Multiphoton Ionization of Nitric Oxide in the Presence of Foreign Gases*

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Abstract. The addition of foreign gases (e.g. Ar, He, and CH₃Cl) is shown to strongly affect the MPI current resulting from excitation of NO through the C₂II(ν=0) intermediate state. The NO excitation spectrum is not affected by a large excess of Ar. Quantitative and specific determination of NO is demonstrated to 6 x 10⁻⁶ Torr in a bulk mixture. Foreign gas effects are interpreted as arising from secondary ionization of neutrals by energetic electrons. The linear dependence of the signal on NO pressure and the quadratic dependence on laser power suggest that the technique can be used to determine reaction rates involving selected states of NO.

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Multiphoton ionization (MPI) of atoms and molecules can be readily induced by focussing high-power laser radiation into a gaseous sample [1-3]. The process is resonantly enhanced when an electronically excited state of the particle lies at an energy nhv where n is a small number (typically ≤ 3) and ν the laser frequency. Because it produces easily detected charged particles, resonantly enhanced MPI(REMPI) can be used as a highly sensitive analytical tool for selectively ionizing one species in a mixture. Thus the detection of single Cs atoms in P-10 gas (90% Ar + 10% CH₄) has been claimed [4].

In addition to its high sensitivity, REMPI may allow time resolved studies on molecules which could not be observed by previous techniques. For example, laser induced fluorescence via one (LIF) [5, 6] or two (TPEF) [7] photon excitation has provided a wealth of kinetic data on molecular reactions and relaxation. Since molecules not possessing a fluorescent upper electronic state cannot be monitored using LIF or TPEF, REMPI may provide a suitable alternative.

The possible application of MPI in following the kinetics of a chemical reaction was considered for the case of molecular beams [8]. The results indicated that the MPI spectrum is broader than the LIF spectrum, and that signal intensity is not readily related to laser intensity nor to the molecular concentration. The present study was motivated by the possibility of using MPI to monitor the concentration of transient species in bulk reactions. In distinction with molecular beams one must now be concerned with complications due to ion and electron-neutral collisions.

Using NO as a molecular prototype we find that the high selectivity is not affected by the addition of foreign gases (i.e. the sharp features of the MPI excitation spectra are maintained), and that the overall signal intensity varies considerably over certain pressure ranges. Notwithstanding, it is shown that the current is linearly proportional to the NO pressure and that calibrations curves can be constructed for the desired operating conditions. That REMPI yields quantitatively reliable results with NO despite the fact that its resonant intermediate state C₂II rapidly predissociates (enhanced even more by high pressure Ar [9]), demonstrates the relevance of the technique for molecules in which LIF or TPEF present difficulties [10].

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Experimental

The apparatus is typical of other dye laser MPI configurations. A Molelectron 400 kW N₂ laser pumped a DL-200 dye laser. When used with the dye BBQ the laser's 5 ns, 1-2 cm⁻¹ bandwidth pulse yielded an energy of ~250 μJ. For the power dependent studies ordinary microscope slides placed between the dye laser output and the MPI cell provided variable attenuation of the laser energy. A 5-cm focal length quartz lens focussed the dye laser beam into the MPI cell. The MPI cell was made from a pyrex tube (22 mm inner diameter) to which two 32 mm ID O ring joints were sealed. The ends of the cell were closed by attaching quartz windows with the appropriate viton O rings. The window-window length of the cell was 9 cm. Two platinum wires (0.7 mm diameter) were epoxied to the cell in a parallel geometry separated by 7 mm over a longitudinal distance of 20 mm. The laser beam propagated along the longitude axis between the wires. When appropriately biased the wires collected the charges created in the focal region of the laser. The cell and attached leads were placed inside a well grounded Faraday box to protect it from rf fields generated by the N₂ laser.

The current was amplified using a charge sensitive preamplifier. The pre-amplifier incorporated a 1 GΩ resistor in the feedback loop of a LF 357 (Texas Inst.) operational amplifier. When capacitively coupled to the bias wires by a 1 pF capacitor the net amplification was approximately 5 × 10⁶ V/Coul. As measured by an oscilloscope having a 1-MΩ input impedance the pre-amplifier signal had about one μs risetime and a FWHM of 1.5 ms. The bias voltage across the platinum electrodes was varied between 15 and 300 V by a Fluke 415 B High Voltage Power Supply. The pre-amplifier signal was processed by a PAR 162 Boxcar integrator and displayed on either a digital voltmeter or an X–Y recorder.

In addition to the MPI spectra, TPEF spectra were also taken by observing the total NO fluorescence as a function of dye laser frequency. For these experiments the beam was first transmitted through a TPEF cell, then focussed into the MPI cell and both spectra recorded simultaneously.

Ar (H.P., 99.995%, Matheson Gas Products) and He (H.P., 99.995% MGP) were used directly from their cylinders. CH₃Cl (99.5%, MGP) was degassed before use and NO (C.P. 99.0%, MGP) cleaned of NO₂ impurities by passing the gas through a methyl cyclohexane slush bath before condensation at liquid N₂ temperatures. After three such distillations the NO solid was absent of any color. All samples were mixed in 1 liter bulbs equipped with greaseless stopcocks prior to use. Pressures were determined with capacitance manometers (MKS, Inc.) having 1, 10 or 100 Torr full scale.

Results

MPI and TPEF spectra of NO were obtained for the following intermediate levels: A²Σ(v=0–3), C²Π(v=0, 1), and D²Σ(v=0, 1). In this paper we confine our attention to the C²Π(v=0) intermediate state. A simultaneous recording of the MPI and TPEF spectra is presented in Fig. 1. The signal to noise ratios in these spectra are of comparable magnitude, but the superior sensitivity of MPI is reflected by the fact that the pressure used was smaller by a factor of 100. We were not able to record the TPEF spectrum from the B²Π state, apparently due to unfavorable Franck-Condon factors. The MPI spectrum of the B²Π(v=9) intermediate level, however, was easily obtained. The line frequencies shown at the bottom of Fig. 1 were calculated using the constants from [11] and assuming that the intermediate C²Π(v=0) could be treated as a ²Σ state [12]. Figure 1 shows that the MPI and TPEF excitation are almost identical in both peak position and relative peak intensities. Both spectra can be readily assigned to the C²Π intermediate spectrum. The close similarity between MPI and TPEF spectra is not always the case as reported elsewhere for several A state transitions [13]. One notable difference between the C²Π spectra shown in Fig. 1 is the P₂₂ + Q₁₃ band head in the C²Π → X²Π₃/₂ at 3828.1 Å which appears weaker in the MPI spectrum relative to TPEF.

The signal intensity was measured as a function of NO pressure (0.005–2 Torr) at the peaks indicated by 1 and 2 in Fig. 1. The signal was found to increase linearly with pressure for bias voltage below 100 V. At higher bias voltage, and particularly when NO pressure exceeded 100 mTorr, the signal intensity increased more rapidly than the NO pressure.

A similar effect was found when a foreign gas was added, keeping the NO pressure constant. Figure 2 shows the effect of added Ar at three bias voltages. When a small bias voltage was used (15–50 V) the signal intensity and temporal characteristics did not change significantly up to 2 Torr Ar. Beyond this pressure the signal began to broaden in time, until at 7 Torr it was indistinguishable from the background. As Fig. 2 shows, the signal intensity increased with Ar pressure up to about 0.6 Torr. The enhancement is strongly dependent on the bias voltage, but P_{max} the pressure at which this maximum is obtained, is not. Further increase of pressure leads to gradual decrease in signal intensity (note the logarithmic pressure scale!), until about 600 Torr when the initial intensity is reached. Although it was not nearly as serious as in