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Photoproduction of $N_2{}^{2+}$ from threshold to 400 eV

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We have measured the relative probability for the production of $N_2{}^{2+}$ using monochromatized synchrotron radiation in the range of 38 to 400 eV. We find the energy dependence of the ratio $N_2{}^{2+}/N_2{}^{+}$ to be very similar to that of the He^{2+}/He^{+} ratio, which indicates a similarity in the double-photoionization mechanism. This may allow us to predict the relative dication production for other simple molecules, such as O_2, without the need to measure an extended photon-energy range. We obtain a threshold for the production of $N_2{}^{2+}$ ions of 42.97(10) eV.

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I. INTRODUCTION

The photon-energy dependence of the simultaneous removal of two electrons from an atom by a single photon has been studied for several cases such as helium [1,2], lithium [3,4], beryllium [5], sodium and potassium [6], and magnesium [7]. It was found that the energy dependence of the relative double-photoionization cross section, i.e., the yield of doubly charged ions relative to the yield of singly charged ions, is very similar for different atoms [6] if the energy and the ratio of doubly to singly charged ions is scaled by suitable constants [8]. This similarity in the photon-energy dependence indicates a common double-photoionization mechanism, namely the knock-out mechanism that has been discussed in the literature [9–11]. Other atoms, in particular noble gases, have also been studied. However, not far from the first double-ionization threshold, usually more double-ionization thresholds exist due to different spin-orbit couplings of the double-hole state, so that in ion measurements different processes contribute to the creation of doubly charged ions. Thus, a clear, unambiguous photon-energy dependence of the double-to-single photoionization ratio for a single process cannot be observed in many cases. A more detailed discussion can be found in Ref. [12].

Recent investigations on large molecules, such as benzene, revealed double-photoionization mechanisms that do not exist in atoms [13,14] and are still under investigation. In this paper we address the question of whether a small molecule such as N_2 behaves in this respect simply like an atom or exhibits any as of yet unknown features unique to molecules. Here, molecular nitrogen not only serves as a test sample for the photon-energy dependence of the ratio of doubly to singly charged ions but also is a molecule of high interest in the astrophysics community [15]. The nitrogen molecule is abundant in our atmosphere but also exists in the upper atmospheres of Titan [16,17] and of some other planets and moons. The doubly charged nitrogen molecule, $N_2{}^{2+}$, present in the ionospheres of these and other astrophysical objects [18] is of high interest for modeling the corresponding atmosphere and for interpreting satellite-based measurements. A review of the importance of doubly charged ions in planetary ionospheres can be found in Ref. [19].

Several experiments have been performed using electron-impact ionization of N_2 with the goal of providing data to model planetary atmospheres. However, the mass-to-charge ratios of N^+ and $N_2{}^{2+}$ are the same and cannot be separated easily with an ion time-of-flight spectrometer. Therefore, Hałas and Adamczyk [20] used the isotopically enriched $^{14}N^{15}N$ molecule to determine the relative cross sections for $N_2{}^{2+}$, N^+, and $N_2{}^{+}$. Using the same molecule, Märk [21] determined the absolute single- and double-ionization cross sections by electron impact as well as the double-ionization threshold. The experiment by Krishnakumar and Srivastava [22] used naturally occurring N_2 and, thus, did not separate N^+ and $N_2{}^{2+}$ ions in their cross-sectional measurements. Also, Straub *et al.* [23] did not separate these ions in their absolute cross-sectional measurements, although they had used a position-sensitive detector with a time-of-flight spectrometer. The fragment ions were not fully separated from the doubly charged parent ions, although the fragment ions have an initial moment, in contrast to the parent ions, and, therefore, will hit the detector at a different position.

Also, photoionization data are needed for modeling planetary atmospheres, but only a few such experiments have been carried out. Fluorescence after photoionization has been observed for $N_2{}^{2+}$ although it is a weak process [24,25], and Ehresmann [26] made an estimate for the double-photoionization cross section from the fluorescence experiment for the photoexcitation energy range of 50–66.5 eV. It is worthwhile to mention an Auger-electron-ion coincidence study around the N *K* edge, in which the lowest $N_2{}^{2+}$ state populated by Auger decay appears at 43.2 eV [27]. More recently, an analysis of the fragmentation dynamics of $N_2{}^{2+}$ ions using electron-electron coincidence measurements has been published for the 42.5- to 54-eV energy range [28].

Modeling of planetary atmospheres is based on equations that accurately describe the production and loss of ions, for which electron-impact and photoabsorption data are needed [17,18,29,30]. Here we present a photoionization study with the goal to measure the production of $N_2{}^{2+}$ ions relative to $N_2{}^{+}$ ions. Only preliminary measurements of that ratio separating the N^+ ions from the $N_2{}^{2+}$ ions based on their initial velocity in the interaction region have been presented in Ref. [12].

II. EXPERIMENT

Two different beamlines at the Synchrotron Radiation Center (SRC) in Stoughton, WI (USA), have been used in this investigation. The experiments were performed on the 6-m toroidal-grating monochromator (6m-TGM) beamline [31]

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with a bending-magnet source for photon energies from 17 to 170 eV and the varied line-spacing plane-grating monochromator (VLS-PGM) beamline with an undulator source [32] for energies from 150 to 400 eV. On the 6m-TGM beamline we employed an Al filter (36–71 eV), an Si_3N_4 filter (71–100 eV), and a C filter (150–170 eV) to suppress higher-order and stray light. On the VLS-PGM beamline we employed a C filter (150–275 eV) and a Ti filter (280–400 eV). The photon energy was calibrated using well-known resonances in Ar, Ne, Kr, and Xe. Knowledge of precise photon energies is not critical in this experiment. The overall accuracy is better than 0.1 eV for the energy range investigated here.

We adjusted the entrance and exit slits of the monochromator so that the total count rate was less than 2500 Hz and, thus, dead time of the detection electronics was not an issue. They were set as narrow as reasonably possible to avoid scattered light (in addition to using filters). The energy resolution was low but sufficient for this investigation.

The experimental setup has been described before [33]. Briefly, monochromatic photons entered through a differential pumping stage into the interaction region inside the vacuum chamber where the beam crossed an effusive beam of nitrogen molecules. A pulsed electric field accelerated the photoions and photofragments towards a drift tube with a Z stack of microchannel plates at its end. The pulse period of the extraction voltage was 0.1 ms so that only long-lived metastable ions, that have a lifetime of at least about 50 μs, or fully stable ions were detected. The flight times for the N_2^+ and N_2^{2+} ions were 3.34 and 2.36 μs, respectively, but the limiting factor for detecting metastable ions was the rather long pulse period. The N_2^{2+} ions are expected to have a lifetime of about 3 s [21].

We have detected N_2^+, N^+, N_2^{2+}, and, at higher photon energies, also Ar^{2+} and Ar^{3+} ions as can be seen in Fig. 1. The Ar ion signal became only noticeable above the Ar L shell. No other ions, such as C^+ or O^+, were detected. This is important as the CO molecule has the same mass as the N_2 molecule and could not be separated if present. Figure 1 shows ion time-of-flight spectra taken above and below the Ar $L_{2,3}$-edge. The Ar^{3+} peak is near the N_2^{2+} peak but still well separated. Although outside the range of Fig. 1 we note here that we did not detect any N^{2+} ions in contrast to observations in Ref. [34]. This could be explained by the insensitivity of our spectrometer to fast ions due to its small entrance aperture and long pulse period of the extracting electric field.

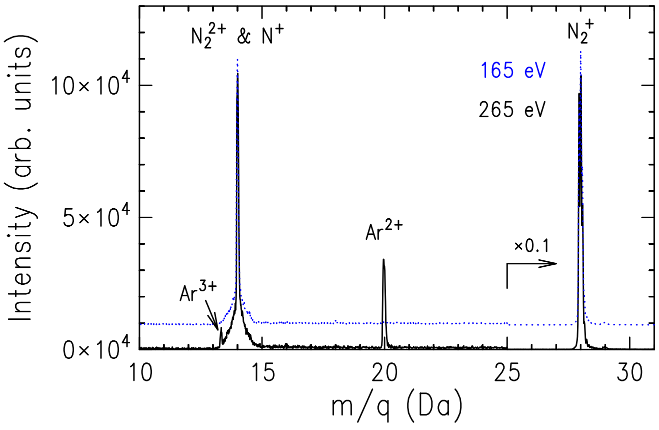

FIG. 1. (Color online) Ion time-of-flight spectra taken at 165 eV (dotted line) and 265 eV (solid line). The baseline of the 165-eV spectrum is offset for easier comparison.

During the experiment on the 6m-TGM beamline the chamber's base pressure was in the low 10^{-9} mbar range with a sample pressure of 2×10^{-7} mbar. On the VLS-PGM beamline the base pressure was in the low 10^{-8} mbar while the sample pressure was about 1.3×10^{-6} mbar.

III. DATA ANALYSIS

We extracted the areas of the N_2^+ peaks in our ion time-of-flight spectra using direct numerical integration. The region of the doubly charged ions around 14 Da shows two different peaks: one broad peak and one narrow peak. Usually, a time-of-flight spectrometer and its electrical potentials are designed such that an ion created in the interaction region with no momentum yields a narrow, focused peak in the spectrum. This is practically the case for the N_2^{2+} peak that gets broadened only by the thermal motion of the nitrogen molecule and by the emission of the two electrons. The broad peak, on the other hand, is caused by the $N^+ + N^+$ dissociation process in which the two fragments have an initial momentum due to their mutual Coulomb repulsion and, thus, are not properly focused by the electric fields of the time-of-flight spectrometer, resulting in a broad peak. In addition, the partially neutral dissociation after photoionization, $N^+ + N$, is also possible [35] and will result in a broad background as well.

The double-ionization region in the time-of-flight spectra was fitted with two Voigt profiles, one broad peak and one narrow peak, at the higher photon energies as shown in Fig. 2(a). We note that the data as well as the fit curves displayed in Fig. 2 were converted from the original time scale to a mass-to-charge scale. The Voigt profile, a convolution of a Gaussian with a Lorentzian profile, was chosen because it is a flexible profile that can accommodate a variety of peak shapes. Note that the shape of the broad dissociation peak is not known and depends on the dissociation dynamic and the detection efficiency of the spectrometer for fast ions. Since the spectrometer is optimized for thermal ions, not all fast ions will reach the detector and the faster ions will be lost. Therefore, in this investigation the broad peak is regarded just as background of the N_2^{2+} peak, which we want to investigate in this paper. At lower photon energies the broad peak exhibits a somewhat structured profile [cf. Fig. 2(b)], most likely due to the angular distribution of the dissociation process. The two N^+ ions seem to have a nonisotropic angular distribution with respect to the polarization vector of the synchrotron light. In order to get a reliable background subtraction for the N_2^{2+} peak, we added four more peaks to the broad peak to model the dissociation peak for the lower photon energies. For all fits, the widths of the N_2^{2+} peak were kept fixed to obtain a reliable result.

Finally, we divided the area of the N_2^{2+} peak by the area of the N_2^+ peak for each photon energy and corrected the photon energy according to our energy calibration.

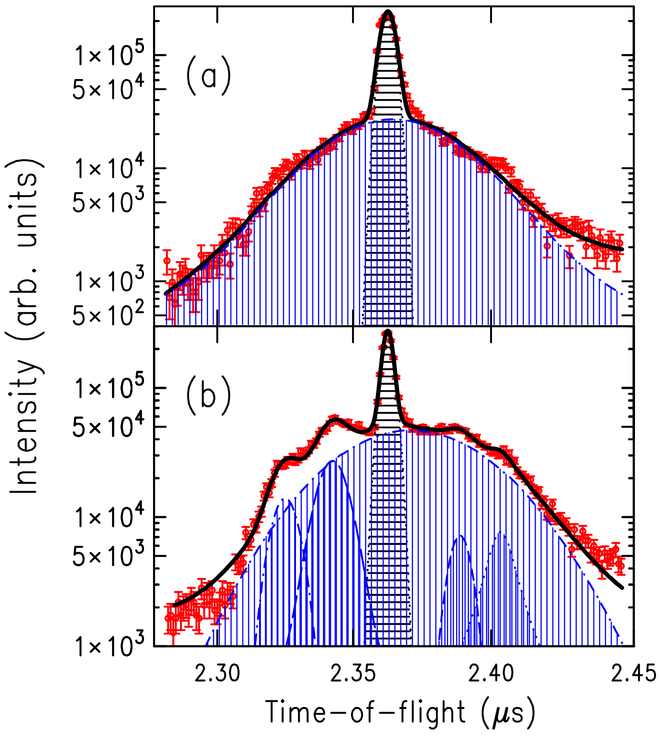

FIG. 2. (Color online) Ion time-of-flight spectra taken at (a) 165 eV and (b) 46 eV in the region of doubly ionized nitrogen molecules displayed on a log scale. The solid lines are the fit curves to the corresponding spectra. The horizontally shaded areas are the peaks created by the N_2^{2+} ions; the vertically shaded areas are fit curves that model the so-called background of the N_2^{2+} peak due to the $N^+ + N^+$ and $N^+ + N$ dissociations. Note that the individual fit curves do not include a common constant background.

IV. RESULTS AND DISCUSSION

Figure 3 shows the ion yield of doubly charged nitrogen molecules relative to the singly charged molecular ions as a function of photon energy from threshold up to the first nitrogen inner-shell excitation, above which sequential double ionization dominates. Unfortunately, above the carbon *K* edge, where we have changed the monochromator's grating and switched from carbon filters to a titanium filter, the ratio is consistently too high, possibly due to higher orders of the grating and/or a pin hole in the Ti filter. By multiplying those affected ratios with a factor of 0.68 we obtain a smooth transition from the ratios below the carbon edge to above the carbon edge. Near the N_2 $1\sigma \rightarrow \pi^*$ resonance at 401.1 eV the ratio steeply rises due to the dominance of sequential processes. Even a tiny contribution of second-order light will affect the ratio below 400 eV, as we indeed can see.

Previous, exploratory measurements performed with the same apparatus (cf. Fig. 3) show results consistent with our new measurements. However, the older measurements exhibit a larger scatter and were taken only below 180 eV. No other such photoionization ratios are available to our knowledge. However, one can derive the double-to-total photoionization ratio for molecular nitrogen from the data of Hellner *et al.* [36] and Cole and Dexter [37]. We divided the relative number of N_2^{2+} ions, normalized at 59 eV to 0.2 Mb [36], by the photoabsorption cross section [37]. The resulting double-to-total photoionization ratio, shown in Fig. 3 as a thin solid line, is slightly higher than our values. Although one would expect a slightly lower rather than higher ratio, the overall agreement is fair, considering the different (imperfect) methods used to derive that ratio. However, its photon-energy dependence is clearly different from our results.

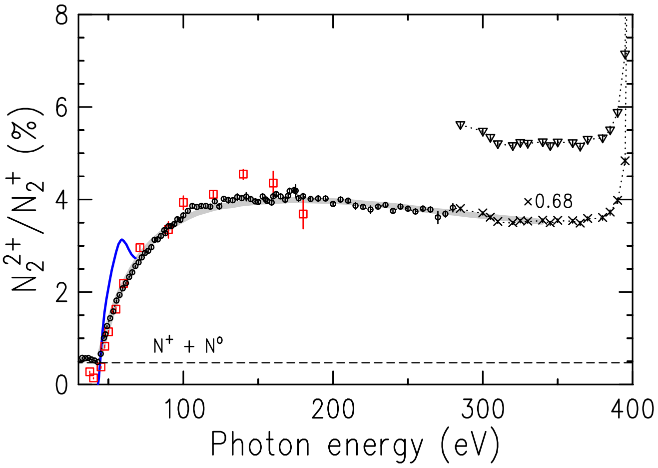

FIG. 3. (Color online) Ratio of doubly to singly charged N_2 ions as a function of photon energy (open circles). The measured ratios above the carbon *K* edge (triangles) were multiplied by 0.68 (crosses) to match the ratios below that edge (see text for details). Previously published data are shown as open squares [12]. The thin solid curve was derived from data of Hellner *et al.* [36] and Cole and Dexter [37] and represents the double-to-total photoionization ratio. The thick gray line is a fit of the helium double-to-single photoionization ratio curve [1] to the nitrogen ratio data.

Below the double-ionization threshold we notice that the ratio values do not go down to zero but stay almost flat at a ratio value of 0.47%. There is no indication that this offset is due to second-order light, but it is possible that the offset is due to a $N^+ + N^o$ dissociation in which we have a singly charged and a neutral fragment. Also autoionization of N_2^{+*} states can occur below the double-ionization threshold, leading to N^+ ions. Low-energetic N^+ fragment ions will appear in the spectrum at the same position as a N_2^{2+} ions. In order to compare the photon-energy dependence of the N_2^{2+}/N_2^+ ratio with the one for helium, we fitted the He^{2+}/He^+ ratio curve [1] to our data, shown as a thick gray curve in Fig. 3.

Here, the helium ratio (starting at zero excess energy) was scaled in energy; i.e., the energy was multiplied by 1.179 and then an energy offset of 42.97 eV was added in order to compare the He with the nitrogen data, which are plotted on a photon-energy scale in Fig. 3. The values for the He ratio [1] were multiplied by 0.936, and a constant offset of 0.47% (indicated as a dashed line in Fig. 3) was added due to the apparent offset in the data as mentioned above. The scaling values 1.179 and 0.936 and the energy offset 42.97 eV were determined in a least-squares fit to our nitrogen data. The resulting fit curve matches the nitrogen ratio very well, indicating that the double-photoionization process in molecular nitrogen is similar to the one in atoms, i.e., it is based on an internal collision in which the photoionized electron knocks out a second electron [38]. In contrast to more complex molecules such as benzene [39], we do not see any deviation from the helium-like behavior. In other words, we do not see any molecular effect in the ratio. As one would expect from Wannier theory [40], the relative double-ionization cross section of N_2 by electron impact rises (approximately) quadratic with excess energy near threshold [41]. Märk [21] plotted the square root of the relative cross section as a function of energy and determined the double-ionization threshold by linear extrapolation as 42.9(3) eV. Correspondingly, we expect an (approximately) linear increase of the relative double-photoionization cross section of N_2 when using photon impact. Indeed, our ratio values follow the helium ratio curve down to threshold. We note that the precise slope corresponds to an $E_{\mathrm{exc}}^{1.056}$ power law [40,42]. The excess energy E_{exc} is defined as the energy above the double-ionization threshold of the molecule. From the fit of the helium ratio curve to our nitrogen data, we obtain a double-ionization threshold of 42.97(10) eV, in excellent agreement with Märk's value [21]. It also agrees well with the adiabatic threshold of double ionization of 43.004 eV [28]. Our threshold is also consistent with the finding that the lowest energy state of ${N_2}^{2+}$ populated by Auger decay is at 43.2 eV [27].

V. SUMMARY

We have measured the ratio of doubly to singly charged N_2 ions from threshold to 400 eV and find a clear similarity in the photon-energy dependence to the corresponding ratio of helium. This indicates that, as is the case for helium and other atoms, the double-photoionization mechanism can be explained by the knock-out model. No indication for a molecular mechanism has been observed for N_2, in contrast to measurements on aromatic hydrocarbons. We obtain a double-ionization threshold of 42.97(10) eV, in agreement with previous values. The threshold region can be described by the Wannier power law with an exponent of 1.11(11) up to a photon energy of 48 eV (or about 5 eV excess energy).

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