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Novel detection of the C_{2v} isomer of carbon tetraoxide (CO_4)

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Abstract

Carbon oxides such as carbon dioxide (CO_2) and carbon trioxide (CO_3) have long been known as important molecules in atmospheric and solid state chemical reactions. Although higher order carbon oxides have been theoretically predicted to be stable and also important, their detection has been difficult. Here, we report on the first spectroscopic detection of the cyclic (C_{2v}) isomer of carbon tetraoxide ($^{12}C^{16}O_4$) via its v_1 vibrational mode centered around 1941 cm^{-1} via low temperature infrared spectroscopy; the identification of the $^{12}C^{18}O_4$, $^{13}C^{16}O_4$, and $^{13}C^{18}O_4$, isotopologues supported by *ab initio* calculations confirms the assignments.

1. Introduction

Radiation-induced chemistry of carbon dioxide (CO_2) has shown to be important in a variety of regions from the atmospheres of Venus, Earth, and Mars to the ices of comets, Mars, and planetary satellites [1–6]. As carbon dioxide molecules are degraded by radiation, carbon monoxide along with high energy oxygen atoms are produced [7]. These oxygen atoms can react with carbon dioxide molecules to produce higher order carbon oxides, CO_n ($n > 2$) [8]. Previous studies have shown carbon trioxide to result as an important reaction product of carbon dioxide irradiation experiments. For example, the cyclic C_{2v} structure has been well studied [9–11]. It has been identified by infrared spectroscopy in matrix isolation studies formed by reaction of carbon dioxide with high energy oxygen atoms that are released from radiolysis. More recently, the D_{3h} isomer was also detected by infrared spectroscopy in a 10 K carbon dioxide ice [12]. These isomers are important intermediates in terrestrial atmospheric chemistry to explain the quenching of $O(^1D)$ atoms and possibly the ^{18}O isotope enrichment in stratospheric carbon dioxide [13–16].

The next higher carbon oxide molecule is carbon tetraoxide (CO_4) where theoretical calculations show the C_{2v} structure lying 138 $kJ\,mol^{-1}$ below the D_{2d} structure (Fig. 1) [8]. The carbon tetraoxide molecule has been assumed to be a key intermediate that is formed in irradiated molecular oxygen–carbon dioxide (CO_2–O_2) mixtures as a prerequisite for ozone (O_3) formation and in explaining the disappearance of oxygen atoms [17]. The CO_4 molecule has also been suggested as a potential high energy molecule (HEM) due to the large amount of energy that would accompany its dissociation [18,19]. Thus far, only one experimental study revealing the existence of a CO_4 molecule has been carried out [20]. Cacace et al. detected the carbon tetraoxide ion at mass-to-charge $m/z = 76$ by neutralization–reionization mass spectrometry (NRMS) indicating the existence of the CO_4 neutral molecule. However, this method could not resolve which structural isomer(s) were produced. Here we report the first detection of the C_{2v} isomer of carbon tetraoxide using infrared spectroscopy in a low temperature carbon dioxide ice and support our assignments with theoretical calculations.

2. Materials and methods

The experiments were carried out in a contamination-free ultra high vacuum stainless steel chamber [11]. The

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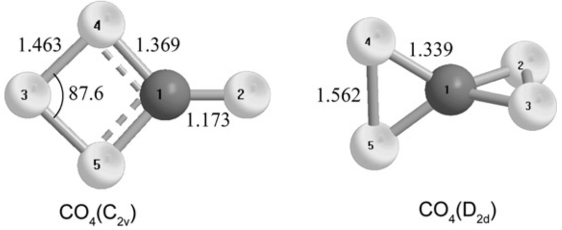

Fig. 1. The two lowest energy isomers of carbon tetraoxide (C_{2v} and D_{2d}) are shown. The central dark gray atoms represent carbon while the light gray atoms are oxygen. Atoms are labeled with numbers to clarify the calculations for the different isotopologues in Tables 1 and 2.

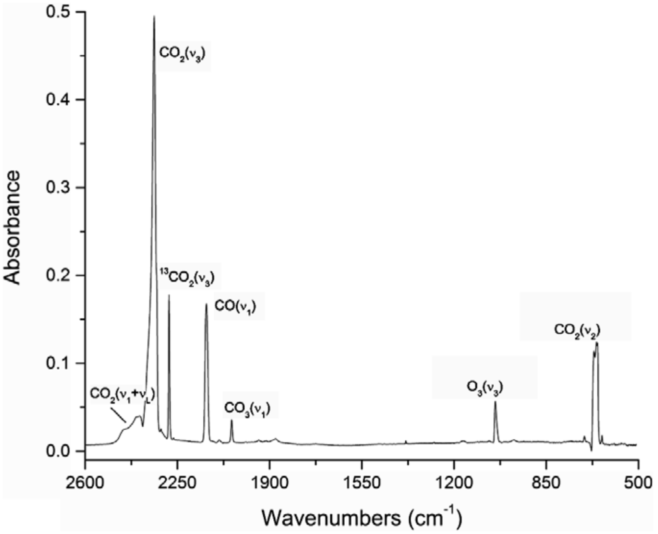

Fig. 2. The infrared absorption spectrum of carbon dioxide ($^{12}C^{16}O_2$) ice after being irradiated to one-hour with 5 keV electrons is shown. New absorptions were observed that are due to carbon monoxide (CO, 2140 cm^{-1}), ozone (O_3, 1043 cm^{-1}) and two isomers of carbon trioxide (C_{2v}, 2044 cm^{-1}, and D_{3h}, 1165 cm^{-1}).

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 directly 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 disburses the gas. The 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. 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 one-hour, 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

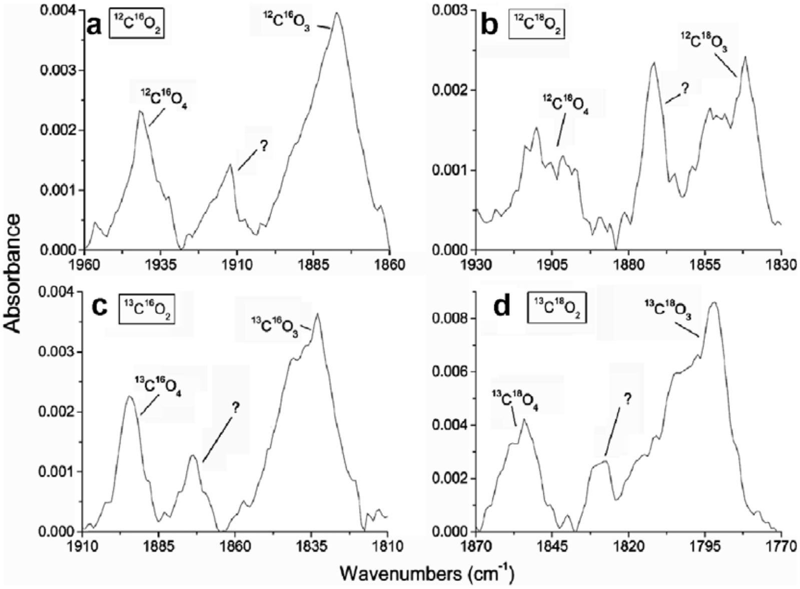

Fig. 3. The infrared absorption features of the ν_1 vibration of four isotopologues of the carbon tetraoxide (C_{2v}) molecule are shown above. A Fermi resonance absorption of the carbon trioxide (C_{2v}) is also labeled in the spectra [11] along with a band that has an unknown carrier. The isotopic compositions of the initial carbon dioxide reactants are boxed.

densities of a molecule can be calculated according to Bennett et al. [11].

The CO_4 (C_{2v} and D_{2d}) structures were minimized by quantum calculations at the B3LYP/6-311G* level of theory. Vibrational frequencies, and infrared intensities were then carried out using the B3LYP level of theory method with the 6-311G* basis set. The calculations were performed employing the GAUSSIAN 98 program package.

3. Results and discussion

First, the carbon dioxide ices were irradiated for one-hour while the experiment was monitored by infrared spectroscopy. Next, the electron beam 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 $CO_4(C_{2v})$ molecule since an investigation of the low mass species produced as a result of the radiolysis has been previously documented by our laboratory [11,12].

After the one-hour irradiation of the carbon dioxide ice a number of new bands were observed in the infrared spectrum (Fig. 2). For example, in the $^{12}C^{16}O_2$ irradiation experiment, carbon monoxide (CO, 2140 cm^{-1}), ozone (O_3, 1043 cm^{-1}) and two isomers of carbon trioxide (C_{2v}, 2044 cm^{-1}, and D_{3h}, 1165 cm^{-1}) were detected [11,12]. Also identified in each of the isotopically labeled experiments are infrared absorptions that we have assigned to the carbon tetraoxide (C_{2v}) molecule (Fig. 3).

In order to validate our infrared assignments of the $CO_4(C_{2v})$ isotopologues, quantum calculations of the vibrational modes and their intensities were performed at the B3LYP/6-311G* level of theory (Table 1). Calculations are also presented for the $CO_4(D_{2d})$ isomer for comparison although this molecule was not observed in our experiments (Table 2). 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 [21] where Irikura et al. [22] 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 example, their results show that at the B3LYP/6-311G(d, p) level of theory, a recommended scaling factor of 0.967 should be used. The error here is reported to be 0.02 in each case. For CO_4, 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.

Table 1
Calculated unscaled wavenumbers (cm^{-1}) are given for several isotopologues of the carbon tetraoxide (C_{2v}) molecule calculated at the B3LYP/6-311G* level of theory

	All ^{16}O	$^{18}O_2$	$^{18}O_3$	$^{18}O_4$	$^{18}(O_2, O_3)$	$^{18}(O_2, O_4)$	$^{18}(O_3, O_4)$	$^{18}(O_4, O_5)$	$^{18}(O_3, O_4, O_5)$	$^{18}(O_2, O_4, O_5)$	$^{18}(O_2, O_3, O_4)$	All ^{18}O	^{13}C, all ^{16}O	^{13}C, all ^{18}O
ω_1	1996	1959	1995	1996	1958	1959	1995	1996	1995	1958	1958	1958	1944	1905
(a_1)	(599.7)	(591.3)	(599.7)	(599.0)	(591.4)	(590.5)	(599.0)	(598.2)	(598.2)	(589.6)	(590.5)	(589.6)	(560.2)	(550.4)
ω_2	1032	1030	1031	1003	1029	1001	1003	978	977	975	1000	974	1031	973
(a_1)	(42.5)	(39.3)	(42.2)	(42.5)	(38.9)	(39.3)	(42.2)	(40.7)	(40.6)	(37.4)	(38.8)	(37.1)	(43.0)	(37.6)
ω_3	913	912	876	909	876	907	871	902	863	899	870	861	913	860
(a_1)	(0.5)	(0.7)	(1.5)	(0.2)	(1.8)	(0.3)	(1.0)	(0.0)	(0.2)	(0.0)	(1.3)	(0.4)	(0.4)	(0.4)
ω_4	789	771	786	778	767	761	766	769	768	752	758	751	784	746
(a_1)	(13.6)	(12.4)	(12.8)	(12.5)	(11.5)	(11.7)	(11.8)	(11.9)	(11.7)	(11.2)	(11.1)	(10.9)	(14.6)	(11.7)
ω_5	1114	1112	1114	1108	1112	1106	1108	1098	1098	1097	1106	1097	1082	1064
(b_2)	(114.0)	(113.1)	(113.9)	(112.1)	(113.0)	(111.2)	(112.1)	(112.3)	(112.2)	(111.4)	(111.2)	(111.3)	(107.1)	(104.4)
ω_6	867	867	844	854	844	853	831	841	818	841	830	818	866	817
(b_2)	(0.9)	(0.9)	(1.0)	(1.4)	(1.0)	(1.2)	(1.4)	(1.0)	(1.0)	(1.0)	(1.1)	(1.0)	(0.8)	(0.9)
ω_7	512	501	510	505	500	494	503	497	496	487	492	485	510	483
(b_2)	(3.4)	(3.3)	(3.4)	(3.2)	(3.3)	(3.0)	(3.1)	(3.0)	(2.9)	(2.8)	(3.0)	(2.8)	(3.6)	(3.0)
ω_8	722	718	721	719	718	715	718	716	716	712	715	712	700	690
(b_1)	(24.2)	(23.6)	(24.2)	(24.2)	(23.6)	(23.6)	(24.2)	(24.2)	(24.2)	(23.6)	(23.6)	(23.6)	(22.6)	(22.1)
ω_9	297	295	290	294	288	292	287	291	284	288	284	281	297	280
(b_1)	(1.5)	(1.5)	(1.5)	(1.4)	(1.5)	(1.4)	(1.4)	(1.4)	(1.4)	(1.3)	(1.4)	(1.3)	(1.6)	(1.3)

Infrared intensities (km mol^{-1}) for the absorptions are also given in parentheses. Oxygen labels (e.g. O_2) correspond to the labels set forth in Fig. 1.

Table 2
Calculated unscaled wavenumbers (cm^{-1}) are given for several isotopologues of the carbon tetraoxide (D_{2d}) molecule calculated at the B3LYP/6-311G* level of theory

	All ^{16}O	$^{18}O_2$	$^{18}(O_2, O_3)$	$^{18}(O_2, O_4)$	$^{18}(O_2, O_3, O_4)$	All ^{18}O
ω_1 (b_2)	1671 (487.5)	1665 (485.6)	1659 (483.7)	1659 (483.9)	1653 (482.1)	1647 (480.3)
ω_2 (b_2)	755 (16.9)	745 (16.0)	735 (15.0)	736 (15.3)	726 (14.5)	716 (13.9)
ω_3 (a_1)	1035 (0.0)	1026 (6.5)	1006 (0.5)	1018 (16.6)	1005 (27.8)	976 (0.0)
ω_4 (a_1)	607 (0.0)	599 (0.2)	589 (0.1)	591 (0.3)	582 (0.2)	572 (0.0)
ω_5 (e)	1005 (49.4)	1005 (49.3)	1005 (49.2)	994 (49.9)	984 (50.3)	984 (50.2)
		990 (43.7)	984 (50.5)	982 (33.2)	980 (22.1)	
ω_6 (e)	540 (12.5)	537 (12.4)	535 (12.3)	528 (11.5)	524 (11.2)	516 (10.6)
		530 (11.4)	521 (10.7)	526 (11.1)	518 (10.7)	
ω_7 (b_1)	344 (0.0)	339 (0.0)	335 (0.0)	334 (0.0)	330 (0.0)	325 (0.0)

Infrared intensities (km mol^{-1}) for the absorptions are also given in parentheses. Oxygen labels (e.g. O_2) correspond to the labels set forth in Fig. 1.

From our calculations, ν_1 vibration of $^{12}C^{16}O_4(C_{2v})$ was computed to be 1936 cm^{-1} after scaling by the recommended value of 0.97. The ν_1 vibration of the heavier isotopologues of carbon tetraoxide show a calculated shift toward lower wavenumbers. For example, after scaling, values of 1899, 1886, and 1847 cm^{-1} are reported for the isotopologues $^{12}C^{18}O_4$, $^{13}C^{16}O_4$, and $^{13}C^{18}O_4$, respectively.

In the $^{12}C^{16}O_2$ irradiation experiment, the ν_1 vibration of $^{12}C^{16}O_4(C_{2v})$ was observed at 1941 cm^{-1} compared to a calculated wavenumber of 1936 cm^{-1} (Table 3). The next most intense absorption of the carbon tetraoxide molecule would be the ν_5 vibration centered at 1114 cm^{-1}. However, no absorption could be identified in this region due to its low intensity. In Table 1, the ν_5 vibration should be more than five times less intense than the ν_1 vibration. The integrated peak of the ν_1 vibration after the one-hour irradiation is about 0.025 cm^{-1} and so the intensity of the ν_5 vibration is calculated to be 0.005 cm^{-1} which puts its intensity at the noise level in the experiment (0.005 cm^{-1}). Therefore, confirmation of our assignment of the $CO_4(C_{2v})$ molecule requires an agreement with the predicted isotope shifts in the ν_1 position. This approach has been utilized recently to detect the novel C_s symmetric OCNO isomer [23] and also the D_{3h} structure of the CO_3 molecule [12]. In the $^{12}C^{18}O_2$ experiment, $^{12}C^{18}O_4$ was observed at 1908 cm^{-1} which compared well to a scaled value of 1899 cm^{-1}. In the $^{13}C^{16}O_2$ experiment, $^{13}C^{16}O_4$ was observed at 1894 cm^{-1} which agrees with the theoretical value of 1886 cm^{-1}. Lastly, in the $^{13}C^{18}O_2$ irradiation experiment $^{13}C^{18}O_4$ was observed at 1855 cm^{-1} compared to the scaled theoretical shift of 1847 cm^{-1}. The consistent agreement of the peak positions of the ν_1 fundamental vibrations of the $CO_4(C_{2v})$ isotopologues with the theoretically predicted shifts confirms our assignment of the carbon tetraoxide molecule.

Table 3
The observed wavenumbers of the ν_1 vibration of the different isotopologues of carbon tetraoxide (CO_4, C_{2v}) are compared to the scaled theoretically calculated values at the B3LYP/6-311G* level of theory

Isotopomer	Observed wavenumber/ cm^{-1}	Calculated wavenumber (scaled)/cm^{-1}
$^{12}C^{16}O_4$	1941	1936
$^{12}C^{18}O_4$	1908	1899
$^{13}C^{16}O_4$	1894	1886
$^{13}C^{18}O_4$	1855	1847

A scaling factor of 0.97 is used.

However, we must address the possibility that other molecules containing C═O functional groups may be responsible for the assigned CO_4 peak. There are several possibilities to consider, notably the CO_n and C_2O_n species. It is worth mentioning that our irradiation experiments on carbon monoxide ice [24] resulted in the formation of several carbon-rich species including C_n (n = 3,6), C_nO (n = 1–6), and C_nO_2 (n = 1,3–5). Besides CO and CO_2, none of the other species were found in the current CO_2 irradiation experiment and so the assignment must be an oxygen rich carbon oxide that contains a C═O functional group. We have performed vibrational frequency calculations of several isomers of the CO_n species (n = 3–6) [12,25]. The C_{2v} isomer of CO_4 provides the best match to the observed peak position and the corresponding isotope shifts. To consider dicarbon oxides, a literature search shows that none of the considered C_2O_n (n = 3,4) molecules agree with the observed peak position. $C_2O_3(C_{2v})$ has its most intense absorption near 1865 cm^{-1} eliminating it as a possible molecule for the 1941 cm^{-1} peak [26]. $C_2O_4(C_{2v})$ has been theoretically investigated [27] where the most intense scaled frequencies were found to be 1898.8 and 1919.8 cm^{-1}. This molecule also has an intense absorption near 1100 cm^{-1}. These absorptions do not match the current results and no feature was observed near 1100 cm^{-1}. Higher order dicarbon oxides are unlikely to form due to their high complexity and so the agreement of the peak position of CO_4 and its isotope shifts seems to justify our assignment.

After the one-hour irradiation phase of the experiment, the ice was left isothermal at 10 K for one-hour to check the stability of the products. There was no observable change in the column density of carbon tetraoxide (C_{2v}) indicating that the product was stable and that there were no residual reactions occurring in the ice to form CO_4. The ice was then heated at a rate of 0.5 K min^{-1} to further check the stability of the carbon tetraoxide molecule. In the infrared spectra, the carbon dioxide matrix was observed to sublime around 92 K, however, the carbon tetraoxide absorptions remained until about 120 K. This high temperature is interesting because $CO_4(C_{2v})$ should be unstable with respect to dissociation to $CO_2(X^1\Sigma_g^+)+O_2(X^3\Sigma_g^-)$ [8,19]. However, Averyanov et al. have found that there is likely a significant barrier to this dissociation due a large singlet–triplet energy gap. A large barrier is also likely to exist for the spin-allowed dissociation to $CO_2(X^1\Sigma_g^+)+O_2(a^1\Delta_g)$ [19].

4. Summary

We have detected the carbon tetraoxide (C_{2v}) molecule by its v_1 vibrational mode in four different isotopically labeled experiments (Fig. 3). Our assignment is supported by an agreement of the observed peak positions of the four isotopologues with our *ab initio* calculations (Table 3). The formation routes might proceed via insertion of a suprathermal oxygen atom into the oxygen–oxygen and/or carbon–oxygen atom of the cyclic substructure of the carbon trioxide molecule; a detailed kinetic investigation is currently in progress. The CO_4 molecule may be an important precursor involved in the formation of ozone or electronically excited molecular oxygen in our own atmosphere [17,19]. Also, the CO_4 anion has been thought to be involved in many reactions in the atmospheres of Earth and Mars [28,29]. The CO_4 molecule detected in our experiment may have reaction channels that lead to its anion. Carbon tetraoxide (C_{2v}) may also be a candidate high energy material with its high oxygen balance (OB) and heat of formation [19,30]. Lastly, in the radiation processed carbon dioxide ices of the outer solar system like on Triton and Ganymede (Neptune's and Jupiter's largest moons, respectively), the carbon tetraoxide (C_{2v}) molecule may be produced and stabilized in these low temperature environments.

Acknowledgements

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