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Ion-ion coincidence studies on multiple ionizations of N₂ and O₂ molecules irradiated by extreme ultraviolet free-electron laser pulses

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We have investigated multiple ionization of N₂ and O₂ molecules by 52 nm extreme-ultraviolet light pulses at the free-electron laser facility SCSS in Japan. Coulomb break-up of parent ions with charge states up to 5+ is found by the ion-ion coincidence technique. The charge-state dependence of kinetic energy release distributions suggests that the electrons are emitted sequentially in competition with the elongation of the bond length. © 2010 American Institute of Physics.

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I. INTRODUCTION

A free-electron laser (FEL) based on self-amplified spontaneous-emission (SASE) in the extreme ultraviolet (EUV) region below $\lambda=100$ nm was first developed in Germany and has proven to be a very powerful tool to explore the interaction of strong EUV laser pulses with molecules.¹⁻³

In May 2008, a new facility, the SPring-8 Compact SASE Source (SCSS) test accelerator in Japan started operation for users.⁴ It provides linearly polarized EUV-FEL pulses (~ 30 μ J per pulse, ~ 100 fs pulse width, and 10–20 Hz repetition rate) in the wavelength region 50–62 nm. In this energy regime, all atoms and molecules can be ionized by just a single photon with huge photoionization cross sections. The first evidence of multiphoton multiple ionization of N₂ by EUV pulses from the SCSS test accelerator was reported by Sato *et al.*⁵ Recently, we have demonstrated that this source is ideal to investigate molecular ionic excited states that are accessible only by sequential EUV photon absorption by the molecules,⁶ by means of ion momentum spectroscopy using a multiparticle detection system.⁷ In the work, dissociative ionization pathways leading into N⁺(O⁺) and N²⁺(O²⁺) ions, and N⁺–N⁺ (O⁺–O⁺) ion-pair formations from the N₂(O₂) molecule were discussed.

In the present work, as an extension of our previous study, we have investigated multiple ionization of N₂ and O₂ molecules caused by multiphoton absorption of the EUV-FEL pulses at 52 nm (photon energy of 24 eV) with standard

deviation of the wavelength fluctuation of ~ 0.5 nm from this light source, by means of photoion-photoion coincidence spectroscopy, using the same detection system in our previous studies.^{6,7} The photon energy employed in the present experiment was set to be in between single and double ionization thresholds of N₂ and O₂, with twice the photon energy being above the double ionization thresholds. Thus, N₂ and O₂ are singly ionized by single-photon absorption, and ionized N₂ and O₂ can be further ionized or excited by absorption of additional photons. Using tightly focused intense FEL pulses, photoabsorption processes can occur several times within a single FEL pulse. Power densities of the focused FEL pulses in the present work are about one order higher than those in the previous study.⁶ Thus, we have found that highly charged parent molecular ions with charge states up to 5+ were produced.

II. EXPERIMENT

The experimental setup used here is almost the same as the one employed in Refs. 6 and 8. The time-of-flight axis of the ion momentum spectrometer is vertical, whereas the supersonic molecular beam is horizontal and crosses the horizontal FEL beam at 45°. The FEL beam is partially blocked by a 1.5 mm wide horizontal beam stopper before the target so that the nonfocused beam does not irradiate the molecular beam directly. The FEL beam is reflected and focused onto the molecular beam by a multilayer focusing mirror fabricated at Lawrence Berkeley National Laboratory, identical to the one employed in Ref. 8. The reflectivity of the mirror at 24 eV was estimated to be $\sim 40\%$. Using electrostatic fields,

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FIG. 1. PIPICO map for N_2 and O_2 irradiated by 24 eV FEL pulses.

ions are projected onto a microchannel plate (MCP) read out by a three-layer type delay-line anode (Roentdek HEX120).⁹ The design of the ion spectrometer is similar to the one described in Refs. 10 and 11. All signals (six from the delay-line anode plus the direct signals from the MCP) are fed to an eight-channel digitizer (Acqiris DC282 $\times 2$) and software CFD (constant fraction discriminator) is employed for extracting the timing signals.⁷ In this way, we minimize the deadtime of our detection system as described previously.⁷

The signal from a gas monitor detector is also fed to the digitizer, as a measure of the laser power for each individual FEL shot during the experiments. Very recently, this device was absolutely calibrated using a cryogenic radiometer in a separate measurement.^{12,13} In the present work, however, the signals give us only relative intensities of the respective FEL pulse because the experiment was performed before this calibration. Taking all the optical elements (steering and focusing mirrors, skimmers, etc.) between the radiation point and the ionization point into account, we estimate the pulse energy at the sample assuming the pulse energy of 30 μJ at the radiation point,⁴ and expect the power density at the focus spot on the molecular beam to be at most 10^{14} W/cm² at full power of the FEL, assuming the diffraction-limited spot size of 3 μm in diameter and the pulse width of 100 fs. We consider this number to be an upper limit and we estimate that the uncertainty may be a factor of four to ten, mostly due to the uncertainties of the spot size and the pulse width. The intensity of the FEL beam was adjusted using a gas attenuator, i.e., an absorption cell filled with Ar gas.

Under the present experimental conditions, event rates for ionization of the target molecule are more than one per shot. Therefore, we use the momentum conservation law to identify ion pairs emitted from single molecules.

III. RESULTS AND DISCUSSION

Figure 1 shows the photoion-photoion coincidence (PIPICO) maps for N_2 and O_2 irradiated by 24 eV FEL pulses. In this figure, ion pairs satisfying the momentum conserva-

FIG. 2. KER distributions for ion-pair formations from O_2 irradiated by 24 eV FEL pulses. Circles: high laser power (10^{14} W/cm² at most). Triangles: low laser power (10^{13} W/cm² at most).

tion law only for a plane perpendicular to the time-of-flight axis are shown. One can clearly see the correlation lines due to N^+-N^+ , N^+-N^{2+} , N^+-N^{3+} , $N^{2+}-N^{2+}$, and $N^{2+}-N^{3+}$ from N_2 , and O^+-O^+ , O^+-O^{2+} , O^+-O^{3+} , $O^{2+}-O^{2+}$, and $O^{2+}-O^{3+}$ from O_2 . Bright spots appeared in the PIPICO map of O_2 are due to false coincidences from combinations of two of CH_3^+ , O^+ , OH^+ , and H_2O^+ from residual gases. These spots were excluded in the kinetic energy analysis.

Figure 2 shows the kinetic energy release (KER) distributions for each of ion-pair formation channel of O_2 found in Fig. 1. The KER means sum of the kinetic energies of the two ions. O^+-O^+ and O^+-O^{2+} were observed at high laser power (10^{14} W/cm² at most) and low laser power (10^{13} W/cm² at most), whereas O^+-O^{3+} , $O^{2+}-O^{2+}$, and $O^{2+}-O^{3+}$ were observed only at high laser power. The horizontal axis indicates the KER divided by Q , where Q is the product of the charges of both ions. For the spectrometer setting in this work, we could collect all singly, doubly, and triply charged ions emitted into 4π sr with kinetic energies up to ~ 20 , ~ 40 , and ~ 60 eV, respectively. An axis on top of the figure indicates the internuclear distance at corresponding KER/ Q estimated by the Coulomb repulsion energy. A vertical broken line indicates the Coulomb repulsion energy at the equilibrium internuclear distance of neutral O_2 in the ground state, $R_0=1.2$ Å.

Let us discuss first O^+-O^+ ion-pair formation. Our result for the O^+-O^+ channel measured in low laser power is in good agreement in shape with those measured at a photon energy of 48.4 eV observed using He II light.¹⁴ This indicates that O^+-O^+ pairs in Fig. 2 are most likely released via the same dicationic states that were measured¹⁴ to lie between 41 and 48 eV within the Franck-Condon region. The lowest state of these O_2^{2+} states is $A^3\Sigma_u^+$. These levels cannot be reached in our case by sequential two-photon absorption via the $X^2\Pi_g$ state of O_2^+ , because the vertical ionization potential to this state is 12.307 eV,¹⁵ more than 24 eV below the measured dicationic states. By contrast, these dicationic

states can be reached from the $b^4\Sigma_g^-$ and $B^2\Sigma_g^-$ states because the vertical ionization potential to these states are 18.171 and 20.296 eV, respectively.¹⁵ Furthermore, partial photoionization cross sections of O_2 to the $b^4\Sigma_g^-$ and $B^2\Sigma_g^-$ states at 24 eV are in the same order of that of the $X^2\Pi_g$ state.¹⁶ In case the first step of the sequential photon absorption yields the excited states of O_2^+ such as the $b^4\Sigma_g^-$ and $B^2\Sigma_g^-$ states, O^+-O^+ can also be produced by sequential two-photon absorption. Although the vertical ionization potential to the $a^4\Pi_u$ state is 16.703 eV,¹⁵ it may be possible to reach the $A^3\Sigma_u^+$ state of O_2^+ due to fluctuation of the photon energy. In the case that first step yields lower states of O_2^+ , O^+-O^+ can also be produced by sequential three-photon absorption. O^+-O^+ ion-pair with KER above 16 eV can be produced more than three photon absorption because difference between twice of the photon energy and lowest dissociation limit of O^+-O^+ [32.351 eV (Refs. 19 and 20)] is lower than 16 eV. Different contributions of two- and three-photon processes manifest themselves in different shapes of the KER distributions at high and low laser powers. It should be noted, however, that we cannot exclude the possibility that the detector efficiency declined by a huge amount of O^+ detections may cause disturbance for the measurements of KER distributions at high laser power. An alternative pathway is fragmentation of highly excited ionic states into O^+ and O^* and subsequent atomic autoionization of the O^* species. These pathways are known to exist from the works of Bolognesi *et al.*¹⁷ and Feifel *et al.*,¹⁸ and they are readily opened up several eVs below the lowest O_2^+ vibrational state, $X^1\Sigma_g^+(\nu=0)$ at 36.13 eV:^{17,18} sequential two-photon absorption of 24 eV photon via the $X^2\Pi_g$ state of O^+ will suffice to create O^+-O^+ ion pairs in this way. However, KER from this process should be lower than ~ 4 eV because the lowest dissociation limit of O^+-O^+ is 32.351 eV.^{19,20} It seems that contributions from this processes would be small from the KER distribution in Fig. 2.

For $O^{2+}-O^{2+}$ and $O^{2+}-O^{3+}$ ion-pair formations, the KER distributions are peaked at values significantly below the Coulomb repulsion energy at R_0 . This indicates that the internuclear distance is elongated during multiple ionization processes. If multiple-ionization was caused by “direct” vertical multiphoton absorption processes, the internuclear distance would be equal to R_0 , leading to KER/Q as high as 12 eV, certainly not found in our result. Thus, the observed KER distributions clearly indicate that multiple ionization occurs via step-wise electron removal proceeding sequentially within the 100 fs pulse duration, i.e., via sequential multiphoton absorption.

Figure 3 shows simplified potential energy curves of multiply ionized O_2 dissociating into the lowest dissociation limits of the ion pairs observed in this study. In this figure, only the Coulomb repulsive potential is taken into account. The lowest dissociation limits are calculated using the dissociation energy of O_2 (Ref. 19) and the ionization energies of O, O^+ , and O^{2+} .²⁰ The length of each arrow indicates the photon energy, 24 eV. The position of each arrow, on the other hand, corresponds to the internuclear distance estimated by solving the differential equation of motion along these potential curves assuming that the electrons are re-

FIG. 3. Coulomb potential energy curves of highly charged dissociative O_2^{n+} .

moved sequentially at every 5 fs. Under this crude hypothesis, KER/Q for $O^{2+}-O^{2+}$ and $O^{2+}-O^{3+}$ are estimated to be 9.6 and 8.2 eV, respectively, resulting fair agreement with the experimental values. This indicates that time evolution of the nuclear motion observed in this study is in order of ~ 10 fs. For O^+-O^{2+} , O^+-O^{3+} , $O^{2+}-O^{2+}$, and $O^{2+}-O^{3+}$ ion pairs, 4, 7, 7, and 10 photons are required in total, respectively.

It is interesting to note that the KER distribution for O^+-O^{3+} ion pairs is located at higher KER/Q than that for $O^{2+}-O^{2+}$, although the charge states of the parent molecules for these pairs are the same. This indicates that O_2^{4+} ions produced at relatively long internuclear distances predominantly dissociate into $O^{2+}-O^{2+}$, whereas those produced at relatively short internuclear distance may fragment into O^+-O^{3+} . We can understand this tendency from the simplified potential curves in Fig. 3. At equilibrium bond length R_0 , the ionization from O_2^{3+} requires three photons, independent of the final charge separation $O^{2+}-O^{2+}$ or O^+-O^{3+} . As the dissociation proceeds along the potential O^+-O^{2+} , two-photon ionization becomes possible to $O^{2+}-O^{2+}$, whereas the ionization to O^+-O^{3+} still requires three photons. Thus $O^{2+}-O^{2+}$ production is strongly enhanced at larger internuclear distances. In this situation, $O^{2+}-O^{2+}$ and $O^{2+}-O^{3+}$ ion-pair productions become to require 6 and 9 photons in total, respectively. Under present experimental conditions, although O^{3+} emitted into 4π with kinetic energy of ~ 60 eV can be measured, O^{3+} in coincidence with O^+ emitted into 4π are limited up to ~ 20 eV because of momentum conservation law. Thus, some parts of O^+-O^{3+} pairs with KER/Q above ~ 13 eV missed our detector and, thus, the high-energy part of the KER distribution is suppressed, not affecting, however, the present discussion.

Figure 4 shows KER distribution for ion-pair formation from N_2 . Let us discuss first N^+-N^+ ion-pair formation. The lowest N_2^{2+} state dissociating into N^++N^+ is the $a^3\Pi_u$ state with the vertical ionization potential of 45.195 eV.²¹ From

FIG. 4. KER distributions for ion-pair formations from N_2 irradiated by 24 eV FEL pulses. Circles: high laser power (10^{14} W/cm² at most). Triangles: low laser power (10^{13} W/cm² at most).

the perspective of excitation energy, N^+-N^+ ion pairs, thus, can be produced by simultaneous two-photon absorption of 24 eV photons. However, it cannot be produced by sequential two-photon absorption via the $X^2\Sigma_g^+$, $A^2\Pi_u$, and $B^2\Sigma_g^+$ states because the vertical ionization potentials to these states are 15.580, 16.926 and 18.751 eV, respectively,²² more than 24 eV below the $a^3\Pi_u$ state of N_2^{2+} . Absorption of one further 24 eV photon by N_2^+ in the $X^2\Sigma_g^+$, $A^2\Pi_u$, and $B^2\Sigma_g^+$ states, may produce highly excited ionic states at ionization potentials of 40, 41, and 43 eV. Aoto *et al.* showed that there are many excited ionic states around this energy region.²³ In line of the discussion so far, the N^+-N^+ ion pairs are then expected to be produced by at least three-photon processes. The three steps are ionization to the lowest three ionic states, excitation to the highly excited ionic states from the lowest three ionic states, and ionization to dissociative N_2^{2+} states from the highly excited ionic states. Contributions from the $C^2\Sigma_u^+$ and $2^2\Pi_g$ states should be small at the photon energy of 24 eV because the vertical ionization potentials to these states are 25.514 and 24.788 eV, respectively, although the adiabatic ionization potentials to these states are 23.583 and 23.755 eV, respectively.²² Incidentally, after the second excitation stage, an alternative pathway is fragmentation of the highly excited ionic states into N^+ and N^* and subsequent atomic autoionization of the N^* species as discussed in the work of Ahmad *et al.*²⁴ This pathway is already opened up below the lowest N_2^{2+} vibrational state, $X^1\Sigma_g^+(\nu=0)$ at 42.88 eV,²⁴ and has an onset at 41.2 ± 0.5 eV;²⁴ sequential two-photon absorption of 24 eV photons via N_2^+ in the $A^2\Pi_u$ and $B^2\Sigma_g^+$ states will suffice to create N^+-N^+ ion pairs in this way. However, KER from the N_2^+ states lower than the lowest N_2^{2+} state should be lower than ~ 4 eV because the lowest dissociation limit of N^+-N^+ is 38.827 eV.^{19,20} There is no such kind of sign in Fig. 4. Thus, we conclude that contributions from these processes would be negligible.

The KER distribution measured at high laser power is different in shape from the one at low laser power. Although

FIG. 5. Coulomb potential energy curves of highly charged dissociative N_2^{m+} .

declined detection efficiency may disturb the low energy part of the KER distribution at high laser power, a tale in the distribution above 20 eV at high power is definitely different from one at low power. This indicates that highly excited N_2^{2+} states that were produced by one additional photon absorption of low lying N_2^{2+} states are involved in the N^+-N^+ ion-pair formation, in addition to the above-discussed channels from the low lying N_2^{2+} states.

The lowest N_2^{3+} level is located around 83 eV at R_0 .²⁵ To produce this state, two photons are required from the lowest N_2^{2+} state, and only one photon from highly excited N_2^{2+} . This means that in total five photons are required for N^+-N^{2+} ion-pair formation. The difference in shape of the KER distributions at high and low laser powers indicates that there are also highly excited N_2^{3+} states dissociating into N^+-N^{2+} ion pairs, which were produced by one-photon absorption from lower N_2^{3+} states.

As in the case of $O^{2+}-O^{2+}$ and $O^{2+}-O^{3+}$ ion-pair formations, the KER distributions for $N^{2+}-N^{2+}$ and $N^{2+}-N^{3+}$ are peaked at values significantly below the Coulomb repulsion energy at R_0 , indicating that the internuclear distance is elongated during the intermediate sequential steps of the multiple ionization processes. Figure 5 shows potential energy curves of ionized N_2 dissociating into the lowest dissociation limits of the individual ion pairs observed in this study obtained by the same way as Fig. 3. The position of each arrow corresponds to the internuclear distance estimated in the same way, as shown in Fig. 3. KER/Q for $N^{2+}-N^{2+}$ and $N^{2+}-N^{3+}$ are estimated to be 9.9 and 8.2 eV, respectively. These values are very similar to those for O_2 and in fair agreement with the experimental values and thus illustrate that the multiple ionization proceeds sequentially along the dissociation.

The KER distribution for N^+-N^{3+} ion pairs is located at higher KER/Q than that for $N^{2+}-N^{2+}$, and indicates that N_2^{4+} ions produced at relatively long internuclear distances predominantly dissociate into $N^{2+}-N^{2+}$, whereas those pro-

duced at relatively short internuclear distance may fragment into N^+-N^{3+} . We can understand this tendency from the same discussion as for O_2 . At equilibrium bond length R_0 , the ionization from N_2^{3+} requires three photons, independent of the final charge separation. As the dissociation proceeds along the potential N^+-N^{2+} , two-photon ionization becomes possible to $N^{2+}-N^{2+}$, whereas the ionization to N^+-N^{3+} still requires three photons. Thus $N^{2+}-N^{2+}$ production is strongly enhanced at larger internuclear distances. It is also worth noting that, for $N^{2+}-N^{2+}$, N^+-N^{3+} , and $N^{2+}-N^{3+}$ ion-pair formations, 7, 8, and 10 photons are required in total, respectively.

IV. CONCLUDING REMARKS

We have investigated multiple ionization of N_2 and O_2 molecules irradiated by EUV-FEL pulses by means of PI-PICO spectroscopy. Up to ten sequential photon absorptions are observed for both N_2 and O_2 . The multiple ionization is found to be predominantly due to sequential electron removal supposed by the elongation of the internuclear distance during intermediate steps caused by Coulomb repulsion during 100 fs pulse. To discuss these processes in further detail, electron spectroscopy and/or electron-ion coincidence spectroscopy are indispensable. Such experiments are under considerations.

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