An ESR Investigation of the $C^{17}O^+$ Cation Radical Isolated in a Neon Matrix at 4 K

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Abstract: The $C^{17}O^+$ radical cation has been trapped in neon matrices at 4 K for ESR investigation. Both photoionization and electron bombardment generation techniques were employed. The $^{17}O(I = {}^5/_2)$ A tensor was fully characterized and compared with various theoretical results. The bonding in CO^+ was compared to other 13-electron diatomic radicals including BO, CN, BeF, and N_2^+. A qualitative correlation between the electronegativity differences of bonded atoms in this series and the electronic properties of the unpaired electron as determined by ESR is presented. The magnetic parameters for ^{17}O in $C^{17}O^+$ are $|A_{\parallel}|$ = 47.6 (9) MHz and $|A_{\perp}|$ = 51.5 (6) MHz. The most reasonable choice of absolute signs is discussed for these parameters.

Recently developed electron bombardment and photoionization experimental methods have enabled the first ESR (electron spin resonance) studies of molecular cation radicals isolated in an inert rare gas matrix at 4 K.[1-3] These initial experiments have reported ESR results for the following molecular cation radicals: $^{12}C^{16}O^+$, $^{13}C^{16}O^+$, $^{14}NH_3^+$, $^{15}NH_3^+$, $H_2^{16}O^+$, $HD^{16}O^+$, $D_2^{16}O^+$, $H_2^{17}O^+$, $^{14}N_2^+$, and $^{15}N_2^+$.[1-3] The methods appear to be generally applicable to a wide range of interesting cation radical types including high-temperature (>1000 K) inorganic species, metal cluster ions, and volatile organics. A few of the systems currently under study are $^{13}CH_4^+$, $H_2^{13}CO^+$, $C_6H_6^+$, F_2CO^+, $Si^{29}O^+$, and $^{25}Mg_2^+$.[4] Under special deposition conditions, the occurrence of ion-neutral reactions has been observed leading to the assignment of such unusual radicals as $^{13}C_2^{17}O_2^+$ and $^{15}N_2^{13}CO^+$.[4] Previous ESR studies have focused on larger molecular cations trapped in less inert media including ionic solids and frozen solutions or glasses such as TCFM (trichlorofluoromethane).[5-8]

Magnetic parameters for cation radicals are extremely difficult or impossible to obtain in the gas phase, although high-resolution microwave measurements for $^{13}C^{16}O^+$ have been reported.[9] This cation radical was the first candidate selected for detailed rare gas matrix isolation studies so that matrix shifts and the degree of isolation for trapped cations could be determined. Neon matrix shifts of only 3–4% in the very large ^{13}C hfs (≈ 1500 MHz) were observed.[1]

This report analyzes recently observed $^{17}O(I = {}^5/_2)$ hyperfine structure for the $C^{17}O^+$ $(X^2\Sigma)$ radical cation, a property which has not been measured in the gas phase. Most ESR studies involving ^{17}O substitution in small radicals have been able to determine only the isotropic components of the ^{17}O A tensor.[8] Fortunately, $C^{17}O^+$ in neon matrices does not undergo motional averaging and determination of the ^{17}O dipolar hyperfine interaction could also be made. These additional ^{17}O data in conjunction with the previously measured ^{13}C hfs of $^{13}C^{16}O^+$ allow a complete description of the unpaired electron in terms of its isotropic and dipolar components on both atoms. Such a complete characterization has been reported for only a very few radicals, with $^{13}C^{14}N$ being the only other first-row diatomic case studied in such detail.[10,11] The magnetic properties of CO^+ and other diatomic isoelectronic radicals are presented, including those of

$BeF,^{12} BO,^{13} CN,^{10,11}$ and $N_2^+.^3$ A comparison between this complete set of magnetic parameters and ab initio spin density calculations is presented. To date, direct comparisons at the ab initio level have been done for only a few cases. Also included are the results of the more commonly reported MNDO-type calculations.

A brief review of progress to date concerning the utilization of rare gas matrices for the study of charged species was given in the $^{13}C^{16}O^+$ report and the references contained therein.[1] The investigation of matrix-isolated neutral radicals by ESR is well established and has been previously reviewed.[14] A comprehensive book on the subject with numerous examples has recently become available.[15]

Experimental

The liquid helium matrix apparatus employing a hydraulic raise-and-lower mechanism and the ESR spectrometer system used in our laboratory have been described elsewhere.[1] The neon matrices (≈ 4 K) containing isolated $C^{17}O^+$ radicals were formed by two different ion generation and trapping schemes. The open-tube neon discharge (17 eV) gas phase photoionization generation method was identical with that used for the original $^{13}C^{16}O^+$ studies.[1] The more recently developed electron bombardment procedure for generating matrix isolated cations, described in the N_2^+ and H_2O^+ reports,[2,3] was also used to produce $C^{17}O^+$ in this study.

In the electron bombardment method, 50–70-eV electrons ($\approx 100 \mu A$) are focused onto the copper rod deposition target (4 K) which is maintained about +50 eV above ground potential. Codeposition of neon matrix gas containing 0.1% $C^{17}O$ and ionizing electrons was found to produce intense ESR signals of $C^{17}O^+$. The penetrating depth of the electrons even at these low energies is at least several monolayers of neon.[16] Likely counterions (-anions) present in the matrix sample and formed by collisions with background amounts of H_2O are H^-, O^-, and OH^-.[17] Unfortunately, these anion candidates cannot be detected by ESR. A previous estimate of the ratio of neon matrix atoms to isolated CO^+ radicals is approximately $10^6:1$.[1]

The CO(g) sample enriched to 30% in $^{12}C^{17}O$ was obtained from Stohler Isotope Chemicals. Matheson research grade neon and the CO sample were passed through liquid nitrogen traps immediately prior to entering the vacuum system. Details of the deposition procedure such as flow rates, times of deposit, etc., have been given previously.[1]

Results

Identical ESR results for $^{13}C^{16}O^+$ and $^{12}C^{17}O$ were obtained by the photoionization and electron bombardment generation

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Table I. Magnetic Parameters^a for C^{17}O$^+$ (X$^2\Sigma$) in Neon Matrix at 4 K

	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	A_{iso}	A_{dip}
^{12}C^{17}O$^+$	2.0011 (4)	1.9995 (2)	47.6 (9)^b	−51.5 (6)^b	−18.5 (5)^b	33.0 (5)^b
^{13}C^{16}O$^{+\ c}$	2.0004 (7)	1.9996 (5)	1665 (2)	1527 (2)	1573 (3)	46 (1)
^{12}C^{16}O$^{+\ c}$	2.0009 (5)	1.9991 (4)				
^{12}C^{16}O$^{+\ d}$	2.0010 (2)	1.9993 (2)				

^{a} MHz. ^{b} Absolute signs of A values for ^{17}O($I = {}^5/_2$) cannot be assigned from these experimental results. Most reasonable signs are shown. Magnetic moments are assumed to be positive. See text. ^{c} Reference 1. ^{d} These values are more accurate measurements for ^{12}C^{16}O$^+$ obtained on these ^{12}C^{17}O$^+$ experiments.
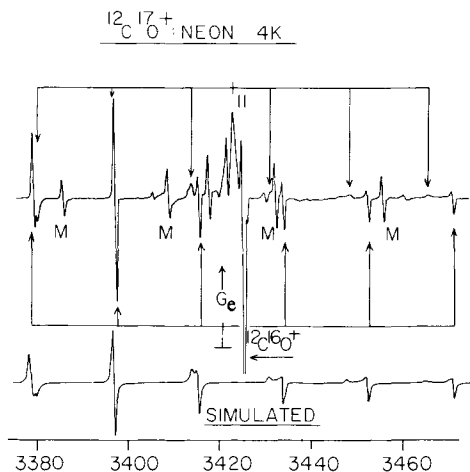

Figure 1. ESR spectrum of ^{12}C^{17}O$^+$ isolated in neon matrix at 4 K. The M denotes methyl (CH$_3$) impurity lines. The computer-simulated second-order powder spectrum for ^{12}C^{17}O$^+$ is shown at the bottom. G_e denotes the magnetic field corresponding to the free spin g value. The spectrometer frequency is 9587.1 (3) MHz.

schemes in neon matrices at 4 K. All attempts to trap small molecular cation radicals by these two methods in argon matrices for ESR studies have been unsuccessful. Apparently, the difference in ionization energies between argon and the neutral precursors is too small, although other factors might be involved. Optical and IR spectroscopic detection of larger cations with electron affinities less than 10–11 eV have been trapped in argon matrices.[18,19]

Figure 1 presents the neon matrix ESR spectrum observed for ^{12}C^{17}O$^+$. An anisotropic ^{17}O($I = {}^5/_2$) nuclear hyperfine powder pattern consisting of six perpendicular and six parallel lines is clearly discernible. The relative phases of the parallel and perpendicular lines, the peak height intensity distribution, and the line positions are in excellent agreement with a computer-simulated spectrum also shown in Figure 1. A combination of g and ^{17}O A tensor anisotropy is responsible for the extremely weak nature of the high-field parallel transitions, although the lines are clearly descernible on expanded spectra. The simulated spectrum very nicely reproduces this line-shape characteristic. The magnetic parameters for ^{12}C^{17}O$^+$ and ^{13}C^{16}O$^+$ are listed in Table I. The molecular g values obtained from these ^{12}C^{17}O$^+$ results are consistent with those obtained for the earlier ^{13}C^{16}O$^+$ and ^{12}C^{16}O$^+$ studies.[1] All observed ^{12}C^{17}O$^+$ line positions agree within the experimental uncertainty of ±0.3 G to calculated positions utilizing the magnetic parameters in Table I and the following second-order solutions to the standard axially symmetric spin Hamiltonian neglecting nuclear quadrupole interaction[20]

$$H_\parallel = H^\circ_\parallel - M_I A_\parallel - \frac{A_\perp^2}{2H^\circ_\parallel}[I(I+1) - M_I^2]$$

$$H_\perp = H^\circ_\perp - M_I A_\perp - \frac{A_\parallel^2 + A_\perp^2}{4H^\circ_\perp}[I(I+1) - M_I^2]$$

where $H^\circ_\parallel = h\nu/g_\parallel\beta$ and $H^\circ_\perp = h\nu/g_\perp\beta$. The absolute signs of the ^{17}O nuclear hyperfine parameters, $A_\parallel$ and $A_\perp$, cannot be determined from these experimental results alone; however, the most reasonable assignment can be deduced from other considerations discussed below.

A discussion of the g tensor for CO$^+$ has been presented previously.[1] More accurate values were obtained in this C^{17}O$^+$ study as shown by the data listed in Table I.

A distinguishing feature of cation radicals trapped in neon matrices is the loss of ESR signal following brief exposures (20–30 min) of low-intensity visible light.[1-3] This dramatic photobleaching effect was also observed for the ESR lines assigned to ^{12}C^{17}O$^+$. None of the matrix-isolated neutral radicals previously studied in our laboratory have shown such an effect. Apparently, visible light in the 500–600-nm region (2–2.5 eV) is sufficiently energetic to photoionize the negatively charged matrix-isolated counterions or electron traps. The liberated electrons have sufficient mobility to neutralize cation radicals throughout the solid neon lattice. A detailed wavelength-dependent study of this phenomenon might offer a useful means of determining electron affinities if the selection of various A$^-$ species could be controlled. ESR studies of a similar photobleaching phenomenon have been previously reported for charged radicals trapped in condensed media other than rare gas matrices.[21] Photobleaching of electronic and vibrational bands has also been observed by others for charged species in rare gas matrices.[22]

Discussion

Given the low natural abundance of ^{17}O (0.02%) and the expense of isotopic enrichment in most compounds, its nuclear hyperfine structure has not been studied in detail for many radicals. In most cases where it has been observed, only the isotropic part of its nuclear hyperfine tensor has been measured on account of motional averaging effects. One of the main objectives of this C^{17}O$^+$ study was to obtain both the isotropic and dipolar components for such a simple and fundamentally important molecular cation radical and to compare such findings to theoretical results.

The experimental observation that $|A_\parallel| < |A_\perp|$ for ^{17}O (see Table I) coupled with a high probability that A_{dip} is inherently positive leaves only two sign choices for $A_\parallel$ and $A_\perp$. The A_{dip} parameter must be positive when the anisotropy on a given atom is dominanted by spin density in a local p$_\sigma$ orbital which is certainly the most likely case for first-row diatomics. If both $A_\parallel$ and $A_\perp$ are negative, $A_{dip} = +1.3$ (5) and $A_{iso} = -50.3$ (5), and for $A_\parallel > 0$ and $A_\perp < 0$, $A_{di+} = +33.0$ (5) and $A_{iso} = -18.5$ (5) MHz. These conclusions can be verified by examining the following equations:

$$A_{dip} = \frac{1}{3}(A_\parallel - A_\perp)$$

$$A_{iso} = \frac{1}{3}(A_\parallel + 2A_\perp)$$

where

$$A_{dip} = \frac{1}{2}g_e g_n \beta_e \beta_n \left\langle \frac{3\cos^2\theta - 1}{r^3} \right\rangle$$

$$A_{iso} = \frac{8}{3}\pi g_e g_n \beta_e \beta_n |\psi^2(0)|$$

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Table II. Comparison of 13-Electron First-Row Diatomic Radicals (X²Σ)

	$g_\parallel$	$g_\perp$	A_{iso}[a]	A_{dip}[a]	% orbital character[b] 2s	2p
CO⁺: ¹³C[c]	2.0010 (2)	1.993 (2)	1573 (3)	46 (1)	42	43
¹⁷O			−18.5 (3)	33.0 (3)	(−0.35)	20
CN: ¹³C[d]	2.0015 (5)	2.0003 (5)	588.1 (3)	45 (3)	16	42
¹⁴N			−12.6 (3)	15.4 (3)	(−0.70)	28
BO: ¹¹B[e]	2.0018 (3)	2.0020 (5)	1026 (1)	13.5 (8)	40	22
¹⁷O			±14 (2)		(±0.27)	
N₂⁺: ¹⁴N[f]	2.0004 (2)		104.1 (6)		5.7	(44)[g]
BeF: ⁹Be[h]	2.001 (1)		294 (2)		65	
¹⁹F			230 (2)		0.43	

[a] MHz. Nuclear magnetic moments are assumed to be positive. See text. [b] On the basis of a comparison of molecular parameters with atomic values of A_{iso} and A_{dip}. See text and ref 21. [c] Neon, 4 K. [d] Argon, 4 K. Reference 10. [e] Neon, 4 K. Reference 13. [f] Neon, 4 K. g value is g_{iso}. Reference 3. [g] Value was determined by the difference and is not a direct reflection of an experimental quantity. [h] Argon, 12 K. g value is g_{iso}. Reference 12.

The latter sign choice is highly favored since it produces an A_{dip} value in good agreement with theoretical results, causes the total spin density to be closer to unity, and is consistent with ¹⁴N results for the CN radical ($A_\parallel = +18.2$ (4) and $A_\perp = -28.0$ (3) MHz).[10]

A direct comparison between these neon matrix experimental results and recent CI ab initio calculations by Davidson and Feller yields the following (theoretical values are listed after the experimental results):[23] ¹³C (A_{iso}) 1573 (3) vs. 1520 MHz; ¹³C (A_{dip}), 46 (1) vs. 51 MHz; ¹⁷O (A_{iso}), −18.5 (5) vs. −13.7 MHz; ¹⁷O (A_{dip}), 33.0 (5) vs. 29.7 MHz. The nuclear hfs parameters listed here in Tables I and II assume positive magnetic moments for ¹³C($I = 1/2$) and ¹⁷O($I = 5/2$). Even though this is not the correct sign for ¹⁷O, such an assumption facilitates the comparison of electronic structure information based on such parameters for related radicals.

Comparison of "experimental spin densities" with those obtained by a MNDO/3 (UHF) calculation shown in parentheses yields the following: C(2s), 0.42 (0.35); C(2p$_\sigma$), 0.43 (0.42); O(2s), −0.0035 (−0.012); and O(2p$_\sigma$), 0.20 (0.23). The optimized bond length determined in the MNDO calculation was 1.14 Å compared to an experimental value of 1.12 Å.[24] While the apparent agreement with theory is excellent except for the very small O(2s) value, it should be emphasized that the "experimental spin density" values were obtained by using the set of atomic parameters for neutral atoms listed by Preston and Morton.[25] For example, the C(2s) value of 0.42 is obtained by the ratio A_{iso}(molecule)/ A_{iso}(atom). To correct for the partial positive charge existing on each atom in the CO⁺ radical, a modified set of atomic parameters for A_{iso} and A_{dip} should be employed. The atomic parameters would definitely increase with charge, but a calculated set of values considering such an effect is apparently not available. The MNDO results for CO indicate a +0.81 charge on carbon and +0.19 on oxygen. The total orbital occupation percentages listed in Table II for CO⁺ is ≈105%. Utilization of "charge corrected" atomic values would definitely reduce this total, although given the numerous approximations involved the 105% value is certainly not unreasonably high. The calculated negative spin density on oxygen is consistent with the above analysis of the signs for $A_\parallel$ and $A_\perp$ and the negative value observed and calculated for ¹⁴N in CN.[10]

A comparison of first-row diatomic 13-electron ²Σ radicals is presented in Table II for CO⁺, CN, BO, N₂⁺, and BeF. The experimental trends illustrate nicely the predictions of a simple MO diagram for the composition of the orbital formally containing the unpaired electrons. The homonuclear case, N₂⁺, with zero

electronegativity difference (Δ) between the bonded atoms exhibits a very large p/s ratio indicating a small degree of hybridization since the p valence levels on each atom are energy equivalent. As Δ increases (in the order N₂⁺, CN, BO, and BeF) the p/s ratio on the more electropositive atom decreases significantly in the order 7.7, 2.6, 0.5, and ≈0.3, respectively. On this "scale", CO⁺ with p/s ≈ 1 resembles BO more closely than the other diatomics as might be expected given the formal charge distribution on CO⁺ indicated above by the MNDO calculation. The "2s" character of the more electropositive atom shows a large decrease as Δ approaches zero. Also, on this scale the percent "2s" value for C in CO⁺ of 42 closely resembles the value of 40 for B in BO.

For BeF, the most ionic case (greatest Δ), the valence "p" orbital of F lies considerably below the 2s level of Be. Thus a transfer of one of the two Be 2s electrons to F through bonding orbitals leaves the unpaired electron primarily on an antibonding Be 2s orbital thereby accounting for the large "s" spin density on Be in BeF. A gradual transition in the relative amounts of A(2s) and B(2p) character for the unpaired electron occurs from ionic BeF to covalent N₂⁺. For example, in CO⁺ the values are 42% "s" on C and 20% "p" on O, those for CN are 16% "s" on C and 28% "p" on N, and those for N₂⁺ are 6% "s" on N and 44% "p" on N. It is also apparent from the data in Table II that a greater degree of local hybridization occurs on the more electropositive atom. A detailed theoretical treatment of this diatomic series should be conducted to obtain a better understanding of the various factors involved.

Summary

The C¹⁷O⁺ cation radical has been generated by two independent methods and studied by ESR in neon matrices at 4 K. These results coupled with existing ¹³C¹⁶O⁺ data allow a complete characterization of the MO containing the unpaired electron in terms of a simple valence orbital description. The experimental spin densities were compared with the results of both ab initio CI and MNDO type calculations. General bonding trends for five 13-electron first-row diatomic radicals were qualitatively compared as a function of electronegativity differences.

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