Assignment of Carbon Chain Molecules in Cryogenic Matrices by Selective Laser-Induced Oxidation

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We tested and applied a laser-induced oxidation method for identifying the IR-active stretching mode absorptions of linear C_{2n+1} molecules which have known strong UV−vis absorptions. For this purpose, we trapped the molecules of carbon vapor in non-inert matrices (pure O_2 and Ar−O_2 mixtures) at temperatures providing molecular growth. The matrix was exposed to laser light tuned to the wavelength of the UV−vis transition of a specific carbon species. We observed a bleaching of that UV−vis absorption and a correlated decrease of lines in the IR spectra for C_9, C_{11}, C_{13}, C_{15}, and C_{21}. The data suggest that the strongest IR absorptions of the C_{2n+1} ($n \geq 4$) chains form a regular pattern with increasing n. To obtain information about IR absorptions of carbon chain oxides, oxygen matrices with replaced $^{16}O \rightarrow {}^{18}O$ isotopes were applied. Our data revise some of the IR assignments existing in the literature.

1. Introduction

Carbon molecules play a role in combustion, cometary, stellar, and interstellar chemistry.[1−6] More recently, interest in carbon species has considerably increased in connection with fullerene and nanotube formation.[7−9] Several reviews cover the field of spectroscopy of carbon molecules in the range $C_2 \cdots C_{15}$.[10−12]

For the molecules of concern, carbon exhibits exclusively sp hybridization and forms linear chains and monocyclic rings. The linear chains of an odd number of atoms show singlet, those of an even number show triplet ground states. In particular, each of the odd species exhibits a rather intense absorption in the UV−vis which belongs to the electronic ground state $^1\Sigma_u \leftarrow X^1\Sigma_g$ transition. As shown by Maier and co-workers by matrix-isolation spectroscopy of mass-selected species, the wavelength position of this transition increases linearly with n up to C_{15}.[13] Most likely this relation is valid for even longer species, ranging up to C_{21}.[14] Such long chains are formed from matrix-isolated carbon vapor molecules either after matrix annealing[15] or when the deposition is performed at elevated matrix temperatures.

The observed IR absorptions of linear species usually belong to stretching modes. Nothing is known about such modes for chains beyond C_{13}. This latter molecule has been observed in the gas phase by high-resolution laser spectroscopy, and its size and structure have been derived from the observed rotational pattern of a strong IR transition at 1809 cm^{-1}.[16] The position of that line in cryogenic matrices is still matter of debate.[17,18]

In this work, we attempt to locate the IR lines of linear C_{13} and other large odd chains.

2. Approach

The exposure of matrix-isolated carbon species to laser radiation at a wavelength which corresponds to the electronic absorption of a certain C_n chain may lead to a bleaching of this absorption and a decrease in the corresponding IR lines. Wakabayashi observed such an effect for the first time when linear C_6 in solid Ne was exposed to 235 nm laser light.[19] Apparently, the electronic excitation from the ground state can trigger molecular fragmentation or a chemical reaction with surrounding non-inert trace molecules. We suspected that molecular oxygen may be such a trace compound, since it is known that oxidation of pure carbon molecules is energetically favorable and that oxygen affects sp carbon chains.[20] Our experiments with pure O_2 matrices confirm this view, and we will show in this study that it is possible to deplete selectively carbon molecules by suitable laser exposures.[21] As a result we obtained various carbon oxides as reaction products.

Besides chemical reactivity, the use of oxygen matrices introduces further effects. Under low pressure conditions, there are two stable phases, namely, α at lower (<23.8 K) and β at higher temperatures (23.8 < T < 43.8 K), both with antiferromagnetic properties.[22] We usually preferred to work with β oxygen, in which the site splittings of IR lines appeared to be less complicated. For easier comparison with the Ar data we also applied mixtures (90% Ar + 10% O_2) as matrices. Under such conditions argon is known to prefer hexagonal close packed structure.[23]

3. Experiment

Our experimental setup was designed to measure the IR and UV spectra of the same sample of matrix-isolated carbon molecules.[24] All experiments were performed under low temperature (usually 7−40 K) and vacuum (order of 10^{-7} mbar) conditions.

Carbon vapor molecules were co-deposited either with pure oxygen (99.998%) or with an argon−oxygen mixture (90% Ar + 10% O_2) on a Rh-coated sapphire substrate at 25 K. The ratio of carbon to matrix molecules was kept at about 1:1000. IR and UV−vis spectra were measured by a Fourier transform infrared (FTIR) and OMA spectrometer, respectively. The UV−vis spectra were recorded during 60 s in order to minimize the effect from UV irradiation by our deuterium lamp light source.

After deposition, the matrix was exposed to the beam of an XeCl excimer pumped dye laser which was tuned to the desired

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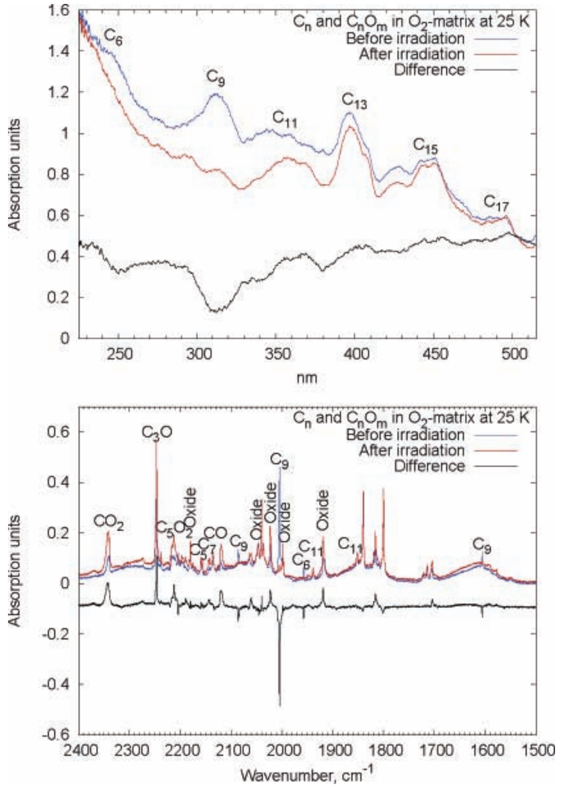

Figure 1. UV−vis and IR spectrum. Depletion of C_9 by 308 nm laser in a pure O_2 matrix during 80 min at $T = 25$ K. The almost complete disappearance of C_9 indicates good selectivity of its photooxidation.

wavelengths. IR and UV−vis absorption spectra (with 0.3 cm^{-1} and 0.5 nm resolution, respectively) were measured before and after laser irradiation.

For photooxidation of C_9, the pump beam of the excimer laser at a 308 nm wavelength was used attenuated to an average power of ~10 mW. For other molecules, the dye laser with different dye solutions was applied:[25] DMQ (LC3590) for C_{11} (~5 mW), QUI (LC3690) and PBBO (LC4000) for C_{13} (~6 mW and ~4 mW, respectively), and Coumarin 2 (LC4500) for C_{15} (~8 mW).

In our experience, better selectivity of the oxidation can be achieved if shorter carbon chains are depleted before longer ones. We frequently applied this strategy of photobleaching, even though the spectra became more complicated because of the increased contribution of chain oxides.

4. Results and Discussion

4.1. C_n Absorption Spectra in Solid Oxygen. Figure 1 shows the UV−vis spectrum of carbon molecules isolated in a pure O_2 matrix. One observes a sequence of absorptions which looks very similar to that of the $^1\Sigma_u \leftarrow X^1\Sigma_g$ transitions of C_n clusters in argon.[26] Their positions are close to those in an Ar matrix. This similarity suggests that pure carbon species at least partly survive in an oxygen surrounding.

IR data support this assumption. The vibrational absorptions of pure carbon molecules are discernible in the O_2 matrix (see IR spectrum on Figure 1), however shifted in the range −10 to +10 cm^{-1} relative to an Ar matrix. Several new lines appearing in oxygen-containing matrices can be assigned to carbon oxides (see section 4.5).

4.2. Oxidation of Carbon Chains with Known UV−vis and IR Absorptions. *C_6*. The concentration of C_6 in an O_2 matrix decreases spontaneously even without laser irradiation. There are also small changes in other carbon species, but only C_6 disappears almost completely. Laser irradiation with different UV frequencies or irradiation with a deuterium lamp just accelerates the process of C_6 depletion.

The high reactivity of this molecule may originate from its triplet ground state. That IR lines of the other even species (C_8 and C_{10}) in oxygen are weak or absent may have the same reason.

C_9. Here, for the first time, we observed selective photobleaching after irradiation with 308 nm laser light, which is in the vicinity of the main electronic absorption of this molecule (Figure 1). The decrease of the C_9 absorptions in the IR spectrum was roughly 95%. In the UV region, the decrease was similar (80%), though baseline changes limit the accuracy of this estimate. Additional features in the difference spectrum of Figure 1 at 350 and 380 nm indicate the presence of weaker C_9 absorptions, as already reported in neon matrices.[13]

A more than 90% decrease is a very striking depletion. All increasing lines in the IR spectrum probably belong to oxides since they do not appear in rare-gas matrices. Among the growing absorptions are those of CO_2, C_3O, and C_5O_2,[27] indicating that there are several possible reactions of electronically excited C_9 with O_2. For C_9, the selectivity of photooxidation appears to be quite good.

C_{11}. For bleaching, the laser was applied in a scanning regime between 350 and 364 nm. In pure oxygen matrices, the lines of C_{11} at 1938 and 1851 cm^{-1} (1938.6 and 1853.4 cm^{-1} in neon[28]) could be depleted entirely. The observed simultaneous depletion of C_5, C_7, C_3O, C_9, and some other unidentified oxide molecules means that reactions involving several carbon species took place. The possible reason is the presence of weak electronic absorptions of these species in the region of excitation, yielding, in this case, poor selectivity.

Laser-induced oxidation in a mixed matrix (90% Ar + 10% O_2) has shown better selectivity. Only C_{11}, C_9, and C_6 were depleted. The decrease of C_9 probably originates from C_9 absorption at the irradiation wavelengths. A 50% decrease of C_{11} indicates sufficient selectivity of the photooxidation of this molecule.

C_{13}. Irradiation at the maximum of the UV−vis band at 397 nm leads to a decrease of the IR lines at 1800 (82%) and 1840 cm^{-1} (78%). These two lines are shown in Figure 6. The increased lines are all oxides: CO_2, C_3O, C_5O_2, and other unidentified oxide species. In the UV−vis, we observed the decrease of the absorption at 397 nm. This feature has a width of 20 nm. One would be tempted to associate these two IR lines with C_{13}, but as will be shown later (section 4.5), these absorptions definitively belong to oxide(s). We name the carrier(s) by “1800/1840 oxide(s)”.

The 1819 and 1816 cm^{-1} pattern of absorptions in O_2 (1818 cm^{-1} in Ar) probably belongs to the IR-active C_{13} stretching mode (see Figures 6 and 2). There are no other candidates in the region around 1809 cm^{-1}, that is, the band position reported for C_{13} in the gas phase.[16] Indeed, after the complete depletion of the “1800/1840 oxide(s)”, we irradiated the same sample in the scanning mode at 390−406 nm, that is, within the expected region of C_{13} absorption. A 43% decrease of the absorptions at 1816 and 1819 cm^{-1} and the depletion of a wide region from 365 to 440 nm in UV−vis were observed. We thus are confident to have located the C_{13} absorption in our matrices.

The assignment of the absorption at 1818 cm^{-1} in argon to cyclic C_8[17] is in conflict with other assignments[30,18] and with our C_{13} assignment.

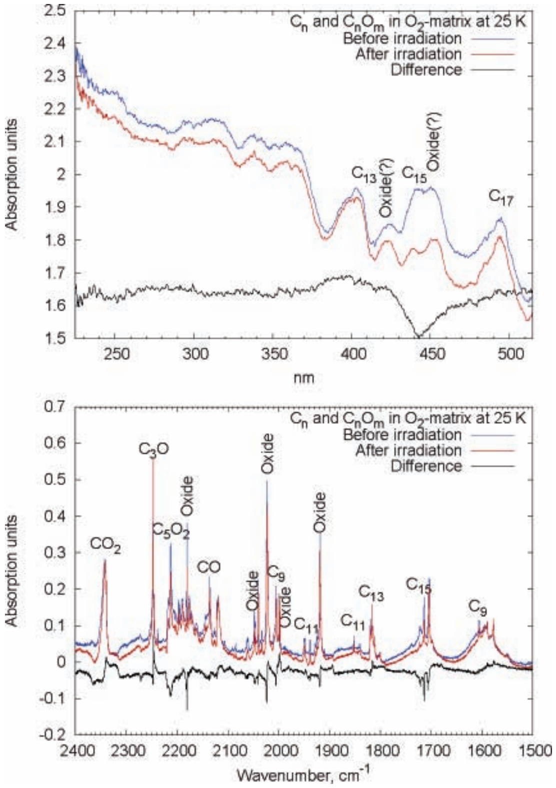

Figure 2. UV−vis and IR spectrum. Depletion of C_{15} by 438−454 nm laser in a pure oxygen matrix during 80 min at $T = 25$ K. Decreased absorption lines at 1721, 1714, and 1707 cm^{-1} probably belong to site peaks of C_{15} in a β-phase solid oxygen.

In conclusion, the photooxidation method applied to carbon molecules C_9, C_{11}, and C_{13} is sufficiently selective for identification purposes. In the following, molecules with known electronic absorptions, but unknown vibrational transitions, will be investigated.

4.3. Application of the Method to Longer Odd Chains. The electronic absorption of C_{15} is centered at ∼440 nm, with a width of about 10 nm. Laser irradiation of this absorption region was performed employing two different types of matrices, namely, pure O_2 at 25 K and at 20 K and a mixed (Ar + 10 O_2) matrix at 25 K. We followed the strategy of depleting shorter carbon chains before longer ones: C_9 (by 308 nm for 120 min) → C_{11} (by 350−364 nm for 160 min) → "1800/1840" oxide(s) (by 397 nm for 140 min) → C_{15} (by 438−454 nm for 80 min).

C_{15} in a Pure O_2 Matrix. After irradiation in the scanning mode between 438 and 454 nm, we observed a decrease of the absorption (Figure 2) with a peak at 442 nm. We think that this feature originates from C_{15}. An additional absorption with a maximum at 452 nm slightly decreased. This latter absorption very likely comes from an oxide (see below). The C_{15} decrease in the visible spectrum is between 40 and 80%; the uncertainty comes from baseline changes and from the overlap with the oxide absorption at 452 nm. In the IR spectrum, significantly decreased lines are C_5O_2 (30%), the oxide at 2180 cm^{-1} (52%), the oxide at 1704 cm^{-1} (25%), and a bundle of lines at 1721, 1714, and 1707 cm^{-1} (40 ± 10%). Among increased lines are C_3O (6%), the oxide at 1998 and 1997 cm^{-1} (35%), and CO_2 (roughly 4%). All other changes in the IR spectrum are negligible.

Therefore, the only decreased lines in the IR, which could belong to a pure carbon molecule (no shift in an $^{18}O_2$ matrix,[29] see section 4.5), are 1721, 1714, and 1707 cm^{-1}.

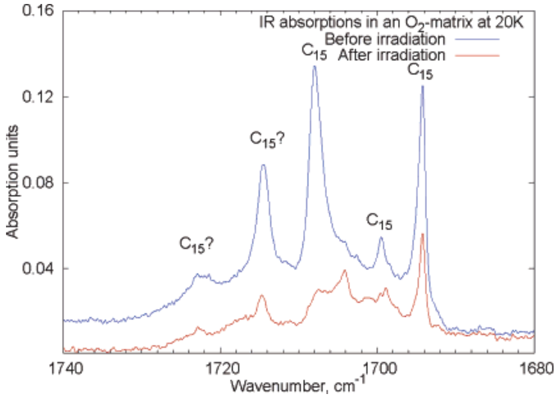

Figure 3. Region C_{15} absorption before and after laser irradiation in a α-phase oxygen matrix at 20 K. Notice the presence of the site peak at 1694 cm^{-1}. The 1721 and 1714 cm^{-1} lines may come from an oxide since they are very weak in a pure Ar matrix and increase after addition of O_2.

Additional exposures of the sample were performed in order to locate the electronic absorption of the carrier of the IR absorptions at 1721, 1714, and 1707 cm^{-1} more precisely. The irradiation at 436−444 nm led to a correlated decrease of the 439 nm feature and the residual absorption at 1714 cm^{-1}. Another irradiation at 450−455 nm led to a correlated decrease of 452 nm and 1704 cm^{-1} absorptions, both belonging to an oxide (the IR line shifts after $^{16}O \rightarrow {}^{18}O$, see section 4.5).

The bundle of three IR lines at 1721, 1714, and 1707 cm^{-1}, which correlates with the UV absorption between 436 and 444 nm, probably belongs to C_{15} absorptions in the β-phase oxygen matrix. In α-phase oxygen (Figure 3), there is one more site peak of C_{15} at 1694 cm^{-1} which shows considerable intensity and which, in position, is very close to a strong carbon chain absorption in an Ar matrix.

C_{15} in a Mixed Ar + 10% O_2 Matrix and a Pure Ar Matrix. The same experiments as described above performed in the mixed matrix yielded absorptions at 1713, 1700, and 1695 cm^{-1}. We conclude that the absorptions at 1700 and 1695 cm^{-1} in a pure Ar matrix belong to linear C_{15}. The 1713 cm^{-1} line in a pure Ar matrix is very weak, and it considerably increases after a small addition of oxygen indicating that the carrier may be an oxide.

Our assignment of the 1695 cm^{-1} absorption is in conflict with previous identification attempts. On the basis of the apparent agreement between measured and calculated ^{12}C, ^{13}C isotopomeric data obtained in Ar matrices, it was claimed that this line originates from the cyclic (D_{3h}) C_6 molecule.[31,32] We think that the complexity of matrix spectra leads to great uncertainties in such comparisons and that the deduced assignments remain tentative.

In favor of our assignment, we note two facts: First, the observed correlation between the UV−vis absorption of C_{15} and the IR band which relates to the 1695 feature in Ar. Second, we find that the strongest IR absorptions of odd chains form a regular sequence into which C_{15} readily fits (see below).

C_{21}. The electronic absorption of C_{21} extrapolated from shorter chains should occur at around 588 nm. The peak there has a width of about 20 nm. Laser irradiation in the scanning mode in the range of 585−590 nm during 1 h leads to correlated depletion of UV−vis absorption between 580 and 605 nm and the IR absorptions at 1317, 1308, 1297, 1295.5, and 1285 cm^{-1} (Figure 4). The later absorptions we assign as site peaks of C_{21} in a $^{16}O_2$ matrix. However, some of these absorptions may come from oxides. We assume that the absorption at 1283 cm^{-1} in a pure Ar matrix belongs to C_{21}.

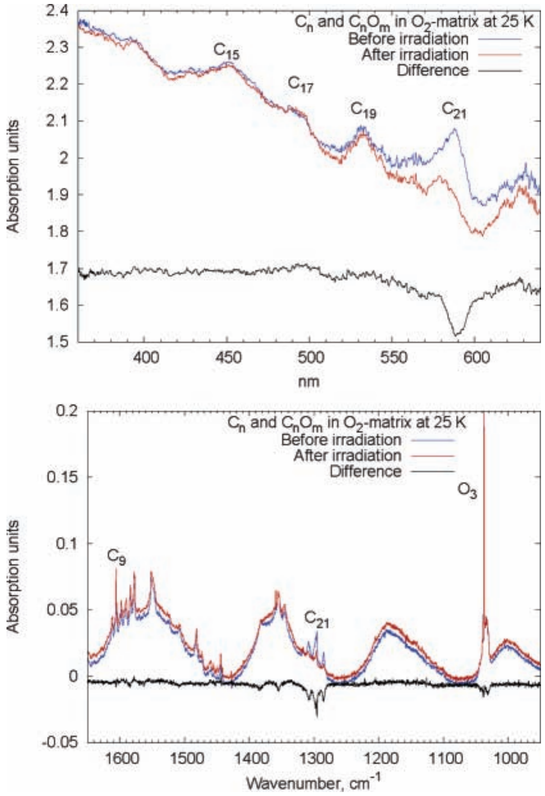

Figure 4. UV−vis and IR spectrum. Depletion of C_{21} by 585−590 nm laser in a pure oxygen matrix during 60 min at $T = 25$ K. To decreased absorption lines at 1317, 1308, 1297, 1295.5, and 1285 cm^{-1}, we assign site peaks of C_{21} in a β-phase solid oxygen.

TABLE 1: IR Frequencies and Intensities (in parentheses) of the Most Intense Modes of Long Carbon Chains: Calculation and Experiment

molecule	DFT, cm^{-1}	PM3, cm^{-1}	exp, cm^{-1}
C_9	2128 (5815), 2207 (3886)	2107 (22941)	2004
C_{11}	2112 (14973), 1939 (2435)	1922 (45134)	1944, 1851
C_{13}	2027 (22736), 2089 (2660)	1729 (77821)	1816
C_{15}	1983 (27580), 1915 (8579)	1502 (129379)	1721, 1714, 1707, 1694
C_{17}	1917 (46278), 2237 (3058)	1215 (206426)	
C_{19}	1848 (60974), 2211 (7748)	788 (318451)	
C_{21}		777 (357293)	1317, 1308, 1297, 1295.5, 1285

4.4. Comparison between Theory and Experiment. A chain molecule C_n has $n - 1$ stretching modes of which for odd chains $(n - 1)/2$ are IR active. For long chains, one expects a correspondingly large number of lines, but it appears from our experimental results and calculations that only very few are intense.

DFT (B3LYP/6-311G(d))[33] and PM3[34] quantum-mechanical calculations predict the positions and intensities of IR-active vibrational modes, which are displayed in Table 1. Experimental data are for an oxygen matrix at 25 K.

It is interesting to note that according to the calculation there is one absorption of dominating intensity. In the case of PM3 calculation, the second intense IR line of odd C_n chains ($n \geq 13$) is weaker at least by a factor of 10. The position of the most intense absorption shifts with increasing chain length to longer wavelengths, forming a regular sequence. This absorption corresponds to the totally alternating stretching mode which produces a maximal change in the dipole moment. The atomic displacement pattern of this mode is shown in Figure 5.

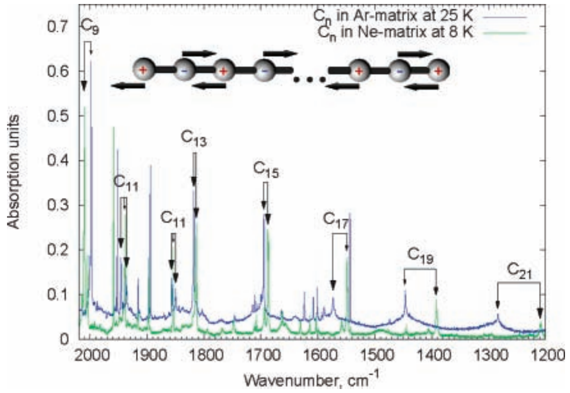

Figure 5. Most intensive IR mode of a long carbon chain is the totally alternating vibration, in which the displacement vectors turn by 180° in going from one atom to the next. With an increase in chain length, the position of this absorption shifts to lower energies.

One can easily understand this feature by taking into account the eigenvectors of the normal modes and the Mulliken atomic charges, as calculated, for example, by the PM3 method. The Mulliken charges in a linear chain with an odd number of carbon atoms alternate in sign going from one atom of the chain to the next.

This suggests that a normal vibration with maximal change of dipole moment and maximal IR intensity will be likewise alternating. In such a case, all atoms with charges of one sign move against all others with charges of the opposite sign. Strong absorptions based on a similar collective motion of charges also occur in other fields of spectroscopy as, for example, in surface plasmons in small particles or in giant dipole resonances in atomic nuclei.[35]

The strength of this vibration increases with increasing molecular chain length. This explains why the absorptions of long chains are observable despite their low abundance. The frequency of this vibration seems to decrease steadily with the number of carbon atoms in the chain, yielding a strikingly simple sequence of IR lines as shown in Figure 5.

To estimate the positions of the IR absorptions in the gas phase, Figure 5 compares the line positions in argon and neon. Notice that the lines in neon are blue shifted with respect to argon for C_9 and red shifted for the larger chains. If it is assumed, as is usually the case, that the line positions are going into the direction argon → neon → gas phase, then the chains longer than C_{11} should have gas-phase absorptions redward of their positions in neon.

The IR absorptions of C_{11} are exceptional: first, because there are two intense lines and, second, the "Ne to Ar" shift goes in both directions (there are two site peaks of C_{11} in Ar for every observable IR active mode). We expect that the gas-phase absorption of C_{11} should be quite close to that in Ne.

4.5. Isotopic Substitution of $^{16}O_2$ by $^{18}O_2$: Implications Regarding Carbon Chain Oxides. In our depletion experiments in oxygen matrices different oxides were produced. The IR spectra of some of these, mostly monoxides and dioxides of short carbon chains, are already known.[27]

For the purpose of identifying oxides and distinguishing between oxides and pure carbon molecules, several experiments were performed using $^{18}O_2$ matrices. The expected qualitative effects for IR absorptions are the shift of oxides to the red and no shift of pure carbon species.[29] Furthermore, mixtures of $^{16}O_2$ and $^{18}O_2$ can provide information about the number of oxygen atoms in the molecule, and the magnitude of the shift allows one to estimate the number of carbon atoms in the oxide

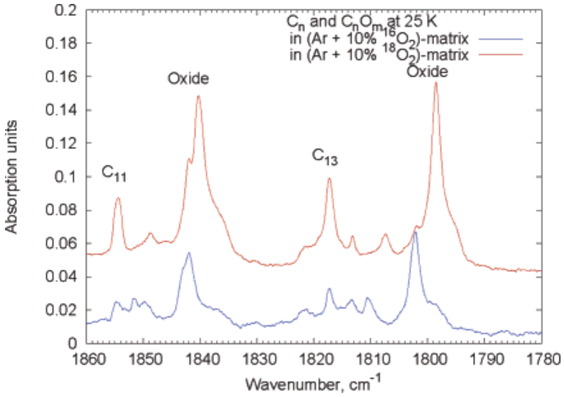

Figure 6. IR spectra of carbon species in a (Ar + 10 $^{18}O_2$)-matrix and in a (Ar + 10% $^{16}O_2$)-matrix at $T = 25$ K. The substantial shift of the absorptions at 1842 and 1802 cm^{-1} indicates that the carrier of this features is/are (an) oxide(s).

molecule, provided that the vibrational mode is known. Using this approach we found that an absorption at 2180 cm^{-1} in $^{16}O_2$ matrix probably belongs to the C_6O_2 molecule.[21]

A list of the IR absorptions shifted after isotopic substitution can be found in the Supporting Information. Some of the lines which are not shifted in an $^{18}O_2$ matrix are, nevertheless, definitely oxides, namely, the lines at 2020 and 1918 cm^{-1}. The reason that these lines should be oxides is their absence in inert matrices such as Ar, Ne, Kr, and N_2. Such lines (which show very small shifts), according to the qualitative estimates from PM3 calculations, may belong to monoxides of long chains, that is, C_9O, $C_{11}O$, and others.

As already mentioned in section 4.2, the absorptions at 1803 and 1844 cm^{-1} in an Ar matrix are from oxides since these lines are red shifted upon $^{16}O_2$ by $^{18}O_2$ substitution (Figure 6). The exact positions of these lines in a mixed (Ar + 10% $^{16}O_2$) matrix are 1802.1 and 1841.9 cm^{-1}. The previous assumption that these lines belong to pure carbon species thus has to be revised.[17,30,36] As possible carriers for these two absorptions we suggest $C_{13}O$, $C_{13}O_2$, $C_{11}O$, or $C_{11}O_2$. The assumed number of carbon atoms is based on the position of electronic absorption (397 nm, see section 4.2) and configuration interaction singles[34] (with PM3 optimized geometries) calculations which yield 402 nm for $C_{13}O_2$ and 357 nm for $C_{11}O_2$. In the literature, the IR absorptions at 1803 and 1844 cm^{-1} were tentatively assigned to C_{13}.[17] The absorption at 1844 cm^{-1} was also assigned to cyclic C_8.[30,18] We have shown that these absorptions are oxides, so the presence of 1803 and 1844 cm^{-1} lines in the Ar matrix is probably due to oxygen impurities.

5. Conclusion

We have found that pure carbon molecules at least partly survive in oxygen and mixed rare-gas oxygen matrices. The reason for the low abundance of even-numbered carbon chains in oxygen matrices is their high reactivity which probably originates from their triplet electronic ground state.

The laser-induced oxidation method was successfully tested on linear C_9, C_{11}, and C_{13} molecules, confirming the existing data on the IR absorptions of these species.

Application of the oxidation method to linear C_{15} and C_{21} yielded new information about the IR active transition of these molecules.

From our data, it appears that the IR absorptions of very long odd chains are very intense and are concentrated in a single vibrational mode. The frequency of this vibration seems to decrease steadily with the number of carbon atoms in the chain yielding a strikingly simple sequence of IR lines.

The technique of ^{18}O isotopic substitution has provided information about the positions of IR absorptions of carbon oxides in an O_2 matrix and has revised some of the assignments in the literature.

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Supporting Information Available: List of infrared absorptions shifted after ^{18}O isotopic substitution. This material is available free of charge via the Internet at http://pubs.acs.org.

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