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Microwave Scattering from Laser Ionized Molecules: A New Approach to Nonintrusive Diagnostics

Richard B. Miles,* Zhili Zhang,† Sohail H. Zaidi,‡ and Mikhail N. Shneider§
Princeton University, Princeton, New Jersey 08544

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Introduction

WE PRESENT here a new nonintrusive diagnostic, "radar resonant enhanced, multiphoton ionization (REMPI)," that has the promise of providing localized measurements of both dominant and trace species with high-sensitivity and with high-selectivity. High-sensitivity is achieved by using microwave scattering for detection. High-selectivity is achieved through a resonant laser interaction with selected molecular electronic states. The excitation and detection have nanosecond time response, making radar REMPI robust to quenching and useful for the measurement of ionization and recombination processes. Visible or infrared light can be used to access ultraviolet resonances, thus providing the capability of observing molecules whose spectra would otherwise be obscured by other molecular species. Radar REMPI can potentially be used for the detection of hazardous gases or pollutants in air, the measurement of major and minor species densities in reacting environments, and the determination of temperature. The combination of laser excitation and microwave detection may permit this diagnostic to be used for remote detection for airborne gases, for pollution measurements, and for threat identification. The application of the radar REMPI technique is demonstrated through the spectroscopy of pure nitric oxide and the trace detection of nitric oxide in nitrogen.

Discussion

Radar REMPI uses resonant enhanced, multiphoton ionization to selectively ionize a particular molecular species of interest [1] and microwave scattering to see that ionized plasma. A short pulse laser is focused to the point where the measurement is to be made. Ionization is generated through an m-photon multiphoton excitation step to an intermediate electronic state, followed by an n-photon second multiphoton ionization step from that electronic state to the continuum, leading to what is termed m + n REMPI ionization. Through this process a weakly ionized, small volume plasma is generated within the focal volume of the laser. As the laser is tuned in frequency through the resonance associated with the m-photon multiphoton excitation of the electronic state, the ionization density of this plasma dramatically changes, strongly peaking at the resonant condition. The multiphoton nature of the REMPI process makes it possible to generate ionization from resonances in regions that would otherwise be opaque by using laser excitation at a subharmonic of the transition frequency.

Microwave radiation illuminates the focal volume, and the microwave radiation that is scattered from the small plasma is detected using standard radar homodyne or heterodyne technologies. Because the dimension of this weakly ionized plasma is much less than the wavelength of the microwaves and much smaller than the skin depth, the scattering falls into the Rayleigh range, and the electrons collectively act as an induced point dipole scatterer of the microwaves [2,3]. The scattered electric field amplitude is directly proportional to the number of electrons. This field is scattered into a classical dipole scattering pattern which is symmetric around the polarization vector of the microwave field [4]. Detectivity is significantly increased and shot noise significantly reduced in the microwave region compared to detection in the ultraviolet because the photons have much lower energy; 1 nW detected in 1 ns corresponds to 10^5 microwave photons, but only 1 UV photon. This permits the time evolution of the plasma to be followed by the microwave scattering.

Experimental Setup and Results

Experiments in nitric oxide (NO) were undertaken to demonstrate the capability of this new diagnostic for nonintrusive spectroscopy and for the detection of trace species. Both 1 + 1 and 2 + 1 radar REMPI signals were measured. For the 1 + 1 radar REMPI, an Nd: YAG-pumped, frequency-doubled dye laser (Sirah Cobra-Stretch) was mixed with residual 1.064 μm Nd: YAG to generate light in the 226 nm spectral region with a bandwidth of approximately 1 cm^{-1}. This laser could be scanned electronically in frequency, and it provided a capability of doing spectroscopy on the nitric oxide in a test cell. The microwave was a 10 mW, 12.6 GHz source placed 15 cm from the sample point and detected at a distance of 30 cm, and homodyne detection was used to measure the signal. The 2 + 1

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*Professor, Mechanical & Aerospace Engineering, Olden Street. AIAA Fellow.
†Graduate Student, Mechanical & Aerospace Engineering, Olden Street. AIAA Student Member.
‡Research Scientist, Mechanical & Aerospace Engineering, Olden Street. AIAA Member.
§Research Scientist, Mechanical & Aerospace Engineering, Olden Street. AIAA Senior Member.

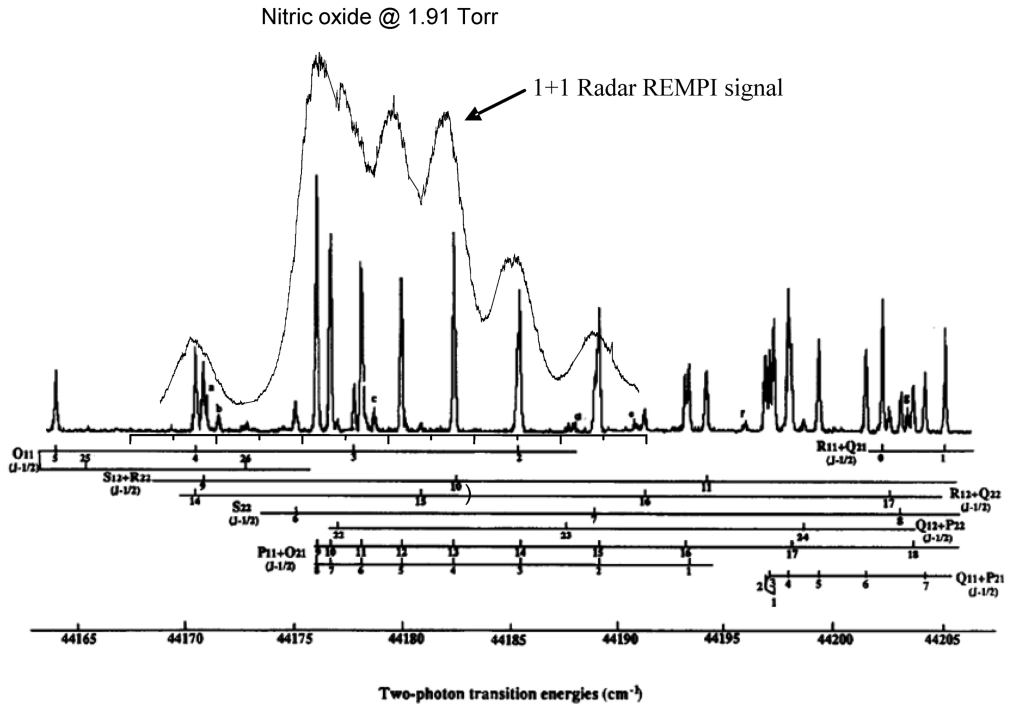

Fig. 1 1 + 1 radar REMPI signal of 1.91 torr of NO compared with high resolution 1 + 1 REMPI spectrum from [6].

REMPI line of xenon at 226.36 nm (44176.1 cm^{-1}) was used to calibrate the spectrum [5]. Experiments were conducted in nitric oxide at a few torr. The experimentally measured spectrum is shown in Fig. 1, together with the classical nitric oxide spectrum from the literature [6]. The broadening seen with the radar REMPI curve is due to the 1 cm^{-1} linewidth of the laser. This curve demonstrates that radar REMPI can be used for spectroscopy. Similar experiments were conducted in a flame, indicating that the microwave scattering is still effective in that environment.

The second set of experiments was to demonstrate trace species detection and was undertaken using 2 + 1 REMPI, in which the two-photon resonance was with the ($C^2\Pi \leftarrow X$) nitric oxide transitions in the vicinity of 190 nm. The laser is a Ti: Sapphire laser, operated in the region of 760 nm, and frequency-doubled to the UV around 380 nm. This laser has a broad bandwidth and is hand tuned, so it is not particularly useful for spectroscopy, but can be used to identify the presence of nitric oxide by tuning on and off the nitric oxide two-photon resonance. Air is not transparent at 190 nm, but it is at 380 nm, so this detection uses the subharmonic capability of REMPI. The experimentally measured spectra of 720 and 160 ppb of nitric oxide in 200 torr of nitrogen are shown in Fig. 2, together with the 2 + 1 classical REMPI spectrum of NO from the literature [1]. This mixture was prepared by diluting a 20% NO plus 80% nitrogen mixture several times. For this experiment, the laser pulse energy was approximately 20 mJ/pulse, and it was focused into the cell with a 10 cm focal length lens. The microwave power was 50 mW, and the receiver was located 30 cm away from the plasma region. The figure shows the spectrum as the laser is hand tuned across the NO resonance. Each point represents an integration of 32 laser pulses.

The time dependence of the signal is directly related to the number of electrons. Figure 3 shows the time evolution of the 2 + 1 radar

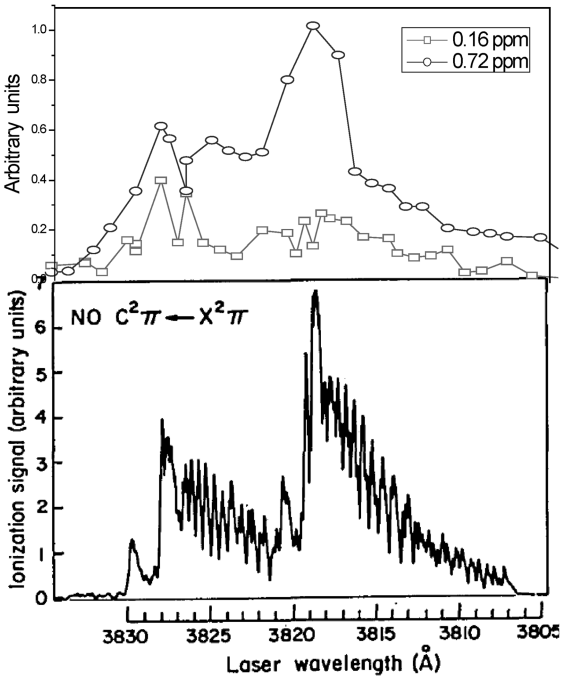

Fig. 2 2 + 1 radar REMPI signal at the top compared with 2 + 1 REMPI spectrum on the bottom [1]. Radar REMPI spectra are rough because the laser and frequency upconversion crystals were hand tuned.

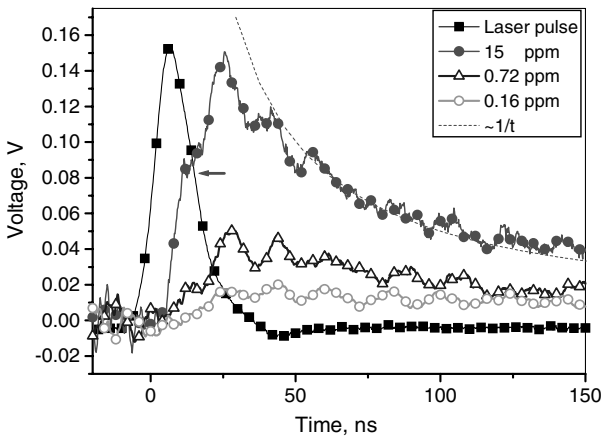

Fig. 3 Time dependence of the excitation laser pulse and the 2 + 1 radar REMPI signals. The arrow shows the initial REMPI ionization before the subsequent avalanche ionization process, and the $1/t$ dependence that is characteristic of dissociative recombination is shown by the dotted line.

REMPI microwave scattering signal from nitric oxide at 15 ppm, and 720 and 160 ppb during and after the laser pulse. The ionization takes place in two steps: REMPI ionization of NO, followed by avalanche ionization of the nitrogen. With high-intensity, short pulse excitation, the initial state of the particular molecular species that is probed can be fully depleted by REMPI in a time that is short compared with collisional refilling time, providing a measure of that state population. (The accuracy of this measurement can be improved by splitting the REMPI laser pulse and simultaneously producing a radar REMPI signal in a reference calibration cell.) The subsequent avalanche process is dominated by the electrons that were generated in the REMPI process. We believe that these two mechanisms are directly observable in the rise time of the microwave scattering, in which the shoulder of the ionization indicated by the arrow corresponds to the REMPI process, and the subsequent rise in the signal is due to the avalanche process. Shorter laser pulses ($\sim$0.1 ns) or reduced laser beam intensities are expected to suppress the avalanche component and will provide for better quantitative measurements, however, the avalanche process may be of interest for achieving higher sensitivity for trace species detection. The decay rates of the signals are directly related to the loss rate of electrons. As shown by the dotted line in the figure, the decay rate of electrons in the NO and nitrogen mixture is close to the $1/t$ dependence expected for dissociative recombination.

Conclusions

In summary, a new nonintrusive diagnostic technology has been developed that is capable of detecting trace species and doing spectroscopy. The detected signal is by microwave scattering, so it can be made highly sensitive and time accurate, and it is less affected by constraints which are common to optical diagnostics, such as quenching and background light scattering. Microwaves pass through nonmetallic surfaces and are easily reflected from metallic surfaces, so that many problems associated with optical access can be alleviated.

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E. Oran
Associate Editor