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Differentiation of Positional Isomers of Propyl Alcohols Using Filament-Induced Fluorescence *

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We experimentally demonstrate the recognition of positional isomers of propyl alcohol vapor through nonlinear fluorescence induced by high-intensity femtosecond laser filaments in air. By measuring characteristic fluorescence of n-propyl and isopropyl alcohol vapors produced by femtosecond filament excitation, it is found that they show identical spectra, that is, those from molecular bands of CH, C_2, NH, OH and CN, while the relative intensities are different. By comparing the ratios of the CH and C_2 signals, the two propyl alcohol isomers are differentiated. The different signal intensities are ascribed to different ionization potentials of the two isomer molecules, leading to different production efficiencies of fluorescing fragments.

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Structures of positional isomers, which influence the chemical and biological actions of the compounds, are of significance in chemistry and toxicology.[1] So far, a variety of methods have been proposed for differentiating the positional isomers, such as nuclear magnetic resonance (NMR), terahertz spectroscopy and mass-spectrometry-based techniques due to their high-sensitivity and rapid distinction capacities.[2–4] For example, by using high-energy and low-energy collisional-activated dissociation tandem mass spectrometry with electrospray ionization, inositol phosphate isomers have been distinguished from each other.[4]

Recently, femtosecond laser-based spectroscopy techniques such as filament-induced nonlinear spectroscopy (FINS) and remote filament-induced breakdown spectroscopy (R-FIBS) have demonstrated the feasibility for applications to remote sensing.[5–8] This is based on a unique optical phenomenon called femtosecond laser filamentation, resulting from the dynamic balance between the optical Kerr self-focusing and the defocusing effect induced by the self-generated weak plasma of air molecules.[9–11] This phenomenon gives rise to a high nearly constant laser intensity of about 10^{13}–10^{14} W/cm^2 inside the filament core that can induce a variety of nonlinear optical effects, such as ultrafast few-cycle pulse compression,[12] lasing,[8,13–15] THz and high harmonic generation.[16,17] In particular, such peak intensity is high enough to induce ionization and fragmentation of molecules inside the filament, resulting in the emission of the characteristic 'fingerprint' fluorescence for sensing trace gases,[18,19] chemical and biological agents,[20,21] metallic samples,[22,23] combustion intermediates,[24] and so forth.

However, the molecular species to be differentiated in previous investigations are generally different. Even the molecules are constituted with the same chemical compositions, the element abundances are distinct, e.g., in the identification of the two hydrocarbon molecules of methane (CH_4) and acetylene (C_2H_2),[19] and the recognition of the similar biological samples of barley, corn and wheat.[21] Therefore, in this Letter we investigate the feasibility to distinguish the positional isomers that possess both the same chemical compositions and the same element abundances by using the FINS technique. We measure the filament-induced nonlinear spectra of propyl alcohol isomers, n-propyl and isopropyl in a gas phase and compare their spectral differences. The fluorescence signals from molecular bands of CH, C_2 and CN are recorded. These spectral bands reveal identical chemical composition, while the relative intensities are different, showing the possibility to recognize the positional isomers by FINS.

The experiment was performed with a Ti:sapphire femtosecond laser system (Spectra Physics, Spitfire), which delivered the laser pulse train with a repetition rate of 1 kHz, a pulse duration of 35 fs, an energy of up to 5 mJ, and a central wavelength at 800 nm. A beam splitter was inserted into the laser beam to modify the laser pulse energy to 2.2 mJ. The laser pulses were focused by a fused silica lens of 50 cm focal length to form a single filament with the length of 5 cm in air. The filament was located above the surface of a top-opened bottle with an open area of 6 cm in diameter. The bottle was filled fully with n-propyl or isopropyl

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alcohol. The distance between the filament and the liquid surface was set to 10 mm. The fluorescence induced by the filament was collected perpendicularly to the laser propagation direction by using a fused silica lens (6 cm focal length; 5.08 cm in diameter) in a $2f$–$2f$ imaging system. The fluorescence focused onto the entrance slit of a spectrometer (Andor Shamrock SR-750) was dispersed by a holographic grating of 1800 grooves/mm and then recorded by a gated intensified charge coupled device (ICCD Andor iStar). The entrance slit width of the spectrometer was set to 100 μm. All the measured spectra were averaged over 10000 laser shots.

The femtosecond filament-induced fluorescence spectra of n-propyl and isopropyl alcohols are presented in Figs. 1(a) and 1(b) in the spectral range of 300–600 nm, respectively. The ICCD gate width and delay were set to $\Delta t = 200$ ns and $t = -3$ ns, respectively (note that the laser pulse arriving time at the interaction zone is $t = 0$). It should be pointed out that the spectra in Fig. 1 are very clean and free plasma continuum which is consistent with previous observations of filament-induced spectra in air and other gases.[19]

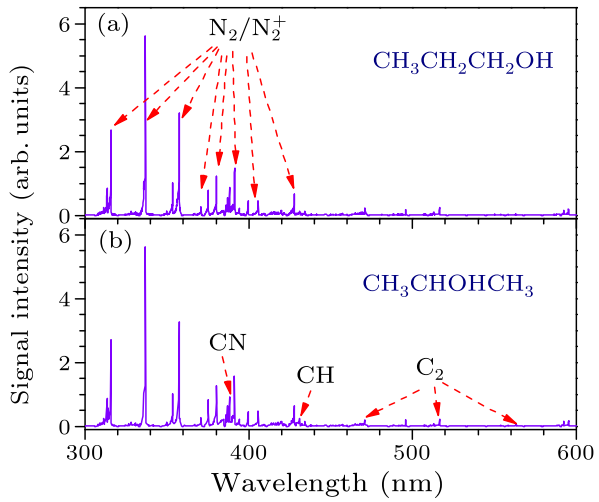

Fig. 1. Spectra of (a) n-propyl and (b) isopropyl alcohol vapors with femtosecond filament excitation.

Analysis of the spectrum reveals that the emissions result from several different species. The several strongest spectral bands are assigned to the first negative band of N_2^+ ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) and the second positive band of N_2 ($C^3\Pi_u \rightarrow B^3\Pi_g$) of the nitrogen molecules in air. The three spectral bands around 563, 516, and 466 nm originate from the Swan band ($d^3\Pi_g \rightarrow a^3\Pi_u$) of the C_2 radical; the spectral band around 430 nm is assigned to the $A^2\Delta \rightarrow X^2\Pi$ transitions of the CH radical and the spectral band at around 388 nm comes from the $B^2\Sigma^+ - X^2\Sigma^+$ transition of the cyano radical CN.[24] Since the n-propyl and isopropyl alcohol molecules do not contain the nitrogen element, the CN and NH should result from the interaction between the parent and/or fragmented alcohol molecules with the nitrogen molecules in air.

It can be noted from Fig. 1 that the fluorescence from nitrogen molecules in air dominates the FINS spectra. To obtain 'pure' characteristic FINS spectra of the n-propyl and isopropyl alcohol vapors without the nitrogen fluorescence contamination, we also measured the FINS spectrum of pure air. By subtracting the air background, clean fluorescence spectra from the n-propyl and isopropyl alcohol vapors are obtained, as shown in Fig. 2, in which the fluorescence emissions from the free radicals CN, C_2, CH, OH, NH, as well as the two-order diffractions of the C (I) atomic lines at 247.4 nm (not shown) can be clearly seen in both the cases. The identical spectral bands presented in these two spectra clearly show that these two molecules possess the same chemical compositions and that the characteristic spectral bands could not be directly used to distinguish the positional isomers of n-propyl and isopropyl alcohol molecules.

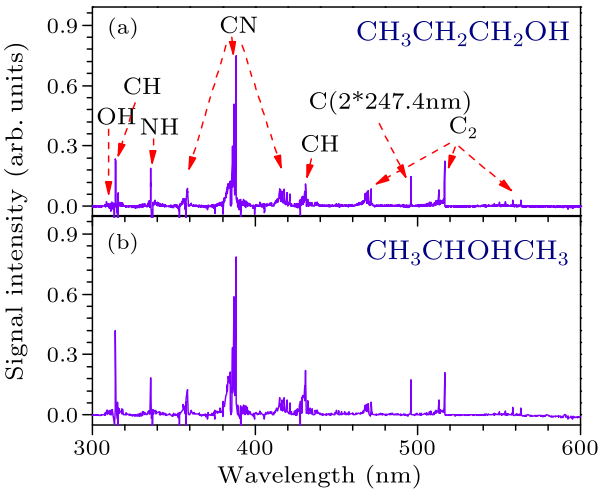

Fig. 2. Clean FINS spectra of (a) n-propyl and (b) isopropyl alcohol vapors after subtracting the air background.

On the other hand, it can be seen from Figs. 2(a) and 2(b) that the signal intensities from different spectral bands are obviously different, although the element abundances in these two molecules are the same. Therefore, the intensity ratios of different spectral bands could be used to identify the two molecules. Since the observed molecular species, CN, OH and NH are strongly related to the interaction of the parent and fragmented alcohol molecules with air molecules (O_2, N_2 and H_2O), we selected the CH and C_2 radicals that are less influenced by the air molecules to check the possibility of discriminating the n-propyl and isopropyl alcohols by comparing the CH/C_2 fluorescence intensity ratios.

For the radical C_2, the signal intensity is from the spectral band head at 516.8 nm; for the radical CH,

the signal intensity is from the spectral band head at 431.5 nm. The calculation result reveals that the CH/C_2 intensity ratio (0.99) for the isopropyl alcohol molecule is about twice higher than that (0.50) for the n-propyl alcohol molecule. The signal uncertainty is about 10%–20%. This demonstrates the possibility of the FINS technique for distinguishing the positional isomers with the excitation of the femtosecond laser filament.

To minimize the air background, we carried out the decay time measurements of the molecular CH at about 431 nm, C_2 at about 516 nm and N_2 at about 337 nm, as shown in Fig. 3. In the measurements, both of the ICCD gate width and the delay step were set to 2 ns. It can be observed from Fig. 3 that the N_2 fluorescence at 337 nm has a short lifetime of 1–2 ns (limited by the temporal resolution of the ICCD) and the CH and C_2 radicals have a longer lifetime of about 7–10 ns, in which the almost identical decay curves of the measured CH and C_2 fluorescence in Fig. 3 are limited by the temporal resolution of the ICCD.[19] This indicates that the air background can be isolated by performing the time-resolved measurements.

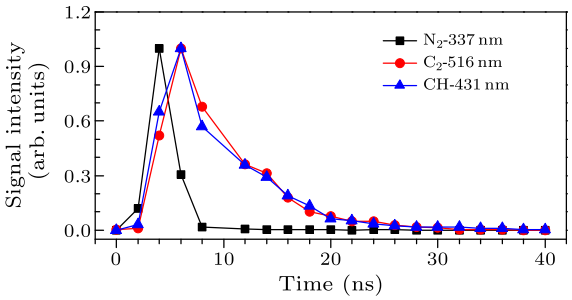

Fig. 3. Fluorescence lifetime of N_2, CH and C_2 radicals at 337, 431, and 516 nm, respectively.

Figure 4 presents the time-resolved filament-induced fluorescence of n-propyl and isopropyl vapors. In this measurement, the ICCD gate delay is set to +7 ns, while all other parameters are kept unchanged. It can be seen from Fig. 4 that the spectral bands from CH, C_2, CN, NH, and OH are very clean, in which the fluorescence emissions from the nitrogen molecules are almost unobservable. In this case, we calculate the ratio of CH/C_2 signal intensity and find that the ratio is about 0.77 for the isopropyl alcohol molecule, which is 1.8 times larger than that (0.45) for the n-propyl alcohol molecule, indicating results similar to Fig. 2. The slight difference of the ratios between the two measurements shown in Figs. 2 and 4 may result from the different lifetimes of CH and C_2 radicals in the filament.[19]

In the filament core, the intensity of 10^{13}–10^{14} W/cm^2 is high enough to ionize/fragment the n-propyl and isopropyl alcohol molecules, and the different intensities of the CH and C_2 spectral bands may result from the following scheme. Since the excitation and ionization processes are highly nonlinear, and are strongly dependent on the ionization potentials of the two molecules, the different ionization potential of the isomer molecules (10.17 and 10.22 eV for n-propyl and isopropyl alcohol molecules, respectively[25]) may thus lead to the different ionization yields of the n-propyl and isopropyl alcohol molecules. Although the mechanisms for producing the fluorescing CH and C_2 radicals from the n-propyl and isopropyl alcohol molecules in the filament are very complicated, and could be contributed from several different reaction channels such as neutral dissociations, recombination of electrons with resultant fragments and direct disintegration of ions,[26] they all strongly depend on the ionization yields. Therefore, the ionization potentials of these two molecules play crucial roles in determining the production efficiency of the fluorescing fragments, leading to different signal intensities of CH and C_2. On the other hand, due to the fact that the excitation and ionization processes are highly nonlinear, it should be pointed out that the ratio of the fluorescence intensities of C_2 and CH may slightly change as the external focal condition varies, so that the laser intensity inside the filament can be changed.[27]

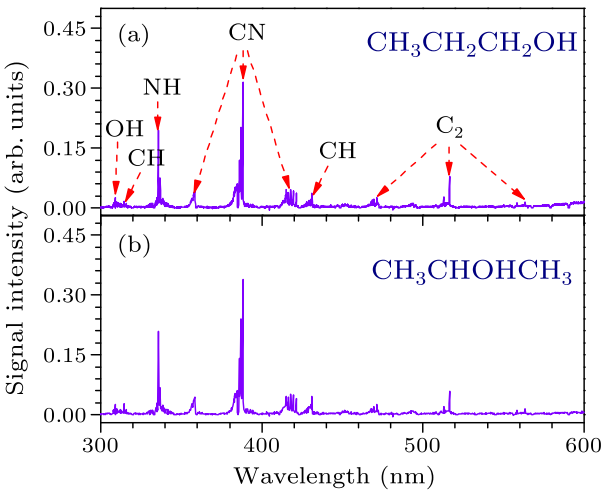

Fig. 4. Time-resolved filament-induced fluorescence spectra of (a) n-propyl and (b) isopropyl vapors in air with the delay time +7 ns, respectively.

In summary, we have experimentally demonstrated the feasibility of distinguishing the positional isomers of propyl alcohol vapors using filament-induced nonlinear fluorescence based on the non-gated and time-resolved measurements. The products of CH and C_2 from the n-propyl/isopropyl alcohols show different characteristic fluorescence intensities, which result from the highly nonlinear light-molecule interaction in femtosecond laser filaments, and can be utilized for differentiating positional isomers of propyl alcohols. Unlike NMR and mass spectrometry that need high-end and complex equipment, the filament-based

spectroscopic technique only needs simple optical geometry, which opens up a new way for the distinction of positional isomers.

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