

CO₄: An MS and Theoretical Study

Carbon Tetraoxide: Theoretically Predicted and Experimentally Detected**

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The current interest in CO_n ($n > 2$) oxides reflects the growing recognition of their role in different research areas. First, CO_n species are key intermediates in the reactions of atomic and molecular oxygen with the lower oxides of carbon, hydrocarbons, and other organic molecules.^[1] Furthermore, CO_n oxides and their ions are relevant to the chemistry of the terrestrial^[2] and planetary^[3] atmospheres. More importantly, members of the CO_n family are potential high-energy density materials (HEDM), the next generation of environmentally benign propellants and explosives.^[4] CO₄ is of special interest, since ab initio MP2, QCISD and MP2/6-31G* calculations^[5–7] have identified a CO₄ D_{2d} ¹A₁ singlet as a metastable species that releases from 80 to 93 kcal mol^{–1} upon dissociation into CO₂ (X ¹Σ⁺) and O₂ (a¹Δ). Another isomer of C_{2v} symmetry has been identified on the potential energy surface (PES) of the lowest ¹A₁ singlet state, and two local C_{2v} minima have been located on the low-lying, excited triplet PES.^[7] In summary, the available theoretical results identify two singlets of D_{2d} and C_{2v} symmetry as the lowest energy CO₄

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isomers and suggest that these molecules, albeit metastable, might be detectable. So far, however, CO_4 has been experimentally elusive, the only species observed being a weakly bonded $\text{CO}\cdots\text{O}_3$ van der Waals complex formed by codeposition of CO and O_3 in an Ar matrix, stable only below 10 K, as at higher temperatures its monomers react yielding CO_2 .^[8]

We report herein the experimental discovery of CO_4 , a metastable molecule sufficiently long-lived to allow its positive detection as an isolated species in the gas state. We utilized a well-established technique, neutralization–reionization mass spectrometry (NRMS),^[9] implemented on a highly sensitive instrument previously used for the detection of other elusive molecules, including N_4 , O_4 , HO_3 , and the $[\text{H}_2\text{O}^+\text{O}_2^-]$ CT complex.^[10,11]

First, a population containing, among other ions, a CO_4^+ precursor amenable to neutralization was prepared. Next, the structure of the mass-selected CO_4^+ ions was assayed by collision techniques. In the third step, the actual neutralization–reionization sequence was performed, which detected a significant CO_4 “recovery” peak. Confirmatory experiments were carried out with ^{18}O -labeled reagents to rule out the conceivable interference from isobaric contaminants. Finally, the results of NRMS experiments were compared with those of the computational study of the CO_4^{+0} system at the B3 LYP and CCSD(T) level of theory.

The CO_4^+ cation, m/z 76, was obtained from two reactions that involved the ionization of CO_2/O_2 and CO_2/O_3 mixtures by 70 eV electrons. The first route, that conceivably involves two distinct processes [Eq. (1a), (1b)]



requires association of the reagents, and therefore was studied by chemical ionization (CI) at sufficiently high pressures as to ensure partial collisional stabilization of the adduct. The second reaction



was studied also in the low-pressure range, accessible to Fourier-transform ion cyclotron resonance (FTICR) spectrometry. This technique allowed us to unambiguously identify the charged reagent and to positively assign the charged product of m/z 76 as $^{12}\text{C}^{16}\text{O}_4^+$ by accurate mass measurements, consistent with the shift from m/z 76 to 80 of the charged product noted in CI experiments, in which $^{16}\text{O}_2$ is replaced by $^{18}\text{O}_2$ (Figure 1).

Irrespective of the preparation method, the CO_4^+ populations probed by collisionally activated dissociation (CAD) and multistage mass-spectrometry (MS^3) techniques show the same collisional fragmentation pattern, whose salient features can be summarized as follows: the CAD spectra display signals arising from the O_2^+ ion as the major fragment, together with less intense signals from CO_2^+ , CO^+ and O^+ ions, and weak signals ($<1\%$) from O_3^+ and CO_3^+ ions (Figure 2). The CAD spectra of the $\text{C}^{16}\text{O}_2^{18}\text{O}_2^+$ population obtained from reactions (1a)/(1b) when using $^{18}\text{O}_2$ display signals from $^{18}\text{O}_2^+$ ions as the most abundant fragment, together with signals from $\text{C}^{16}\text{O}_2^+$, C^{16}O^+ , $^{16}\text{O}^+$, $^{18}\text{O}^+$ ions and

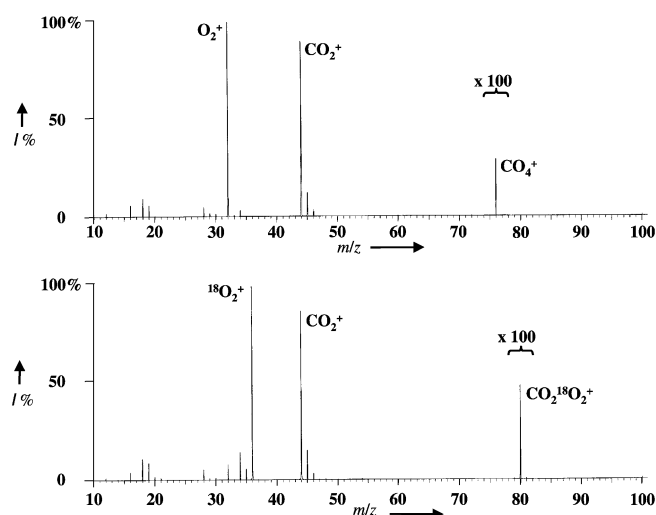


Figure 1. CI spectra of (top) $\text{CO}_2/^{16}\text{O}_2$, (bottom) $\text{CO}_2/^{18}\text{O}_2$ mixtures.

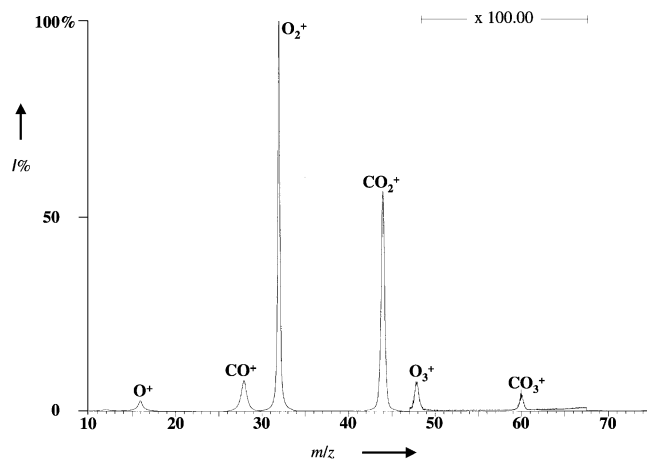


Figure 2. CAD spectra of the CO_4^+ population, see text.

weak signals from the $\text{C}^{16}\text{O}_2^{18}\text{O}^+$ and $\text{C}^{16}\text{O}^{18}\text{O}_2^+$ isotopomers and from the $^{16}\text{O}^{18}\text{O}_2^+$ ion.

NRMS of CO_4^+ , performed by using CH_4 and O_2 as the collision gases in the neutralization and reionization cell, respectively, gives a significant “recovery” peak of m/z = 76 (Figure 3). To rule out conceivable interferences from isobaric adventitious contaminants, the NR spectra of $^{12}\text{C}^{18}\text{O}_4^+$ (from $^{12}\text{C}^{18}\text{O}_2$ and $^{18}\text{O}_2$), and of $^{12}\text{C}^{16}\text{O}_2^{18}\text{O}_2^+$ (from $^{12}\text{C}^{16}\text{O}_2$ and $^{18}\text{O}_2$) were recorded (Figure 3). Invariably, the m/z ratio of the “recovery” peak undergoes the shift expected for the specific isotopomer used, thus confirming that neutral CO_4 does exist in the gas state, with a lifetime exceeding the flight time from the neutralization to the reionization cell, namely about 1 μs .

Figure 4 illustrates the geometries and relative energies of the CO_4^+ ion and CO_4 species identified. On the doublet PES the most stable species is the $\text{C}_s^2\text{A}'$ ion **1**, in essence a cluster formed by CO_2 and O_2 units joined by electrostatic forces and characterized by a large separation of the monomers. The $\text{C}_s^2\text{A}'$ ion **2** and the $\text{C}_{2v}^2\text{A}_2$ doublet **3** lie at considerably higher energies (some 4 eV). Another cluster, the $\text{C}_s^4\text{A}''$ species **4**, was identified on the quartet PES.

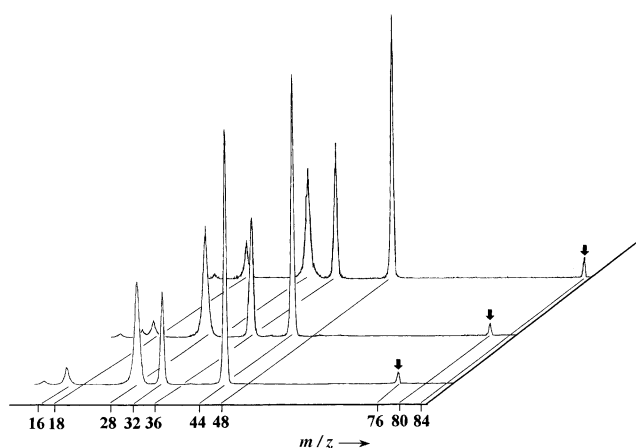


Figure 3. NR spectra of $^{12}\text{C}^{16}\text{O}_4^+$, m/z 76 (bottom trace), $^{12}\text{C}^{16}\text{O}_2^{18}\text{O}_2^+$, m/z 80 (middle trace) and $^{12}\text{C}^{18}\text{O}_4^+$, m/z 84 (top trace). The arrows indicate the "recovery" peaks at the appropriate m/z ratios.

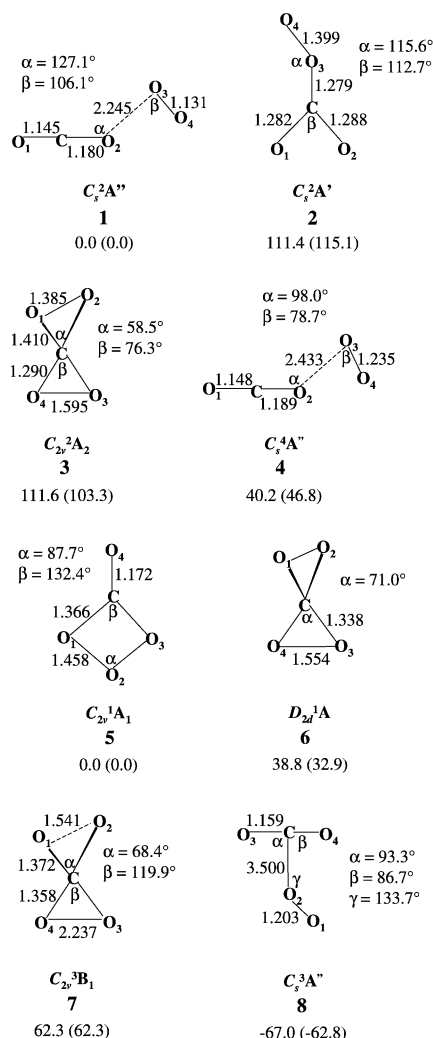
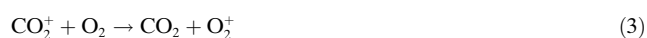


Figure 4. Optimized geometries and relative energies of the CO_4^+ and CO_4 species calculated at the B3LYP and the CCSD(T) (in parentheses) level.

With regards to neutral CO_4 , the most stable species on the singlet PES is the $C_{2v}^1A_1$ molecule **5**, which is unstable with respect to the spin forbidden dissociation into CO_2 and O_2 in their ground states by 67.5 and 62.7 kcal mol $^{-1}$ at the B3LYP and CCSD(T) level, respectively. By using higher energy calculations (38.8 and 32.9 kcal mol $^{-1}$ at the B3LYP and the CCSD(T) level, respectively) we localized **6**, a singlet of D_{2d} symmetry. Based on the experimental separation between $\text{O}_2(^3\Sigma_g^-)$ and $\text{O}_2(^1\Delta_g)$, 22.64 kcal mol $^{-1}$,^[22] **5** is also unstable towards dissociation into ground-state CO_2 and singlet O_2 . On the triplet PES we localized the weakly bound cluster **8**, which is unstable against dissociation once the zero point energy correction is included. Both processes (1a) and (1b) can contribute to the formation of CO_4^+ ions in a O_2/CO_2 mixture ionized by electron impact. Indeed, despite the higher ionization energy (IE) of CO_2 , primary CO_2^+ ions are not efficiently depleted by the remarkably slow, $k_3=5.5 \times 10^{-11}$ cm 3 s $^{-1}$ charge exchange [Eq. (3)].^[23]

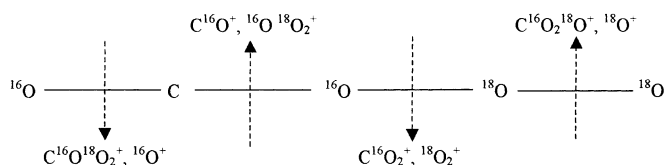


Thus, two processes, different with respect to the charged reagent and the energetics, contribute to the formation of CO_4^+ ions in the EI of O_2/CO_2 mixtures. As to process (1a), association of a ground-state O_2^+ ($^2\Pi_g$) with CO_2 is known to yield a $[\text{O}_2^+ \text{CO}_2]$ cluster, characterized by a binding energy (BE) of the monomers estimated as 0.48 eV,^[24] ≥ 0.46 eV,^[25] and 0.4 ± 0.05 eV.^[26] Another source of CO_4^+ ions is process (1b), as discussed above. Furthermore, CO_4^+ ions of unknown structure and stability can arise from excited precursors. Indeed, under conditions similar to those prevailing in this study, CO_2^{*+} ^[27] and O_2^{*+} ions^[27c,28] are known to be formed in excited states, for example, $\text{O}_2^+(^4\Pi_u)$, which is sufficiently long-lived to promote processes energetically inaccessible to ground-state reagents.^[29] We conclude that reactions promoted by excited species can yield CO_4^+ ions, of unknown structure and stability, other than those arising from ground-state reagents. This view is supported by the results of photoexcitation studies, which show that irradiation of the $[\text{O}_2^+(\text{X}^2\Pi) \text{CO}_2(\text{X}^1\Sigma)]$ adduct with 375–590 nm photons causes its dissociation into $\text{CO}_2^+(\text{X}^2\Pi)$ and $\text{O}_2(\text{X}^3\Sigma)$,^[25,26,30] rather than into O_2^+ and CO_2 , despite the large (1.7 eV) energetic bias in favor of the latter process. Of particular interest to the present discussion, 10% to 25% of the photoexcited CO_4^+ species are estimated to be formed in a *bound* state, and subsequently undergo predissociation, eventually yielding $\text{CO}_2(\text{X}^2\Pi)$ and $\text{O}_2(\text{a}^1\Delta)$.^[26] In summary, EI of an O_2/CO_2 mixture is expected to yield a complex population of CO_4^+ ions of different stability, structure and lifetime.

The structural information on the composition of the CO_4^+ population provided by CAD and MS 3 spectrometry is hardly conclusive. Let's consider the cluster(s) of O–C–O–O–O connectivity formed by O_2 and CO_2 units joined by essentially electrostatic forces, in which the bond between the monomers is considerably longer and weaker than the O–C–O and O–O bonds. The cluster is probably the most abundant component of the CO_4^+ population sampled, and its predominant fragmentation channel gives back the CO_2 and O_2 monomers,

with the charge mainly located on the latter one, characterized by the lower IE.

Furthermore, all signals from the fragments displayed by the CAD spectra of $\text{C}^{16}\text{O}_4^+$ ion, and its $\text{C}^{16}\text{O}_2^{18}\text{O}_2^+$ isotopomer, can in principle be accounted for by the fission of one bond of the cluster, for example, in the case of the $\text{C}^{16}\text{O}_2^{18}\text{O}_2^+$ ion.



However, the CAD and MS/MS results do not exclude the presence of CO_4^+ ions other than the cluster of O-C-O-O-O connectivity. Apart from the possibility that several of the charged fragments may arise from other isomers, the mixed character of the CO_4^+ population is suggested by certain experimental observations, for example, the intensity ratio of the $\text{C}^{16}\text{O}_2^{18}\text{O}^+$ and $\text{C}^{16}\text{O}^{18}\text{O}_2^+$ fragments from the $\text{C}^{16}\text{O}_2^{18}\text{O}_2^+$ isotopomer shows large variations (from 1:1 to 1:3), well above those noted for other fragments. Despite the low absolute intensity of the peaks from $\text{C}^{16}\text{O}_2^{18}\text{O}^+$ and $\text{C}^{16}\text{O}^{18}\text{O}_2^+$ ions, this suggests that the two isotopomers arise from the fragmentation of different CO_4^+ species, whose relative abundances are critically affected by small changes in the experimental conditions in the ion source.

The results of the NR experiments conclusively show that neutral CO_4 does exist in the gas phase with a lifetime in excess of about 1 μs , a long time on the molecular scale, being sufficient for an exhaustive exploration of the entire rovibrational manifold. It is natural, at this point, to inquire as to the structure of the CO_4 species detected. Although a rigorous assignment is impossible, a reasonable hypothesis can be based on the available theoretical results and the specific features of NR experiments. As neutralization is a vertical process, the parent ion and the neutral molecule must be structurally alike to ensure sufficiently favorable Franck-Condon overlap of the transition. The theoretically predicted CO_4 species include the singlets **5** and **6**, the triplet **7** and the van der Waals complex **8**. Complex **8** will not be discussed further, because the low binding energy of its monomers would not allow its survival in the neutralization step. Indeed, the neutral species must reside in a sufficiently deep energy well to be detectable by NRMS.^[31] As to triplet **7**, its exothermic dissociation into $\text{CO}_2(\text{X}^1\Sigma^+)$ and $\text{O}_2(\text{X}^3\Sigma^-)$ is expected to be very fast, as no kinetic barrier could be identified, and hence **7** is not detectable in NR experiments. Thus, one is left with singlets **5** and **6**, whose dissociation into $\text{CO}_2(\text{X}^1\Sigma^+)$ and $\text{O}_2(\text{a}^1\Delta)$ is also exothermic, and hence their detectability depends on the existence of sizable kinetic barriers to dissociation. This rules out **5**, as no such a barrier could be identified, thus restricting the choice to singlet **6**, whose dissociation into $\text{CO}_2(\text{X}^1\Sigma_g^+)$ and $\text{O}_2(\text{a}^1\Delta_g)$ is forbidden by orbital symmetry rules^[5,7] and hence can be expected to have a significant barrier,^[32] in addition to that presumably arising from steric factors.^[7] However, an indirect route to dissociation could involve fast nonradiative singlet-triplet

decay of **6** into **7**, prone to dissociation into $\text{CO}_2(\text{X}^1\Sigma_g^+)$ and $\text{O}_2(\text{X}^3\Sigma_g^-)$. Fortunately, the barrier to the nonradiative decay of **6** into **7**, and hence the barrier to dissociation of **6**, has been investigated in details by Averyanov, Khait and Puzanov,^[7] whose estimate sets the barrier height in the range from 15.0 to 27.3 kcal mol^{-1} . Among the ionic precursors of **6** in our NR experiments, only **3** has the same connectivity as **6**, whereas its geometry is similar but not identical to that of the neutral molecule. Consequently, **6** formed from the vertical neutralization process is expected to contain excess energy (the Franck-Condon energy), that we have calculated to amount to 15.5 and 17.0 kcal mol^{-1} at B3LYP and the CCSD(T) levels of theory, respectively. These results show that following neutralization of **3**, the $D_{2d} \text{ } ^1\text{A}_1$ singlet should survive dissociation, and hence it represents the most likely (indeed, the only) candidate, although a more rigorous assignment requires additional studies, in particular a more detailed theoretical analysis of the difficult CO_4 system.

In conclusion, the present results demonstrate the existence of a metastable CO_4 molecule with a lifetime exceeding 1 μs in the isolate gas state, whose structure can tentatively be assigned as a $D_{2d} \text{ } ^1\text{A}_1$ singlet, based on the available experimental and theoretical evidence.

Apart from its intrinsic interest, the discovery of CO_4 , long theoretically predicted but so far experimentally elusive, may be significant to atmospheric chemistry and especially to the high energy density materials (HEDM) field, in that the CO_4 isomer detected, that is, the D_{2d} singlet, is a metastable species calculated to release more than 80 kcal mol^{-1} upon dissociation into CO_2 and O_2 .^[7]

Experimental Section

The experiments were performed by using a modified ZABSpec oa-TOF instrument (VG Micromass) of EBE-TOF configuration, where E, B stand for electric and magnetic sectors and TOF for orthogonal time-of-flight mass spectrometer. The instrument was fitted with EI and CI ion sources, a gas cell located in the first field free region and two pairs of gas cells located after the magnet along the beam path. Typical operating conditions of the CI source were as follows: source temperature: 373 K, repeller voltage: 0 V, emission current 1 mA, nominal electron energy: 50 eV. Typical EI source conditions were: source temperature: 373 K, trap current: 200 μA , electron energy: 50 eV. The ions from the source were accelerated to 6–8 kV and their CAD and NR spectra recorded, by using the first of the collision cells pair, located between the magnet and the second E sector. The target gas used in the CAD experiments was He, which was admitted into the first cell at a pressure adjusted to obtain a 80 % transmittance. In the NR experiments CH_4 , used as the neutralizing gas, was also admitted into the first of the cells pair at such a pressure to obtain a beam transmittance of 80 %. All ions were then removed by a pair of high voltage ($\pm 0.8 \text{ kV}$) deflecting electrodes, and the beam of fast neutral species entered the second cell, in which reionization was achieved by using O_2 as the stationary collider. The NR spectra were averaged over 100 acquisitions to improve the signal-to-noise ratio. The following MS³ (multi-stage mass spectrometry) experiments were performed: 1) The selected precursor ion underwent decomposition by collision with He in one of the cells located in the second field free region, and the energy-selected daughter ions were structurally analyzed by CAD-TOF in the cell located in the TOF mass spectrometer; 2) The same experiment was performed by selecting the charged fragments formed by collisions occurring in the cell

located in the first field free region. An Apex 47e spectrometer, (Bruker Spectrospin AG), equipped with an external CI/EI ion source and a cylindrical infinity cell^[33] was used in FTICR experiments. The ions generated in the source and driven into the resonance cell, were mass-selected by soft ejection techniques and allowed to react with the neutral species at pressures ranging from 10^{-8} to 10^{-7} Torr. Accurate mass analyses were performed to unambiguously identify the charged products. The gases, research-grade products with a stated purity in excess of 99.95 mol%, were used as such without further purification. Ozone was prepared by passing UHP oxygen through a commercial ozonizer, collected over silica in a trap cooled to 77 K, and released by gradual warming of the trap. The $^{18}\text{O}_2$ (99 ^{18}O atom%) and the C^{18}O_2 (98.7 ^{18}O atom%) samples were obtained from Ikon Stable Isotopes, Inc.

Computational Methods: Density functional theory, by using the hybrid^[12] B3LYP functional,^[13] was used to localize the stationary points of the investigated systems and to evaluate the vibrational frequencies. Although it is well known that density functional methods that use nonhybrid functionals sometimes tend to overestimate bond lengths,^[14] hybrid functionals as B3LYP usually provide geometrical parameters in excellent agreement with experiment.^[15] Single point energy calculations at the optimized geometries were performed using the coupled-cluster single and double excitation method^[16] with a perturbational estimate of the triple excitations [CCSD(T) approach]^[17] in order to include extensively correlated contributions.^[18] Transition states were located by using the synchronous transit-guided quasi-Newton method reported by Schlegel and co-workers.^[19] The 6-311+G(3df) basis set^[20] was used. Zero point energy corrections evaluated at the B3LYP6-311+(3df) level were added to the CCSD(T) energies. The 0 K total energies of the species of interest were corrected to 298 K by adding translational, rotational and vibrational contributions. The absolute entropies were calculated by using standard statistical-mechanical procedures from scaled harmonic frequencies and moments of inertia relative to B3LYP6-311+G(3df) optimised geometries. All calculations were performed using Gaussian 98.^[21]

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