of comparison with the optical absorption spectrum of Judge and Moule.[5] The most intense band corresponds to the electronic origin of the $\tilde{a}^3A_2 \rightarrow \tilde{X}^1A_1$ transition and is located at 833.3 ± 1.2 nm (12, 146 ± 18 cm^{-1}), measured at the band maximum. The bands located at 693 ± 25 cm^{-1} and 1357 ± 25 cm^{-1} to the blue of the origin are consistent with emission from excited vibrational levels in the $\tilde{a}$ state. The band at 693 cm^{-1} is consistent with the overlapping 3^1_0 (C=S stretch) and 4^2_0 (out-of-plane bend) bands that were observed in absorption[5] at 707 and 687 cm^{-1}, respectively. These bands appear to be merged into one because of the resolution of this study ($\sim$60 cm^{-1}). The feature at 1357 cm^{-1} is also consistent with the merged 3^2_0 and $3^1_0 4^2_0$ bands of Moule and Walsh.[5] A weak feature, 517 ± 25 cm^{-1} to the blue of the origin, is not assigned and may be a combination band. The overlap of the two transitions in the minor bands at 693 and 1357 cm^{-1} above the origin interferes with what might be observed as red shading in the bands.

It is notable that no bands to the red of the origin corresponding to transitions of the kind $v' = 0 \rightarrow v'' = n$ ($n \neq 0$) are identifiable in the spectrum. The 2^0_1 and 3^0_1 bands might especially be expected to appear because of their presence in the CH$_2$S phosphorescence spectrum. Two factors may affect the observability of any CH$_2$Se bands to the red of the origin: the potential presence of the HF (3-0) band at 879 nm and the greatly reduced response of the diode array spectrophotometer beyond 880 nm. We have assigned the band at 870 nm to HF (3-0), but have not ruled out the possibility that CH$_2$Se transitions may account for some of the intensity under the band.

The upper trace of Figure 1 is a spectrum obtained from the reaction of 10 mtorr of DMDSe with 370 mtorr of the 10% F$_2$/He mixture. The two traces are markedly different, although the major features of the lower trace can be discerned in the upper trace. The CH$_2$Se bands and HF (3-0) band are visible in the red shoulder of the extensive band of the upper trace. The HCF ($\tilde{A}^1A'' \rightarrow \tilde{X}^1A'$) spectrum is also observed and is clearly identifiable by its $0n0 \rightarrow 000$ (bending mode) progresssion between 475 and 600 nm and the 000 → 010 band at 630 nm.[11]

The features located between 650 and 800 nm in the upper trace of Figure 1 are difficult to identify at this low resolution. Certain identities of this feature can be ruled out. The CF$_2$,[12] CF$_2$Se,[13] and SeF$_2$[14] molecules have electronic spectra that are known or can be estimated to lie to much higher energies. We have obtained evidence for the formation of FCS radical in the reactions of F$_2$ with organosulfur compounds[10] and speculate that FCSe* may contribute to some of the intensity in this region. It is also possible that CH$_2$Se in the $\tilde{A}^1A_2$ state may be formed in this reaction; however, the oscillator strength for fluorescence from CH$_2$Se is expected to be less than that for phosphorescence according to arguments given previously.[5] But fluorescence from CH$_2$S ($\tilde{A}^1A_2$) is not observed in the CH$_3$SH/F$_2$ system,[3] and the fluorescence and phosphorescence are expected to be of similar intensity for CH$_2$S* in contrast to CH$_2$Se*.

Using the formation of CH$_2$S* in the (CH$_3$S)$_2$ system as a guide,[3] we suggest that CH$_3$Se radicals react with F$_2$ molecules to produce CH$_2$Se*, HF, and F atoms. The chain is initiated by F$_2$ attack on (CH$_3$Se)$_2$ and carried by F atoms and CH$_3$Se radicals. This scheme proved to be thermochemically acceptable for forming CH$_2$S in its $\tilde{a}^3A_2$ state in the organosulfur systems.[3,10]

In summary, we have recorded a spectrum of the $\tilde{a}^3A_2 \rightarrow \tilde{X}^1A_1$ transition in selenoformaldehyde. The HF (3-0) band and, under slightly more fuel lean conditions, HCF ($\tilde{A}^1A'' \rightarrow \tilde{X}^1A'$) features were also observed. The acquisition of these spectra by sampling

an approximately 1-cm^3 reaction volume for a 12-min intergration time demonstrates the utility of the chemiluminescent technique in observing spectra of hard-to-study species. It is hoped that improved mechanistic and dynamical predictability of chemiluminescent reactions will also be useful to the spectroscopist.

## Diminished Solution Electron Affinities of ^{13}C- and Deuterium-Substituted Anion Radical Precursors Allow Isotopic Enrichment

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Since the dawn of the nuclear age, the problem of isotopic separation has been of considerable interest.

An ESR study carried out in tetrahydrofuran (THF) and dimethoxyethane (DME) has shown that even the substitution of a hydrogen by a deuterium on the benzene anion radical (BZ$^-$·) removes the degeneracy of the symmetry (S) and antisymmetric (A) wavefunctions.[1] This apparent electron-releasing nature of the deuterium creates a splitting of about 0.05 kcal/mol in the two wavefunctions.[1] Alkyl groups produce a much larger splitting in the degeneracy of the S and A wavefunctions of benzene$^-$·.[2-6] However, this effect is not purely an electronic one as was shown by the vibronic coupling calculations of Alper and Silbey.[7] Further, alkyl groups appear to destabilize both the S and A wavefunctions, as evidenced by the fact that toluene has a smaller solution electron affinity than does benzene.[8] It must be kept in mind that the relative electron affinities in solution are due to counterion and/or solvent interactions, as toluene has a larger EA than benzene in the gas phase.[9] We were motivated to see if deuteration analogously diminishes the solution electron affinity and if this decreased solution EA could be utilized for isotopic enhancement. Both of these situations were realized. In fact, not only are the relative solution EA's of benzene and naphthalene diminised upon substitution of the protons by deuteriums, but also replacement of the ^{12}C atoms with ^{13}C has a similar effect. Further, this diminished solution EA caused by the addition of neutrons to the carbon or hydrogen nuclei can be utilized to enhance isotopic abundance.

When mixtures of carefully measured quantities of naphthalene (NP) and perdeuterated naphthalene (NP-d_8) were reduced with very deficient amounts of potassium metal in THF, the relative intensities of the two simultaneously observed ESR spectra (Figure 1) show that the equilibrium constant at −120 °C for reaction 1 is 0.26 ± 0.04 and $\Delta G°$, which is identical with the enthalpy change,[10] is 0.41 ± 0.15 kcal/mol.

$$NP^-,K^+ + NP\text{-}d_8 \rightarrow NP + NP\text{-}d_8^-,K^+ \qquad (1)$$
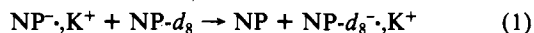
We have used this threefold diminished capacity for the capture of electrons to enhance the concentration of NP-d_8 from mixtures of NP and the deuterated species. The reduction of a 1:1 mixture of the deuterated and undeuterated naphthalenes with 0.5 mol

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(10) The entropy of electron transfer between two similar species to generate similar anion radicals is considered to be very close to zero. For example, see ref 7.
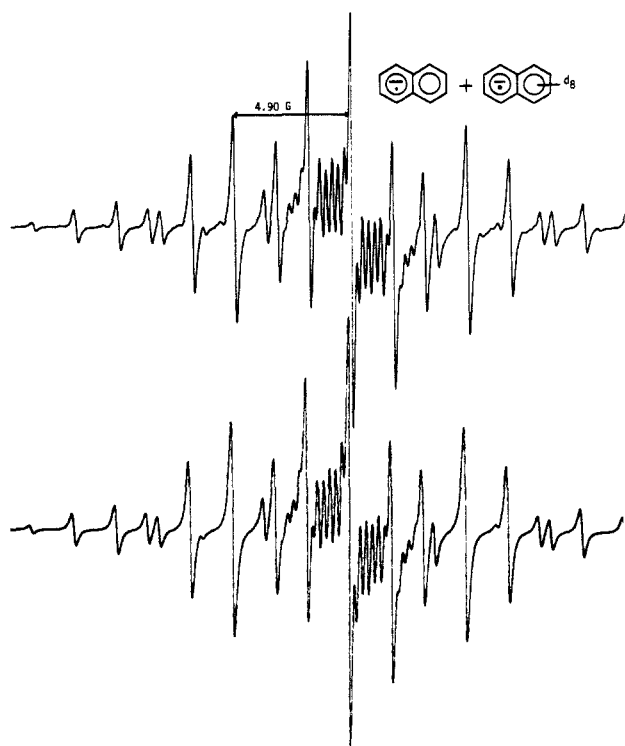
Figure 1. ESR spectrum at −2 °C of a solution of 3.4 × 10^{-3} M NP plus 2.1 × 10^{-2} M NP-d_8 in hexamethylphosphoramide (HMPA) reduced with a very deficient amount of potassium metal. The lower spectrum is a computer simulation that was generated by using a 1.0:1.8 ratio of NP⁻· to NP-d_8⁻·. The equilibrium constant in HMPA is well within experimental error of that found in THF. Coupling constants of 4.90 and 1.79 G were used for NP⁻· and 0.76 and 0.28 for NP-d_8⁻·. All of the ratios of unsubstituted to isotopically substituted anion radicals were obtained by using similar computer simulations. These simulations rigorously account for line broadening due to electron exchange.

of K per mol of hydrocarbon was carried out. The addition of water to this anion radical solution leads to the Birch reduction[11] of the NP and NP-d_8 that are in the reduced state. Since the concentration of NP⁻· is larger than that of NP-d_8⁻·, more NPH_2 than NPH_2-d_8 is formed. Even if this reduction involves protonation of the dianion rather than the radical anion this same argument holds. The isolated naphthalenes remaining after the water addition prove to contain an enhanced ratio of NP-d_8 to NP.

The analogous equilibrium for the benzene (BZ) system also yields an equilibrium constant that is well below unity (K_{eq} = 0.26 ± 0.10, reaction 2. Very similar results were observed from

$$BZ^-·,K^+ + BZ\text{-}d_6 \rightarrow BZ + BZ\text{-}d_6^-·,K^+ \qquad (2)$$
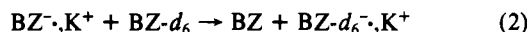
$$\Delta G° = 0.41 ± 0.12 \text{ kcal/mol at } -120 °C$$

mixtures of benzene and BZ-$^{13}C_6$. The ESR spectrum of benzene containing six ^{13}C atoms (98.2% ^{13}C) can be readily generated via the reduction of BZ-$^{13}C_6$ in THF with K, and it consists of two heptets, one due to six protons with a coupling constant of 3.75 G and the other due to six ^{13}C's with a splitting of 2.70 G. The potassium reduction of 4.5:1 [BZ-$^{13}C_6$]/[BZ] mixtures yields ESR spectra consistent with a ratio of anion radicals [BZ-$^{13}C_6$⁻·]/[BZ⁻·] of $^1/_2$. Thus, the decrease in solution EA is slightly less when the six neutrons are added to the carbon atoms.

$$BZ^-·,K^+ + BZ\text{-}^{13}C_6 \rightarrow BZ + BZ\text{-}^{13}C_6^-·,K^+ \qquad (3)$$
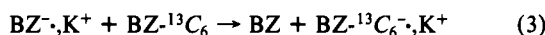
$$\Delta G° = 0.24 ± 0.08 \text{ kcal/mol}$$

$$K_{eq} = 0.45 ± 0.12 \text{ at } -120 °C$$

The measured equilibrium constant for reaction 3 is very dependent upon small impurities of benzene in the solvent or metal

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(11) Birch, A. J.; Smith, H. Q. *Rev., Chem. Soc.* **1958**, *12*, 17.

due to the fact that the BZ⁻· lines exactly superimpose upon the most intense lines from the BZ-$^{13}C_6$⁻·. To varify the value of $\Delta G°$ for reaction 3, mixtures of BZ-$^{13}C_6$ and BZ-d_6 were reduced. The equilibrium constant for reaction 4 was found to be 0.51 ± 0.09.

$$BZ\text{-}^{13}C_6^-·,K^+ + BZ\text{-}d_6 \rightarrow BZ\text{-}d_6^-·,K^+ + BZ\text{-}^{13}C_6 \qquad (4)$$
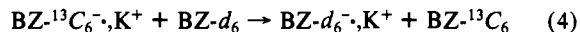
The division of K_{eq} for reaction 2 by that of reaction 4 is equal to 0.51, thus providing an independent confirmation of K_{eq} for reaction 3.

Raman spectra[12] of anion radical systems indicate that the presence of an added electron could increase the zero point energy (ZPE) of the C–C stretch in BZ⁻· relative to that of BZ by as much as 25 cm⁻¹. Considering the fact that six such bonds are present this ZPE effect could account for up to 0.02 kcal/mol of the free energy of reaction 3.

From the work described here it appears that the presence of heavier isotopes in anion radical precursors significantly reduces their solution EA, which allows a means for isotope enrichment via the different reactivities of the reduced and unreduced materials. This reduction of solution EA is probably due to a combination of electronic, ZPE, and solvent/counterion effects. Further, studies into the mechanism of this effect are in progress.

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Remarkable Oxygen Affinity of a Mixed Valence Dicobalt Cofacial Porphyrin Co^III Co^II FTF4

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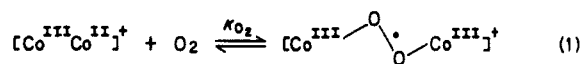*Université de Bretagne Occidentale*
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When the dicobalt cofacial porphyrin complex **1**, Co_2FTF4 (Figure 1), is adsorbed on a graphite electrode in aqueous acid, it is an efficient catalyst for the four-electron reduction of dioxygen.[1] A dioxygen adduct is thought to be an important intermediate in the catalytic cycle.[1] We have shown that *in nonaqueous solutions* the mixed-valence (Co^III Co^II FTF4) complex of **1** forms a stable dioxygen adduct.[2] We now report the equilibrium affinity of this mixed-valence derivative for O_2. Our data reveal three major points: (a) the high equilibrium affinity is unprecedented for cobalt porphyrin derivatives, (b) axial ligands have no measured effect on the magnitude of the O_2 binding constant, and (c) water is a competitive inhibitor of O_2 binding.

The equilibrium constant, K_{O_2}, for oxygen complex formation in benzonitrile (BN) has been measured both spectrophotometrically and potentiometrically.[3]

$$[Co^{III}Co^{II}]^+ + O_2 \underset{}{\overset{K_{O_2}}{\rightleftharpoons}} [Co^{III}\overset{\text{O}}{\underset{\text{O}}{\diagup\diagdown}}Co^{III}]^+ \qquad (1)$$

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(2) Le Mest, Y.; L'Her, M.; Courtot-Coupez, J.; Collman, J. P.; Evitt, E.; Bencosme, C. S. *J. Chem. Soc., Chem. Comm.* **1983**, 1286. Surprisingly, the Co^II Co^II derivative does not show measurable O_2 binding in nonaqueous media.