Stable Isotope Ratio Analysis at Trace Concentrations Using Degenerate Four-Wave Mixing with a Circularly Polarized Pulsed Probe Beam

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Stable isotope analysis based on vectorial optical-phase conjugation by resonant degenerate four-wave mixing (D4WM) is reported by using a D4WM method with vertically polarized pump beams and a circularly polarized probe beam. Since the polarization of the signal beam is different from that of the pump beams, the background radiation is suppressed more effectively. Excellent sensitivity, high spectral resolution, and efficient optical detection make this an effective and unusually convenient nonlinear spectrometric method for the analysis of trace amounts of stable isotopes. Using an excimer-pumped pulsed dye laser, the fine structures of lithium are examined. A detection limit of 2.5 ng/mL lithium is observed while a Doppler-free resolution is maintained by using transient "coherent-grating" based D4WM spectroscopy.

INTRODUCTION

Reliable analysis of stable isotopes is essential in the successful use of nonradioactive and nonhazardous isotopes in many areas, including biomedical and environmental sciences. Currently, mass spectrometry (1, 2) and atomic absorption spectrometry (3, 4) have been most commonly used for the measurement of nonradioactive stable isotopes. Laser-based spectroscopic methods (5, 6) that can measure fine or hyperfine structures offer more reliable and unambiguous results in isotope analysis, since hyperfine structures are the spectroscopic fingerprints of isotopes/atoms. Unlike mass spectrometry, these laser-based methods do not encounter chemical interference problems, since these very characteristic analyte hyperfine structures are unique and they can be precisely scanned and measured. Conventional nonlaser-based atomic absorption methods lack spectral resolution and detection sensitivity needed for stable isotope analysis of many elements.

A nonlinear laser spectroscopic method that offers high spectral resolution necessary for hyperfine structure and isotope ratio analysis is optical-phase conjugation by resonant degenerate four-wave mixing (D4WM) (7). Optical-phase conjugation is a process that incorporates nonlinear optical effects to reverse precisely both the direction of propagation and the overall phase factor of an input wave. D4WM is one of the most versatile methods to induce optical-phase conjugation in a nonlinear medium (7–10). D4WM offers several interesting properties including high-resolution Doppler-free spectral information and excellent detection sensitivity. In addition, D4WM offers a convenient and effective optical signal detection, since the signal is a laser beam. Recently, we reported resonant D4WM in a low-pressure hollow cathode discharge plasma and an analytical flame (6, 11–13). This unusually sensitive nonlinear laser technique offers good detection limits even when a relatively low-power continu-

ous-wave dye laser is used, such as a single-frequency ring dye laser. We have also demonstrated the use of D4WM as a sensitive analytical method for the condensed-phase analyte and reported a 2×10^{-11} M (or 2.9 amol in a probe volume of 0.14 μL) detection limit for eosin B in a continuously flowing liquid cell at room temperature (14). Since the D4WM signal is a laser beam and it is only present when the laser frequency is tuned to an absorption line, the signal is measured virtually against a dark background, and it can be effectively extracted with excellent signal-to-noise ratios. When a continuous-wave ring dye laser is used as the excitation source, the detection sensitivity can be significantly improved by modulating either the probe beam or the forward pump beam at high frequency to suppress scattered stray radiation from the optics, laser flicker, and Mie scattering from the flame (12, 13). When a pulsed dye laser is used as the excitation source, the signal-to-noise ratio can be improved by taking advantage of the polarization properties of D4WM and using polarization discrimination techniques to suppress optical noise. Polarization characteristics of optical-phase conjugation by resonant D4WM have been studied previously (15–19). According to the polarization conservation rule, when all input beams are vertically plane-polarized, the output signal beam is also vertically plane-polarized. When one of the pump beams is rotated by 90° so that it is horizontally polarized, the output signal beam is expected to be horizontally polarized. When the two pump beams are vertically polarized and the probe beam is circularly polarized, the output signal beam will be circularly or elliptically polarized (15). The polarization properties of D4WM provide an excellent opportunity for introducing polarization discrimination techniques to eliminate background scattering.

Resonant D4WM, when performed in low-pressure atomizers, offers the highest spectral resolution suitable for isotope and hyperfine structure analysis for many elements. It has been demonstrated in low-pressure discharge plasmas (6, 12) and a low-pressure flame atomizer (20) using an argon-ion laser pumped single-frequency ring dye laser.

In this paper, we report a simple stable isotope analysis technique using vectorial optical-phase conjugation by coherent-grating-based D4WM with a XeCl excimer laser pumped pulsed dye laser. Simpler and less crowded Doppler-free fine structures can be observed by selectively measuring certain fine lines. We demonstrate that optical noise can be suppressed by using vertically polarized pump beams and a circularly polarized probe beam. A detection limit of 2.5 ng/mL ($S/N = 2$) lithium with Doppler-free spectral resolution is observed in a conventional atmospheric pressure air–acetylene flame with an excimer-pumped pulsed dye laser.

EXPERIMENTAL SECTION

A schematic diagram of the experimental arrangement is shown in Figure 1. An excimer laser operating at the XeCl 308-nm line (Lumonics, Ontario, Model HyperEx 460SM-A) is used to pump a pulsed dye laser (Lumonics, Ontario, Model HyperDYE-300)

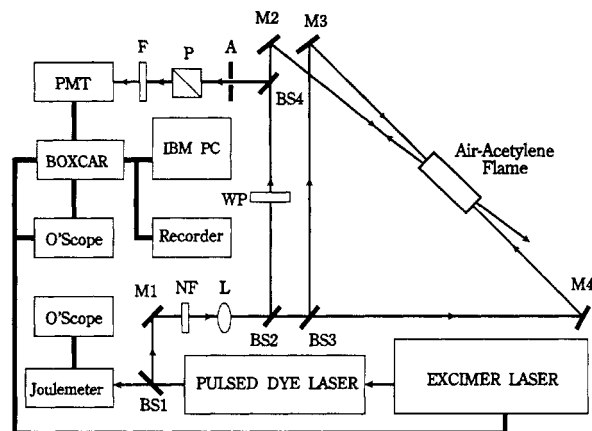*To whom correspondence should be addressed.

Figure 1. Experimental arrangement for coherent-grating-based degenerate four-wave mixing: BS1, BS2, BS3, and BS4, beam splitters; M1, M2, M3, and M4, mirrors; F, lithium-line filter; NF, neutral density filter; L, focusing lens; WP, quarter-wave plate; A, aperture; P, polarizer; PMT, photomultiplier tube.

using DCM dye. The line width of the dye laser is approximately 0.08 cm^{-1}, and the pulse width is 15 ns. The dye laser beam is initially split by a 10/90 (R/T) beam splitter (BS1). The transmitted laser beam is sent to a joulemeter (Molectron Detector, Inc., Campbell, CA, Model J50) and then an oscilloscope (Tektronix, Inc., Marlow, England, Model 2225) for monitoring the laser pulse energy. The reflected laser beam (i.e., 10%) is then split by beam splitters (BS2 and BS3) into three beams, the forward pump beam, E_f, the backward pump beam, E_b, and the probe beam, E_p. The three input beams arriving at the atomizer are of equal intensity. Neutral density filters are placed in front of the BS2 beam splitter to adjust the laser energy. A 2 m focal length lens is used to focus the laser beam so that the beam diameter at the center of the atomizer is about 1.5 mm. The air–acetylene slot burner (Varian Techtron, Palo Alto, CA, Model Mark 5) is mounted on a X-Y translation stage to allow micro-positioning of the flame along horizontal and vertical axes. A Fresnel rhomb is inserted in the path of probe beam to convert the laser beam polarization from linear to circular polarization. The probe beam crosses the counterpropagating pump beams at an angle of less than 0.5°. The resonant D4WM signal generated in the sample cell is directed by the BS4 beam splitter to a photomultiplier tube (Hamamatsu Corp., Middlesex, NJ, Model R928) through a polarizer and an aperture. The photomultiplier tube signal is sent to a boxcar averager (Stanford Research Systems, Inc., Sunnyvale, CA, Model SR250-280), averaged, digitized, and stored on an IBM personal computer. An oscilloscope (Tektronix, Guernsey, Ltd., Channel Islands, Model 2225) is used to monitor the signal and the boxcar averager gate. The synchronous output of the excimer laser is used to trigger the boxcar averager and the oscilloscope. Resonant D4WM arrangement with all vertically polarized input beams is also used to compare its features and results with those of the arrangement with the vertically polarized pump beams and a circularly polarized probe beam. Inserting or removing the Fresnel rhomb allows one to switch between these two different optical arrangements.

Isotopically enriched lithium carbonate (99.54% ^{6}Li and 99.5% ^{7}Li) are purchased from Isotec Inc., OH. Natural abundance lithium solution is prepared by dissolving reagent grade lithium carbonate in 1:1 HCl solution and then diluting with deionized–distilled water.

RESULTS AND DISCUSSION

Lithium has two isotopes, ^{6}Li and ^{7}Li, with natural abundances of approximately 7.4% and 92.6%, respectively. The fine energy splitting for the 670.784-nm transition line of ^{7}Li is shown in Figure 2. The fine structure splitting between the 2p $^2P_{1/2}$ and 2p $^2P_{3/2}$ levels is 10.05 GHz (21) (i.e., the energy level difference between the D_1 and D_2 transitions for ^{7}Li isotope is 10.05 GHz). The isotope shift value between the ^{6}Li D_1 peak and the ^{7}Li D_1 peak is also approximately 10 GHz. Hence, the D_1 peak of the ^{7}Li isotope and the D_2 peak
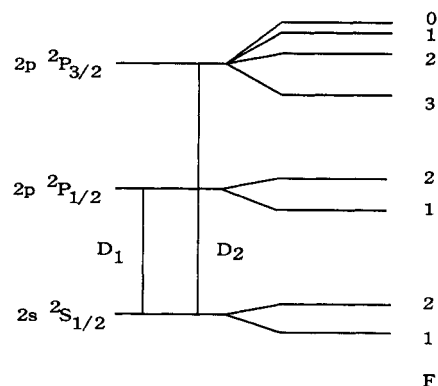

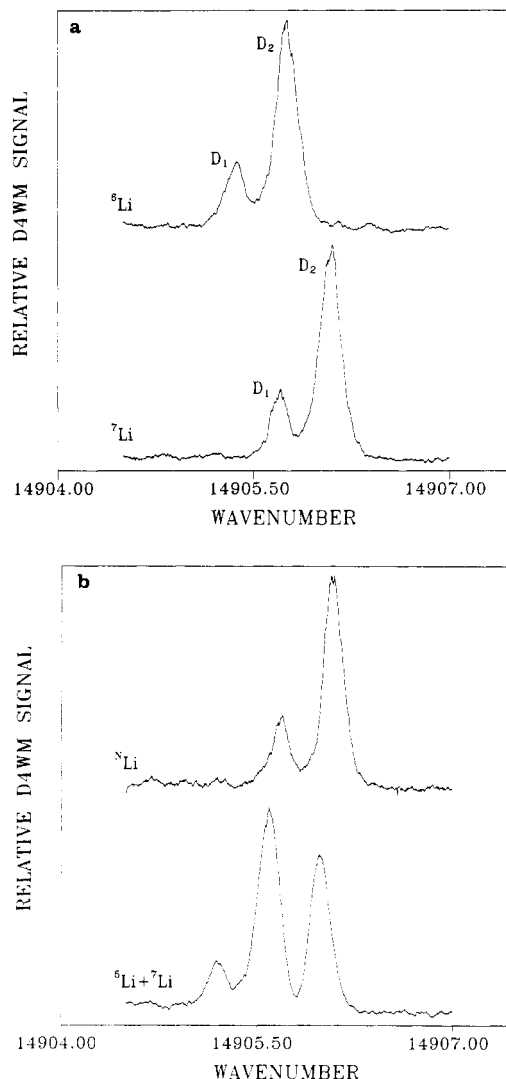**Figure 2.** Energy level splitting of ^{7}Li isotope for 670.784-nm transition.

Figure 3. (a) Degenerate four-wave mixing spectra of fine structures of individual lithium isotopes collected by using all vertically polarized input beams. (b) Degenerate four-wave mixing spectra of fine structures of mixed lithium isotopes collected by using all vertically polarized input beams.

of the ^{6}Li isotope are located approximately at the same position and consequently convoluted in a complete fine structure for lithium (21–23). Parts a and b of Figure 3 show D4WM spectra of lithium fine structures collected by using all vertically polarized excimer dye laser input beams. The fine structures shown are for 99.54%-enriched ^{6}Li isotope (Figure 3a, upper trace), 99.50%-enriched ^{7}Li isotope (Figure 3a, bottom trace), natural-abundance lithium, i.e., 92.6% ^{7}Li
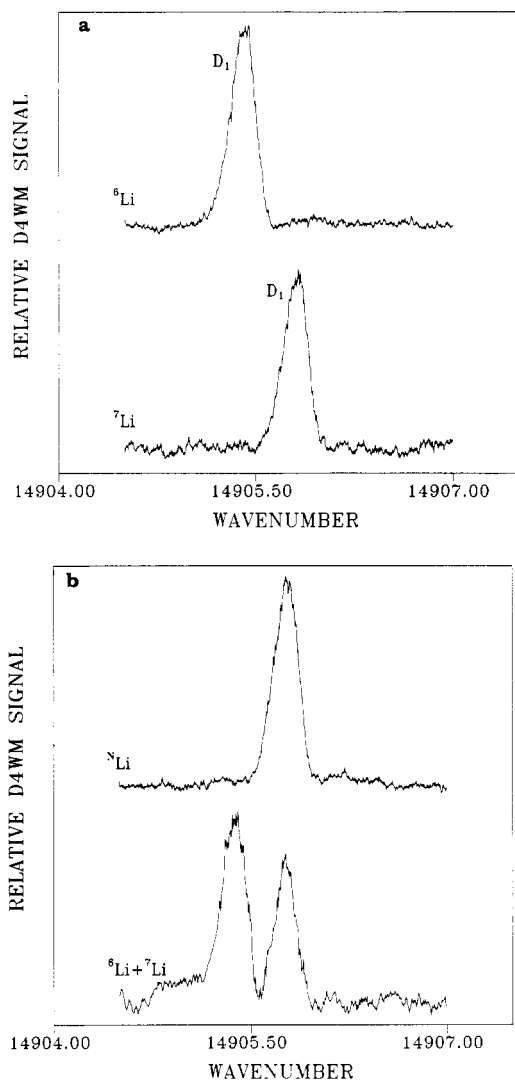
Figure 4. (a) Degenerate four-wave mixing spectra of fine structures of individual lithium isotopes collected by using a circularly polarized probe beam and vertically polarized pump beams. (b) Degenerate four-wave mixing spectra of fine structures of mixed lithium isotopes collected by using a circularly polarized probe beam and vertically polarized pump beams.

(Figure 3b, upper trace), and a mixture of ^6Li and ^7Li (1:1 in concentration) (Figure 3b, bottom trace). The middle peak in the bottom spectrum of Figure 3b is the convoluted signal from the ^7Li D_1 and ^6Li D_2 transitions.

Parts a and b of Figure 4 show D4WM spectra of lithium fine structures collected by using vertically polarized forward and backward pump beams and a circularly polarized probe beam. The spectra shown are for 99.54%-enriched ^6Li isotope (Figure 4a, upper trace), 99.50%-enriched ^7Li isotope (Figure 4a, bottom trace), natural-abundance lithium, i.e., 92.6% ^7Li (Figure 4b, upper trace), and a mixture of ^6Li and ^7Li (1:1 in concentration) (Figure 4b, bottom trace). All the D4WM spectra of lithium fine structures shown in Figures 3 and 4 are collected by using a pulse repetition rate of 50 Hz for the excimer-pumped dye laser and a dye laser wavelength scanning rate of 0.002 cm^{-1}/s.

The spectra shown in Figure 3a,b are collected by using 5 ppm ^6Li, 5 ppm ^7Li, 5 ppm ^NLi, 4 ppm ^6Li and ^7Li mixture, 100-nJ total laser energy, 400-V PMT voltage, and boxcar averaging of 300 times. The spectra shown in Figure 4a,b are collected by using 5 ppm ^6Li, 5 ppm ^7Li, 5 ppm ^NLi, 0.75 ppm ^6Li and ^7Li mixture, 100-nJ total laser energy, 370-V PMT voltage, and boxcar averaging of only 100 times. It should be noted that the boxcar averaging time and the concentration

for the ^6Li and ^7Li mixture solution are much lower for the spectra in Figure 4 as compared to those in Figure 3.

Comparing corresponding fine structures from Figures 3 and 4, one finds that the D_2 peak (i.e., 2s $^2S_{1/2}$–2p $^2P_{3/2}$ transition) is absent for all isotopes in Figure 4, where a circularly polarized probe beam is used. The absence of the D_2 peak can be described by using the unique properties of nonlinear phase conjugation based on a "coherent-grating" generated D4WM signal.

Generation of the D4WM signal has usually been explained by the formation of "population gratings" involving excited analyte atoms. However, when a pulsed laser is used and when certain polarization arrangements are used for input beams, another grating, known as the coherent grating, plays a major role in the generation of the D4WM signal. This new component in the D4WM signal results not from excited atoms but rather from coherently aligned, but not optically pumped, ground-state atoms. These two different signal-generating mechanism/gratings will be briefly described below (19).

For a D4WM arrangement, the complex D4WM signal vector amplitude, $P^{(3)}$, can be described as

$$P^{(3)} \propto (A e_b e_p{}^* \cdot e_f + B e_f e_p{}^* \cdot e_b + C e_p{}^* \cdot e_f e_b) E_f E_b E_p{}^* \qquad (1)$$

where A, B, and C are constants depending on the nonlinear susceptibility of the medium, and e_f, e_b, and e_p are polarization-state vectors of the forward pump, backward pump, and probe beams, respectively. Polarization-state vectors are normalized so that $e_f{}^* \cdot e_f = 1$, etc. In a D4WM medium, the interference between the forward pump beam, E_f, and the probe beam, E_p, creates a population grating, from which the background pump beam, E_b, is scattered to produce the phase conjugation signal beam, E_s. This process is described by the first term with the constant A in eq 1. Similarly, E_b interferes with E_p to form a population grating, from which E_f is scattered, and this process is described by the second term with the constant B in eq 1. The grating period for the $E_f E_p$ grating ($D = \lambda/\{2 \sin (\theta/2)\}$, where λ is the laser wavelength and θ is the angle between pump and probe laser beams) is much wider than that of the $E_b E_p$ grating ($D = \lambda/\{2 \cos (\theta/2)\}$). Hence, the $E_f E_p$ grating is more stable and less susceptible to grating washout due to thermal motion of atoms across the grating when a high-temperature atomizer such as a flame is used (13). Thus, the $E_f E_p$ grating contributes more in the signal generation process and coefficient A is much larger than coefficient B accordingly in eq 1. Forward and backward pump beams, E_f and E_b, are colinearly counterpropagating, and intensity beats between them are both temporal (at 2ω) and spatial and, therefore, produce no population grating (19). Therefore, contribution from coefficient C and the third term in eq 1 is negligible for the signal generated by population gratings. When all vertically polarized input beams are used, $A \gg B$ and $C = 0$. However, when the probe beam polarization plane is orthogonal to pump beam polarization planes, even $E_p E_f$ and $E_p E_b$ population gratings will not be formed and therefore no population-grating-based signal will be generated.

However, a coherent grating can still be formed even if the probe beam polarization is orthogonal to those of the pump beams. This is an important feature that is different from the population-grating system. When a pulsed dye laser is used in the D4WM experiment, where the dye laser pulse is much shorter than the decay time of an excited atom, the D4WM signal is primarily generated from the coherent grating (15, 18, 19). The D4WM signal is generated here by the scattering of one input beam from a grating of ground-state atoms in coherent superpositions of ground-state m sublevels. When two input beams are orthogonally polarized, no significant "intensity" beats are produced and hence no population grating is created. However, "spatial" beats can be

produced by two orthogonally polarized input beams and hence one can still observe D4WM signal via coherent gratings. The coherent grating is different from the population grating in that there is negligible population redistribution since there is negligible optical pumping of ground-state sublevels in this transient (pulse) regime. When the D4WM signal is mainly generated from the coherent grating, A, B, and C can be expressed as (19)

$$A = B \equiv g_0^{-1} \sum |\alpha_m^+|^4 \tag{2}$$

$$C \equiv g_0^{-1} \sum (|\alpha_m^+|^2 |\alpha_m^-|^2 + |\alpha_{m+2}^-|^2 |\alpha_m^+|^2) - A \tag{3}$$

where g_0 is the ground state degeneracy and

$$\alpha_m^\pm = 2^{-1/2} \langle m + 1, J' | M_x \pm i M_y | m, J \rangle \tag{4}$$

are matrix elements between ground states $|m, J\rangle$ and excited states $|m \pm 1, J'\rangle$ of components of the electric-dipole-moment operator M of an atom. When sodium is used as the nonlinear medium, A, B, and C have the relative values of $A:B:C \simeq 1:1:-1$ for the sodium 2s $^2S_{1/2}$–2p $^2P_{1/2}$ transition (D$_1$), and $A:B:C \simeq 5:5:-2$ for the sodium 2s $^2S_{1/2}$–2p $^2P_{3/2}$ transition (D$_2$), respectively (19). When the polarization plane of the probe beam is parallel to that of the pump beams, the signal is proportional to $|A + B + C|^2$, since all three gratings contribute in the generation of the phase conjugate signal. If the polarization plane of the probe beam is orthogonal to that of the pump beams, only the grating formed by forward and backward pump beams contributes in the generation of signal, and therefore the signal is proportional to $|C|^2$. Since $|A + B + C|^2 > |C|^2$ for the D$_1$ line and $|A + B + C|^2 \gg |C|^2$ for the D$_2$ line, the D$_1$ line signal intensity should be smaller and the D$_2$ line signal intensity should become insignificant when orthogonal probe polarization is used instead of all parallel input beam polarization arrangements. Experimental observations agree with this prediction, since the sodium D$_1$ line signal for $E_p \perp E_f \| E_b$ polarization is only about one-fifth that of $E_p \| E_f \| E_b$ polarization arrangement and no sodium D$_2$ line signal is observed for the $E_p \perp E_f \| E_b$ polarization setup.

For the investigation of coherent D4WM gratings of lithium D lines in the transient situation (i.e., with pulsed lasers), we use a circularly polarized probe beam and vertically polarized pump beams. The pulse width of the dye laser used is about 15 ns and the lifetime of the lithium D line is reported to be 27 ns (23). This lifetime could be reduced in the flame environment employed in this experiment due to the higher rate of collisional deactivation. However, the lifetime is still longer than the laser pulse width, hence allowing the generation of the coherent-grating D4WM signal, as observed experimentally.

A circularly polarized light consists of vertical and horizontal polarization components, and therefore, two different processes contribute in the generation of the D4WM signal. The vertical polarization component of the probe beam is parallel to the polarization of vertically polarized pump beams and hence the signal intensity is proportional to $|A + B + C|^2$. The horizontal polarization component of the probe beam is orthogonal to the polarization of vertically polarized pump beams, and the signal is proportional to $|C|^2$. The signal generated from these two processes can be experimentally identified by placing a polarizer in front of the photomultiplier tube. When the polarizer is rotated to pass through the horizontally polarized component of the signal, the D4WM signal is proportional to $|C|^2$, and only the lithium D$_1$ line is observed as expected. When the polarizer is rotated to pass through the vertically polarized component of the signal, the D4WM signal is proportional to $|A + B + C|^2$, and both the lithium D$_1$ and D$_2$ lines are observed as expected. The relative signal amplitude generated by these two processes are also

measured. For the D$_1$ line, the peak signal intensity with the polarizer crossed to pump polarization is about one-fifth that with the polarizer parallel to pump polarization. Also, as expected, no signal is observed for the D$_2$ line when the polarizer is crossed to the pump polarization. By using the circularly polarized probe, vertically polarized pump beam arrangement with pulse lasers (i.e., transient coherent-grating D4WM method), one can selectively measure only certain fine lines of an element. Lithium has only two fine lines, D$_1$ and D$_2$, for each isotope, as shown in Figure 3. However, when the D4WM signal is detected in the circular-probe-vertical-pump polarization configuration, only the D$_1$ transition (2s $^2S_{1/2}$–2p $^2P_{1/2}$) is observed for each isotope as shown in Figure 4. The isotope ratio of ^{6}Li and ^{7}Li can be easily determined by just measuring the D$_1$ peak from each isotope. Apparently, this capability of selectively measuring certain fine or hyperfine lines could simplify some fine or hyperfine structures that are more crowded, improve spectral resolving power, and allow convenient isotope ratio determination for elements with relatively complicated fine or hyperfine structures.

One of the most important characteristics of the D4WM signal is its cubic dependence on the laser energy. In our experiment, the excitation laser energy is adjusted by inserting neutral-density filters with different optical density values in the optical path. As expected, the cubic laser energy dependence of the D4WM signal is observed with a slope of 3.07. At laser excitation energy of about 100 nJ/pulse or higher, the analyte line width is broadened due to energy saturation. Without laser energy saturation, the resonant D4WM spectrum is inherently Doppler-free and the analyte line width in an atmospheric pressure flame consists mainly of Lorentzian (pressure) broadening. The fine structure of the lithium 2s $^2S_{1/2}$–2p $^2P_{3/2}$ transition is relatively simple and spread out. Hence, spectral resolution available from room-pressure analytical flame atomizers is sufficient to resolve the fine lines. For isotopes with more crowded fine or hyperfine structures, one could use a low-pressure atomizer, such as a hollow cathode discharge (12, 13) to minimize Lorentzian broadening and obtain sufficient spectral resolution. Or one could use some spectral deconvolution methods (5) to determine isotope ratios, since all hyperfine structure parameters could be calculated and precise theoretical profiles could be determined and matched with experimental convoluted profiles.

Degenerate four-wave mixing using a circularly polarized probe beam provides not only convenient measurement of lithium isotopes but also a very efficient method to isolate optical noise caused by the scattered stray radiation from the optics and the Mie scattering from the flame. In a D4WM experiment, the interference of these optical background sources is the main limiting factor in obtaining better detection sensitivity, since both the optical noise and the signal have the same wavelength. When a continuous-wave laser is used as the excitation source, the signal-to-noise ratio can be improved by using amplitude or polarization modulation at high modulation frequency (12, 13). When using a pulsed laser in a D4WM experiment, one can use appropriate polarization arrangements for the input beams to minimize optical noise and improve the signal-to-noise ratio. In a typical D4WM experiment, most of the background radiation is caused by the backward pump mirror (M$_4$ in Figure 1), since the scattered light from M$_4$ has a propagation direction similar to that of the signal beam. The background radiation caused by the forward pump beam and the probe beam is insignificant. In our D4WM experiment, two vertically polarized pump beams and a circularly polarized probe beam are used to generate a circularly (or elliptically) polarized conjugate signal beam. Hence, when the polarizer in front of the photomultiplier tube is rotated to cross the vertically polarized pump beams, most

of the background noise from the mirror M_4 can be suppressed. Although the signal intensity is only one-fifth of that produced by the $E_p \| E_f \| E_b$ polarization configuration, much more background is suppressed and hence the signal-to-noise ratio is effectively enhanced. To demonstrate that the background noise from the backward pump beam can be efficiently rejected by using this polarization discrimination configuration with a circularly polarized probe beam, the signal-to-noise ratios are measured with and without a polarizer in front of the photomultiplier tube. The S/N with the polarizer in front of the photomultiplier tube is 50 times as high as that without the polarizer in front of the photomultiplier tube. A detection limit of 2.5 ng/mL lithium is observed while Doppler-free resolution is maintained by using this transient coherent-grating-based D4WM spectroscopy. Reasonably good accuracy and precision are also observed in measuring individual isotope contents. Relative standard deviations of 0.2%, 0.3%, 0.5%, 0.7%, and 1.0% are observed for ^6Li isotopes in samples enriched with 50%, 40%, 30%, 20%, and 10% (by weight) ^6Li, respectively.

In conclusion, D4WM offers not only high spectral resolution but also excellent detection sensitivity, as demonstrated here and with different atomizers reported previously (12–14). By using vertically polarized pump beams and a circularly polarized probe beam, one can improve the signal-to-noise ratio and also simplify fine or hyperfine spectra by selectively measuring only certain fine or hyperfine lines. A room-pressure flame atomizer provides stable, fast, continuous, and convenient sample introduction.

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Comparative and Complementary Plasma Desorption Mass Spectrometry/Secondary Ion Mass Spectrometry Investigations of Polymer Materials

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Thick layers of various polymer materials have been investigated by static secondary ion mass spectrometry (SIMS) and plasma desorption mass spectrometry (PDMS) with a new combination time-of-flight (TOF) SIMS/PDMS instrument. For all polymers investigated, characteristic spectra could be obtained with both desorption techniques. The yield (number of detected secondary ions divided by number of primary ions) of characteristic secondary ions for PDMS turned out to be 1–2 orders of magnitude higher than for SIMS. Oligomers of PEG (cationized with sodium), of PMTFMA (protonated), and in the negative spectra of PMMA (methylene splitting) have been desorbed from thick layers with both desorption techniques, but only the PDMS measurements show correct distributions. The sensitivity for surface contamination in SIMS is greater than in PDMS.

INTRODUCTION

Static secondary ion mass spectrometry (SIMS) has been applied in analytical investigations of polymers for several years. Most of these SIMS investigations have been carried out with quadrupole mass spectrometers (1). Recently, also time-of-flight (TOF) analyzers have been used (2, 3). The polymer spectra obtained by static SIMS in general provide a lot of chemical information, especially for optimally prepared SIMS samples, i.e. monolayer preparation on noble metal substrates.

Characteristic secondary ions can be desorbed from polymers over a large mass range. Generally, the positive polymer secondary ion spectrum can be divided into three parts: oligomer, fragment, and fingerprint regions. This is illustrated by Figure 1, showing a positive SIMS spectrum of polystyrene prepared as a monolayer on an etched silver target. Intact oligomer chains consisting of several repeat units and two end groups are generally detected as positive cationized ions. Cations often originate from the substrate. As the chain length varies over a certain mass range, a corresponding oligomer distribution can be seen in the higher mass region of the spectrum, provided that the molecular weight is not too high. Fragment ions produced by bombardment-induced chain cleavage consist of a number of repeat units with one or without any end group. In general they appear in the positive spectrum as a series of cationized ions. Uncationized fragment