First detection of the C$_2$ symmetric isomer of carbon pentaoxide (CO$_5$) at 10 K

Corey S. Jamieson [a], Alexander M. Mebel [b], Ralf I. Kaiser [a,*]

[a] Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI 96822, USA
[b] Department of Chemistry and Biochemistry, Florida International University, Miami FL 33199, USA

Abstract

Carbon oxides of the form CO$_n$ ($n = 2$–8) have long been known as important molecules in atmospheric and solid state chemical reactions. These higher order carbon oxides have been theoretically predicted to be stable, however, their detection has been difficult. Here, we report on the first spectroscopic detection of the cyclic (C$_2$) isomer of carbon pentaoxide (^{12}C^{16}O$_5$) via its v_1 vibrational mode centered around 1912 cm^{-1} under matrix isolation conditions; the identification of the ^{12}C^{18}O$_5$, ^{13}C^{16}O$_5$, and ^{13}C^{18}O$_5$, isotopologues supported by ab initio calculations confirms the assignments. We also discuss possible formation routes of this molecule.
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1. Introduction

During the last decade, intensive research has been carried out to develop new high-energy materials (HEMs) to meet needs for future defense and space science applications such as novel explosives and rocket propellants [1–6]. Particular attention has been devoted to cyclic carbon oxides of the generic formula CO$_n$ ($n = 3$–8). These higher-order oxides of the main group IV element carbon are highly energetic and therefore candidates for high energy density materials. The carbon oxides and their corresponding anions are also of interest to the atmospheric [7,8] and planetary science communities [9]. For instance, the lowest order of these species, the C$_{2v}$ and D$_{3h}$ symmetric CO$_3$ isomers, have been shown to be key intermediates in the ^{18}O isotopic enrichment in atmospheric carbon dioxide and also in the quenching of electronically excited oxygen atoms (O(^{1}D)) in the terrestrial and Martian atmospheres [10]. The higher order oxides hold an increased oxygen balance (OB) and have been suggested

to act as reaction intermediates involving bi- and termolecular reactions of mono- and diatomic oxygen with lower carbon oxides and organic molecules in the atmosphere [11]. Finally, Shkrob suggested these oxides as model compounds to study high velocities of detonation (VOD) and to possibly control the energy release from high energy density material [12].

Previous computational studies suggest that carbon oxide structures based on a central carbon atom, bound oxygen rings, and a carbonyl functional group are indeed (meta) stable molecules [13,14]. These include the well-know C$_{2v}$ symmetric CO$_3$ isomer [15] and the C$_2$ symmetric CO$_4$ structure, which were detected recently in our laboratory via infrared spectroscopy in low-temperature carbon dioxide ices after irradiating the samples with high energy electrons [16]. However, despite the importance of the higher carbon oxides as high-energy density molecules and their role in atmospheric and planetary chemistry, an experimental verification of the formation routes, a spectroscopic characterization, and an investigation of the stability of the CO$_n$ isomers ($n = 5$–8) together with their anions has remained elusive so far. Here we report the first experimental detection of one isomer of the next higher order carbon oxide specie, the C$_2$ symmetric carbon

* Corresponding author.
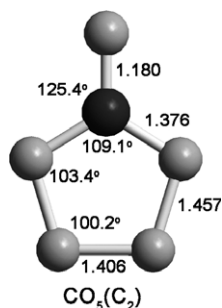 E-mail address: kaiser@gold.chem.hawaii.edu (R.I. Kaiser).

Fig. 1. The lowest energy isomer of the C_2 symmetric carbon pentaoxide molecule is shown. The central black atom represents carbon while the gray atoms are oxygen. Calculated bond lengths (Å) and bond angles (in degrees) are also shown.

pentaoxide molecule (CO_5, C_2), via low temperature, infrared spectroscopy (Fig. 1). We will also discuss the production routes of this molecule.

2. Experimental and computational details

The experiments were carried out in a contamination-free ultra high vacuum stainless steel chamber [15]. The chamber can reach pressures down to 5×10^{-11} Torr by use of a magnetically suspended turbo molecular pump (TMP) that is backed by a scroll pump. All pumps used are oil-free to ensure no hydrocarbon contaminants enter the system. Temperatures down to 10 K are reached using a two-stage closed-cycle helium refrigerator that is interfaced to a polished single crystal silver mirror onto which the ices are condensed. The silver substrate is suspended by a differentially pumped rotatable feedthrough, which aligns the wafer in the center of the main chamber. Gas condensation is carried out at 10 K where the pressure is regulated by a thermovalve that lets gas through the linear transfer mechanism and to the gas capillary array which evenly disperses the gas. Carbon dioxide gases were condensed for 3 min at a pressure of 1.0×10^{-7} Torr at 10 K to a total thickness of 250 ± 50 nm. This averaged thickness was derived using an equation provided in Bennett et al. [15], where the average column density of the initial ice was calculated by integrating several absorption features in the carbon dioxide infrared spectrum and dividing by their respective absorption coefficients. The ice sample was then irradiated isothermally with 5 keV electrons to cleave the carbon–oxygen bond. The electron beam was operated at a nominal current of 1 μA with an extraction efficiency of 78.8% and scanned over the sample area 1.8 ± 0.3 cm^2 to avoid heating the ice. The sample was irradiated for 1 h, which exposed the target to 1.8×10^{16} electrons. In this work, four carbon dioxide irradiation experiments were performed using (a) $^{12}C^{16}O_2$, (b) $^{12}C^{18}O_2$, (c) $^{13}C^{16}O_2$, and (d) $^{13}C^{18}O_2$. The progress of the reaction was monitored using a Nicolet 510 DX Fourier Transform Infrared Spectrometer (FTIR). The spectrometer has a wavenumber range of 6000–500 cm^{-1} and

operates in absorption–reflection–absorption mode with a reflection angle of 75° from the normal relative to the mirror surface. The infrared spectra of the ice were recorded online and in situ at an integrated time of 2.5 min and at a resolution of 2 cm^{-1}. The column densities of a molecule can be calculated according to Bennett et al. [15].

The minimized structure of the C_2 symmetric CO_5 molecule was calculated at the B3LYP [17,18] level of theory with the 6-311 G* basis set. Quantum calculations including vibrational frequencies and infrared intensities of the carbon pentaoxide molecule were then carried out at the B3LYP/6-311G* and the QCISD/6-311G* levels of theory. The calculations were performed employing the GAUSSIAN 98 program package [19].

3. Results

The experiments were carried out in three phases. First, the carbon dioxide ices were irradiated for 1 h while the experiment was monitored continuously by infrared spectroscopy. The temporal developments of the infrared bands of each molecule were quantified to help us understand the kinetics of the reactions that occur. Next, the electron source was turned off, and the ice was left at 10 K to check the stability and/or reactivity of the molecular species produced. Finally the ice was warmed at a rate of 0.5 K min^{-1} to observe any reaction, dissociation, and/or sublimation of the products. In this work specific attention is devoted to the $CO_5(C_2)$ molecule since an investigation of the low mass species ozone, carbon monoxide, carbon trioxide, and carbon tetraoxide produced as a result of the radiolysis has been previously documented [15,16,20]. This procedure has been applied previously in our laboratory and assisted the identification of the $ONCO(X^2A')$ molecule [21].

3.1. Infrared band assignment

We will first review our infrared band assignments of the carbon pentaoxide (C_2) molecule in our experiments. In order to validate our assignments, calculations of the positions of the vibrational modes and their intensities were performed at the B3LYP/6-311 G* and QCISD/6-311G* levels of theory for the different isotopologues that are expected to result from the four isotopically labeled experiments (Table 1). In order to compare the calculated vibrational frequencies with our observed peak positions, scaling factors are used since the calculated frequencies are often larger than the observed frequencies. The scaling factors account for anharmonicity effects that are neglected in the theoretical calculations, an inadequate description of electron correlation, and the use of finite basis sets. The recommended value of the scaling factor is dependent on the level of theory [22] where Irikura et al. [23] have determined these values by comparing observed vibrational frequencies available through the computational chemistry comparison and benchmark database (CCCBDB) with the calculated values at several levels of theory. For exam-

Table 1
Calculated unscaled wavenumbers (cm^{-1}) are given for several isotopologues of the carbon pentaoxide (C$_2$) molecule calculated at the B3LYP/6-311G* and the QCISD/6-311G* levels of theory

Symmetry	^{12}C^{16}O$_5$		^{12}C^{18}O$_5$		^{13}C^{16}O$_5$		^{13}C^{18}O$_5$	
	B3LYP/6-311 + G*	QCISD/6-311G*	B3LYP/6-311 + G*	QCISD/6-311G*	B3LYP/6-311 + G*	QCISD/6-311G*	B3LYP/6-311 + G*	QCISD/6-311G*
B	201 (0.7)	199 (0.7)	189 (0.6)	188 (0.6)	201 (0.7)	199 (0.7)	189 (0.6)	188 (0.6)
A	408 (1.5)	440 (0.1)	384 (1.3)	414 (0.1)	408 (1.5)	440 (0.1)	384 (1.3)	414 (0.1)
B	489 (3.7)	504 (5.0)	464 (3.0)	478 (4.1)	487 (4.0)	502 (5.2)	462 (3.2)	476 (4.3)
A	663 (8.1)	706 (0.2)	628 (8.7)	670 (0.5)	661 (6.9)	702 (0.1)	626 (7.7)	667 (0.3)
B	695 (12.7)	732 (23.0)	662 (7.7)	710 (12.6)	687 (17.0)	718 (27.4)	658 (9.8)	695 (17.7)
B	746 (19.4)	770 (11.5)	733 (22.1)	751 (19.7)	729 (14.0)	760 (5.9)	712 (19.1)	733 (13.5)
A	760 (19.0)	822 (11.0)	720 (14.1)	776 (8.7)	757 (21.3)	822 (11.9)	717 (15.9)	776 (9.4)
B	860 (9.5)	907 (10.9)	811 (8.5)	857 (9.8)	859 (9.8)	906 (11.2)	811 (8.4)	856 (9.7)
A	887 (52.2)	906 (34.7)	838 (44.8)	855 (28.9)	886 (53.3)	905 (36.2)	837 (45.9)	854 (30.2)
A	939 (15.5)	967 (47.1)	886 (14.9)	913 (42.7)	937 (14.6)	966 (46.3)	885 (14.1)	912 (42.1)
B	1090 (130.0)	1168 (124.4)	1069 (128.6)	1146 (123.6)	1063 (120.7)	1139 (115.1)	1041 (119.6)	1115 (114.6)
A	1929 (477.9)	1979 (444.0)	1891 (471.2)	1941 (438.5)	1880 (445.5)	1929 (413.4)	1841 (439.0)	1889 (408.1)

Infrared intensities (km mol^{-1}) for the absorptions are also given in parenthesis.

Table 2
The observed wavenumbers of the v_1 vibration of the different isotopologues of carbon pentaoxide (CO$_5$, C$_2$) are compared to the scaled theoretically calculated values at the B3LYP/6-311G* (scaling factor 0.992) and the QCISD/6-311G* (scaling factor 0.967) levels of theory

Isotopomer	Observed wavenumber/cm^{-1}	B3LYP/6-311G* calculated wavenumber/cm^{-1}	QCISD/6-311G* calculated wavenumber/cm^{-1}
^{12}C^{16}O$_5$	1912	1914	1914
^{12}C^{18}O$_5$	1872	1876	1877
^{13}C^{16}O$_5$	1873	1865	1865
^{13}C^{18}O$_5$	1829	1826	1827

ple, their results show that at the B3LYP/6-311G(d, p) and QCISD/6-311G(d, p) levels of theory, recommended scaling factors of 0.967 and 0.954, respectively should be used. The errors here are reported to be 0.02 in each case. For CO$_5$, the 6-311G(d, p) basis set is identical to the 6-311G* basis set used in this letter; in addition, Irikura et al. have found that the scaling factor is not greatly affected by changing the basis set.

In the following comparison between our experimentally determined frequencies with the theoretically calculated values, the more accurate B3LYP/6-311G* level of theory will be used (Table 2). In the ^{12}C^{16}O$_2$ irradiation experiment, the v_1 vibration of ^{12}C^{16}O$_5$(C$_2$) was observed at 1912 cm^{-1} (Fig. 2) compared to a calculated wavenumber of 1914 cm^{-1} after being scaled by a factor of 0.992. Table 3 summarizes the peaks positions and molecule assignments that are observed in Fig. 2. In comparing our chosen scaling factor with the aforementioned value of 0.967 found by Irikura et al., we see that they differ by 0.025, just outside of the error limits reported for the calculated value. However, these suggested scaling factors and the calculated frequencies cannot be taken as absolute since several variables can shift the expected absorption. For instance, the calculated frequencies assume that the molecule does not interact with its surrounding environment. In the solid state, neighboring molecules can alter the electronic environment in which the molecule of interest vibrates, thereby shifting the observed band position. Second, it has been assumed that one scaling factor should be used for a given level of theory, where in fact, the scaling factor is not only dependent on the type of molecule but can also be different for different types of vibrations [24]. Third, although the basis set does not greatly affect the scaling factor, there is slight variation which would change the suggested scaling factor of 0.967. Lastly, errors may exist in the data set of observed frequencies used to calculate the scaling factors from Irikura et al. [23] as well as in our own determination of the CO$_5$ peak position. With these considerations, our chosen scaling factor of 0.992 for the B3LYP/6-311G* level of theory seems reasonable. Also a scaling factor of 0.967 was chosen for the QCISD/6-311G* level of theory which compares well with the recommended value of 0.954.

After the v_1 vibration of CO$_5$, the next most intense absorption of the carbon pentaoxide molecule would be
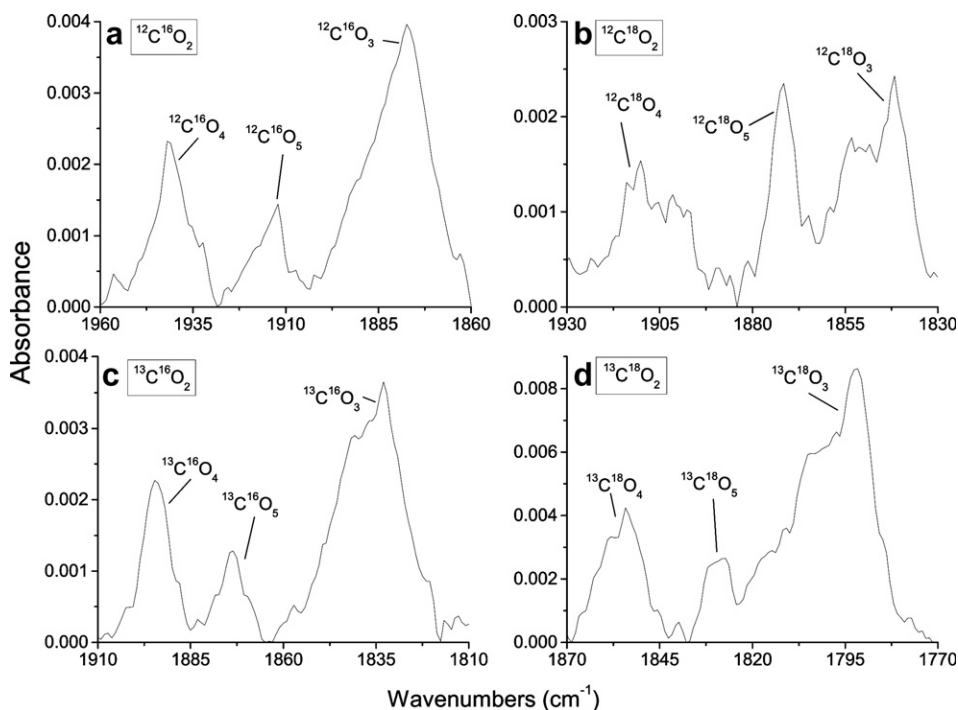
Fig. 2. The infrared absorption features of the v_1 vibration of four isotopologues of the carbon pentaoxide (C_2) molecule are shown above. Also labeled in the spectra are a Fermi resonance absorption of carbon trioxide (C_{2v}), and the carbon tetraoxide (C_{2v}) molecule. The isotopic compositions of the initial carbon dioxide reactants are boxed.

the v_7 vibration centered at 1092 cm^{-1} [13]. However, no absorption could be identified in this region due to its low intensity. The v_7 vibration should be almost four times less intense than the v_1 vibration. The integrated peak of the v_1 vibration is about 0.013 cm^{-1} and so the intensity of the v_7 vibration is calculated to 0.004 cm^{-1} which puts its intensity at the noise level in the experiment. Therefore, confirmation of our assignment of the $CO_5(C_2)$ molecule requires an agreement with the predicted isotope shifts in the v_1 position. In the $^{12}C^{18}O_2$ experiment, $^{12}C^{18}O_5$ was observed at 1872 cm^{-1} which agrees with the scaled value of 1876 cm^{-1} (0.992 scaling factor). In the $^{13}C^{16}O_2$ experiment, $^{13}C^{16}O_5$ was observed at 1873 cm^{-1} which agrees with the scaled theoretical value of 1865 cm^{-1}. Lastly, in the $^{13}C^{18}O_2$ irradiation experiment, $^{13}C^{18}O_5$ was observed at 1829 cm^{-1} compared to the scaled theoretical shift of 1826 cm^{-1}. The consistent agreement of the peak positions

of the v_1 fundamental vibrations of the $CO_5(C_2)$ isotopologues with the theoretically predicted shifts confirms or assignment of the carbon pentaoxide molecule. As will be discussed in the following sections, the analysis of the kinetics and energetics of the formation pathways to carbon pentaoxide (C_2) also support our assignment.

In order to develop a complete reaction model describing the formation of the $CO_5(C_2)$ molecule, it is also necessary to identify other molecules that are relevant to the formation pathways. For example, ozone (O_3), two isomers of carbon trioxide (C_{2v} and D_{3h}), and carbon tetraoxide (C_{2v}) were detected in each of the four isotopically labeled experiments, however, an analysis of their band assignment as well as an investigation into their formation pathways can be found in our previous works and will not be further discussed [15,16,20]. Note, the following kinetic analysis investigating the formation of the $CO_5(C_2)$ molecule is based on the $^{12}C^{16}O_2$ experiment.

4. Discussion

4.1. Reaction dynamics and kinetics

As this is the first detection of the carbon pentaoxide molecule (only one theoretical work could be found) [13], we must review the possible formation pathways and weigh the probability of each occurring. In order to do this, we will attempt to quantify the kinetics of the important reaction pathways to elucidate the major formation route(s) of $CO_5(C_2)$. A reaction model was developed to relate the

Table 3
The observed wavenumbers of the absorptions found in Fig. 2 are given

Carbon dioxide irradiation experiment	CO$_3$(C$_{2v}$) observed wavenumber/ cm^{-1}	CO$_4$(C$_{2v}$) observed wavenumber/ cm^{-1}	CO$_5$(C$_2$) observed wavenumber/ cm^{-1}
$^{12}C^{16}O_2$	1878	1941	1912
$^{12}C^{18}O_2$	1841	1908	1872
$^{13}C^{16}O_2$	1833	1894	1873
$^{13}C^{18}O_2$	1792	1855	1829

The identified molecules include isotopologues of carbon trioxide (CO$_3$, C$_{2v}$), carbon tetraoxide (CO$_4$, C$_{2v}$), and carbon pentaoxide (CO$_5$, C$_2$).
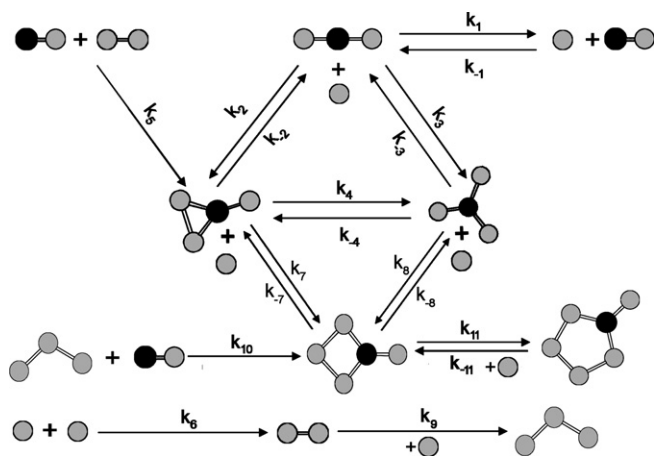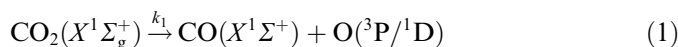
Fig. 3. A reaction model was developed to kinetically relate the species present in the ice that are important for the formation/destruction channels of carbon pentaoxide (C_2). Here, gray atoms are oxygen where black atoms are carbon. The reaction model is initiated by the radiation-induced destruction of carbon dioxide (top-center).
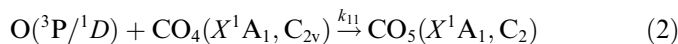
observed species in the ice in terms of formation and destruction channels (Fig. 3). For this study, only the formation pathways involving carbon pentaoxide are discussed although the rate constants that are relevant for the formations of CO_3 (C_{2v} and D_{3h}), CO_4, and CO_5 are given for comparison (Table 4). Molecular abundances (column densities) in units of molecules cm^{-2} were derived to quantify the abundance of each observable specie relevant for the formation of the $CO_5(C_2)$ molecule (excluding molecular oxygen and oxygen atoms which were undetectable in our infrared spectra). The column densities of the observable species were plotted over the 1 h irradiation. In order to kinetically fit the column densities, rate equations were derived that relate the molecular species that are important to the formation of carbon pentaoxide. From these rate equations, differential equations can be derived to fit the temporal development of the column densities of the observed molecular species during the irradiation phase of the experiment. The column densities of CO, CO_2, CO_3 (C_{2v} and D_{3h}), CO_4, CO_5, and O_3 were calculated using a solution mapping method in which differential equations are substituted by polynomial functions which

Table 4
The following rate constants were derived using the solution mapping technique as described in the text according to the reaction model given in Fig. 3

Reaction	Product	Rate constant
$CO_2 + O$	$CO_3(C_{2v})$	$k_2 = 6.4 \times 10^{-17}$
$CO_2 + O$	$CO_3(D_{3h})$	$k_3 = 9.4 \times 10^{-18}$
$CO + O_3$	$CO_4(C_{2v})$	$k_{10} = 7.3 \times 10^{-21}$
$CO_4 + O$	$CO_5(C_2)$	$k_{11} = 7.0 \times 10^{-15}$

Only the rate constants (in units of cm^2 molecule^{-1} s^{-1}) of the most important formation pathways for the carbon oxide species are shown for comparison. Note the rate constant for the $O + CO_3$ reaction to form $CO_4(C_{2v})$ was found to be negligible in comparison to the $CO + O_3$ rate constant.
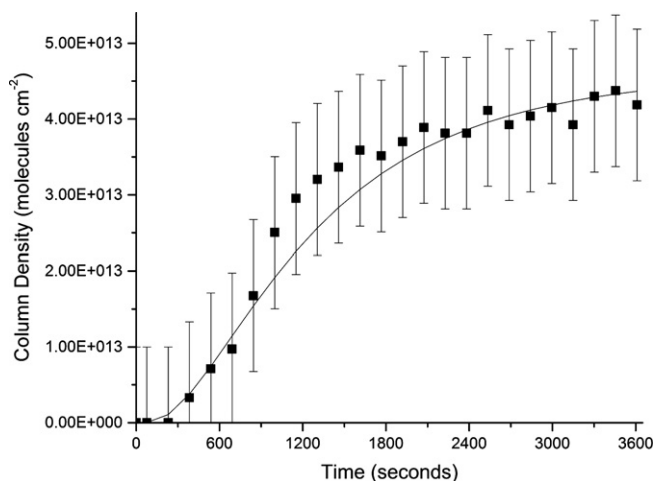
are simpler to solve (the column densities of molecular and atomic oxygen were not experimentally determined but were derived from the rate constant data that resulted from the modeling calculations). From this, rate constants were derived for the pathways set forth in the reaction model. As this paper is focused on the formation of carbon pentaoxide we will report only its formation rate.

Briefly, we will summarize the preliminary reactions that may be relevant to the formation of carbon pentaoxide. As carbon dioxide undergoes radiation induced dissociation, carbon monoxide and oxygen atoms are produced with rate constant k_1 (Eq. (1)). The oxygen atoms may be either in their ground electronic state (^3P) or electronically excited (^1D), both of which may be suprathermal (excess kinetic energy). These oxygen atoms can react via multiple reaction pathways with carbon dioxide molecules to form both carbon trioxide isomers as well as carbon tetraoxide (Fig. 3) [15,20].

$$CO_2(X^1\Sigma_g^+) \xrightarrow{k_1} CO(X^1\Sigma^+) + O(^3P/^1D) \qquad (1)$$

With the aforementioned atoms/molecules as reactants (CO_4, CO_3, CO_2, CO, O, O_2, O_3), one may consider a number of reaction pathways that could possibly form carbon pentaoxide. Previously, Elliott and Boldyrev [13] have calculated the reaction energies for carbon dioxide and ozone ($CO_2 + O_3$) and carbon trioxide and molecular oxygen [$CO_3(C_{2v}) + O_2$] at the CCSD(T)/6-311 + G* level of theory but they were both found to be endoergic (by 165.9 and 31.6 kJ mol^{-1}, respectively) and are not likely to play a large role in the formation of carbon pentaoxide. However, one plausible reaction was identified that was found to be exoergic. Here, carbon pentaoxide could be produced after atomic oxygen reacts with carbon tetraoxide (Eq. (2)).

$$O(^3P/^1D) + CO_4(X^1A_1, C_{2v}) \xrightarrow{k_{11}} CO_5(X^1A_1, C_2) \qquad (2)$$

The reaction was found by Elliot and Boldyrev to be exoergic by 174.0 kJ mol^{-1} with respect to a ground state oxygen atom. In order for the reactants to proceed to the C_2 symmetric CO_5 molecule, an oxygen atom must attack CO_4 at its four-membered ring and insert into either one of the C–O or O–O bonds. This means that reaction (2) likely has little steric hindrance since there are four reaction sites available to an attacking oxygen atom (four bonds to insert). If this attack occurs by an electronically excited oxygen atom (^1D), this should allow a barrierless insertion process. On the other hand, an oxygen attack in the electronic ground state (^3P) could overcome an energy barrier – possibly through a conical intersection – to reaction if the atom was suprathermal (excess kinetic energy); recall that as carbon dioxide dissociates (Eq. (1)), excess energy is to be transferred to kinetic energy of the oxygen atom. The rate constant that was derived for the formation of carbon pentaoxide is 7.0×10^{-15} cm^2 molecule^{-1} s^{-1} (Fig. 4). This represents the rate constant of an oxygen atom inserting into either of the C–O or the O–O bonds of carbon tetraoxide to form carbon pentaoxide.

Fig. 4. The temporal development of the column density of carbon pentaoxide (CO_5, C_2) is shown during the 1 h irradiation phase of the experiment. A best fit curve is also plotted according to the proposed reaction model as discussed in the text. Error bars are $\pm 10^{13}$ molecules cm^{-2}; calculated by integrating a featureless region of the infrared spectrum and propagating the error through the column density calculations.

4.2. Stability

After the 1 h irradiation phase of the experiment, the ice was left isothermal at 10 K for 1 h to check the stability of the products. There was no observable change in the column density of carbon pentaoxide (C_2) indicating that the product was stable at 10 K and that there were no reactions occurring in the ice to form or destroy CO_5. The ice was then slowly heated at a rate of 0.5 K min^{-1} to further check the stability of the carbon pentaoxide molecule. In the infrared spectra, the carbon dioxide matrix was observed to sublime around 92 K, however, the carbon pentaoxide absorptions remained until about 106 K. This high temperature is interesting because according to the calculations carried out by Elliot and Boldyrev, there are three exoergic dissociation pathways of $CO_5(C_2)$ including to $CO_2 + O_3$, $CO + 2O_2$, and $CO_3 + O_2$. Our experiments suggest that significant energy barriers are involved in these reactions to dissociate to carbon pentaoxide.

5. Conclusion

We have detected the carbon pentaoxide (C_2) molecule by its v_1 vibrational mode in four different isotopically labeled experiments (Fig. 2). Our assignments are supported by an excellent agreement of the observed peak positions of the four isotopologues with our ab initio calculations (Table 3). From our kinetics analysis, the $CO_5(C_2)$ molecule is likely formed via the insertion of oxygen atoms

into the ring structure of the C_{2v} isomer of carbon tetraoxide. The spectroscopically verified existence of high-order carbon oxide species from this and preceding works (CO_3 isomers, CO_4) [15,20] confirms the stability of these species as has been previously predicted by theoretical studies [13,14]. This lends support to the idea that CO_5 and other carbon oxide species may be useful high-energy molecules in which a large amount of potential energy can be stored. Also with high oxygen balances, they would be very efficient oxidizers. Carbon pentaoxide may also be produced and stabilized in the low temperature, radiation processed carbon dioxide ices of the outer solar system like on Triton and Ganymede (Neptune's and Jupiter's largest moons, respectively).

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