Temperature-Dependent Infrared Photodissociation Spectroscopy of $(CO_2)_3^+$ Cation

Xin Lei,[†,‡,||] Xiangtao Kong,[†,||] Bingbing Zhang,[†,‡,§] Zhi Zhao,[†] Dongxu Dai,[†] Xueming Yang,[†] and Ling Jiang*,[†] (ID)

[†]State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

[‡]University of Chinese Academy of Sciences, 19A Yuquan Road, Beijing 100049, China

[§]State Key Laboratory of Fine Chemicals, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China

ABSTRACT: Infrared photodissociation spectra of He-buffer-gas-cooled $(CO_2)_3^+$ were measured at ion trap temperatures of 15, 50, 150, and 280 K. Electronic structure calculations at the mPW2PLYPD/aug-cc-pVDZ level were performed to identify the structures of the low-lying isomers and to assign the observed spectral features. The experimental and calculated infrared spectra show that the $(CO_2)_3^+$ cations formed in the source are primarily dominated by the charge partially delocalized $C_2O_4^+$ motif, in which the positive charge is partially delocalized over the two CO_2 molecules. Thermal heating at elevated internal temperature supplies sufficient energy to overcome the isomerization barriers and gives access to the charge completely delocalized $(CO_2)_n^+$ ($n = 3$) motif, in which the positive charge is almost completely delocalized over all of the constituent CO_2 molecules.
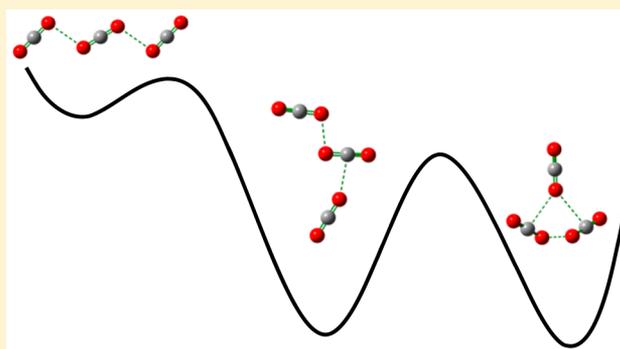
1. INTRODUCTION

The study of charge distributions is of fundamental interest because of their crucial roles in various processes, such as atmospheric chemistry, biomedicine, electronics, and materials science.[1,2] Various experimental (mass spectrometry, absorption spectroscopy, photoelectron spectroscopy (PES), infrared photodissociation (IRPD) spectroscopy, etc.) and theoretical methods have been used to analyze charge resonance interactions in complexes, providing detailed structural and dynamical information. Previous studies of the $(C_6H_6)_n^+$,[3] $(CO_2)_n^{\mp}$,[4,5] and $(CS_2)_n^+$ cluster ions[6] exhibited the feature of intermolecular charge resonance in the dimer ion core.

The $(CO_2)_n^+$ cluster is considered here because of its importance in energy and the environment. Thermochemical investigations of the association reaction $(CO_2)_{n-1}^+ + CO_2 \rightarrow (CO_2)_n^+$[7−10] and ionization potential measurements on the neutral $(CO_2)_n$ clusters[11−15] showed that the binding energy of $(CO_2)_2^+$ is higher than that of $(CO_2)_n^+$ ($n > 2$), suggesting the preferential formation of the $(CO_2)_2^+$ dimer ion core structure. For the $(CO_2)_2^+$ structure, two models of charge distribution were suggested. One is the CO_2^+ motif with the positive charge localized on a CO_2 molecule, and the other is the $C_2O_4^+$ motif with the positive charge delocalized over the two CO_2 molecules.[16−20] The CO_2 antisymmetric stretching vibration was observed at ~1423 cm^{-1} in the gas phase and in the solid Ne matrix,[21−24] implying the existence of CO_2^+ motif. The IR band characteristic of $C_2O_4^+$ was found at ~2131 cm^{-1} in the solid Ne matrix.[23,24] IRPD spectra of $(CO_2)_n^+$ ($n = 3-8$)

cations suggested the existence of the $C_2O_4^+$ ion core structure.[5]

B3LYP/6-311+G(d) calculations on $(CO_2)_n^+$ ($n = 2-4$) predicted that the positive charge is almost equally delocalized over all of the constituent molecules (named the charge completely delocalized $(CO_2)_n^+$ motif).[5,25] However, geometry optimization at the MP2/6-311+G(d) level yielded three motifs with the involvement of CO_2^+ core, $C_2O_4^+$ core, and the charge completely delocalized $(CO_2)_n^+$ motifs.[5] The question regarding the charge distribution of $(CO_2)_3^+$ remains open. Herein we report experimental IRPD spectra of thermalized $(CO_2)_3^+$ ions in the region of 2000−2600 cm^{-1} measured at ion trap temperatures from 15 to 280 K, in which only the fundamental vibrations appear in this characteristic spectral range.[26] Quantum-chemical calculations were carried out to understand the experimental spectral features and to identify the isomers present at various ion trap temperatures. The combination of experimental and calculated IR spectra reveals the coexistence of two motifs, in which the positive charge is delocalized over the two CO_2 molecules ($C_2O_4^+$ motif) and over the three CO_2 molecules ($(CO_2)_n^+$ motif), respectively.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

The experiments were carried out on an infrared photo-dissociation spectroscopic apparatus that includes a dielectric barrier discharge (DBD) source, a quadrupole mass spectrometer, a cryogenic ion trap, and a time-of-flight (TOF) mass spectrometer. The experimental setup has been previously described in detail,[27] and a brief description is given here. The $(CO_2)_3^+$ cations were generated by discharge from the supersonic expansion of a 4% CO_2/He gaseous mixture. The generated ions were introduced into a quadrupole mass spectrometer. The cluster ion of interest was mass-selected by a quadrupole mass filter, deflected by 90°, and focused into a 3D Paul ion trap filled with He buffer gas held at a constant temperature of 15, 50, 150, or 280 K. Collisions with He atoms thermalized the cations, which were accumulated in the trap for 98 ms and then extracted into the TOF mass spectrometer, where they were irradiated by a single pass of a tunable IR laser. The dissociation fragments and the remaining parent ions were mass-analyzed by the TOF mass spectrometer. Fragment yields were normalized by the intensities of the parent ions and the IR power. IRPD spectra of parent ions were acquired by plotting the normalized yields of fragment ions as a function of the dissociation IR laser wavelength. Typical IRPD spectra were obtained by scanning the dissociation laser in steps of 3 cm^{-1} and averaging over 1200 laser shots at each wavelength.

The tunable IR laser beam was generated by a KTP/KTA optical parametric oscillator/amplifier (OPO/OPA) system (LaserVision)[28] pumped by an injection-seeded Nd:YAG laser (Continuum Surelite EX). The system provides tunable IR output radiation from 700 to 7000 cm^{-1} with a 7 ns pulse width. The line width of the mid-IR output was ~1 cm^{-1}. The wavelength of the OPO laser output was calibrated using a laser spectrum analyzer (HighFinesse, OSA).

In order to assign the experimental spectra, quantum-chemical calculations were carried out using the Gaussian 09 package.[29] The mPW2PLYPD functional and the aug-cc-pVDZ basis set were employed. Relative energies, binding energies, dissociation energies, and energy barriers were calculated at 0 K with zero-point vibrational energies. A scaling factor of 0.982 was used for the vibrational frequencies calculated. The resulting stick spectra were convoluted with a Gaussian line shape function with a full width at half-maximum of 8 cm^{-1}.

3. RESULTS AND DISCUSSION

The experimental IRPD spectra of $(CO_2)_3^+$ at ion trap temperatures of 15, 50, 150, and 280 K are shown in the bottom four rows in Figure 1. The band positions are summarized in Table 1. Band D is the most intense feature at all of the temperatures studied here. Band A is poorly resolved. Weak features of bands B, C, and G are observed in the 15 K spectrum. Bands E−H gain their intensities in the 280 K spectrum.

The calculated IR spectra of the four lowest-energy isomers are depicted in the top four rows in Figure 1, and the optimized structures are shown in Figure 2. The lowest-energy isomer, labeled 3-I, is a C_2-symmetric structure (Figure 2), which is consistent with the previous MP2/6-311+G(d) calculations. In isomer 3-I, the neutral CO_2 molecule is located along the C_2 axis. In isomer 3-II, which lies only 0.28
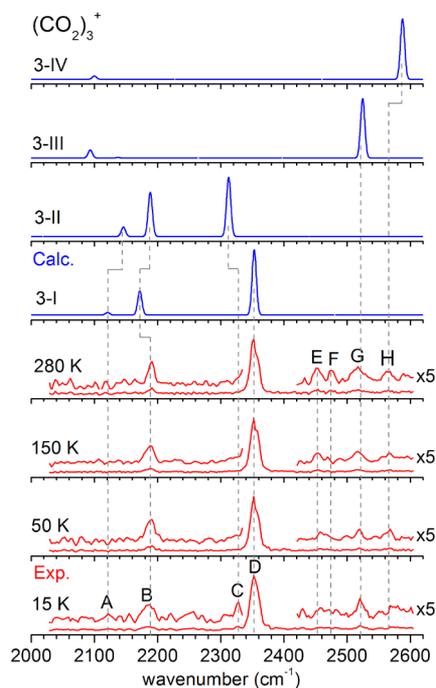
Figure 1. Experimental IRPD spectra of $(CO_2)_3^+$ measured at ion trap temperatures of 15, 50, 150, and 280 K (bottom four rows, red curves) and calculated IR spectra of the four lowest-energy isomers (top four rows, blue curves).

kJ/mol higher than 3-I at the mPW2PLYPD/aug-cc-pVDZ level, the solvent CO_2 molecule is located in the plane of the $C_2O_4^+$ ion core. Isomer 3-III (+3.48 kJ/mol) is a side-by-side planar structure with C_{2v} symmetry. Isomer 3-IV (+7.83 kJ/mol) is a "ladder" type structure.[25] It can be seen from Figure 2 that in isomers 3-I and 3-II, the positive charge is partially delocalized over two CO_2 molecules, which is named the charge partially delocalized $C_2O_4^+$ motif. In isomers 3-III and 3-IV, the positive charge is almost completely delocalized over all three CO_2 molecules, which is named the charge completely delocalized $(CO_2)_n^+$ motif.

Isomer 3-I yields calculated positions of bands A, B, and D that are in agreement with the experimental values (Figure 1 and Table 1). Bands A and B are assigned to the in-phase and out-of-phase combinations, respectively, of the CO_2 antisymmetric stretches of the two CO_2 constituent molecules in the $C_2O_4^+$ core (Table 1). Band D (2352 cm^{-1}) is due to the CO_2 antisymmetric stretch of the neutral CO_2, which is blue-shifted by 3 cm^{-1} from that of the free carbon dioxide molecule (2349 cm^{-1}).[26] The three absorption features of isomer 3-II are slightly shifted from the experimental values for bands A−C. Band C is due to the CO_2 antisymmetric stretch of the solvent CO_2. The most intense bands in the calculated IR spectra of isomers 3-III (2524 cm^{-1}) and 3-IV (2587 cm^{-1}) are responsible for the observed bands G (~2517 cm^{-1}) and H (2565 cm^{-1}), respectively, which are attributed to the CO_2 antisymmetric stretch of less-charged CO_2 with the out-of-phase combinations of the CO_2 antisymmetric stretches of the two CO_2 constituent molecules.

The above analysis leaves bands E and F unassigned, as these cannot be attributed to normal modes of either structure 3-I, 3-II, 3-III, or 3-IV. Previous MP2/6-311+G(d) calculations on the C_{2h} structure of the $C_2O_4^+$ ion core predicted a band at 2473 cm^{-1} without IR intensity, which is due to the CO_2

Table 1. Experimental IRPD Band Positions (in cm^{-1}) of (CO$_2$)$_3^+$ Measured at Ion Trap Temperatures of 15, 50, 150, and 280 K and Assignments Compared to the mPW2PLYPD/aug-cc-pVDZ-Calculated Vibrational Frequencies (in cm^{-1})

label	15 K	50 K	150 K	280 K	3-I	3-II	3-III	3-IV	Assignment
A	2122	–	–	–	2120	2145	–	–	in-phase combinations of the CO$_2$ antisymmetric stretches of the two CO$_2$ components in the (CO$_2$)$_2^+$ core
B	2186	2188	2189	2191	2172	2188	–	–	out-of-phase combinations of the CO$_2$ antisymmetric stretches of the two CO$_2$ components in the (CO$_2$)$_2^+$ core
C	2328	–	2257	2258	–	2312	–	–	CO$_2$ antisymmetric stretch of the solvent CO$_2$
D	2352	2352	2352	2352	2352	–	–	–	CO$_2$ antisymmetric stretch of neutral CO$_2$
E	2458	2457	2454	2452	–	–	–	–	CO$_2$ antisymmetric stretch of the C$_2$O$_4^+$ core
F	2471	2467	2470	2475	–	–	–	–	CO$_2$ antisymmetric stretch of the C$_2$O$_4^+$ core
G	2520	2520	2517	2517	–	–	2524	–	CO$_2$ antisymmetric stretch of the less-charged CO$_2$ with the out-of-phase combinations of the CO$_2$ antisymmetric stretches of the two CO$_2$ components
H	2568	2568	2566	2565	–	–	–	2587	CO$_2$ antisymmetric stretch of the less-charged CO$_2$ with the out-of-phase combinations of the CO$_2$ antisymmetric stretches of the two CO$_2$ components
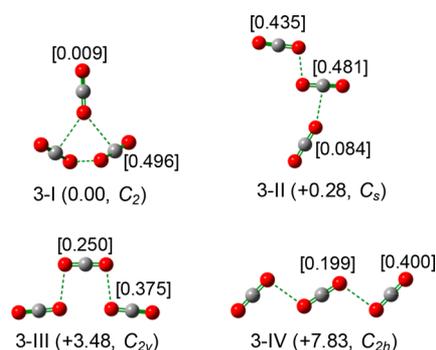
Figure 2. mPW2PLYPD/aug-cc-pVDZ-optimized structures of (CO$_2$)$_3^+$. Relative energies (in kJ/mol) are given inside parentheses, and the natural charges of the constituent CO$_2$ molecules are listed inside square brackets.

antisymmetric stretching mode.[5] Upon the attachment of one CO$_2$ to the C$_2$O$_4^+$ ion core, the C$_{2h}$ symmetry of the C$_2$O$_4^+$ ion core is broken, and consequently, this CO$_2$ antisymmetric stretching mode could gain some IR intensity. The experimental bands E and F are tentatively assigned to the CO$_2$ antisymmetric stretch of the C$_2$O$_4^+$ core. On the basis of the previously reported difficulty in the calculations of force constants for the normal modes of the (CO$_2$)$_n^+$ systems,[5] the IR intensities and frequencies of such weakly bound cluster ions are expected to be accurately computed by higher-level calculations.

The 3-I and 3-II isomers with a C$_2$O$_4^+$ core are responsible for the observed features in the 15 K spectra, which is consistent with the previous IRPD studies. In the present work, we observe the weak but distinct absorption features of bands G and H, providing evidence for the existence of the 3-III and 3-IV structures with the charge completely delocalized (CO$_2$)$_3^+$ motif. Isomer 3-I is mainly produced in the cold ion beams generated by the DBD source. At 50 K, sufficient internal energy could be present to overcome the small isomerization barrier between isomers 3-I and 3-II and shift the isomer population. The intensities of bands G and H increased when the temperature of ion trap was raised to 280 K, implying that heating at elevated internal temperature gives access to isomers 3-III and 3-IV via internal conversion. It should be noted that as a result of RF heating and/or inefficient collisional cooling, the internal temperature of the ions is typically somewhat higher than the measured temperature of the ion trap.[30,31] The barrier for the isomerization from 3-II to 3-I was calculated to be 6.25 kJ/mol at the mPW2PLYPD/aug-

cc-pVDZ level. This suggests that 3-II could not be readily converted to 3-I at 15 K, resulting in the larger population of the lower-energy structure 3-I and the smaller population of the higher-energy structure 3-II. The barrier for the isomerization from 3-II to 3-IV was calculated to be 8.46 kJ/mol at the mPW2PLYPD/aug-cc-pVDZ level, indicating that the transformation between the dimer core and trimer core structures becomes facile at higher ion trap temperatures. These theoretical predictions support the experimental observations mentioned above.

In summary, the present results show the effect of temperature on the isomerization for (CO$_2$)$_3^+$, would have important implications for understanding of the charge distributions of weakly bounded complexes. Previous studies on (CS$_2$)$_2^-$ have also shown the influence of thermal heating on the isomer populations.[32] The weakly bound CS$_2$·CS$_2^-$ ion−molecule complex is mainly produced in the supersonic expansion. Thermal heating shifts the isomer population via a weakly bound isomer, in which the electron is delocalized over the complete complex, to lower-energy covalently bound structures. Our recent ion-trap IRPD spectroscopy study of the trimethylamine (TMA) complexes (TMA)$_n^+$ revealed a strong preference for the formation of a stable charge-shared N···N-type (TMA)$_2^+$ ion core rather than the proton-transferred C···HN-type ion core, evidencing that the source conditions have a remarkable effect on the kinetic stability of the isomers.[27]

4. CONCLUSION

In this work, we investigated how thermal heating affects the isomer population of (CO$_2$)$_3^+$ using temperature-dependent infrared photodissociation spectroscopy and quantum-chemical calculations. The structures with a C$_2$O$_4^+$ ion core are mainly produced in the supersonic expansion, which is consistent with the results of previous IRPD studies. Weak but distinct absorption features at 2517 and 2565 cm^{-1} were also observed, and their intensities increased with increasing internal temperature, providing evidence for the existence of a C$_3$O$_6^+$ motif in which the positive charge is almost completely delocalized over all three CO$_2$ molecules. The present system provides a model for the study of the charge distributions of molecular clusters.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: ljiang@dicp.ac.cn.

ORCID ⦿

Ling Jiang: 0000-0002-8485-8893

Author Contributions

‖X.L. and X.K. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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