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 $CO_n$ ($n = 2–8$) 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 ($^{12}C^{16}O_6$) via its $v_1$ vibrational mode centered around 1876 cm$^{-1}$ under matrix isolation conditions; the identification of the $^{12}C^{18}O_6$, $^{13}C^{16}O_6$, and $^{13}C^{18}O_6$, isotopologues supported by $ab$ initio calculations confirm the assignments. We also discuss possible formation routes of this molecule.

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 ($O(1D)$) 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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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 $5 \times 10^{-11}$ 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 thermostable 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 $1.0 \times 10^{-7}$ Torr at 10 K to a total thickness of $250 \pm 50$ 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 $1.8 \times 10^{16}$ 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 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 $\exp(2\gamma X)$ where $\gamma$ 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 $C_6$ 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 CO$_6(C_6)$ 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 ($C_6$) 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/6-31G* 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

Fig. 1. The $C_6$ 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 (°) are also shown.
The QCISD/6-311G* levels of theory

The QCISD/6-311G** (scaling factor 0.969) levels of theory

logues of carbon hexaoxide (CO$_6$)

The observed wavenumbers of the $v_1$ vibration of the different isotopologues of carbon hexoxide (CO$_6$, C$_x$) 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

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>Observed wavenumber (cm$^{-1}$)</th>
<th>B3LYP/6-311G$^*$</th>
<th>QCISD/6-311G$^{**}$</th>
<th>B3LYP/6-311G$^*$</th>
<th>QCISD/6-311G$^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^2$C$^{16}$O$_6$</td>
<td>1876</td>
<td>1877 (1890)</td>
<td>1877 (1937)</td>
<td>1876 (1890)</td>
<td>1877 (1937)</td>
</tr>
<tr>
<td>1$^2$C$^{18}$O$_6$</td>
<td>1837</td>
<td>1837 (1850)</td>
<td>1839 (1898)</td>
<td>1837 (1850)</td>
<td>1839 (1898)</td>
</tr>
<tr>
<td>1$^2$C$^{16}$O$_6$</td>
<td>1832</td>
<td>1831 (1844)</td>
<td>1830 (1889)</td>
<td>1831 (1844)</td>
<td>1830 (1889)</td>
</tr>
<tr>
<td>1$^2$C$^{12}$O$_6$</td>
<td>1791</td>
<td>1790 (1803)</td>
<td>1791 (1848)</td>
<td>1790 (1803)</td>
<td>1791 (1848)</td>
</tr>
</tbody>
</table>

The unscaled theoretical values are shown in parentheses.
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 $v_1$ fundamental vibrations of the CO$_6(\text{Cs})$ 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 hexoxide isomers [13]. In their paper, Elliot and Boldyrev found that most stable CO$_6$ isomer has a C$_2$ symmetric bi-cyclic structure, O$_2$CO$_4$ (not the isomer presented in this Letter). They also found stability in a D$_{2d}$ symmetric bi-cyclic structure, O$_2$CO$_3$ (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$_2$), 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 hexoxide 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 hexoxide. 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].

$$\text{CO}_2(X^1\Sigma_g^+) \rightarrow \text{CO}(X^1\Sigma_g^+) + \text{O}(^3P/^1D)$$ (1)

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 hexoxide. A look at the formation routes found by our laboratory for the cyclic CO$_4$(C$_2$) and CO$_5$(C$_2$) molecules may give us insight to the likely formation pathways of carbon hexoxide. For example, both CO$_4$ and CO$_3$ were suggested to be formed by oxygen
insertion into the ring structure of the next lower-order carbon oxide molecule (i.e., OCO$_2$ + O → OCO$_3$, and OCO$_3$ + O → OCO$_4$). We would therefore predict that the Cs 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)).

$$\text{O}^i(\text{P}^3/\text{D}) + \text{CO}_3(X^1\text{A}^1, C_2^+) \rightarrow \text{CO}_6(X^1\text{A}^1, C_s) \quad (2)$$

If this attack occurs by an electronically excited oxygen atom ($^1\text{D}$), this should allow a barrierless insertion process. On the other hand, an oxygen attack in the electronic ground state ($^3\text{P}$) 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. 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 CO$_6(C_s)$ molecule throughout the irradiation phase of the experiment. Only the temporal developments of the $^{12}$C$^{16}$O$_6$ and $^{13}$C$^{18}$O$_6$ bands are plotted since there were larger errors in deconvoluting the bands of $^{12}$C$^{18}$O$_6$ and $^{13}$C$^{16}$O$_6$ throughout the irradiation. It is seen from Fig. 3 that the CO$_6$ $v_1$ 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 (1905–1850 cm$^{-1}$ in the $^{12}$C$^{16}$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 $v_1$ 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 2). The CO$_6(C_s)$ molecule is likely formed via the insertion of oxygen atoms into the ring structure of the $C_s$ 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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References