

First detection of the C_s symmetric isomer of carbon hexaoxide (CO_6) at 10 K

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Abstract

Carbon oxides of the form CO_n ($n = 2\text{--}8$) have long been known as important molecules in atmospheric and solid state chemical reactions. Here, we report on the first infrared spectroscopic detection of the cyclic (C_s) isomer of carbon hexaoxide ($^{12}\text{C}^{16}\text{O}_6$) via its ν_1 vibrational mode centered around 1876 cm^{-1} under matrix isolation conditions; the identification of the $^{12}\text{C}^{18}\text{O}_6$, $^{13}\text{C}^{16}\text{O}_6$, and $^{13}\text{C}^{18}\text{O}_6$ isotopologues supported by *ab initio* calculations confirm the assignments. We also discuss possible formation routes of this molecule. © 2007 Elsevier B.V. All rights reserved.

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 ($n = 3\text{--}8$). 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 ($\text{O}(^1\text{D})$) 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 stable molecules [13,14]. These include the well-known C_{2v} symmetric CO_3 isomer [15], the C_{2v} symmetric CO_4 structure [17], and the C_2 symmetric CO_5 molecule [18], which were detected recently in our laboratory via infrared spectroscopy in low-temperature carbon dioxide ices. 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 higher-order carbon oxides CO_n isomers ($n > 5$) has been difficult. Here we report the first experimental detection of one isomer of the next higher-order carbon oxide species, the C_s symmetric carbon hexaoxide molecule (CO_6 , C_s), via low-temperature, infrared spectroscopy (Fig. 1). The spectral identification is supported with isotopic substitutions and theoretical calculations. The stability and the kinetics of the observed CO_6 molecule are also addressed.

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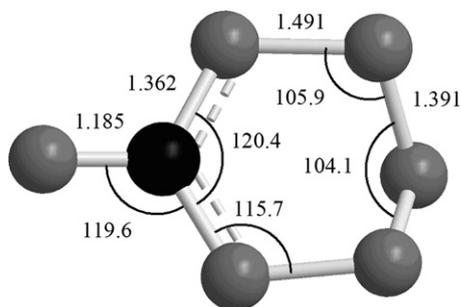


Fig. 1. The C_s symmetric carbon hexaoxide molecule is shown. The central black atom represents carbon while the gray atoms are oxygen. Calculated bond lengths (Å) and bond angles ($^\circ$) are also shown.

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 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 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) $^{12}\text{C}^{16}\text{O}_2$, (b) $^{12}\text{C}^{18}\text{O}_2$, (c) $^{13}\text{C}^{16}\text{O}_2$, and (d) $^{13}\text{C}^{18}\text{O}_2$. The progress of the reaction was monitored using a Nicolet 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 infrared features were deconvoluted utilizing the Fourier self-deconvolution GRAMS/AI (7.02) Program Package (Thermo Galactic, 1991–2002). The deconvolution filter is a simple exponential filter of the form

$\exp(2\pi\gamma X)$ where γ is the deconvolution filter constant and X is the data file. This function is multiplied by the Fourier transformed trace, and the data is then reverse Fourier transformed to give the result.

The minimized structure of the C_s symmetric CO_6 molecule was calculated at the B3LYP [19,20] level of theory with the 6-311G* basis set. Quantum calculations including vibrational frequencies and infrared intensities of the carbon hexaoxide 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 [21].

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 allow for a kinetic interpretation of the product. 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. This work is specifically devoted to the spectroscopic characterization of the $\text{CO}_6(C_s)$ molecule. An investigation of the low mass species (ozone, carbon monoxide, two isomers of carbon trioxide, carbon tetraoxide, and carbon pentaoxide) produced as a result of the radiolysis has been previously documented [15–18].

3.1. Infrared band assignment

We will first review our infrared band assignments of the carbon hexaoxide (C_s) 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/6-311G* 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 example, 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

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

Symmetry	$^{12}\text{C}^{16}\text{O}_6$		$^{12}\text{C}^{18}\text{O}_6$		$^{13}\text{C}^{16}\text{O}_6$		$^{13}\text{C}^{18}\text{O}_6$	
	B3LYP/6-311G*	QCISD/6-311G**	B3LYP/6-311G*	QCISD/6-311G**	B3LYP/6-311G*	QCISD/6-311G**	B3LYP/6-311G*	QCISD/6-311G**
A'	155 (0.6)	141 (1.3)	146 (0.5)	133 (1.1)	155 (0.6)	141 (1.3)	146 (0.5)	133 (1.1)
A''	165 (0.3)	181 (0.6)	155 (0.3)	170 (0.5)	165 (0.3)	181 (0.6)	155 (0.3)	170 (0.5)
A''	414 (8.4)	458 (7.8)	392 (7.2)	435 (6.6)	412 (8.6)	456 (8.0)	391 (7.4)	433 (6.8)
A'	466 (1.2)	499 (0.4)	441 (1.1)	473 (0.5)	464 (1.1)	497 (0.3)	440 (1.1)	471 (0.4)
A''	534 (0.004)	562 (0.2)	504 (0.005)	530 (0.2)	533 (0.003)	562 (0.2)	503 (0.004)	530 (0.2)
A''	577 (0.1)	600 (0.1)	544 (0.1)	567 (0.2)	577 (0.1)	599 (0.1)	544 (0.1)	566 (0.1)
A'	583 (1.1)	700 (22.5)	551 (1.2)	680 (13.5)	582 (1.0)	684 (25.3)	550 (1.0)	667 (18.2)
A'	665 (14.3)	730 (1.8)	636 (8.3)	688 (1.6)	655 (18.4)	730 (1.8)	630 (11.1)	688 (1.6)
A'	740 (24.1)	778 (21.2)	720 (29.5)	747 (28.5)	727 (17.8)	771 (16.1)	704 (24.1)	737 (21.6)
A''	812 (18.0)	873 (16.4)	766 (15.1)	824 (17.1)	812 (18.7)	872 (14.9)	766 (15.7)	823 (15.3)
A'	841 (13.8)	875 (12.1)	799 (9.4)	826 (9.7)	836 (15.8)	874 (13.1)	795 (11.4)	826 (10.4)
A'	862 (30.0)	908 (30.3)	813 (27.6)	860 (22.3)	862 (29.5)	905 (33.6)	813 (27.0)	857 (25.5)
A'	975 (4.1)	992 (27.9)	920 (3.6)	936 (25.1)	975 (4.2)	991 (27.7)	919 (3.7)	935 (24.9)
A''	1174 (151)	1223 (159.1)	1154 (150.0)	1201 (158.4)	1143 (139.6)	1190 (147.1)	1122 (139.0)	1168 (146.7)
A'	1890 (328.3)	1937 (374.0)	1850 (320.3)	1898 (367.0)	1844 (308.4)	1889 (349.8)	1803 (300.5)	1848 (343.0)

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

errors here are reported to be 0.02 in each case. For CO_6 , 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 $^{12}\text{C}^{16}\text{O}_2$ irradiation experiment, the ν_1 vibration of $^{12}\text{C}^{16}\text{O}_6(C_s)$ was observed at 1876 cm^{-1} (Fig. 2) compared to a calculated wavenumber of 1877 cm^{-1} after being scaled by a factor of 0.993. In comparing our chosen scaling factor with the aforementioned value of 0.967 found by Irikura et al., we see that they differ by 0.026, 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_6 peak position. With these considerations, our chosen scaling factor of 0.993 for the B3LYP/6-311G* level of theory seems reasonable. Also, a scaling factor of 0.969 was chosen for the QCISD/6-311G* level of theory. These scaling factors compare very well with those used in our identification of the C_2 symmetric carbon pentaoxide molecule (0.992 for B3LYP and 0.967 for QCISD) by its ν_1 vibrations [21]. This agreement in scaling factors supports our assignments since the CO stretching of the C_2 symmetric CO_5 and C_s symmetric CO_6 molecules occur in similar electronic (carbonyl attached to an oxygen ring) and physical environments (carbon dioxide ice matrix at 10 K), the resulting scaling factors at the two levels of theory are expected to be nearly equivalent.

After the ν_1 vibration of CO_6 , the next most intense absorption of the carbon hexaoxide molecule is the A'' symmetric vibration centered at an unscaled value of 1174 cm^{-1} (Table 1). However, no absorption could be identified in this region due to its low intensity, which should be less than half the intensity of the ν_1 vibration. Therefore, confirmation of our assignment of the $\text{CO}_6(C_s)$ molecule requires an agreement with the predicted isotope shifts in the ν_1 position. In the $^{12}\text{C}^{18}\text{O}_2$ experiment, $^{12}\text{C}^{18}\text{O}_6$ was observed at 1837 cm^{-1} which agrees with the scaled value of 1837 cm^{-1} (0.993 scaling factor). In the $^{13}\text{C}^{16}\text{O}_2$

Table 2

The observed wavenumbers of the ν_1 vibration of the different isotopologues of carbon hexaoxide (CO_6 , C_s) are compared to the scaled theoretically calculated values at the B3LYP/6-311G* (scaling factor 0.993) and the QCISD/6-311G** (scaling factor 0.969) levels of theory

Isotopologue	Observed wavenumber (cm^{-1})	B3LYP/6-311G* calculated wavenumber (cm^{-1})	QCISD/6-311G* calculated wavenumber (cm^{-1})
$^{12}\text{C}^{16}\text{O}_6$	1876	1877 (1890)	1877 (1937)
$^{12}\text{C}^{18}\text{O}_6$	1837	1837 (1850)	1839 (1898)
$^{13}\text{C}^{16}\text{O}_6$	1832	1831 (1844)	1830 (1889)
$^{13}\text{C}^{18}\text{O}_6$	1791	1790 (1803)	1791 (1848)

The unscaled theoretical values are shown in parentheses.

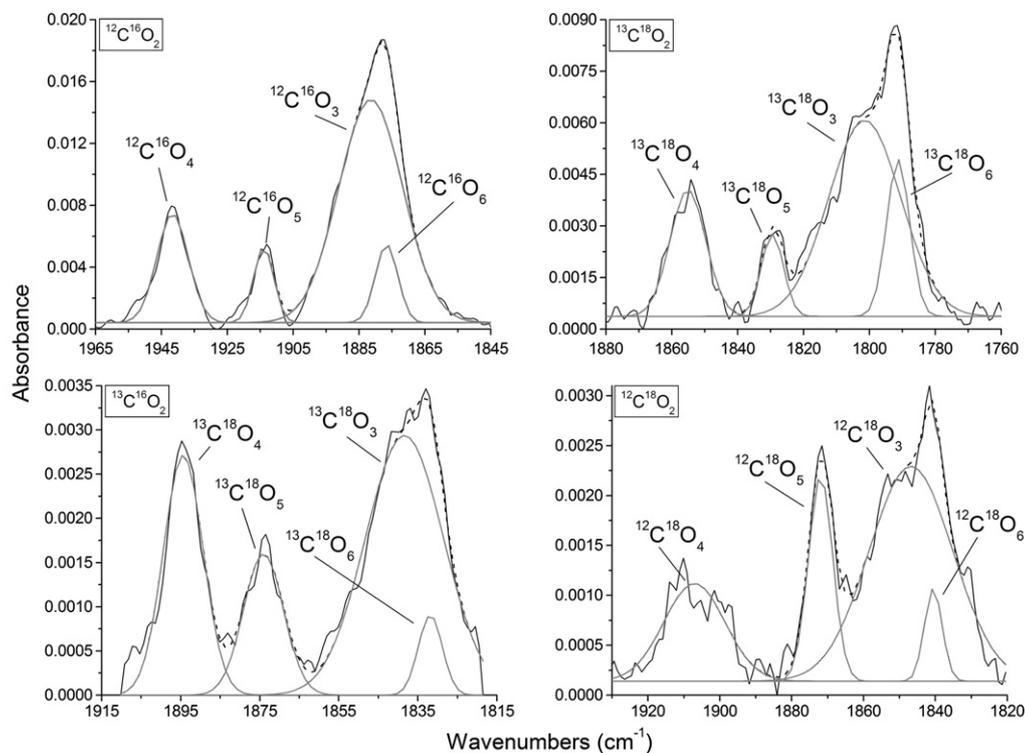


Fig. 2. The infrared absorption features of the ν_1 vibration of four isotopologues of the carbon hexaoxide (C_6) molecule are shown above. Also labeled in the spectra are a Fermi resonance absorption of carbon trioxide (C_{2v}), and the carbon tetraoxide (C_{2v}) molecule, and the carbon pentaoxide (C_2) molecule. The isotopic compositions of the initial carbon dioxide reactants are boxed.

experiment, $^{13}C^{16}O_6$ was observed at 1832 cm^{-1} which agrees with the scaled theoretical value of 1831 cm^{-1} . Lastly, in the $^{13}C^{18}O_2$ irradiation experiment $^{13}C^{18}O_6$ was observed at 1791 cm^{-1} compared to the scaled theoretical shift of 1790 cm^{-1} . The consistent agreement of the peak positions of the ν_1 fundamental vibrations of the $CO_6(C_s)$ isotopologues with the theoretically predicted shifts confirms or assignment of the C_s symmetric carbon hexaoxide molecule.

4. Discussion

4.1. Formation and stability

A literature search on the CO_6 molecule reveals very little. Only one paper could be found, which addressed the theoretical formation and stability of two carbon hexaoxide isomers [13]. In their paper, Elliot and Boldyrev found that most stable CO_6 isomer has a C_2 symmetric bi-cyclic structure, O_2CO_4 (not the isomer presented in this Letter). They also found stability in a D_{2d} symmetric bi-cyclic structure, O_3CO_3 (lying 59 kJ mol^{-1} higher in energy than the C_2 symmetric bi-cyclic structure). However, neither of these isomers correspond to the one observed in our experiments. Elliot and Boldyrev found that our structure, a six-membered ring opposing a carbonyl functional group (OCO_5), had one imaginary frequency and that the molecule would dissociate into carbon dioxide and molecular oxygen upon

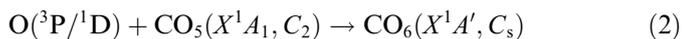
vibration. This is in obvious conflict with our own calculations since we were able to derive a stable structure with real vibrational frequencies both at the B3LYP/6-311G* and QCISD/6-311G* levels of theory (Table 1).

As this is the first detection of the carbon hexaoxide molecule (only one theoretical work could be found) [13], it is useful for us to identify the likely formation pathways within our irradiated ice. Briefly, we will summarize the preliminary reactions that may be relevant to the formation of carbon hexaoxide. Initially, carbon dioxide may undergo radiation-induced dissociation producing carbon monoxide and an oxygen atom (Eq. (1)). The oxygen atom may be either in its ground electronic state (3P) or electronically excited (1D), both of which may be suprathermal (excess kinetic energy). The oxygen atoms produced can react via multiple reaction pathways with carbon dioxide molecules to form carbon trioxide isomers, carbon tetraoxide, and carbon pentaoxide, as previously reported [15–18].



With the aforementioned atoms/molecules as reactants (CO_5 , CO_4 , CO_3 , CO_2 , CO , O , as well as O_2 , O_3), one may consider a number of reaction pathways that could possibly form carbon hexaoxide. A look at the formation routes found by our laboratory for the cyclic $CO_4(C_{2v})$ and $CO_5(C_2)$ molecules may give us insight to the likely formation pathways of carbon hexaoxide. For example, both CO_4 and CO_5 were suggested to be formed by oxygen

insertion into the ring structure of the next lower-order carbon oxide molecule (i.e., $\text{OCO}_2 + \text{O} \rightarrow \text{OCO}_3$, and $\text{OCO}_3 + \text{O} \rightarrow \text{OCO}_4$). We would therefore predict that the C_s symmetric isomer of carbon hexaoxide that was observed in this experiment could be formed via a similar pathway where an oxygen atom would insert into one of the C–O or O–O bonds in the five-membered ring of carbon pentaoxide (Eq. (2)).



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 suprathreshold (excess kinetic energy); recall that as carbon dioxide dissociates (Eq. (1)), excess energy is to be transferred to kinetic energy of the oxygen atom. This reaction (Eq. (2)) was calculated to be exoergic by 181 and 371 kJ mol^{-1} for ground and excited state oxygen atoms, respectively.

Since several reactions likely precede the formation of carbon hexaoxide (i.e., the formation of CO_3 , CO_4 , and CO_5), it would support our assignment then to confirm the delayed development of the infrared absorption feature of carbon hexaoxide that should be expected after the start of the irradiation. In order to do this, molecular abundances (column densities) in units of molecules cm^{-2} were derived to quantify the abundance of the $\text{CO}_6(C_s)$ molecule throughout the irradiation phase of the experiment. Only the temporal developments of the $^{12}\text{C}^{16}\text{O}_6$ and $^{13}\text{C}^{18}\text{O}_6$ bands are plotted since there were larger errors in deconvoluting the bands of $^{12}\text{C}^{18}\text{O}_6$ and $^{13}\text{C}^{16}\text{O}_6$ throughout the irradiation. It is seen from Fig. 3 that the CO_6 ν_1 band does

not appear until 400 s into the irradiation. This is in agreement with the high-order kinetics expected for the development of the carbon hexaoxide molecule.

After the one hour 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 hexaoxide (C_s) indicating that the product was stable at 10 K and that there were no reactions occurring in the ice to form or destroy CO_6 . The ice was then slowly heated at a rate of 0.5 K min^{-1} to further check the stability of the carbon hexaoxide molecule. In the infrared spectra, the carbon dioxide matrix was not observed to sublime until around 92 K, however, the band region containing the carbon trioxide (C_{2v}) and carbon hexaoxide absorptions ($1905\text{--}1850 \text{ cm}^{-1}$ in the $^{12}\text{C}^{16}\text{O}_2$ irradiation experiment) (Fig. 2) was observed to change shape and intensity around 60 K, although carbon trioxide (C_{2v}) is known not to sublime until around 80 K [15]. This may be an indication of the instability of carbon hexaoxide above 60 K.

5. Conclusion

We have detected the carbon hexaoxide (C_s) molecule by its ν_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 2). The $\text{CO}_6(C_s)$ molecule is likely formed via the insertion of oxygen atoms into the ring structure of the C_2 isomer of carbon pentaoxide. The spectroscopically verified existence of high-order carbon oxide species from this and preceding works (CO_3 isomers, CO_4 , CO_5) [15–18] confirms the stability of these species as has been previously predicted by theoretical studies [13,14]. This lends support to the idea that CO_6 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 hexaoxide 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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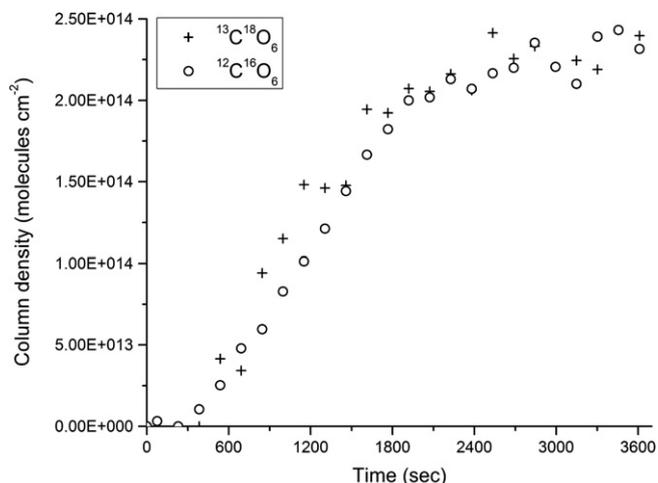


Fig. 3. The temporal development of the column density of carbon hexaoxide (CO_6, C_s) is shown during the 1 h irradiation phase of the experiment. Error bars, which are omitted for clarity, are $\pm 2 \times 10^{13}$ molecules cm^{-2} ; calculated by integrating a featureless region of the infrared spectrum and propagating the error through the column density calculations.

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