CHARACTERIZATION OF THE CN(B) AND CH(A) RADICAL FORMATION IN PLASMA GENERATED BY FEMTOSECOND LASER PULSES VIA STEP-SCAN FT-UV-VIS SPECTROSCOPY

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1. INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) is mostly used for simultaneous analysis of multiple elements measuring the atomic emission lines or the emitted light from diatomic radicals in excited states [Rao 2015, Moros 2019]. Typical LIBS measurements apply nanosecond laser pulses [Dong 2011] however, recent publications suggest potential benefits of using femtosecond lasers [Moros 2019, Kotzagianni 2013]. Seven explosive nitropyrazoles were studied by fs-LIBS technique (~40 fs, 800 nm, 1 kHz, ~2.5 mJ pulse energy) [Rao 2015]. Rao et al. studied the atomic emission lines from C, H, O, and N, the molecular emissions of cyanide (CN, violet bands) and diatomic carbon (C_2, Swan bands). Authors collected time-resolved spectral data for the characterization of the plasma dynamics in different atmospheres, such as air, argon and nitrogen. They found a clear decreasing trend in the CN and C_2 decay times with the increasing number of nitro groups. Moros et al. concluded in their review work about the LIBS of organic compounds that the molecular emission from CN and C_2 radicals is stronger with fs-LIBS technique compared with those obtained using nanosecond laser pulses [Moros 2019].

We report a novel approach producing CN(B) and CH(A) radicals from different small organic molecules in gas phase with a high repetition rate femtosecond laser (100 kHz, 1030 nm, ~43 fs, 250 μJ/pulse). The emission spectra can be collected with high temporal and spectral resolution (5 ns and 1 cm^{-1}) with a Fourier transform UV-Vis spectrometer in step-scan measurement mode [Mogyorosi 2020].

2. EXPERIMENTAL

The experiments were performed in a vacuum chamber typically at 5-100 mbar total pressures in argon or nitrogen gas in the presence of organic vapors (bromoform, methanol or acetonitrile) introduced through a bubbler. The HR-1 laser beam at ELI-ALPS with 1030 nm central wavelength, 100 kHz repetition rate, ~43 fs pulse length and 25 W average power was focused into the vacuum chamber with an achromatic lens (f = 10 cm). The intensity in the focal point was estimated to be 1.1×10^{16} W/cm^2. Overview spectra were monitored with a QEPro spectrometer. The emitted light was also collected with a collimating lens and measured with a Bruker Vertex80 FT-UV-Vis spectrometer with high resolution in step-scan mode (5 ns and 1 cm^{-1}).

3. RESULTS AND DISCUSSION

3.1. CN(B) radical formation

The overview emission spectra from acetonitrile in nitrogen and argon are shown in **Figure 1**. The CN violet system ($B^2\Sigma$-$X^2\Sigma$, $\Delta\nu$ = 0, -1 and +1; 370-395 nm, 350-365 nm and 410-425 nm, respectively) and the C_2 Swan system ($d^3\Pi_g$-$a^3\Pi_u$, $\Delta\nu$ = 0, -1 and +1; 450-480 nm, 500-520 nm and 540-570 nm, respectively) can be observed.

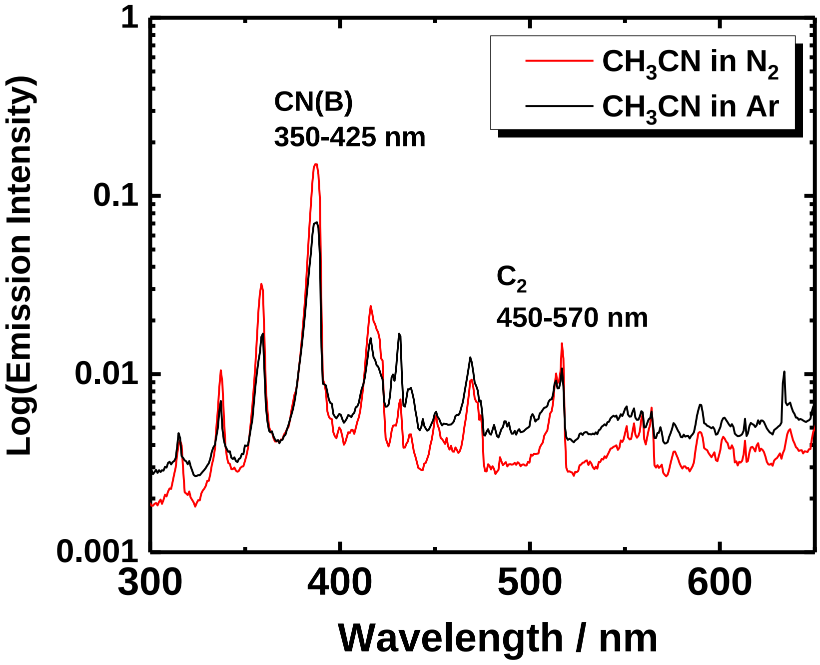

Figure 1. Overview spectra of CN(B) and C_2 radicals generated from acetonitrile.

The highest intensity of CN(B) radicals was observed from bromoform in nitrogen plasma due to the production of reactive carbon atoms and CH radicals. The experimental data obtained with time-resolved Fourier transform spectroscopy were used for the determination of the rotational and vibrational temperatures via fitting (**Figure 2.**) [Western 2017].

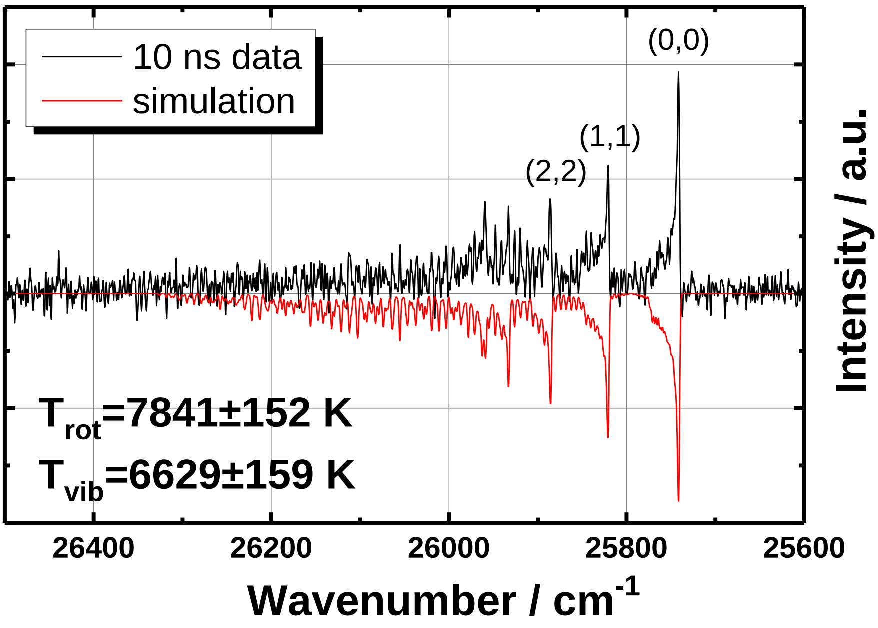

Figure 2. Measured and simulated ro-vibrational spectra of CN from acetonitrile 5 mbar - N_2 95 mbar mixture at 10 ns time point.

The rotational and vibrational temperatures were very high (T_{rot}~6000-8500 K and T_{vib}~4500-8000 K) at about 10 ns for the CN(B) radicals generated from all organic molecules. T_{rot} determined for bromoform and acetonitrile rapidly decreased in all instances within 40 ns. The time-dependent integrated fluorescence signal of the (0,0) band of acetonitrile/Ar (5 mbar/95 mbar) sample is fitted with a mono-exponential curve with a time constant of 87 ns. The CN(B) emission in nitrogen follows a bi-exponential decay. The shorter time constant of this decay (35-40 ns) is close to the natural lifetime of CN(B) emission (~30-90 ns). The longer time constant (130-160 ns) probably belongs to slower chemical reactions involving carbon atoms, C_2 radicals and nitrogen containing species.

3.2. CH(A) radical formation

Based on the overview spectrum of bromoform/Ar (5 mbar/5 mbar) plasma, the formation of CH(A) radicals was confirmed by the observation of a peak at 431 nm. The atomic lines of hydrogen (H-alpha, 656.8 nm) and bromine (827.8 nm) were also noticed. In the case of methanol/Ar (5 mbar/5 mbar), the P-, Q- and R-branches are also recognizable in the high-resolution static spectra. The CH(A) formation kinetic curves are shown in **Figure 3**.

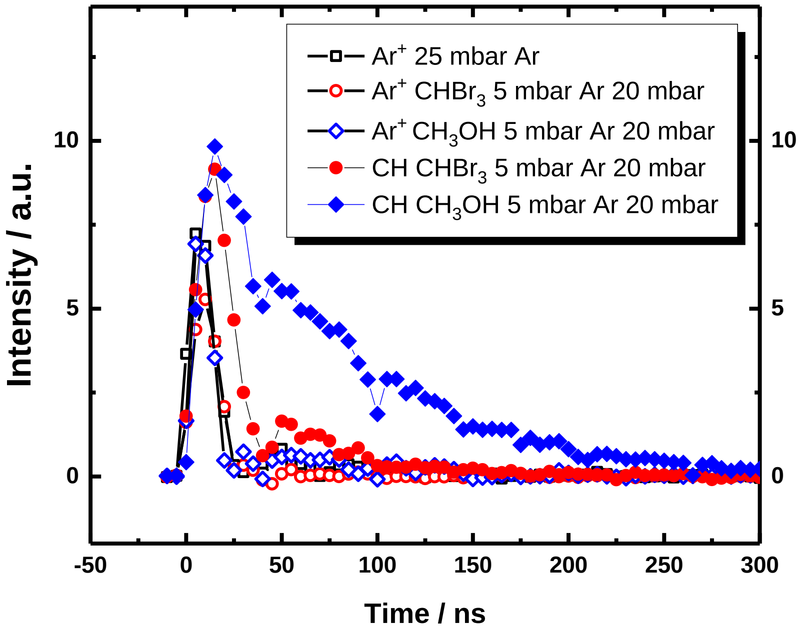

Figure 3. CH(A) formation kinetics in bromoform/argon and methanol/argon mixtures (5 mbar organics/20 mbar argon).

The appearance of the Ar^+ signal occurs in the 5-10 ns time range (that is about the instrument response time). The CH(A) signal formation is similarly fast but the emission decay is different for the bromoform/argon mixture (t = 10.4 (2.2) ns) compared to that of methanol/argon mixture (t_1 = 7.8 (2.2) ns and t_2 = 81.5 (1.7) ns). In the case of methanol, it is likely that the stepwise loss of hydrogen atoms from the CH_3 group results in slower decay of the CH(A) emission.

4. CONCLUSIONS

The step-scan Fourier transform UV-Vis spectroscopy combined with the high repetition rate femtosecond laser (100 kHz, ~43 fs) is an excellent tool for the determination of atomic and molecular composition of samples. The method can be applied for gas, liquid and solid phase samples as well. Due to the localization of the pulse energy of the femtosecond pulse, small quantities can be analyzed with high rate. The main advantage of using femtosecond laser pulses is due to the high starting temperatures (4500-8000 K). This allows the detection of multiple elements and radicals simultaneously, including those which are hardly measurable with the traditional ns-LIBS techniques. It has been demonstrated on model samples that the kinetics of the formation and decomposition of light emitting species can be monitored with high temporal resolution.

5. ACKNOWLEDGEMENTS

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