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Identifying isomers of carbon-dioxide clusters by laser-driven Coulomb explosion

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Clusters usually exhibit unique structures as an intermediate form of matter. However, their structures are still difficult to be determined with available experimental techniques. There are many structure distinct isomers for carbon-dioxide clusters. Here we report an experimental and theoretical joint study to determine the structures of the lowest-energy isomers. In the experiment, we exploded carbon-dioxide clusters by laser-driven multiple ionization and obtained precise momentum vectors of explosion fragments for each explosion channel. In the theory, we calculated low-energy structures of carbon-dioxide clusters and simulated their explosion dynamics. In comparison with the momentum vectors of explosion fragments, the lowest-energy isomers were identified for carbon-dioxide dimers, trimers, and tetramers.

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I. INTRODUCTION

As an intermediate form of matter, clusters are aggregates of atoms, molecules, or ions that are bound together by different kinds of forces ranging from very weak van der Waals bonds to strong ionic bonds. By measuring the chemical and physical properties as a function of cluster size, one can bridge the gap between the isolated-molecule behavior and that in the bulk phase. Clusters usually exhibit unique structures, which can be changed by adding a single atom or electron. One of the fundamental goals of cluster study is to build the relationship among structure, dynamics, and thermodynamics. However, the structure of clusters remains difficult to determine with available experimental techniques. Theoretical calculation still plays an indispensable role in predicting the geometric structure of this intermediate form of matter [1,2]. Unfortunately, the number of local minima on the potential energy surface can be very large when the cluster contains many atoms [3]. Generally each local minimum corresponds to a structure distinct isomer. Therefore the number of isomers tends to increase rapidly with increasing cluster size. The predicted energy order of isomers depends on theoretical models as well as the assumed potential function describing the forces between the cluster components. One of the biggest challenges of cluster study is the global search of the lowest-energy isomer. Therefore, identifying isomers in the experiment remains essential for testing theoretical predictions and guiding the development of theoretical methods.

Because of the important role of carbon dioxide in the field of atmospheric science and supercritical solvation, the study of the aggregation of carbon dioxide has attracted much attention. The first observation of carbon-dioxide clusters can be dated back to 1961, in which cationic clusters of carbon dioxide $(\mathrm{CO}_2)_n{}^+$, $n = 2-23$, were detected in the mass spectrometry experiment [4]. Since then, a number of experimental and theoretical efforts have been made to explore the structure of the carbon-dioxide cluster. Among them spectroscopic analysis is the most precise experimental method. However, different isomers are reported depending on the experimental condition. In the case of the carbon-dioxide dimer, a T-shaped structure with an intermolecular distance of 4.1 Å was first proposed by Welsh and co-workers based on the measurement of a low-resolution infrared spectrum [5]. Later, it was confirmed that the carbon-dioxide dimer has a planar slipped parallel structure, rather than the T-shaped geometry based on the assignment of a sub-Doppler resolution infrared spectrum [6]. In the case of the carbon-dioxide trimer, both the planar cyclic structure with C_{3h} symmetry [7] and the nonplanar twisted barrel shape with C_2 symmetry [8,9] have been identified based on the assignments of rotation-resolved high-resolution infrared spectra. In the case of the carbon-dioxide tetramer, the structure is still debated due to the lack of support of an experimentally assigned spectrum. Very recently, Moazzen-Ahmadi and co-workers summarized the high-resolution infrared spectroscopy of carbon-dioxide clusters [10,11].

Femtosecond laser Coulomb explosion imaging has been exhibited to be a novel approach for monitoring molecular structure, in which the molecule is rapidly ionized by an intense femtosecond laser field. Then the multiply charged molecular ion is quickly fragmented, undergoing the process of so-called Coulomb explosion. The molecular structure is deduced from momentum vectors of correlated explosion fragments. Laser-based Coulomb explosion has been applied to image the structure of small molecules [12,13], small van der Waals complexes [14–16], as well as chiral molecules [17]. In this article, we extend the Coulomb explosion imaging technique to molecular clusters and determine the lowest-energy structure of carbon-dioxide clusters.

II. THEORY

The low-energy structures of $(\mathrm{CO}_2)_n$ $(n = 2-4)$ were calculated by using a basin-hopping (BH) global minimum search program combined with density functional theory

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geometric optimization [18–20]. The basic principle of the BH algorithm is the Metropolis rule adding a local optimization procedure. In the process of coarse structure optimization, we chose the "pure" generalized gradient approximation with Becke-Lee-Yang-Parr exchange-correlation functional and the double-numerical polarized basis set with effective core potentials. The evolution of several random initial structures generated sets of low-lying isomers for each cluster with a given size. Then the structures of these low-lying isomers were further optimized using the double hybrid functional with empirical dispersion corrected variation Becke two-parameter Lee-Yang-Parr (B2PLYPD) and dunning type correlation consistent basis set aug-cc-pVDZ implemented in the GAUSSIAN 09 software package [21]. Figure 1 shows the predicted low-energy structures of CO_2 dimers, trimmers, and tetramers, in which the anharmonic vibrational correction has been included [22,23]. All the reported clusters are local minima on the potential energy surface and there is no imaginary frequency for the optimized structures.

In order to explore the energy order of these isomers for each cluster with a given size, their single-point energies were respectively calculated using the B2PLYPD (aug-cc-pVQZ) functional (basis set), MP4(SDQ) (aug-cc-pVQZ) four-order Moller-Plesset perturbation theory (basis set), and CCSD(T) (aug-cc-pVTZ) coupled cluster singles, doubles, and perturbative triples theory (basis set), implemented in the GAUSSIAN 09 software package [21]. Table I lists relative energies of predicted lower-lying isomers of carbon-dioxide clusters. Correspondingly, the structures of these isomers were displayed in Fig. 1. It can be seen that there are some discrepancies for relative energies of these isomers predicted by different theory levels. However, the lowest-energy isomers are consistent for each cluster with a given size. The carbon-dioxide dimer has a planar slipped parallel structure. The carbon-dioxide trimer has a planar cyclic structure with C_{3h} symmetry. The carbon-dioxide tetramer has a triangular pyramid structure.

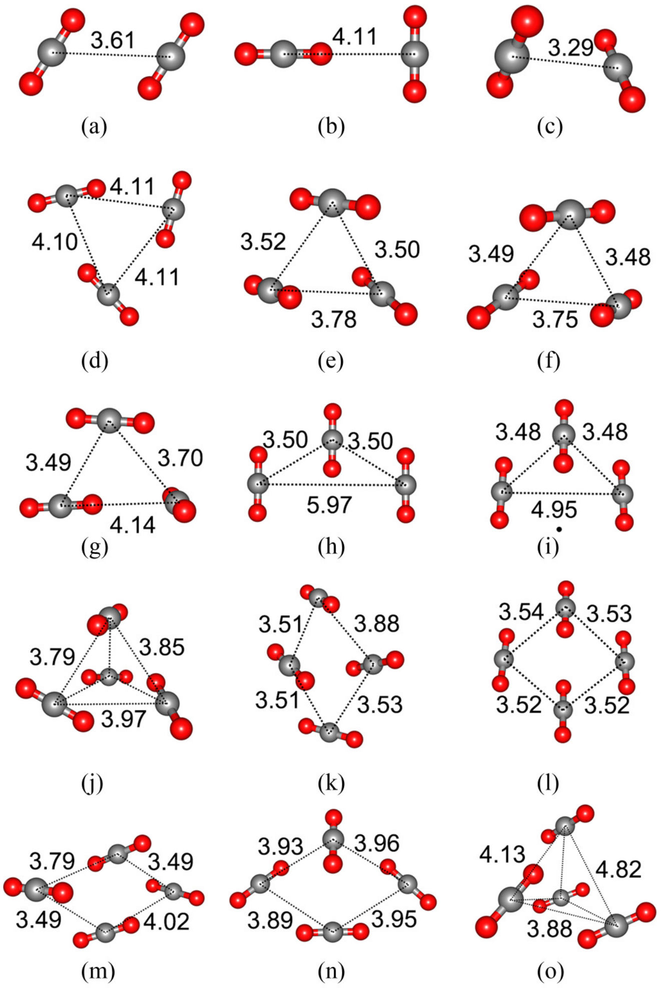

FIG. 1. (Color online) Predicted low-energy structures of CO_2 dimers, trimers, and tetramers.

III. EXPERIMENT

In the experiment, we combined an intense femtosecond laser amplifier and a newly built cold target recoil ion momentum spectroscopy (COLTRIMS) [24] to identify the structure of CO_2 clusters with laser-based Coulomb explosion imaging. The CO_2 clusters were generated by the supersonic expansion of CO_2 gas through a 30 μm nozzle with a driving pressure of 8 bars. The laser pulse with 25 fs duration centered at 780 nm was produced from a Ti:sapphire laser system (Femtolasers, GmbH). Multiple ionization and Coulomb explosion occurred when CO_2 clusters were irradiated by intense femtosecond laser fields. Correlated fragmental ions were therefore generated. To ensure that all fragmental ions originated from the same target molecule, we controlled the reaction chamber pressure to be lower than 3×10^{-10} mbar so that there was less than one ionization event within one laser pulse. The ions produced in the laser-molecule interaction were collected by a temporal and position-sensitive detector (RoentDek, Germany). By measuring the time of flight and the position in the detector, the ions can be identified and their initial three-dimensional momentum vectors can be determined. This information was then recorded in the event-by-event list-mode file. One of the advantages of COLTRIMS is that the data of all reaction channels can be recorded in one experiment. In the off-line analysis, the data from different reaction channels can be disentangled by designing some constraints to filter the experimental data. For example, when we analyze Coulomb explosion of the CO_2 dimer described by channel (1), we can design the following constraints. (1) Only two CO_2^+ ions were detected in one laser pulse. (2) The momentum sum of these two CO_2^+ ions was less than 30 atomic units to meet the requirement of the momentum conservation of two-body explosion. (3) The momentum of each CO_2^+ ion was greater than 30 atomic units to rule out false coincidence events. These false coincidence events came from the single ionization of two CO_2 molecules in one laser pulse. With these constraints to filter the experimental data, we can obtain precise data for Coulomb explosion of the CO_2 dimer described by channel (1). However, such data processes cannot completely rule out the contamination from the dissociation of larger clusters. This contamination is evaluated to be smaller than 5% according to our data analysis.

TABLE I. Relative energies for isomers of carbon-dioxide clusters calculated by the B2PLYPD/aug-cc-pVQZ level of theory, the MP4(SDQ)/aug-cc-pVQZ level of theory, and the CCSD(T)/aug-cc-pVTZ level of theory, respectively. The relative energies of the lowest-energy isomers are highlighted by bold font.

Clusters	Isomers	B2PLYPD (eV)	MP4(SDQ) (eV)	CCSD(T) (eV)
$(CO_2)_2$	a	**0.000**	**0.000**	**0.000**
	b	0.069	0.029	0.026
	c	0.137	0.074	0.075
$(CO_2)_3$	d	**0.000**	**0.000**	**0.000**
	e	0.015	0.005	0.010
	f	0.015	0.055	0.054
	g	0.023	0.067	0.064
	h	0.044	0.095	0.097
	i	0.048	0.096	0.099
$(CO_2)_4$	j	**0.000**	**0.000**	**0.000**
	k	0.177	0.098	0.099
	l	0.185	0.097	0.098
	m	0.186	0.094	0.094
	n	0.189	0.099	0.099
	o	0.191	0.097	0.101

IV. RESULTS AND DISCUSSION

Figure 2 shows the time-of-flight mass spectra of a supersonic carbon-dioxide beam irradiated by 780 nm, 25 fs laser pulses at an intensity of 5×10^{14} W/cm^2. In addition to the ion of CO_2 monomer, cationic clusters of carbon dioxide, up to $(CO_2)_{13}{}^+$, were observed. The observation demonstrated that the distribution of cluster sizes is broad inside the supersonic beam. The observed cationic clusters of carbon dioxide can be produced through direct ionization of a corresponding neutral cluster or through dissociative ionization of a larger neutral cluster by intense laser pulses. Here, we analyze the following explosion channels to identify isomers of carbon-dioxide dimers, trimmers, and tetramers.

$$(CO_2)_2{}^{2+} \rightarrow CO_2{}^+ + CO_2{}^+, \tag{1}$$

$$(CO_2)_3{}^{3+} \rightarrow CO_2{}^+ + CO_2{}^+ + CO_2{}^+, \tag{2}$$

$$(CO_2)_4{}^{4+} \rightarrow CO_2{}^+ + CO_2{}^+ + CO_2{}^+ + CO_2{}^+. \tag{3}$$

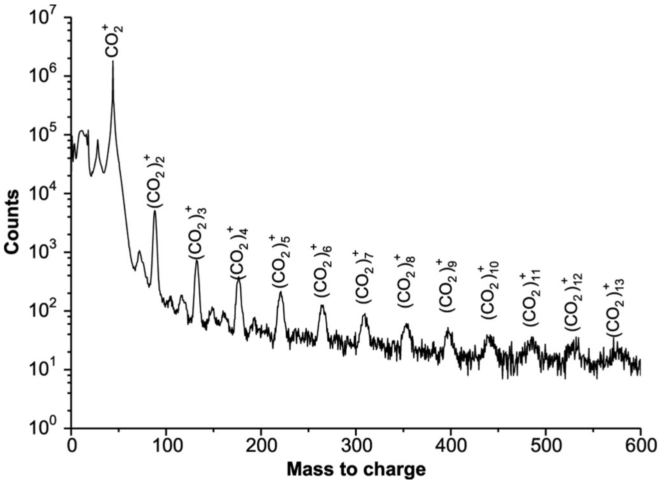

FIG. 2. Time-of-flight mass spectra of a supersonic carbon-dioxide beam irradiated by 780 nm, 25 fs laser pulses at an intensity of 5×10^{14} W/cm^2.

Figure 3 shows the total kinetic energy release (KER) distribution for the explosion channels of carbon-dioxide dimers, trimmers, and tetramers as described by channels (1)–(3), which can be obtained through the equation of KER $=(1/2m)\Sigma|P|^2$ with P and m being the momentum and the mass of $CO_2{}^+$. In the case of the carbon-dioxide dimer, the distribution can be well simulated by a Gaussian function with one peak at 3.8 eV. The single-peak distribution indicates that there is one isomer in the supersonic carbon-dioxide beam. In the case of the carbon-dioxide trimer, the distribution can be simulated by Gaussian function with double peaks, which locate at 10.8 and 11.6 eV, respectively. The double-peak distribution indicates that there is more than one isomer. In the case of the carbon-dioxide tetramer, the data is not abundant because of the limited events for four-body Coulomb explosion. The distribution still can be simulated by Gaussian function with one peak at 21.3 eV. The single-peak distribution indicates that there is one isomer.

To make a comparison between the theoretical calculation and the experimental measurement, we convert KERs and momentum vectors into the structural parameters of

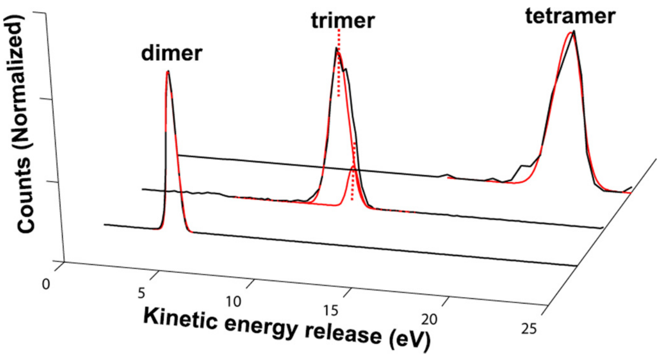

FIG. 3. (Color online) Kinetic energy release distribution for the ions produced in the explosion channels of carbon-dioxide dimers, trimers, and tetramers. Black lines represent experimental data and red lines represent the fitting data with Gaussian function.

carbon-dioxide clusters. Our recent study indicates that Coulomb potential approaches the *ab initio* potential closely when the internuclear distance is larger than 2.1 Å [13]. It is known that the bond length is larger than 3 Å for the weak van der Waals bond of a carbon-dioxide cluster. Then, the explosion dynamics as shown by channels (1)–(3) can be described by Coulomb potential. Based on the Coulomb potential approximation, the internuclear distance between the two C atoms is derived to be 3.7 Å for the carbon-dioxide dimer. Here, each cluster component, i.e., CO_2^+, is treated as a point charge and the charge is assumed to be in the mass center. Usually molecular ions have complicated charge distributions. We calculate the Mulliken charge distribution of CO_2^+, for which the charge is, respectively, 0.6887 and 0.1557 for C and O. When the Mulliken charge distribution and the point charge distribution are respectively applied, the difference of the KERs is less than 0.1 eV and can be neglected. Therefore, we calculate the KER distribution with point change distribution without special statement.

The laser-molecule interaction is very complicated for molecules in intense laser fields [25]. One might think that the molecular structure is modified during the multiple ionization. The derived structural parameters for ions cannot represent the structure of the neutral molecules before the laser irradiation. If the molecular structure is modified during the ionization process, the derived structural parameters will depend on the channel from which the molecular structure is reconstructed [26]. Our recent results demonstrate that the channel-independent reconstructed structures can be utilized as a criterion to judge the molecular structure is kept unchanged during the multiple ionization [16]. Therefore, we compare the explosion channels (1,1) $(CO_2)^{2+} \rightarrow CO_2^+ + CO_2^+$ and (2,1) $(CO_2)^{3+} \rightarrow CO_2^{2+} + CO_2^+$. The KER of the (2,1) channel is 7.5 eV, twice that of 3.8 eV of the (1,1) channel. Thus the derived internuclear distance between the two C atoms is almost the same and exhibits channel independence. The channel-independent derived structural parameters indicate that the structural modification can be neglected for carbon-dioxide clusters during the multiple ionization process driven by intense femtosecond laser pulses. Thus the internuclear distance between the two C atoms before explosion, which is determined to be 3.7 Å, represents the internuclear distance between the C atoms of the neutral carbon-dioxide dimer. In comparison with low-energy isomers predicted by theoretical calculations, the slipped parallel structure agrees with the experimental measurement best. Therefore, we conclude that the lowest-energy isomer has a slipped parallel structure for the carbon-dioxide dimer, which is shown in Fig. 1(a). These results further confirmed previous assignments by a high-resolution infrared spectrum [6].

Symmetry is another important property for clusters. The symmetry in the geometry configuration can be preserved in the momentum configuration if the identical cluster components carry the same charge in the Coulomb explosion process [27]. To visualize the symmetry in the momentum configuration, we replot the experimental data using the Newton diagram. In the Newton diagram for three-body fragmentation of the carbon-dioxide trimer, every CO_2 monomer is regarded as a mass point and the momentum vector of the first CO_2^+ ion is represented by an arrow fixed at one arbitrary unit. The momentum vectors of other CO_2^+ ions are normalized according to that of the first one. KER distribution indicates that there are at least two isomers for the carbon-dioxide trimer. Figures 4(a) and 4(b) show the Newton diagrams for three-body fragmentation of the carbon-dioxide trimer with KER smaller than 10.8 eV and larger than 11.6 eV, respectively. It can be seen that the momentum amplitudes of the three CO_2^+ ions are almost equal. The angle between the momentum vectors of any two CO_2^+ ions is almost 120°. Based on the Coulomb potential approximation, we simulate the explosion dynamics of isomers of carbon-dioxide trimers. In comparison with the experimental measured momentum vectors of the three CO_2^+ ions, the events with the KER smaller than 10.8 eV can be assigned to the isomer which has a planar cyclic structure with C_{3h} symmetry and is shown in Fig. 1(d). The events with the KER larger than 11.6 eV can be assigned to two isomers which exhibit a nonplanar twisted barrel shape. These two isomers have mirror symmetry and their structures are shown in Figs. 1(e) and 1(f), respectively. The present measurement provides direct evidence of the coexistence of these isomers. The ratio is about 3:1 for the isomer with a planar cyclic structure to that with a nonplanar twisted barrel shape under our experimental condition. However, the nonplanar twisted barrel shape belongs to two isomers with mirror symmetry, which cannot be separated in the present stage.

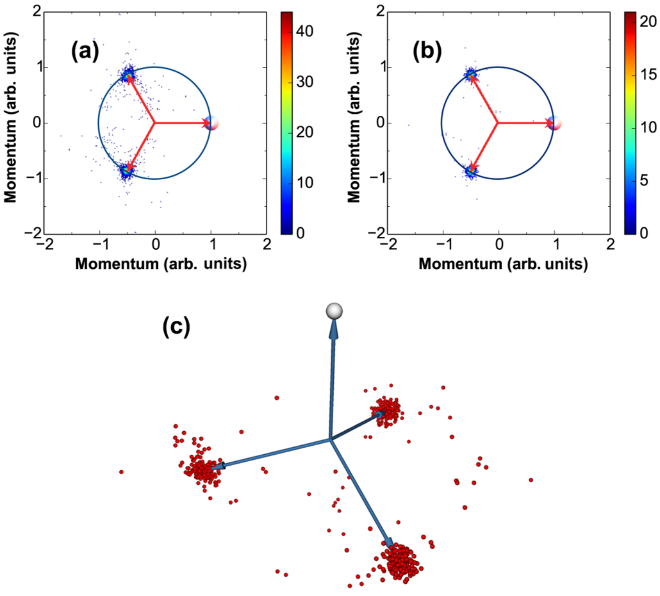

FIG. 4. (Color online) Newton diagram for Coulomb explosion of carbon-dioxide trimers and tetramers (see text).

Figure 4(c) shows the Newton diagram for four-body fragmentation of the carbon-dioxide tetramer. Some mathematical rotation operations were carried out during the plotting process of the three-dimensional Newton diagram. However, the operation does not change the absolute value of each momentum vector nor the angle between either of them. The momentum vector of the first CO_2^+ is fixed along the upward direction after the rotation operations. Then the momentum vectors of the four CO_2^+ ions are normalized to the amplitude of the first CO_2^+ momentum vector. When we connect the center of mass and the areas with the highest density, a triangular pyramid is exhibited in the Newton diagram. Based on the Coulomb potential approximation, we simulate the explosion dynamics of isomers of carbon-dioxide tetramers. In comparison with the experimental measured momentum vectors of the four ${CO_2}^+$ ions, we conclude that the lowest-energy isomer has a triangular pyramid structure for the CO_2 tetramer as shown in Fig. 1(j).

Molecular clusters usually have novel properties because of their unique structures. Exploring the relationship between properties and structures has important scientific significance as well as practical application value. Through these studies, we can reveal the intermolecular forces between molecules and understand complicated phenomena such as solvation. However, the structure of molecular clusters is difficult to directly probe with available experimental techniques, especially for some floppy van der Waals complexes. Coulomb explosion provides a novel approach to determine the structure of molecular clusters after combining with theoretical calculations. Because of the same detection efficiency for all isomers with the same cluster size, the energy order for these isomers can be determined and the lowest-energy isomer can be directly identified through experimental measurements. The identification of the lowest-energy isomer is important to test the theoretical calculation for molecular clusters.

V. CONCLUSIONS

In summary, we have experimentally studied Coulomb explosion dynamics of carbon-dioxide clusters driven by intense femtosecond laser fields. Precise momentum vectors of explosion fragments were obtained for each explosion channel. In the Meanwhile, we theoretically calculate the low-energy structures of carbon-dioxide clusters. Based on the Coulomb potential approximation, we simulate the explosion dynamics of these carbon-dioxide clusters. In comparison with the momentum vectors of explosion fragments, we identify the lowest-energy isomers of carbon-dioxide clusters and determine their structures. The present study provides a feasible approach to determine the structure of molecular clusters.

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