation of molecular chlorine. To our knowledge, multiphoton dissociation has never been investigated by PBD. In gas phase studies, microphones have normally been the first choice as a probe of acoustic wave due to its high sensitivity.

Experimental

The experimental setup is shown in Figure 1. Chlorine molecules were dissociated by absorption of 1064 nm pulsed Nd:YAG laser (Quanta-Ray GCR 150) with pulse duration of 7 ns operating at 10 Hz. Doubling and mixing crystals in the laser head were removed to eliminate any possible interference by 355 nm laser light. A HeNe laser (Uniphase 1105P, 5 mW) was used as a probe laser. Both YAG and HeNe laser beam were focused at the center of the reaction chamber, while the probe laser was aligned such that it propagates perpendicular to the pump laser.

A quadrant cell photodiode (UDT SPOT 9D) was modified to make it work as a position-sensitive detector. Each two outputs were hooked together such that it worked as a bi-cell. The probe laser beam is centered at the bi-cell surface. As the pump beam passes through the reaction medium, the acoustic wave produced by photodissociation propagates toward the region of the probe laser, where the index of refraction changes due to the temporal variation of local pressure. The bi-cell thus detects the deflection of the

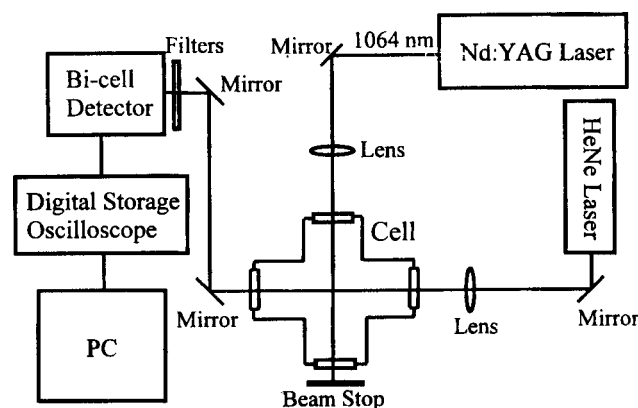


Figure 1. The setup of PBD experiment.

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HeNe laser. The output signals were amplified by a home-made fast difference amplifier (100 MHz)¹² and stored in an oscilloscope (300 MHz, LeCroy 9361). The response time of the position-sensitive detector after amplification as measured by laser pulse is about 20 ns. A color filter and an interference filter of bandwidth 3 nm at HeNe laser wavelength were placed in front of the bi-cell to avoid scattered laser photons and room light. The reaction chamber consists of stainless-steel 6-way cross (MDC, 2.75") with fused silica windows. The pressure was measured by capacitance manometer (MKS 122AA-01000AD).

Results and Discussion

A typical signal shape obtained by PBD is shown in Figure 2. The amplitude of the deflection signal is proportional to the energy released by photodissociation, or thermalization of recoil momenta of chlorine atoms and mole number increase due to dissociation of diatomic molecules.⁶ The time-domain signal reflects the time-dependent change of the local index of refraction, of which integration gives the temporal pressure change.¹³ The acoustic transit time is defined as the delay time taken until the acoustic was generated at the pump beam region launches the probe beam spot. From the acoustic transit time and the distance between the pump and probe beam spot, the sound velocity of the medium can be derived. It was confirmed that the acoustic transit time changed linearly with the distance between the pump and probe laser beam, which implies that the signal is "acoustic" in its character.

To detect acoustic wave only, the two laser beams were aligned such that they do not cross. Instead, they were few millimeters away with each other at the center of the chamber. Translational stages with micrometers were employed to adjust the pump-probe distance continuously. In case they cross, slow photothermal signal overrides the photoacoustic signal necessitating the resolution of the two effects.⁷ Partial overlap of the two laser beams is necessary in

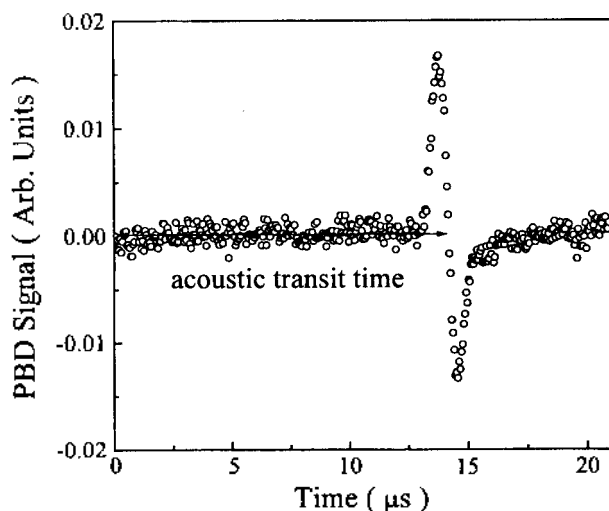


Figure 2. Typical signal of PBD from multiphoton dissociation of chlorine molecules at 1064 nm. The laser fluence was 0.23 J/cm². The total pressure of the cell was 700 Torr with chlorine partial pressure of 50 Torr.

order to obtain informations on the slow heat release processes like recombination or quenching of electronically excited atoms or vibrationally excited molecules produced by recombination, where the analysis is totally different. The study of chemical kinetics regarding recombination of chlorine atoms by photothermal probe beam deflection spectroscopy is also in progress.¹⁴

In order to confirm that the PBD signal originates from multiphoton dissociation of chlorine molecules, the magnitude of the signal was measured as a function of laser fluence. Figure 3 shows the dependence of the signal magnitude on the laser fluence. The solid line is the best fit of $y = cx^n$, where y is the signal magnitude, c is a constant, x is the concentration of chlorine molecule, and n is a fitting parameter. According to the best fit, the signal was found to be proportional to $x^{3.29}$. Therefore, it is believed that chlorine molecules are dissociated mostly by absorption of three 1064 nm photons. The possibility of dissociation of chlorine molecules from any higher electronic states is small, if any. The linear dependence of signal magnitude vs. laser fluence when chlorine molecules were irradiated by 355 nm was confirmed by a separate experiment.

This work has been motivated in part as a detection method of coherent laser control¹⁵ experiment in a cell. Since chlorine molecules can be dissociated by absorption of either single 355 nm photon or three 1064 nm photons, quantum interference effects are expected in the dissociation pathways when they occur simultaneously. Indistinguishable multiple pathways always accompany the quantum interference effect. Although chlorine molecule is known to have major dissociation channel producing two ground state (²P_{3/2}) chlorine atoms at 355 nm² (¹Π←¹Σ transition), the other minor dissociation channel of generating one ground and one spin-orbit excited state (²P_{1/2}) atoms (³Π←¹Σ transition) may be open by the interference effect when the coherent 355 nm and 1064 nm laser light propagate collinearly with proper phase mismatch between the two.¹⁵ The two pathways will show differences in the temporal behav-

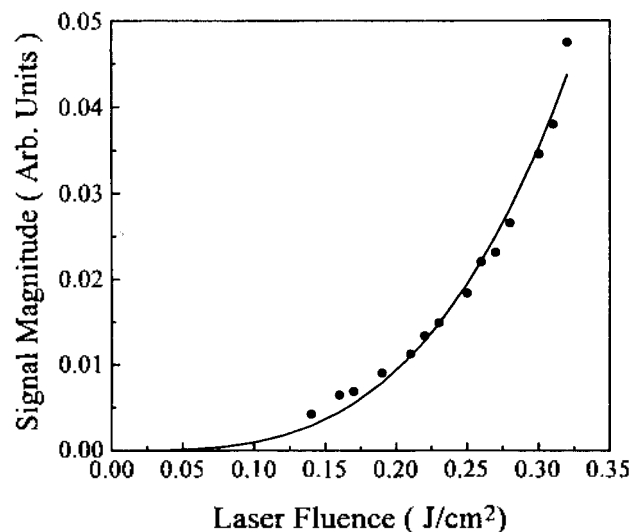


Figure 3. PBD signal magnitude vs. laser fluence at 1064 nm. The total pressure of the cell was 700 Torr and the partial pressure of chlorine was 50 Torr. The solid line is the best fit.

ior of heat release or thermalization of photofragments. This kind of quantum interference effects are to be found even in the cell experiment,¹⁶ where the different dissociation channels can be investigated by detection of photoacoustic or photothermal signals.

Summary

We have shown that the acoustic wave generated by multiphoton dissociation of chlorine molecules in argon can be detected by PBD. Since PBD is a noncontact technique, this detection method can be used in the corrosive environment where the diaphragm of microphone can be easily destroyed. Detection of acoustic wave or heat release by PBD can be an alternative choice of studying photodissociation of molecules with high sensitivity and even quantum interference effect in the cell may have good reason to be studied by PBD.

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Effect of Electrolyte and Solvent in Axial Ligation of Tetrakis(2,6-dichlorophenyl)porphyrinato Manganese(III) and -(II) Complexes

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Manganese porphyrins have several interesting aspects of physical, chemical, and biological properties which distinguish them from other metalloporphyrins.¹⁻³ Manganese porphyrins are of interest as catalysts for the epoxidation of olefins and for hydrocarbon oxygenation,⁴⁻⁸ as models for the behavior of cytochrome P-450,⁹ photosystem II,¹⁰ and superoxide dismutase.¹¹ Particularly axial ligation of manganese porphyrins coupled with their redox chemistry is very crucial in diverse biological functions.¹²⁻¹⁷ Recently we investigated the redox chemistry and autoreduction of Mn^{III}(Cl₈TPP)Cl by hydroxide ion.¹⁸ Electrochemistry, spectrophotometry, and conductometry were used for determining the state of axial ligation of Mn^{III}(TPP)Cl in solutions, they reveal that the axial Cl⁻ ligand is bound to Mn^{III} and Mn^{II} oxidation states in non-ligating solvents, but Cl⁻ is dissociated from Mn^{III}(TPP)Cl in stronger ligating solvents.¹⁹⁻²³ In this study, thin-layer spectroelectrochemistry has been used to probe the effect of electrolyte and solvent on axial ligation of manganese substituted tetra-phenyl porphyrins [Mn^{III}(Cl₈TPP)Cl and Mn^{III}(Me₁₂TPP)Cl].

Experimental

Reagents. Mn^{III}(Cl₈TPP)Cl and Mn^{III}(Me₁₂TPP)Cl were synthesized by literature procedures.^{16,24} Anhydrous acetonitrile (MeCN), methylene chloride (CH₂Cl₂), tetrahydrofuran (THF), dimethyl formamide (DMF), and dimethylsulfoxide (DMSO) were used as received from Aldrich. As supporting electrolytes, tetrabutyl ammonium hexafluorophosphate (Bu₄NPF₆) and tetrabutyl ammonium tetrafluoroborate (Bu₄NBF₄) were used as received from Aldrich, and tetrabutyl ammonium perchlorate (Bu₄NClO₄) and tetraethyl ammonium chloride (Et₄NCl) were purchased from Tokyo Chemical Inc. and vacuum desiccated before use.

Equipment and Procedures. Spectroelectrochemical experiments were carried out in an optically transparent thin-layer cell containing a Pt mesh working electrode *via* controlled potential electrolysis using three electrode potentiostat (Bioanalytical Systems, Model CV-27). A platinum-wire electrode separated from the analyte compartment by a medium porosity glass frit was used as an auxiliary elec-