

Measurements of Photoabsorption Cross Sections of Nitric Oxide by Using Double-Ionization Chamber

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A synchrotron light source is useful in the vacuum ultraviolet (VUV) regime for molecular spectroscopy, such as photoabsorption, photoionization, and dissociative photoionization. In this research, we used a double-ion chamber (DIC) to measure photoabsorption cross sections of a NO molecule in the wavelength range from 90 to 135 nm of 3B1 beam-line of the Pohang synchrotron light source with the resolution of the monochromator being 0.06 nm. The appearance wavelength for ionization was measured to be 134.19 ± 0.09 nm that is placed in the middle of the reported values though they don't agree with each other within the relative error limits. The auxiliary experimental works have been done to test if there are any systematic error sources. The resultant cross-sections agree with previous results in general.

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I. INTRODUCTION

Although experimental studies of molecular total photoabsorption and photoionization cross sections in the vacuum ultraviolet (VUV) and soft X-ray regions have progressed steadily since the early 1950s, quantitatively reliable absolute photoionization and photo-dissociation cross sections have been achieved with techniques based on synchrotron radiation [1]. These enable studies of molecular spectroscopy in the VUV region with a continuous range of incident photon energy [2-3]. Another widely employed experimental approach is low-resolution dipole (e, e) spectroscopy that uses fast electrons as a virtual photon source [4]. These real- and virtual-photon experiments are complementary to each other when it comes to understanding the essential features of the interaction of VUV photons with molecules.

The traditional method used to measure the absorption of radiations to monitor the intensities I_0 and I of the radiation incident upon and transmitted by a gas cell of length L . The absorption cross section σ is then given by

$$\sigma = \frac{1}{nL} \ln \frac{I_0}{I}, \quad (1)$$

where n is the number density of the gas. Although L can be measured with high precision, the accuracy of the ratio I_0/I depends on the accuracy of the picoammeter used to measure the light intensity. The number density of the gas can be measured to an accuracy of approximately 1-2% by use of a capacitance manometer. However, other sources of error can exist, such as the use of a windowless absorption cell that is commonly used in VUV, detection of the stray fluorescence light, and the time lag between measurements of I_0 and I [5]. On the contrary, the double-ion chamber (DIC) simulates a windowed cell, because the product ions relate only to the radiation absorbed within the ion chamber. The time lag problem is naturally removed because there is no need to evacuate the gas cell to measure I_0 . The other merit of using the DIC is that the currents are read directly from electrodes while the photon-flux-measurement method needs a photodiode that needs to be tested and calibrated for the linearity in its dynamic range.

NO plays an essential role in the physics and chemistry of the earth's upper atmospheres [6] and is closely related to pollution problems. The dissociative recombination processes of NO, where Rydberg states are directly involved, are relevant, for example, in the E and F regions of the ionosphere [7]. NO^+ is one of the most abundant molecular ions in the ionosphere,

and the hot oxygen thus produced in the photodissociation of NO contributes to the maintenance of the nighttime ionosphere [8]. In addition to their intrinsic spectroscopic interest, the quantitative aspects of the interaction of NO with UV and soft X-ray radiation are of practical importance in several other contexts. Furthermore, the fact that the ground state of NO exhibits an open-shell electron configuration with symmetry other than Σ , represents a formidable challenge to theorists in the accurate calculation of partial photoionization oscillator strengths [9].

In the present paper we present the measurements of the absorption cross sections of NO with relatively small error by use of a windowless double-ion chamber. We studied the effects of the bias voltage on the apparent cross sections, and discussed the optimum experimental parameters. Also, the appearance wavelength for ionization is measured and compared with other experimental results.

II. EXPERIMENT

The present measurements were performed at the Pohang synchrotron Accelerator Laboratory beamline 3B1. The light was monochromatized by using a

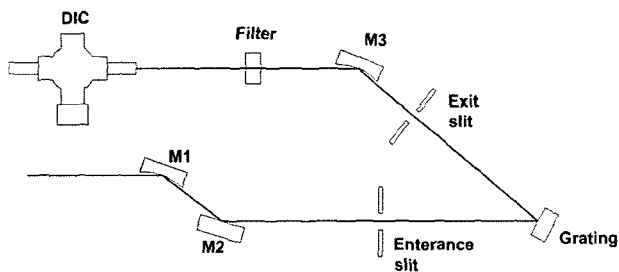


FIG. 1. A schematic diagram of the beam path (not scaled). DIC is the double-ion chamber, and M1, 2, 3 are mirrors.

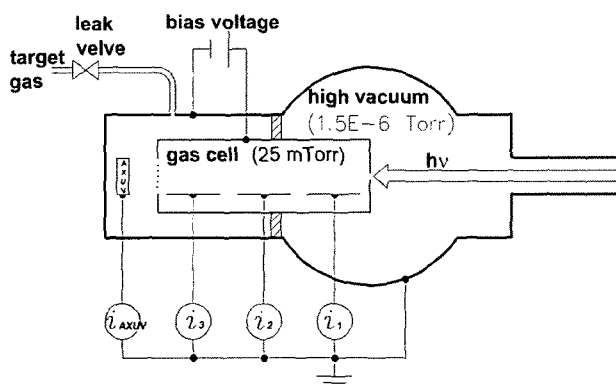


FIG. 2. A schematic diagram of the double-ion chamber (not scaled).

three-meter normal incidence monochromator with a 1200 lines/mm silicon carbide grating. The schematic diagram of the beam path is shown in the Fig. 1. The beam was focused and directed by a toroidal (M1) and a flat (M2) mirrors before it entered the monochromator, and focused with a toroidal mirror (M3) was used to focus the beam to the DIC after the exit slit of the monochromator. The DIC was filled with about 25 mTorr of the target gas whose pressures were measured using an MKS capacitance manometer. The inlet of DIC is 1 mm diameter aperture which is the entrance of the photon beam. The chamber connected to the DIC was differentially pumped by a 2000 l/s turbomolecular pump that kept the pressure at low 10^{-6} Torr. The pressure of the upstream right before the differential pumping chamber was kept at mid 10^{-9} Torr or better. The whole chamber was baked at 80°C for 10 hours before introducing NO gas to minimize the outgas from the surfaces. The purity of NO was 99.5%. The schematic diagram of the DIC is shown in the Fig. 2. It consists of stainless cylinder 4.75 cm in diameter and 53.25 cm in an internal length which is divided into three sections by three electrodes that are 1.8 cm off center from the cylinder and 0.6 cm in diameter. Each electrode is separated by 0.1 cm. The ion collector electrodes are maintained at ground potential through their respective picoammeters. The currents to the electrodes are labeled i_1, i_2, i_3 in order from the upstream. The third current was not crucial for determining the cross section, but used as a reference data. The ion chamber cylinder and ends are held at a positive bias potential. This arrangement gives a symmetrical distribution of the equipotential lines within the DIC, which push the ions to the proper collector electrodes. The ends of electrode 2 have parallel equipotential lines because of the large length-to-diameter ratio of the ion chamber cylinder. The ion chamber is terminated with a 95% transparent electroformed mesh. A silicon photodiode (denoted as AXUV in the Fig. 2) is placed about 10 cm behind the end of the ion chamber for monitoring the beam intensity.

The principle of the DIC uses the Lambert-Beer Law [10]. Photons are allowed to pass through the ion chamber consisting of the ion repeller electrode and two ion collector electrodes of known length. The photon is absorbed by sample gas, thus decays exponentially, as shown by Eq. (1). Ions are produced along its path if the photon has higher energy than ionization potential. The amount of ions is proportional to the intensity of radiation at the position. When both ion collector electrodes are of equal length, and provided that each electrode collects all the ions directly above it, the total absorption cross section of the gas is given by the relation

$$\sigma = \frac{1}{nL} \ln \frac{i_1}{i_2}, \quad (2)$$

where i_1 and i_2 are the actual currents flowing from the ion collector plates. Eq. (2) shows that the photon intensity does not need to be measured, which is one of the merits of this technique.

Two of the most important experimental parameters are the sample pressure and the bias potential. The pressure changes the ratio i_1/i_2 according to the absorption cross section, but i_2 should not be too small in practice because the error gets dramatically large in the ratio when the current gets below 10^{-14} A. The appropriate i_1/i_2 ratio was found to be in between 2 to 10 for reliable results. The corresponding pressure was about 25 mTorr for NO. The variation of the ion currents i_1 and i_2 with the bias voltage was checked to ensure that the potential was sufficiently large to prevent energetic photoelectrons from reaching the ion collectors. Also, Coulomb explosion results in production of energetic ions that can move to the ion chamber wall instead of being collected at electrodes. Fig. 3 shows the graph of the ion current to the first electrode and the apparent cross section in function of the bias potential. It shows that the apparent cross section and the ion current substantially decrease as the bias voltage gets lower than 5 V. This means that the energetic photoelectrons and photoions due to Coulomb explosions overcome the bias potential and are collected to a nearby electrode. An interesting fact is that the apparent cross section decreases only about 9% while the ion current decreases about 61% at 2 V from their saturated values. The saturation voltage is about 5 V for the cross section; however, it is about 15 V for the ion current. This suggests that insufficient bias voltage

still results in “right” ratio of ion currents by losing the same ratios of the currents in each electrode. The photoions or the photoelectrons can ionize the residual gas during they move to the electrodes or the chamber wall if the bias potential is too large. Fig. 3 shows that such a process does not happen up to 40 V of bias voltage. We used 25 V for the bias voltage.

III. RESULTS AND DISCUSSIONS

1. Photoabsorption cross sections.

The measured photoabsorption cross sections of NO are shown in Fig. 4. The error bar represents 90% of the confidence limit. Experimental data of Iida *et al.* [11] are compared in the graph. The general trend of data agrees fairly though the compared data lack the error limit. The relatively large error bar is due to the sharp change of the cross section around the data point. The ionization threshold wavelength is denoted as Th_{ion} where the currents quickly decrease as the wavelength increases, so the error bars are large in the vicinity of the threshold. Measurement of photoabsorption cross sections below ionization energy is impossible with the DIC.

2. Appearance wavelength.

The photoion spectrum is shown in Fig. 5 in the range 120 to 135 nm. The label denoted in the figure is according to Erman *et al.* [12]. It shows a step function behavior at $X^1\Sigma^+ v'=0$ to 3 indicating direct ionization processes. The Rydberg series R ($X^1\Sigma^+$) converging to upper vibrational levels $v'=1$ to 4 of the

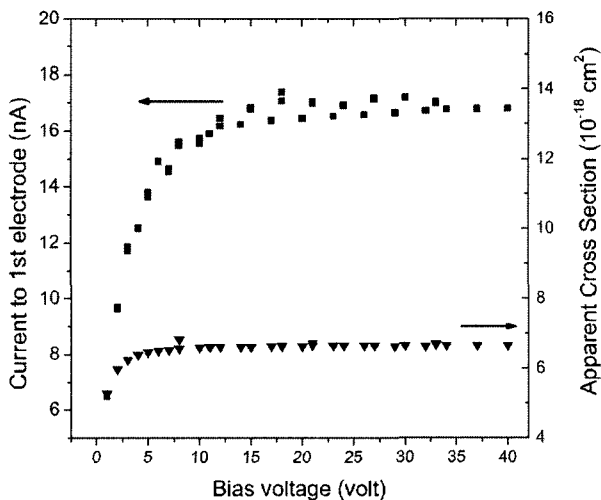


FIG. 3. Current to the first electrode and apparent cross section in function of the bias potential.

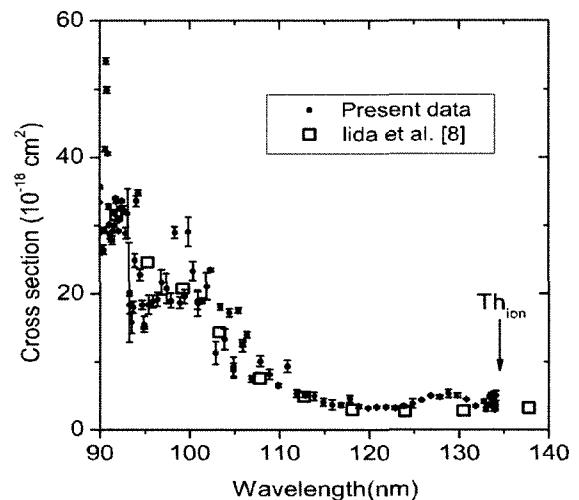


FIG. 4. Absolute photoabsorption cross section of nitric oxide.

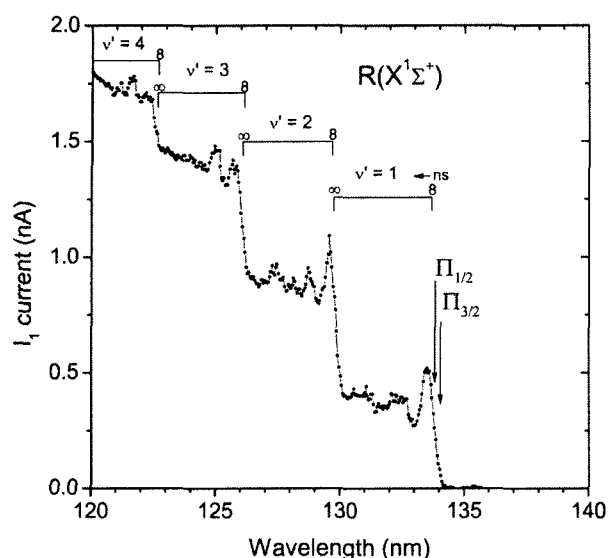


FIG. 5. Photoion current in the first electrode.

TABLE 1. Appearance wavelength for ionization of NO.

	Wavelength (nm)
Present work	134.19±0.09
Reiser <i>et al.</i> [13]	133.8284±0.0007
Sander <i>et al.</i> [14]	133.8332±0.0009
Muller-Dethlefs <i>et al.</i> [15]	133.8363
Ebata <i>et al.</i> [16]	133.8295±0.0029
Fantoni <i>et al.</i> [17]	134.33
Kimura <i>et al.</i> [18]	129.96

NO⁺ ground state are superimposed on this direct ionization continuum. The observed autoionization peaks are associated with a number of Rydberg levels (ns, np σ , np π , nd σ , nd π , nd δ , and nf) converging to NO⁺ (X¹ Σ^+). This yields a very complicated line structure where only the ns series are denoted for comparison. Table I compares the present appearance wavelength and the other experimental works [13-18]. We found the appearance wavelength for ionization to be 134.19±0.09 nm by extrapolation of the linearly decreasing section near threshold. The quoted data in the table 1 do not agree each other within the error limits. The values are scattered in between 129.96 and 134.33 nm. Our measurement is included in this range.

In summary, absolute cross sections for photoabsorption of NO have been measured using the DIC technique in the range of 90 to 135 nm. The appearance wavelength is found to be 134.19±0.09 nm that is one of the mid values among many other measurements.

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