C_4O and C_6O Molecules

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We have observed the triplet linear (or near-linear) CCCCO and corresponding C_6O molecules via electron spin resonance (ESR) in neon and argon matrices at 4 K. Their identities have been made more positive by substitution of ^{13}C ($I = {}^1/_2$) and ^{17}O ($I = {}^5/_2$) isotopes. This is in accord with simple theory, as applied to the C_n series,[1] in that one expects linear structures with triplet ground states for n even and singlet ground states for n odd, as demonstrated by the first three members of this series, $CO(^1\Sigma)$, $C_2O(^3\Sigma)$,[2-4] and $C_3O(^1\Sigma)$.[5,6] Neither C_4O nor C_6O appear in matrices containing carbon molecules and CO without photolysis with blue light. Synthesis requires the specific excitation of the C_3 molecule to induce its reaction with ground-state CO or C_3O.

Matrices containing ^{12}C and ^{13}C carbon species were prepared by vaporization of graphite by laser heating and condensation with neon or argon containing about 1% $^{12}C^{16}O$, $^{13}C^{16}O$, or $^{12}C^{17}O$. The apparatus and procedure have been described in previous publications.[7,8] Photolysis of the formed matrices was carried out with an Oriel 1000-W xenon lamp without filters, with Corning CS-4-70 and 3-70 filters, or with a $^1/_4$-m monochromator with 2.0-mm slits set for 405 nm.

The X-band ESR spectra before photolysis exhibit signals due to C_4, C_6, C_8, C_{10}, HCO, and C_2O as shown in earlier papers.[4,8]

After photolysis a strong new feature, attributed to C_4O, grows in at 6274 G in neon and a weaker signal, assigned to C_6O, at 7155 G (ν = 9.565 GHz). Corresponding signals, but broader and at slightly lower fields, appear in argon. Figure 1 shows the effect of photolysis when ^{12}C molecules are trapped with ^{13}CO in a neon matrix. The C_4O occupies a major site and a few minor sites in the matrix. The site structure in all of these matrices was dependent upon the concentration of CO in the matrix gas. Use of the monochromator during photolysis established that the effective wavelength of excitation to produce these new lines is 405 ± 20 nm. That wavelength corresponds to the strong 0-0 band of the $^1\Pi_u \leftarrow X^1\Sigma_g^+$ system of C_3.[9,10] Preparation of C_4O from various isotopic mixtures is shown in Figure 2. The hyperfine splittings (hfs) discernible there are less apparent on the weaker C_6O signal where only broadening occurred.

Analysis of the ESR spectra on the basis of these being S = 1 molecules[11,12] with zero-field-splitting parameters $|D| > h\nu$ and assuming $g_\perp = g_e = 2.0023$ yields $|D| = 0.759$ (3) cm^{-1} for C_4O and 1.10 (2) cm^{-1} for C_6O (compared to 0.74 cm^{-1} for C_2O).[4] These values are expected to be slightly higher by ~0.03 to 0.05 cm^{-1} in the gas phase.[4] The hfs values $|A_\perp(^{17}O)|$ = 33 (1) MHz and $|A_\perp(^{13}C_\alpha)|$ = 15 (3) MHz for C_4O (the subscript α indicates C nearest O) may be compared to 42 and 26 MHz, respectively, for C_2O.[13] INDO calculations indicate that the principal spin density in these C_nO (n even) molecules lies in the pπ orbitals on the O atom and that it oscillates along the carbon pπ chain such that the terminal carbon has the next-largest population. Thus the observed hfs supports this cumulene-like bonding in $^3\Sigma^-$ C_nO molecules.

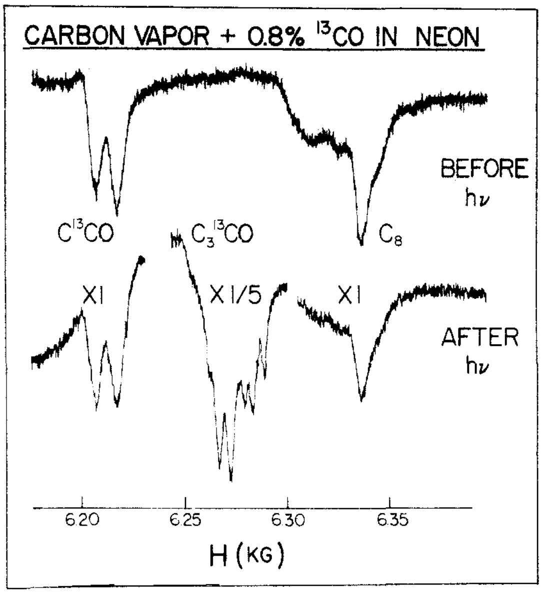

Figure 1. The formation of the $^{12}C_3{}^{13}CO$ molecule in a neon matrix at 4 K containing carbon vapor molecules (formed by laser heating of graphite) and ^{13}CO. Top and bottom spectra are before and after irradiation with 405-nm light. ^{13}C hyperfine splittings are seen on the C_2O and C_4O molecules; in the latter case there is one major and two minor sites in the matrix.

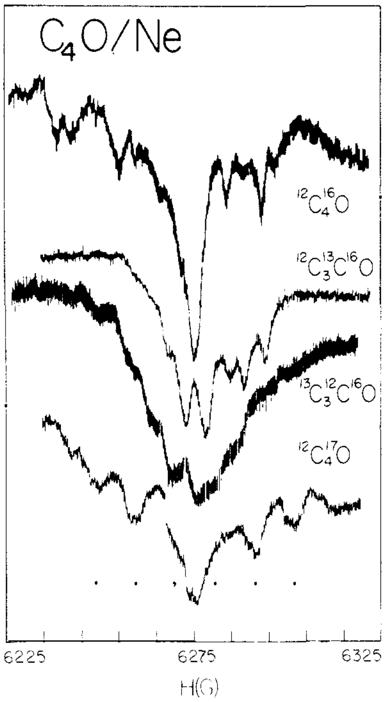

Figure 2. The C_4O "perpendicular" ESR line formed by 405-nm photoexcitation of trapped ^{12}C- or ^{13}C-graphite vapor with $^{12}C^{16}O$, $^{13}C^{16}O$, or partially enriched $^{12}C^{17}O$ in solid neon at 4 K.

The $|D|$ values increase slightly from C_2O to C_4O and more rapidly from C_4O to C_6O. This is similar to the variation in $|D|$ from C_4 to C_6 to C_8 where the values are 0.24, 0.36, and 0.78 cm^{-1}, respectively.[8] As discussed there, this increase is not attributable to spin-spin interaction but rather to spin-orbit contributions as

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the singlet excited states (principally the $^1\Sigma^+$) drop in energy as the chain lengthens. It is noteworthy that the zfs are larger in the C_nO series than in the C_n series, as expected from the increased spin–orbit constant for O relative to C (150 versus 30 cm^{-1}).

$C_2O(^3\Sigma)$[3,4] and $C_3O(^1\Sigma)$[5] can form spontaneously in matrices from the ground-state reactants $C(^3P_{1/2})$, $C_2(^1\Sigma_g)$, and $CO(^1\Sigma)$; however, formation of C_4O and C_6O from $C_3(^1\Sigma_g)$ or $C_5(^1\Sigma)$ and $CO(^1\Sigma)$ is spin forbidden. This is circumvented by excitation of C_3 to the $^1\Pi_u$ state where it can react with CO

$$C_3(^1\Pi_u) + CO(^1\Sigma) \rightarrow C_4O(^1\Pi) \rightsquigarrow C_4O(X^3\Sigma)$$

A similar scheme can be devised for the formation of C_6O either via reaction of excited C_3 with $C_3O(X^1\Sigma)$ by these paths or possibly via excitation of C_5, whose absorption properties are unknown.

The observation of C_3O in interstellar space has been made possible by the efforts of R. D. Brown and his co-workers.[6,14] The proposed mechanisms for its formation[15,16] involve ion–molecule reactions so that it is improbable that the above mechanisms for the formation of C_4O and C_6O could apply there. However, these molecules will have large dipole moments,[17] and like the cyanopolyynes,[18] they should be readily detectable even if present in low concentrations.

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Intercalation of Cationic, Anionic, and Molecular Species by Organic Hosts. Preparation and Crystal Structure of $[NH_4]_6[calix[4]arenesulfonate][MeOSO_3]\cdot(H_2O)_2$

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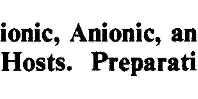
Much interest has recently been shown in the calixarenes (**1**)[1] and, more recently, in water-soluble members of this class of compounds (R = NO_2, SO_3H).[2] Calix[4]arenesulfonate (R = $-SO_3H$, R′ = H, *n* = 4) is usually prepared as the sodium salt of the pentaanion[3,4] (i.e., the four sulfonate protons and a "superacidic" proton[5] from an –OH group are removed at the reaction pH). The salt crystallizes with 12 molecules of water per calixarene unit. Replacement of the sodium ions by use of the appropriate ammonium salt[6] leads to the related pentammonium calix[4]arenesulfonate, the structure of which is the subject of this contribution.[7]



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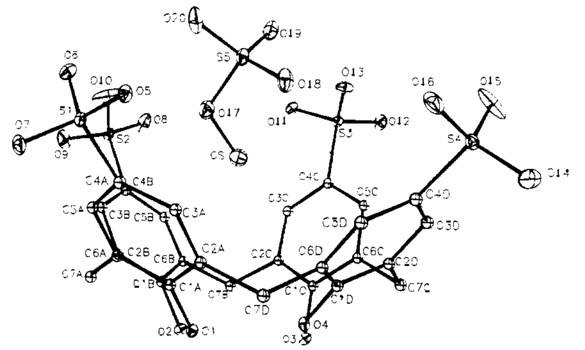

Figure 1. Inclusion of the methyl sulfate anion within the cavity of the calixarene anion.

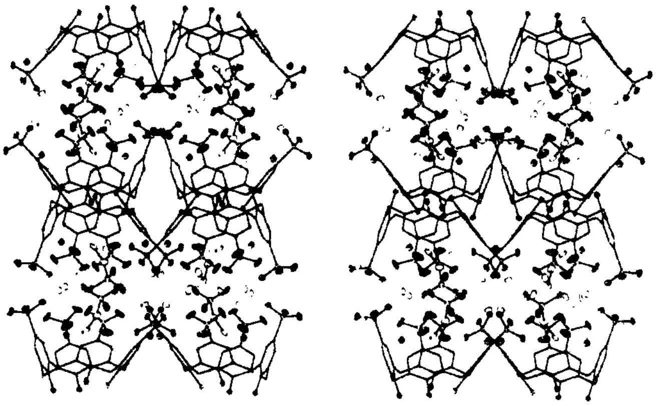

Figure 2. Stereoscopic view of the packing of the layers of calixarene anions and ammonium cations, methyl sulfate anions, and water molecules. Oxygen atoms are represented by dark circles.

The gross structures adopted by the sodium and ammonium species are quite similar, consisting of bilayers of calixarenes alternating with layers composed of ammonium ions and water molecules. The cations and water molecules are responsible for both the inter- and intra-linking of the layers via hydrogen bonds.[8] The composition of the polar layer, however, changes from four sodium ions and eleven water molecules in the sodium salt to five ammonium ions, one water molecule, and a methyl sulfate anion in the ammonium salt.[9,10] The methyl sulfate is oriented such

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(6) A suspension of calix[4]arene (5.0 g) in concentrated H_2SO_4 (50 mL) was heated at 70 °C during 4 h. The solution was filtered and the solid extracted with water (500 mL). This solution was neutralized to pH 7 with $BaCO_3$ and filtered. The filtrate was reduced in volume to ca. 50 mL and $(NH_4)_2CO_3$ was added until the pH was in the range 9–10. The resultant solution was left to slowly evaporate, yielding large, colorless crystals of $[NH_4]_6[calix[4]arenesulfonate][MeOSO_3]\cdot(H_2O)_2$.

(7) The title compound has six ammonium ions, five formally associated with the calixarene anion and one with the methyl sulfate anion. The space group is the monoclinic *C*2/*c* with $a = 22.164$ (5) Å, $b = 25.945$ (6) Å, $c = 17.772$ (7) Å, $\beta = 124.71$ (4)°, and $D_c = 1.28$ g cm^{-3} for $Z = 8$. The cations and anions possess no crystallographically imposed symmetry. Least-squares refinement based on 3590 observed reflections led to a final *R* value of 0.054. The sulfur, oxygen, and nitrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located on a difference Fourier map or placed in calculated positions, but they were not refined. The details of data collection and refinement are given in Holton et al.: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

(8) Both of the structures are quite similar to those found in clays such as montmorillonite: Mason, B.; Berry, L. G. *Elements of Mineralogy*; Freeman: San Francisco, 1968.

(9) One ammonium ion and one water molecule reside between calixarene anions within the calixarene bilayer. The methyl sulfate anion results from dehydration of methanol contained within the lattice of the parent calix[4]arene by H_2SO_4: $CH_3OH + H_2SO_4 \rightarrow CH_3OSO_3H + H_2O$.

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