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Kinetic energy release of diatomic and linear triatomic molecules in intense femtosecond laser fields*

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The kinetic energy release of fragment ions produced by the interaction of femtosecond laser pulse radiation with diatomic and linear triatomic molecules N_2, CO, CO_2 and CS_2 is investigated. In the case of linear polarization, angles at which the kinetic energy release of ions has the maximum value are different from the alignment of molecules though the kinetic energy release of fragment atomic ions depends on the angle between the laser polarization vector and the detection axis of the time-of-flight. For the diatomic molecules, the critical internuclear distance in multielectron dissociative ionization with a circularly polarized light is larger than that with a linearly polarized light. For linear triatomic molecules, our data indicate that a concerted Coulomb explosion process is a universal phenomenon in the interaction of molecules with intense laser fields, even in the circularly polarized regime. During two C–O (or C–S) bonds breaking simultaneously, the C ion obtained larger energy in circular polarization than that in the linear polarization. Different variations of kinetic energy release between the diatomic and the linear triatomic molecules are discussed.

Keywords: kinetic energy release, diatomic and linear triatomic molecules, femtosecond laser
PACC: 3190, 3380, 4260H

1. Introduction

The kinetic energy release (KER) of exploding fragments as the origin of the Coulomb repulsion energy has been the major content for the Coulomb explosion of molecules, especially for diatomic and linear triatomic molecules such as N_2, O_2, CO, CO_2 and CS_2.[1−5] The measured KER is generally weaker than the expected Coulomb repulsion energy starting at the equilibrium internuclear distance of neutral molecules, indicating that the Coulomb explosion begins at a critical internuclear distance larger than the equilibrium internuclear distance. The critical internuclear distance is suggested to be about two times larger than the equilibrium internuclear distance. Recently, experimental investigations on KER of exploding fragments have been performed both in linear and circular light polarizations.[6,7] Hering and Cornaggia [6] reported the laser-induced Coulomb explosion of N_2 and CO_2 using linearly and circularly polarized laser light in the 10^{15}W/cm^2 intensity range at λ=800nm. Their results indicated that the fragmentation KER is identical in both cases using two different experimental methods. This means that the critical internuclear distance is the same in both cases. Banerjee *et al*[7] showed the results of multielectron dissociative ionization (MEDI) of N_2 using 100fs laser pulses (intensity 10^{15}W/cm^2) in linear and circular laser polarizations. They suggested that there are significant differences in both cases and considerably larger critical internuclear distances are favoured in MEDI with the circularly polarized light. The enhanced ionization (EI) of molecules was initially discovered in theoretical simulations of the ionization rates of H_2^+.[8] Recently, theoretical models based on the field-ionization and over-barrier ionization and on the full quantum treatment presented that EI of molecules at the critical distance is poorly dependent on the ionization stage.[9,10] On the other hand, Posthumus *et al*[11,12] have developed the field-ionization Coulomb explosion (FICE) model of diatomic molecules in intense laser fields. For a series of angles made between the laser field and the

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molecule axis in the case of linear polarization, the minimum laser intensity that is required for over-the-barrier ionization as a function of internuclear separation are calculated and indicated that an inertial effect might increase the internuclear distance. A time-dependent Thomas–Fermi model reveals that the kinetic energy defect is a result of screening processes of the departing electrons.[13]

In this paper, the KER of fragment ions generated from diatomic and linear triatomic molecules N_2, CO, CO_2 and CS_2 is investigated. Variation of KER of fragment ions with laser intensity, polarization angle (this refers to the angle between the laser polarization vector and the detection axis of the time-of-fight (TOF)) and ellipticity angle (defined as the angle between the laser field direction and the quarter-wave plate axis) are measured using a TOF mass spectrometer. The differences of KERs between the diatomic and the linear triatomic molecules are discussed.

2. Experimental set-up

The experimental set-up has been described in detail in our previous reports.[14,15] A Ti:sapphire chirped pulse amplifier system (TSA-10, Spectra-Physics Inc., USA) delivered laser pulses with a central wavelength of 800nm, pulse duration of 130fs at a repetition rate of 10Hz. The laser beam was focused into the vacuum chamber of a TOF mass spectrometer by a lens with a focal length of 150mm. To measure the variation of KER of fragment ions with polarization angle, a half-wave plate was inserted into the path of the laser beam to rotate the electric field vector. A quarter-wave plate was inserted into the path of the laser beam in order to obtain the variation of KER of fragment ions with ellipticity angle. A gaseous sample was introduced into the vacuum chamber via a pulsed valve (Park Inc., USA) with a 0.2mm orifice. The generated ions were accelerated by a two-stage electric field and detected by a micro-channel plate (MCP). The signals were recorded using 100MHz data acquisition card and then transferred to a PC for storage and analysis.

3. Results and discussion

3.1. KER of fragment ions as a function of laser intensity

For the diatomic and linear triatomic molecules, the KER of either parent molecular ions or atomic ions increases slightly with increasing laser intensity. The typical laser intensity dependence of the KER of CO_2^+, CO_2^{2+}, O^{m+} $(m \leq 3)$ and $C^{n+}(n \leq 3)$ ions generated from Coulomb explosion of CO_2 is shown in Fig.1. These are consistent with the theoretic predictions [12,16,17] and earlier works on benzene.[18] But they are in conflict with previous reports of Lavancier *et al*[19] and Cornaggia *et al*.[20] They showed that the KER of fragment ions is independent of the laser intensity, which was suggested as the indication of an intensity-tuned resonance process.

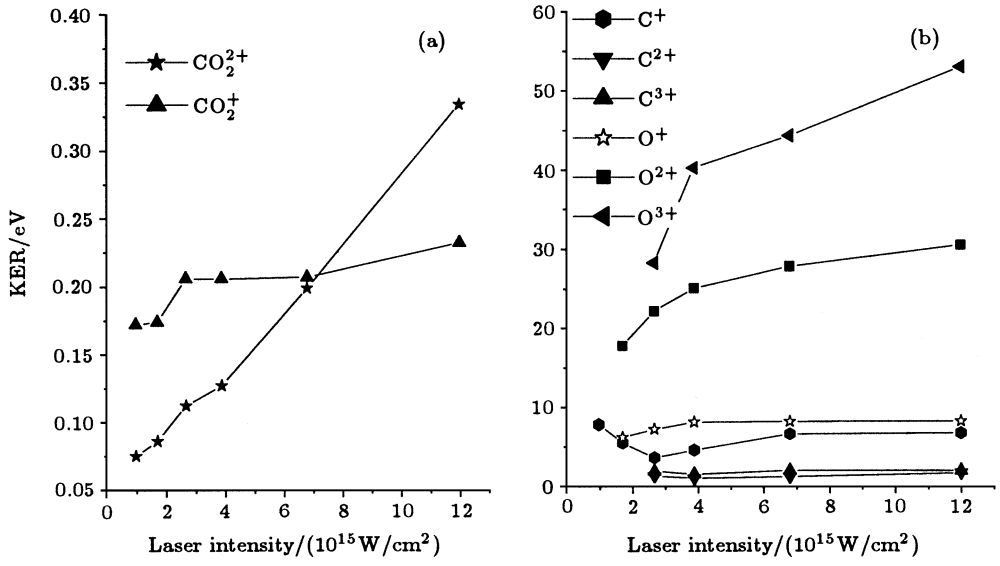


Fig.1. The KER of CO_2^+, CO_2^{2+}, O^{m+} $(m \leq 3)$ and C^{n+} $(n \leq 3)$ ions generated from CO_2 molecule as a function of laser intensity.

3.2. KER of fragment ions as a function of polarization angle

Figure 2 shows the KER of N_2^+, CO^+, CO_2^+ and CS_2^+ parent molecular ions generated from N_2, CO, CO_2 and CS_2 molecules, respectively, as a function of polarization angle. It indicates that the KER of all molecular ions exhibits isotropic distributions. This is the result of a random orientation of the intact parent ions. The KER of fragment atomic ions exhibits a significantly different behaviour from that of the parent molecular ions. Variations of the KER of fragment atomic ions originating from the diatomic molecules N_2 and CO with polarization angle are shown in Figs.3 and 4. The dependence of the KER of atomic ions on polarization angle is observed. The angle where the KER has a maximum value is the same for all the fragment atomic ions and the corresponding direction is parallel to the TOF axis (0° or 180°). It is well known that the origin of the measured KER is Coulomb repulsion energy of highly charged N_2 and CO. So KER reflects the internuclear separation at which dissociation of the multiply charged molecular precursor occurs. These polarization angle dependences are in agreement with the theoretic works of Posthumus *et al* and Springate *et al*, who concluded that internuclear separations differ from a series of angles between the laser field and the molecule axis by using FICE model when the laser is at the threshold intensity for the escape of an electron from the field of two I^+ ions.

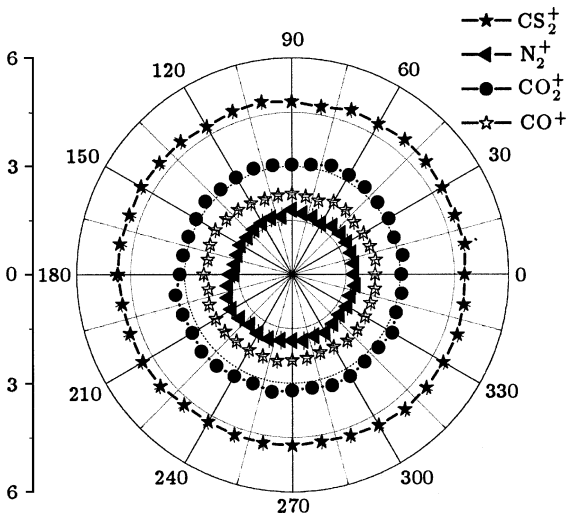


Fig.2. The KER of CO_2^+, N_2^+, CS_2^+ and CO^+ parent molecular ions generated from N_2, CO, CO_2 and CS_2 molecules as a function of polarization angle. The KER of CO_2^+, N_2^+ and CS_2^+ molecular ions has been multiplied by 15, 4 and 4, respectively. The KER of CO^+ ions has been divided by 3, for ease of viewing.

In the case of linear polarization, the N_2 and CO molecules are aligned along the laser electric field (anisotropic angular distributions of fragment atomic ion intensities generated from the N_2 and CO molecules have been proven experimentally [22–24]), and an inertial effect might increase the internuclear distance.[11,21] However, the results presented for N_2 here are at variance with those reported by Hering and Cornaggia,[6] who showed that KER has no significant variation for all the $N^{m+}+N^{n+}$ (m,n=1,2,3) when the direction of the linearly polarized laser field is rotated from $\theta = -90°$ to $\theta = +90°$.

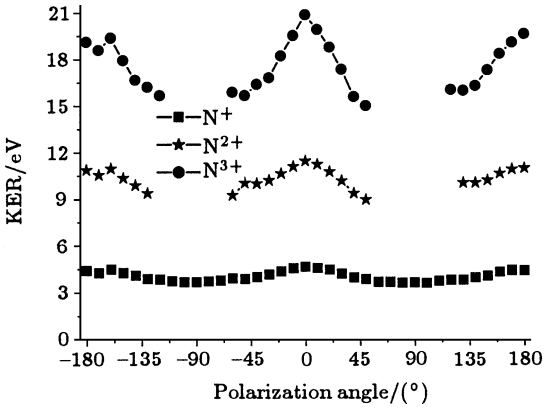


Fig.3. The KER of N^{m+} ($m \leq 3$) fragment ions generated from N_2 molecules as a function of polarization angle.

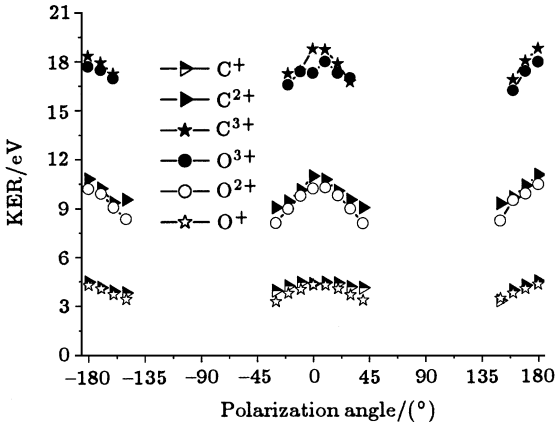


Fig.4. The KER of O^{m+} ($m \leq 3$) and C^{n+}(n≤3) fragment ions generated from CO molecules as a function of polarization angle.

For the linear triatomic molecules CO_2 and CS_2, the behaviour of KER of fragment atomic ions differs significantly from that of diatomic molecules, as shown in Figs.5 and 6. The maximum value of KER for O and S ion fragments is at $\theta = 0°$ and $\theta = 180°$. Conversely, the maximum value is observed at $\theta = 90°$ for C ion fragment.

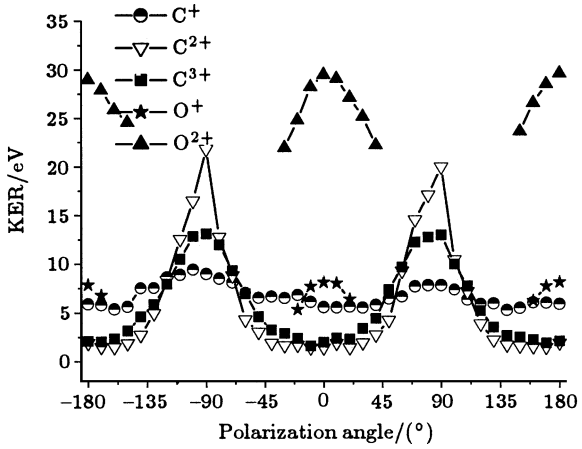


Fig.5. The KER of O^{m+} ($m \leq 2$) and C^{n+}(n≤3) fragment ions generated from CO_2 molecules as a function of polarization angle.

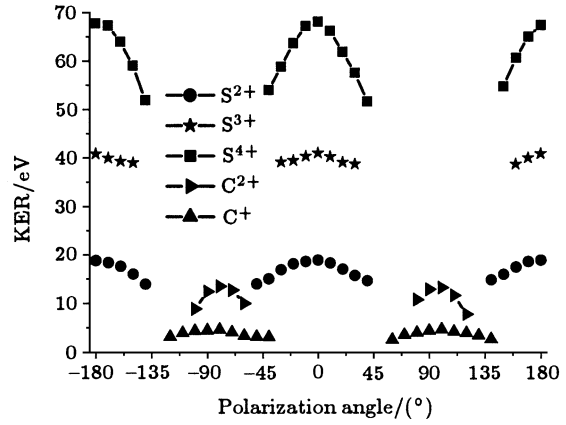


Fig.6. The KER of S^{m+} ($2 \leq m \leq 4$) and C^{n+} ($n \leq 2$) fragment ions generated from CS_2 molecules as a function of polarization angle.

Different variations of KER between the diatomic and the linear triatomic molecules are results of the alignment and geometrical structure of molecules in an intense laser field. The angular distributions of fragment ions have been observed for N_2, CO, CO_2 and CS_2 molecules.[1,22–28] For CO_2 (or CS_2) molecule, the direction of the maximum O^{m+} ($m \leq 3$) (or S^{m+} ($m \leq 3$)) ion count is collinear with the laser polarization vector. Conversely, the direction of the maximum ion count for C^{n+} ($n \leq 3$) ion fragment is perpendicular to the laser polarization vector. However, for the diatomic molecules N_2 and CO, the angular distributions for N^+, N^{2+} and N^{3+} ion are highly anisotropic, peaking along the laser polarization vector and being almost zero normal to the laser polarization vector.[1,22,23] The anisotropic angular distributions of O^{m+} ($m \leq 2$) and C^{n+} ($n \leq 3$) atomic ions produced from CO molecules also have a maximum along the laser polarization vector and a minimum perpendicular to it.[24]

The geometrical structure of molecules also influences the angular distributions of atomic ions. For CO_2 and CS_2 molecules, the carbon atom occupies the central position of the molecule. Many experiments have proven that the geometrical structure of CO_2 and CS_2 molecules will be distorted by an intense laser field and the bond angle ∠O–C–O and ∠S–C–S is not 180° prior to Coulomb explosion.[29–32] This means that the molecule is slightly bent when irradiated by intense femtosecond laser pulses. The two O–C bonds make small angles with the electric field of the laser. The concerted Coulomb explosion process actually occurs in an ultrashort time scale along the stretching coordinates and along the bending coordinates. This will result in the completely opposite behaviours for C and O (or S) ions.

3.3. KER of fragment ions as a function of ellipticity angle

To investigate the KER of fragment ions as a function of ellipticity angle, a quarter-wave plate was inserted into the path of the laser beam in order to obtain the variation of KER of fragment ions with ellipticity angle at a certain intensity. The quarter-wave plate axis is rotated from ϕ=0° to ϕ=180° (ϕ is ellipticity angle) to obtain repeatable experimental results. ϕ=0°, 90°, 180° correspond to linear polarization, ϕ=45°, 135° correspond to circular polarization. The dependence of KER of atomic ions on the ellipticity angle is illustrated for CO in Fig.7. The values of KER for the same atomic ion change with ellipticity angle. The value of KER for linear polarization is larger than that for circular polarization. This suggests that the critical internuclear distance in MEDI with a circularly polarized light is larger than that with a linearly polarized light. Similar results have been obtained for N_2 molecule (in Fig.8; here we only give values of KER for atomic ions when the quarter-wave plate axis is rotated from ϕ=0° to ϕ=45°). These observations are consistent with the results of Banerjee *et al*[7] on N^+ and N^{2+} generated from N_2.

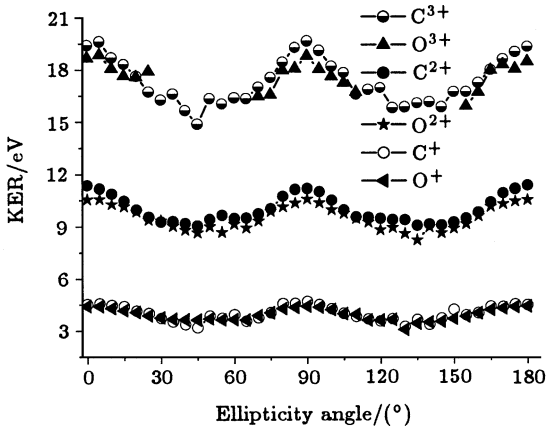


Fig.7. The dependence of KER of atomic ions generated from CO molecules on the ellipticity angle.

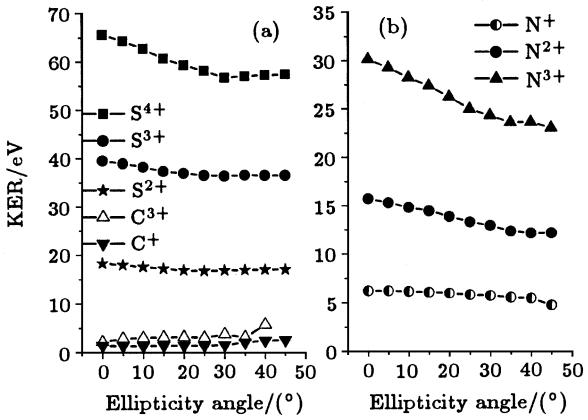


Fig.8. The KER of atomic ions as a function of ellipticity angle for N_2 and CS_2 molecules.

Figure 9 shows the dependence of KER of fragment atomic ions generated from CO_2 molecules on the ellipticity angle. When the ellipticity angle is ϕ=0°, 90°, 180° (corresponding to linear polarization), the O ion has the maximum KER value and the C ion has the minimum value. The C ion has the maximum KER value at near circular polarization. Similar results have been obtained for CS_2 molecules (in Fig.8; here we only give values of KER for atomic ions when the quarter-wave plate axis is rotated from ϕ=0° to ϕ=45°). The different values measured for KER of atomic ions under linearly and circularly polarized laser field for N_2 and CO_2 molecules disagree with those reported previously.[6]

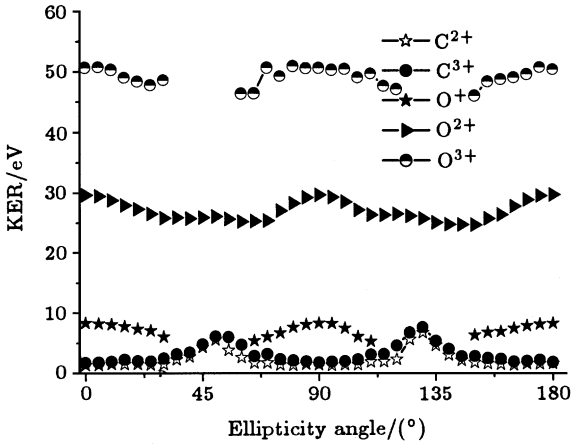


Fig.9. The dependence of KER of atomic ions generated from CO_2 molecules on the ellipticity angle.

Moreover, we also note that C ions always have smaller kinetic energies than O (S) ions at the same charge states (Figs.8 and 9) either in linear polarization or in circular polarization. It has been proven that Coulomb explosion is a concerted process and the two C–S bonds break simultaneously for CS_2 molecules in linear polarization.[25] Our data indicate that a concerted process is a universal phenomenon in the interaction of molecules with intense laser fields, even with a circular polarization. During the two C–O (C–S) bonds breaking simultaneously, the C ions obtain an energy in circular polarization larger than that in the linear polarization.

4. Conclusions

The dependences of the KER of exploding fragments generated from the diatomic and linear triatomic molecules on polarization angle and ellipticity angle have been experimentally investigated. In linear polarization, the polarization angle at which the KER has a maximum value is the same as that at which the ion intensities of fragment ions have a maximum value. The enhanced ionizations and concerted processes occur in an arbitrary elliptical polarization. The critical internuclear distance in MEDI of N_2 and CO with a circularly polarized light is larger than that with a linearly polarized light. During the two C–O (or C–S) bonds breaking simultaneously for CO_2 and CS_2 molecules, the C ions obtain an energy in circular polarization larger than that in linear polarization.

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