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Radical species generation and their lifetime extension by a femtosecond and nanosecond dual-laser system

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Abstract For many material processes, desired radical species at excited states are produced which interact with a given substrate for a certain period of time allowing chemical reactions between them to occur and complete. Hence, it is important to maintain the population of the excited radical species for an extended period of time, i.e., their lifetime, which is defined as the time for emission intensity to decay to $1/e$ of the initial intensity. In this study, a femtosecond–nanosecond (fs–ns) dual-laser system was employed to generate desired radical species via the fs laser and, then, to extend the lifetime of the radical species by the ns laser with different time delays between the two fs–ns laser pulses. The proposed method is demonstrated for a N_2 – CO_2 mixture with CN as the radical species. The results show that the lifetime of CN radical species can be significantly extended, particularly the (3, 3) spectral line which was extended from 30 to 200 ns. By using a wavelength-tunable ns laser, the lifetime of most radical species can be extended which may increase the process efficiency for many material processes.

1 Introduction

In a material process, for example the combustion flame synthesis of diamond, it was found that free radicals such as OH, CH and C_2 at excited states may facilitate the

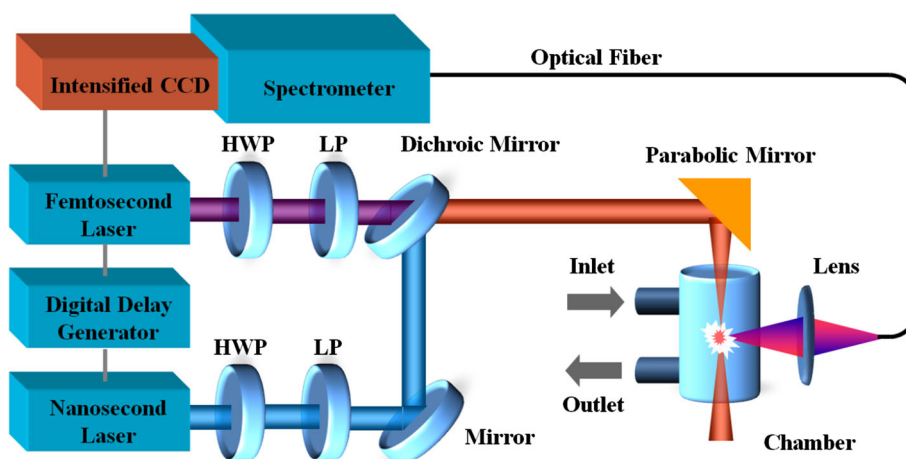
growth of diamond [1–3]. Generally, molecules at excited states would have higher chemical activation energies, as compared to at the ground state, which can enhance chemical reaction rates. However, most radical species at excited states are very reactive which may lead to fast decaying or recombination and, subsequently, the transition to lower excited states or the ground state. As it takes some time for the formation and growth of diamond crystals, the contact time between the substrate and radicals must be long enough allowing chemical reactions to occur and complete. In other words, the lifetime of radical species at excited states must be longer relative to the reaction time. The lifetime of radical species is defined as the time for emission intensity to decay to $1/e$ of the initial intensity for the transition from an excited state to the ground state. In combustion synthesis of diamond, the radical species are continuously generated through the burning of gas mixtures and, hence, in this case the lifetime of free radicals is not critical because fresh radical species are continuously available. However, in a laser-assisted CVD process [4, 5] or diamond synthesis [6, 7], if a pulsed laser is used, free radicals are generated intermittently which decay rapidly. In this case, if the lifetime of radical species is shorter than the laser pulse repetition rate, the chemical reactions between the species and substrate cannot sustain, and it is impossible to grow diamond crystals. Therefore, how to keep the population of radical species at excited states and extend the lifetime of the radical species is important for the success and efficiency of diamond growth and many other material processes.

In this work, a fs–ns dual-laser system was used first to generate radical species by the fs laser and then to re-excite the radical species from the ground electronic state to higher electronic states via the ns laser which extends the lifetime of the radical species.

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Fig. 1 System setup of the dual-laser optical emission spectroscopy. HWP and LP are, respectively, half-wave plate and linear polarizer



2 Experimental

The dual-laser optical emission spectroscopy system consists of a regeneratively amplified Ti:Sapphire fs laser (Legend-F, Coherent), a diode-pumped solid-state ns laser (AVIA-X, Coherent), a spectrometer (Andor) integrated with a time-gated intensified CCD (Andor), and a sample chamber with fused silica windows providing high laser transmittance for holding gas mixtures. The central wavelength, pulse duration, and maximum pulse energy for the fs laser are 800 nm, 120 fs, and 1 mJ, respectively, and are 355 nm, 30 ns, and 0.23 mJ, respectively, for the ns laser. Both the laser beams are in Gaussian distribution and they are synchronized at the repetition rate of 1 kHz. As shown in the schematic diagram Fig. 1, each of the fs and ns pulses first passes through a combination of a half-wave plate and a linear polarizer to adjust the pulse energy. Then, both laser beams are combined into the same optical path via a long-pass dichroic mirror. Next, both the fs and ns laser pulses are focused onto the gas chamber via an off-axis replicated parabolic mirror with a minimum achromatic aberration to reach the same focus spot in space. In order to precisely control the time delay between the fs and ns laser pulses, a digital delay generator (Stanford Research) is employed. A negative time delay is defined as when the ns laser pulse is shot ahead of the fs pulse and a positive time delay implies the ns pulse is shot behind the fs pulse.

A gas mixture of 50 % nitrogen (N_2) and 50 % carbon dioxide (CO_2) was selected because of their stability and inflammability. The gas chamber is continuously flushed and vented with the gas mixture at a constant flow rate. The emission spectra from the gas chamber are collected by a lens and then projected into an optical fiber connected to a spectrometer, and a time-gated intensified CCD camera was used to collect and amplify spectra. In order to efficiently amplify transition signals and eliminate background

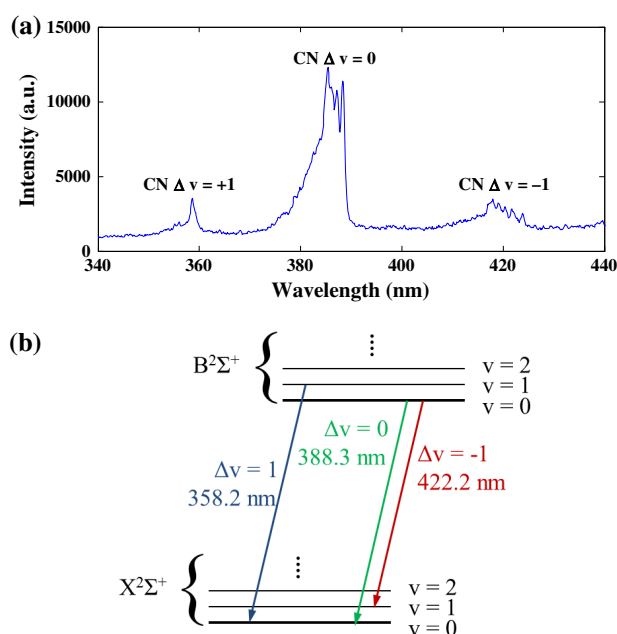


Fig. 2 **a** Optical emission spectrum of CN radical species in N_2 - CO_2 mixture by fs laser irradiations. **b** Energy level diagram for CN radical

noises, the intensifier of the CCD camera is enabled only 10 ns to record each signal with a variety of time delays after every fs laser pulse was fired. Each spectrum is accumulated by 2 s which includes 2,000 intensified signals.

3 Results and discussion

The optical emission spectrum of N_2 - CO_2 excited by a fs laser pulse alone is shown in Fig. 2a. In Fig. 2b we show the energy level diagram of CN at the $B^2\Sigma^+$ and $X^2\Sigma^+$ states [8]. Spectral lines with three CN spectral groups

were observed. Note other spectra may exist in the wavelengths outside the range in Fig. 2. The results in Fig. 2 imply that CN radical species can be generated by the fs laser pulse via multi-photon absorption to dissociate N_2 and CO_2 molecules, and then these dissociated free radicals associated together to become CN species. In this study, spectra measurements were focused on the wavelength ranging from 384 to 389 nm which mainly includes the energy bands of (0, 0), (1, 1), (2, 2), (3, 3), and (4, 4), corresponding to the state transitions of CN free radical at $\Delta v = 0$, where A and B in the expression of (A, B) are, respectively, the vibrational quantum numbers in the $B^2\Sigma^+$ and $X^2\Sigma^+$ states and the difference Δv is defined as $A - B$.

To study the transition dynamics of CN radicals, a sequence of spectra was recorded from time $t = 0$ (immediately after the fs pulse was fired) to $t = 300$ ns to gather the spectral kinetics. Figure 3a represents the

transition spectra of CN violet bands at $\Delta v = 0$ gathered at $t = 0$ (trace 1), $t = 20$ ns (trace 2), $t = 50$ ns (trace 3), and $t = 100$ ns (trace 4). The spectral lines and their relative intensity ratios are similar to the published results [8]. For each trace the peak intensity occurs at (0, 0) and then decreases from (0, 0) through (4, 4). For each spectral line, (0, 0) through (4, 4), the signal intensity decreases as a function of time. However, for each trace the intensity ratios between two wavelengths do not vary too much for different measuring times. This can be seen from the results when the signal intensities of each spectral line are plotted w.r.t. the measured time, as shown in Fig. 3b. Normalized by (0, 0), at $t = 0$, the ratios of (0, 0) through (4, 4) are, respectively, 1, 0.88, 0.75, 0.73, 0.72, and at $t = 300$ ns, and the ratio becomes, respectively, 1, 0.78, 0.54, 0.38, and 0.53. It takes about 25–40 ns for the signal to decay to $1/e$ of the initial intensity ($t = 0$). The (0, 0)

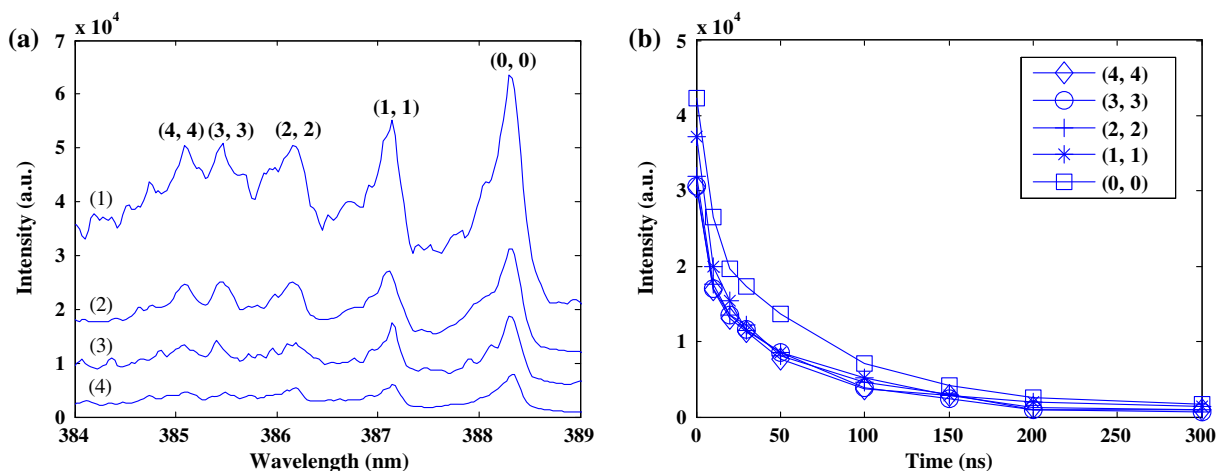


Fig. 3 a Spectra for CN at different measuring times after fs irradiations. Trace (1): 0 ns; trace (2): 20 ns; trace (3): 50 ns; trace (4): 100 ns. b Signal intensity vs. measuring time of CN violet band at $\Delta v = 0$

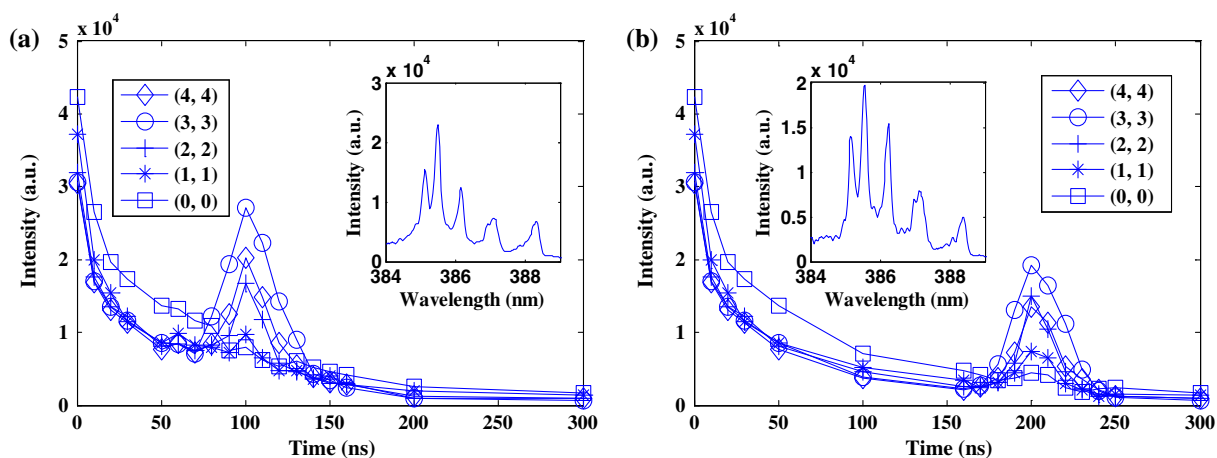


Fig. 4 Dual-laser spectra of CN bands at $\Delta v = 0$. a Ns laser was fired at $t = 100$ ns and the inset is the spectrum measured at $t = 100$ ns. b Ns laser was fired at $t = 200$ ns and the inset is the spectrum measured at $t = 200$ ns

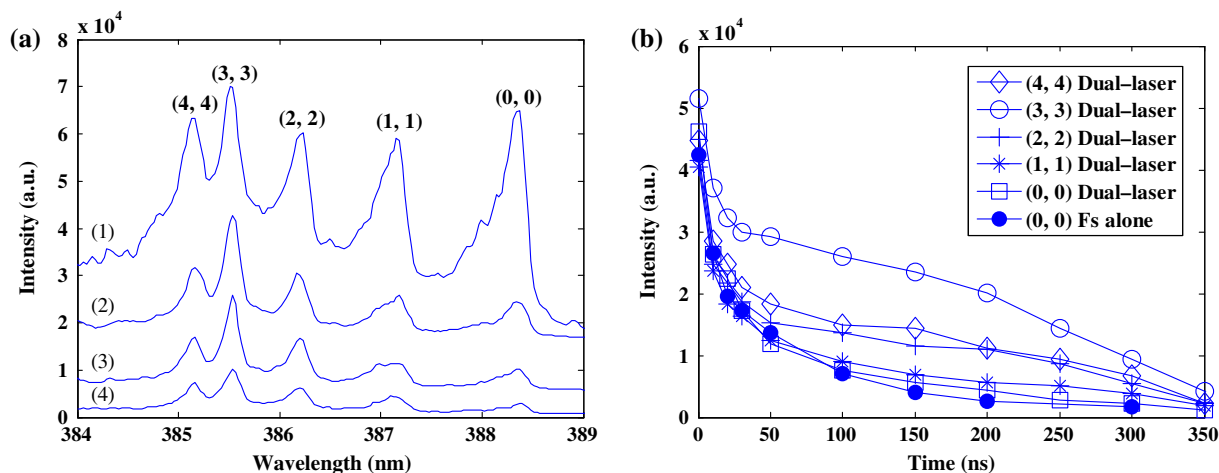


Fig. 5 Dual-laser spectra of CN bands at $\Delta\nu = 0$. **a** Spectra at measuring time of 0 ns (1), 100 ns (2), 200 ns (3), and 300 ns (4). **b** Signal intensity vs. measuring time of CN violet band at $\Delta\nu = 0$

line has the longest lifetime than other lines at $\Delta\nu = 0$ band. The lifetime of CN radicals at $B^2\Sigma^+$ state has been measured to be about 40–60 ns [9, 10] which is slightly greater than our measured result, 40 ns, due to different measuring conditions. The difference may be caused by the combined effect of the state transition from $B^2\Sigma^+$ to $X^2\Sigma^+$ and the plasma expansion and diffusion of CN radicals from the focused volume to its surroundings. Since at the focused volume, the local temperature of generated plasma can be very high; for example, if the local temperature is 2,000 K, the average molecular velocity could achieve 1,300 m/s for CN radicals [11].

Figure 4 illustrates the intensities of spectral lines of (0, 0) through (4, 4) excited by fs–ns dual-laser pulses as a function of time. The ns laser pulse was fired, respectively, at $t = 100$ ns, Fig. 4a, and $t = 200$ ns, Fig. 4b. The inset in Fig. 4a and b shows, respectively, the spectrum at $t = 100$ ns and $t = 200$ ns. After the fs laser pulse was fired, CN radical species were generated and simultaneously excited to the $B^2\Sigma^+$ state, and then the state transition occurred to emit signal and the CN radicals transfer to the lower $X^2\Sigma^+$ state. Then, the ns laser pulse excites the CN radicals from the $X^2\Sigma^+$ state back to the higher $B^2\Sigma^+$ state and subsequently the state transition from $B^2\Sigma^+$ to $X^2\Sigma^+$ state occurs again generating the temporal signal peaks at $t = 100$ ns and $t = 200$ ns in Fig. 4. In Fig. 4a and b, the full widths at half maximum of the temporal peaks of the (3, 3) line are, respectively, 39 and 37 ns which are slightly longer than the pulse width of the ns laser, 30 ns. Hence, once the ns laser pulse completes, the enhancement disappears rapidly. The maximum intensity of the temporal peak excited at 200 ns is lower than the corresponding ones excited at 100 ns. Since the CN radicals in the $X^2\Sigma^+$ state is relatively stable with the binding energy of 7.76 eV, the signal decay is mainly

caused by the nature diffusion which decreases the concentration of CN at the detecting spot. Considering the temporal peaks, the maximum enhancement occurs at the (3, 3) spectral line which means that the energy of the ns laser pulse was directly or indirectly absorbed by the CN radicals which were mostly excited back to the third vibration state of the $B^2\Sigma^+$ state. On the contrary, limited enhancement occurs for the (0, 0) and (1, 1) spectral lines. By comparing the spectral profile of (0, 0) through (4, 4) line, it is seen that the maximum intensity occurs at (0, 0) when only fs pulse was fired, Fig. 3a, and at (3, 3) after the ns laser was fired, insets of Fig. 4. The intensity ratios of the spectrum excited by fs laser alone normalized by the (0, 0) spectral line are, respectively, 1, 0.88, 0.75, 0.73, and 0.72 for the (0, 0) through (4, 4) spectral lines. However, after the ns laser pulse was fired, these ratios change to 1, 1.19, 1.81, 3.42, and 1.97 and 1, 1.29, 2.51, 4.59, and 2.55, respectively, for the inset in Fig. 4a and b. The enhancement generated by the additional ns laser pulse is evident. Note the energy of ns laser pulse alone (200 μ J) is not sufficient to excite any signal in the N_2 – CO_2 gas mixture.

Figure 5a represents the optical emission spectra of N_2 – CO_2 gas mixture excited by fs–ns dual-laser pulses with different time delays. In other words, fs laser pulses were fired at $t = 0$, and ns laser pulses were fired at different t . Trace (1) through trace (4) in Fig. 5a, respectively, represents the spectrum where the ns laser pulse was fired at $t = 0$, $t = 100$ ns, $t = 200$ ns, and $t = 300$ ns, and each measuring interval is 10 ns at the center of the temporal envelope of the ns laser pulse. Similar with Fig. 4, the intensity ratio is significantly different from the ratio excited by fs laser alone. Figure 5b reveals the intensity of each spectral line plotted w.r.t. the measured time. For convenient comparison, the (0, 0) line in Fig. 3b was also put on Fig. 5b. In the first 30 ns, the signal decays fast

because most of the CN radicals have been excited to the $B^2\Sigma^+$ state via the fs laser pulse. Starting at 50 ns, about the lifetime of the CN radicals in $B^2\Sigma^+$ state, the decay rate significantly decreases, especially at the (3, 3) line, because the ns laser pulse plays the role to excite the CN radicals back to the $B^2\Sigma^+$ state and keep more CN radicals at the $B^2\Sigma^+$ state. It takes about 30, 38, 52, 210, and 78 ns, respectively, to decay to $1/e$ of the initial intensities for the (0, 0) through (4, 4) spectral lines. The characteristics of (0, 0) spectral line are similar for cases with or without the ns laser pulse, but the (3, 3) line changes significantly. The intensity at (3, 3) line apparently increases and the lifetime also becomes longer for the case with a ns laser pulse.

Note, in this study, a fs laser is used to generate radical species from the N_2 - CO_2 gas mixture. In fact, the same radical species can be generated by other energy sources and from other target materials which can be in gas, liquid or solid phase. Also, each radical species has its own absorption band for a given ns laser wavelength. Hence, if the ns laser is wavelength tunable or even multi-ns-laser system was employed, it can be used to excite and extend the lifetime of one or more selected radical species. Furthermore, if a pulse-train technology is used, it is possible to significantly increase the lifetime of radical species.

In summary, we have demonstrated that using a fs–ns dual-laser system, the lifetime of selected radical species

can be significantly extended which is very important in many material processes and detection technologies.

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References

1. Z. Xie, Y. Zhou, X. He, Y. Gao, J. Park, H. Ling, L. Jiang, Y. Lu, *Cryst. Growth. Des.* **10**, 1762 (2010)
2. P. Alers, W. Hanni, H.E. Hintermann, *Diam. Relat. Mater.* **2**, 393–396 (1992)
3. T. McKindra, S. Patil, M.J. O’Keefe, Z.Q. Xie, Y.F. Lu, *Mater. Charact.* **61**, 661 (2010)
4. Y. You, A. Ito, T. Goto, *Mater. Lett.* **106**, 11 (2013)
5. A. Ito, H. Kadokura, T. Kimura, T. Goto, *J. Alloy. Compd.* **489**, 469 (2010)
6. K. Kitahama, K. Hirata, H. Nakamatsu, S. Kawai, *Appl. Phys. Lett.* **49**, 634 (1986)
7. J. Narayan, V.P. Godbole, C.W. White, *Science* **252**, 416 (1991)
8. X. Chen, J. Mazumder, A. Purohit, *Appl. Phys. A* **52**, 328 (1991)
9. T.J. Cook, D.H. Levy, *J. Chem. Phys.* **57**, 5059 (1972)
10. W.M. Jackson, *J. Chem. Phys.* **61**, 4177 (1974)
11. J. M. Haile, *Molecular Dynamics Simulation: Elementary Methods*, (Wiley Professional PaperBack Series, New York, 1992)