CHIN. PHYS. LETT. Vol. 37, No. 4 (2020) 043301

Ionic Angular Distributions Induced by Strong-Field Ionization of Tri-Atomic Molecules *

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(Received 19 December 2019)

Angular distributions of fragment ions from ionization of several tri-atomic molecules (CO_2, OCS, N_2O and NO_2) by strong 800-nm laser fields are investigated via a time-of-flight mass spectrometer. Anisotropic angular distributions of fragment ions, especially those of atomic ions, are observed for all of the molecules studied. These anisotropic angular distributions are mainly due to the geometric alignment of molecules in the strong field ionization. Distinct different patterns in ionic angular distributions for different molecules are observed. It is indicated that both molecular geometric structure and ionization channels have effects on the angular distributions of strong field ionization/fragmentation.

PACS: 33.80.Rv DOI: 10.1088/0256-307X/37/4/043301

With the benefit of the rapid development in the laser technique, especially the emergence of chirp amplification technology developed by Mourou and Strickland,[1] the interaction of molecules with femtosecond strong laser fields has attracted considerable experimental and theoretical research interest in the past two decades. Ionization is viewed as a fundamental process in plenty of atomic/molecular strong field phenomena. Knowledge about the strong field ionization is of great importance to reach better insight into other strong-field atomic or molecular phenomena; for example, high-order harmonic generation,[2] high-order above-threshold ionization,[3,4] non-sequential double ionization[5,6] and Rydberg state excitation.[7,8]

The mechanism of the strong field ionization of molecules is much more complicated than that of atoms. Besides the molecular properties such as geometry, type of bonding, molecular size and polarizability, the multicenter interference,[9] multiple orbitals,[10] and molecular nuclear motions[11] can also affect the strong field molecular ionization. In addition, molecules can undergo various processes accompanied with strong field ionization, including excitation, dissociative ionization and so on. Furthermore, it has been shown that the formation of molecular ions is sensitive to the laser wavelength,[12] the pulse duration[13] and the laser polarization.[14] Upon increasing the laser intensity, multiple ionization of molecules followed by a Coulomb explosion will occur, and the anisotropic emission of atomic and molecular ions has been used to reconstruct the structure of multi-charged molecular ions before the Coulomb explosion by covariance mapping,[15,16] momentum imaging techniques[17] and simply considering the kinetic energy release.[18]

Of particular interest in strong field ionization of molecules is the acquirement of experimental information about the angular distribution of various fragment ions. Recently, researchers have shown that the major cause of the anisotropic ion angular distribution in the weak laser field is the geometric alignment[19,20] of the molecules in a tunneling ionization process, even though molecules are randomly oriented in the gas phase. With the laser intensity increasing, the coupling of laser field and the electric dipole moment becomes significant and produces a torque on a molecule due to the anisotropic dipole polarizability. This tends to align the dipole moment of the molecules to the laser field and will change the polarization angle dependence of molecular ionization rate.[16] The coupling would be expected to be stronger for the highly charged molecules, which always undergo Coulomb explosion, resulting in observed narrow angular distributions of fragment ions.[21] Moreover, if the laser-induced electric dipole moments are changed when the molecules bend and/or stretch in the multiple ionization, certain fragment ions may display two maxima in the angular distribution.[22] It should be noted that the emission direction of fragment ions is also dependent on the rotation of the molecules, the molecular structural deformation, the existence of heavy-atom obstacles within a molecule, and the migration of atoms within the framework of the molecules.

In this Letter, we investigate the angular distributions of fragment ions induced by the interaction of strong femtosecond laser with several tri-atomic molecules, CO_2, OCS, N_2O and NO_2. The neutral ground states of CO_2, OCS and N_2O have close shell configurations with linear geometric structure, while that of NO_2 has an open shell configuration with bending structure. Meanwhile, CO_2 and NO_2 molecules are symmetric and the other two are non-symmetric. By performing a comparative study on the angular

*Supported by the National Natural Science Foundation of China (Grant Nos. 11534004, 11874179, and 11704149), and the Natural Science Foundation of Jilin Province (Grant Nos. 20180101289JC and 20190103045JH).

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distributions from different molecules irradiated by 50 fs 800 nm strong laser fields, we aim to add our knowledge on the role of molecular structure in strong-field ionization/fragmentation. Distinct different ionic angular distributions, especially those of the central atom in a tri-atomic molecule, are observed for different molecules. Our study indicates that besides the laser-induced deformation of the molecular geometric structure, ionization channel correlated with different cationic states are also responsible to the anisotropic ionic angular distributions.

The experimental setup used here for femtosecond laser ionization/dissociation is based on a conventional linear TOF spectrometer, which is described in detail in our previous studies.[23,24] Briefly, gas-phase samples were introduced directly into the reaction chamber through a leak valve with a stagnation pressure at 1 atm. The base pressure was 1×10^{-6} Pa, and the operating pressure was about 1×10^{-4} Pa, by a turbo-molecular pump. The linear TOF spectrometer was based on the Wiley–Mclaron configuration and the free field flight distance was about 60 cm. At the end of the flight tube, a pair of micro-channel plates (MCPs) were used to detect the ions (mass resolution $M/\Delta M$ was about 300 at $m/z = 40$). The data were real-time recorded by high speed digitizers (NI5162) into a computer.

The laser system that we used in the experiment was a Ti:sapphire chirped-pulsed amplified laser with a central wavelength of 800 nm, a pulse duration of 50 fs, a repetition of 1 kHz, and a maximum of pulse energy of 4 mJ. A half-wave plate and a Glan prism were introduced into the laser beam to vary the laser intensity continuously. When focused with a 25 cm plane-convex lens, the laser intensity of 6×10^{14} W/cm^2 was achieved. The laser intensity was calibrated by comparing the measured saturation intensity of Xe with that calculated by the Ammosov–Delome–Krainov (ADK) model.[25]

To measure the ionic angular distributions, a 1 mm slit was mounted in front of the MCP detector, and the direction of the slit was parallel to the laser propagation direction. Due to the small aperture and the long flight distance, the angular distribution of different ions could be achieved. The polarization direction of the linearly polarized laser field was controlled by rotating a half-wave plate using a motorized precision rotary stage typically in a 4° step. The horizontal direction was defined to be collinear to the TOF axis. TOF mass spectrum (typically averaged over 10000 shots) was obtained for each polarization angle. Thus, the angular distribution for every fragment was measured with the angle of 0–360° without any further symmertrization of the data.

To investigate the effect of the molecular structure on the angular distribution of fragment ions, we measured the mass spectrum of tri-atomic molecules, CO_2, OCS, N_2O and NO_2 at the intensity of 6×10^{14} W/cm^2. The strong field ionization/dissociation of these tri-atomic molecules has been an attractive topic for a long time. Previous studies focused on the pathway and energy share of dissociation and Coulomb explosion in strong femtosecond laser fields.[21,24,26] In recent years, two-body and three body channels in Coulomb explosion process were identified using coincidence techniques.[27,28] In this study, we first measured the mass spectrum under the strong laser field with both horizontal and vertical polarization directions for all the molecules. Figure 1 presents the results of CO_2 as an example. For each molecule, the parent ion is the dominant peak in the mass spectra of either horizontal or vertical polarizations. Various fragments, including diatomic molecular fragments and atomic fragments with different charge states, appear in the TOF mass spectra. Splitting in the peak of highly charged atomic fragments is observed (see the inset in Fig. 1), which is a signature of Coulomb explosion process. It is interesting to note that for some fragments (e.g., O or C atomic fragments in Fig. 1), apparent different ion yields can be seen for horizontal and vertical polarizations, indicating a strong anisotropic distribution of the fragments. Therefore, we measure the angular distributions of parent and fragment ions from these tri-atomic molecules and the results are presented in Figs. 2–4. The angle in each figure represents the angle between the laser polarization and the TOF axis, with 0° (180°) being the horizontal direction.

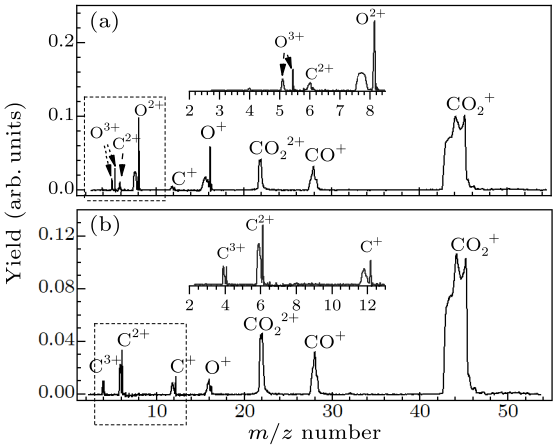

Fig. 1. Time-of-flight mass spectra of CO_2 at 6×10^{14} W/cm^2 measured by 50-fs 800-nm laser linearly polarized laser fields, with the polarization direction horizontal (a) and vertical (b) to the TOF axis. The inset in each figure is an enlarged view showing the peaks of different charged atomic ions.

Figure 2 shows the angular distributions of parent ions and diatomic molecular ions produced by the strong field ionization/fragmentation of these tri-atomic molecules. For either of the molecules, the parent ion has an isotropic angular distribution, which is due to small kinetic energy obtained in the strong field ionization process. Similar angular distributions as those of the parent ions are observed for some diatomic molecular fragment ions, i.e., CO^+ from CO_2, NO^+ from NO_2 (see Figs. 2(a) and 2(d)), indicating a small kinetic energy release that the ions can be ef-

ficiently detected irrespective to the direction of the laser polarization. Meanwhile, CO^+ from OCS and NO^+ from N_2O (see Figs. 2(b) and 2(c)) show more anisotropic angular distributions peaking at 0° and 180°, indicating larger kinetic energy releases of these diatomic fragment ions. We expect that Coulomb explosion could contribute to the formation of these diatomic ions,[27,29] the process that generally leads to a relative large kinetic energy release. For the asymmetric molecule OCS, the angular distribution of CS^+ is not measurable due to its weak peak intensity in the TOF mass spectra, which could be attributed to the minor dissociation channel of $CS^{m+} + O^{n+}$ in strong laser fields.[28]

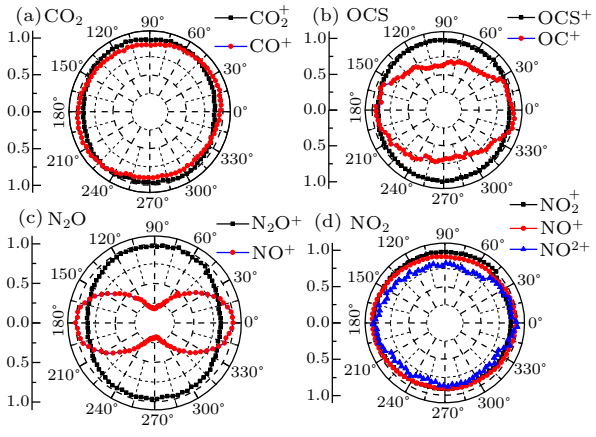

Fig. 2. Angular distributions of the parent and diatomic fragment ions of CO_2 (a), OCS (b), N_2O (c), and NO_2 (d).

The angular distributions of different charged atomic fragment ions are presented in Fig. 3 for the terminal atoms (i.e., O of CO_2, OCS N_2O and NO_2, S of OCS) and in Fig. 4 for the central atoms (i.e., C in CO_2 and OCS, N of NO_2). The observed N^{n+} fragment ions in N_2O can be either from the terminal or the central N atoms, of which the angular distributions are presented in Fig. 4. Apparent anisotropic angular distributions are observed for all the atomic ions, and the distributions become narrower for higher charged atomic ions. This could be understood since Coulomb explosion would be a dominant mechanism for producing highly charged atomic ions in strong laser fields. Similar results have also been observed in angular distributions of other molecules such as SO_2,[15] CO_2[16,30] and CH_2I_2.[31]

The angular distributions for all the terminal atomic ions show a maximum at 0° and 180°, indicating the ions prefer to emit along the laser polarization (Fig. 3). Meanwhile, the angular distributions for the central atomic ions are quite different for different molecules (Fig. 4). An ellipse distribution is obtained for C from CO_2, which show the maxima at 90° and 270°. A four leaf pattern for C from OCS molecules is observed, and the maxima are at neither horizontal nor vertical direction. An orthogonal angular distribution is observed for N from both N_2O and NO_2 molecules. The results indicate that the angular distributions are strongly dependent on the molecular structure, as discussed in the following.

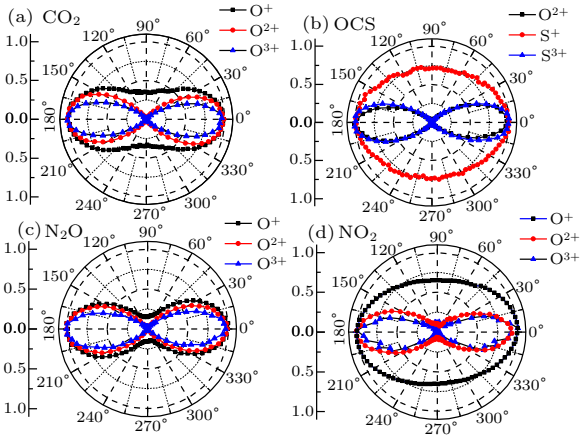

Fig. 3. Angular distributions of the terminal fragment ions of CO_2 (a), OCS (b), N_2O (c), and NO_2 (d).

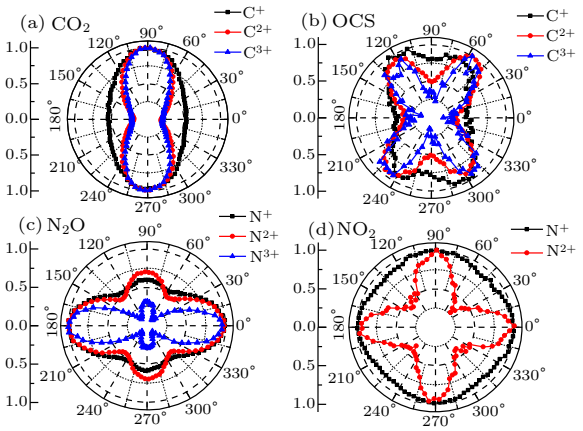

Fig. 4. Angular distributions of the central fragment ions of CO_2 (a), OCS (b), N_2O (c), and NO_2 (d).

It is well-known that the anisotropic ejection of fragment ions depends strongly on the alignment of the molecules in the femtosecond laser fields.[31] Dynamic alignment will be significant if the laser pulse duration is greater than the value of $5\hbar/B$ (B is the rotational constant of the molecule, and it is about 85.3 ps for the CO_2 molecule), thus we can exclude the dynamic alignment in our femtosecond laser experiment. For geometric alignment, the electron is stripped from the large magnitude lobe of electron clouds in the molecule by tunneling ionization, resulting in an angular distribution, which is similar to the HOMO, where the electron is removed. Geometric alignment would only dominant in a short (usually a few cycles) and/or weak laser field. With the laser intensity increasing, the first ionization is already saturated. Further ionizations will be strongly favored for molecules aligned parallel to the electric field, which has been observed in different molecules.[29,32] As mentioned earlier, most high charged ions are ejected along the laser polarization direction, which strongly indicates that the geometric alignment play an im-

portant role in the observed angular distributions of the fragments of the tri-atomic molecules. It is worth mentioning that, for these polyatomic molecules in such a strong laser field, the post-ionization alignment (PIA)[33] could also contribute to the alignment effect of the molecular ionization subsidiary.

Considering the laser induced electronic polarizability and the multi-electron effect of molecules, the Coulomb interaction between the bound/free electrons and the nuclei will produce additional stretching and bending force with an overall torque applied on the nuclear structure.[34] This leads to a bending structure of the molecule at the instant of Coulomb explosion. As a result, the distribution of the central atomic ion would be orthogonal to that of the terminal atomic ions of linear tri-atomic molecules, as we have shown for C from CO_2 (Fig. 4(a)). Similar results have also been observed in other linear molecules, such as C from CS_2.[24] For non-symmetric molecules OCS, however, the angular distributions of C ions peak at an angle 58° (instead of 90°) (Fig. 4(b). Due to its asymmetrical character,[27,35] the S atom has a mass that is twice that of the O atom, thus the kinetic energy shared by the O atom is greater than that by the S atom in the Coulomb explosion process. Thus the C ion from OCS must contain an additional horizontal velocity considering the conservation of momentum, leading to a four-leaf-clover-like angular distribution. It is interesting to see that different charged C ions reach their maximal distribution at almost the same angle, indicating that the highly charged parent ions explode in a similar molecular structure, irrespective of the charge state of the precursor.

For N_2O molecules, the angular distributions of N ions have two maxima at both horizontal and vertical directions. This could be understood since the N ions could be produced from either the terminal atom or the central atom, leading to two orthogonal distributions. This observation has been identified more clearly in a previous study by Graham *et al.*,[29] in which they measured the angular distribution using a labeled molecule ^{15}N–^{14}N–^{16}O. While N_2O is also a non-symmetric molecule, the masses of N and O atoms are close, thus the four-leaf-clover-like angular distribution as in the case of OCS is not significant for the central N atom of N_2O.

Perhaps the most surprising finding is the orthogonal angular distributions of the N ions from NO_2, as shown in Fig. 4(d). For the geometric alignment of molecules in the strong laser field, the angular distribution for the symmetric tri-atomic molecule NO_2 would be expected to be similar to that for CO_2 with a strong anisotropic distribution at a vertical angle for the central atom N. However, additional distribution at horizontal direction is observed, indicating that another mechanism is involved in the strong-field ionization/fragmentation of NO_2.

Considering the strong laser used in the study (intensity $\sim$0.6 PW/cm^2), as well as the fact that the energy difference between HOMO and HOMO-1 of NO_2 is 3.58 eV, which is less than that of CO_2 (4.58 eV), whose HOMO-1 has been found to participate in the strong field ionization,[36] thus one could expect the contribution of both molecular orbitals HOMO and HOMO-1 of NO_2 to the strong-field ionization. Calculations show that the HOMO and HOMO-1 of NO_2 are b_2 and a_1 orbitals, respectively, and the dipole moment of HOMO-1 is perpendicular to that of HOMO. Thus, ionization from HOMO-1 of NO_2 would lead to an orthogonal angular distribution of N atomic ions as shown in Fig. 4(d). However, ionization rate from HOMO-1 is several times lower than HOMO, due to the relatively large ionization energy. Therefore the additional distribution at horizontal direction could not result from the ionization of HOMO-1 orbital.

A similar angular distribution has also been observed for SO_2 molecules in a strong laser field.[37] Both SO_2 and NO_2 have the initial bent structures, which are different from other molecules. According to previous studies, the concerted three-body fragmentation of three-atoms molecules is still with a bent structure, which only results in a vertical emission for central atomic ions;[38] while the sequential three-body breakup would produce a rotational diatomic fragment and lead to an isotropic distribution of central atomic ions.[28] This is further proved by the relative wider angular distribution of C^+ from CO_2 in Fig. 3(a) than that of C^{2+} and C^{3+}, an isotropic distribution component due to the sequential three-body breakup of CO_2[39] is observed. A similar phenomenon is absent in the angular distribution of NO_2, thus the strange angular distribution of N from NO_2 can not be explained by different fragmental pathways with the initial bent structure.

For NO_2 molecules, the strong field ionization from the X^2A_1 ground state of neutral molecular surface to a^3B_2 excited cationic state prefer these molecules whose O...O direction along with the laser polarization.[40] In addition, the ionization of X^2A_1 ground state correlates with the X^1A_1 cationic state at a relative large ∠ONO, where the geometry approaches the linear equilibrium structure of the cationic ground state, prefer these molecules whose O...O bond direction perpendicular to the laser polarization. Normally, those molecules with large bond angles away from the equilibrium structure are rarely populated. However, the evolution of wave-packet through the resonance excited state A^2B_2 would produce lots of "hot" ground states of the neutral. For those molecules with bending vibrations, the strong field ionization to X^1A_1 cationic state would be enhanced, by a good Franck–Condon (FC) overlap for ionization as well as an effectively lower ionization potential. Therefore, the vertical ejection of N atomic ions may come from the ionization channel correlated with the X^1A_1 cationic state at large ∠ONO. While the detail about the strong field ionization of NO_2 could not be obtained due to the insufficient experimental results, further investigation on the relevance of photon-fragment and photon-electron of NO_2

should be implemented.

In summary, we have investigated the angular distributions of different ions produced by strong field ionization/dissociation of several tri-atomic molecules, CO_2, OCS, N_2O and NO_2. Strong anisotropic distributions are observed especially for atomic ions, which would be attributed to the geometric alignment effect in the strong laser fields. By comparing the results of different molecules, we show that the geometric structure would strongly affect the ionization/dissociation in strong laser fields. The strange angular distribution of N atomic ions is explained by the different ionization channel, which correlates with the X^1A_1 cationic state at large bond angles. The detail about the strong-field ionization of N_2O needs further experimental measurement such as photon-fragment and photon-electron joint spectra.

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