culations were carried out using the CASSCF/4-31G method (with six-orbital active space comprising the four ethylenic p^π orbitals and the two C p^σ orbitals of C atoms 2 and 3) as implemented in a development version of Gaussian.[12] We have fully optimized, using the method described in ref 10, *three* conical intersection points: structure **a** similar to that of the reactant, where both π bonds are broken by rotation of the terminal methylenes, thus creating a tetraradicaloid; structure **b** that corresponds to a rhomboid arrangement of the two ethylenic π systems (i.e., with a partial *cross* σ-bond between atoms 1 and 4 in **1**); and structure **c** (shown in Figure 1), the lowest energy conical intersection that occurs in the region of **3**. Decay from **a** (23 kcal mol^{-1} higher than **c**) would lead only to cis–trans isomerization or back to starting material. Structure **b** (31 kcal mol^{-1} higher than **c**) has a geometry similar to the conical intersection[9h,i] for the ethylene + ethylene [2 + 2] cycloaddition. Decay from **b** could lead to [2 + 2] cycloaddition products or the 1,4-diradical **2** (which arises from an asynchronous [2 + 2] cycloaddition of the two π bonds). However, this intersection point will probably be unimportant (except in the case of structural constraint) because of its high energy and the fact that the reactant must assume an eclipsed conformation. Structure **c** would be reached via a formal 1,2-vinyl shift and can lead to **3** and **4**. The two directions that define the space of the double cone for structure **c** are plotted in Figure 1 and correspond to bond stretching in the allylic fragment and the motion of the ethene fragment to form the central bond of the 1,3-diradical. We attempted to follow reaction paths in the plane of these two directions using the IRC method. The only path that did not lead to disproportion is shown in Figure 2. It can be seen that the ground-state reaction path leads directly to the 1,3-diradical region of the potential energy surface.

We now briefly discuss the way in which the various experimental features are consistent with a concerted pathway which passes through a conical intersection point with the structure given in Figure 1. Firstly, the regiospecificity observed in 1,5-substituted reactants is readily rationalized via the different stability of the two different conical intersections leading to the 1,3-diradicaloids (**3** in Scheme 1). The most stable conical intersection will be the one with the most stable allyl radical moiety so that the vinyl radical that migrates will be the one without radical stabilizing substituents. Secondly, the integrity of the migrating vinyl radical double bond is found to be maintained. The optimized conical intersection structure and the structures optimized on the IRC show that this double bond does indeed retain its original geometry along the excited-ground-state relaxation pathway. A third "classical" stereochemical feature is the observed inversion of configuration of carbon 3 (where the migrating vinyl radical corresponds to carbon 1 and 2). This feature can be seen in the IRC (Figure 2) involving the evolution of the conical intersection structure toward the 1,3-diradicaloid structure. The final 1,3-diradicaloid structure on the IRC has the two terminal methylene radical centres oriented to form a new σ-bond (via a barrierless process). From Figure 2, it is obvious that this σ-bond will be formed on the *opposite side* of the -CH$_2$ fragment from the position where the migrating vinyl radical was initially attached.

We have assumed that the product of the reaction is determined by the point where the system returns to S_0 and the nature of the subsequent ground-state reaction path beginning at this point. Further, one assumes that the excess energy of the reaction is rapidly removed by equilibration in solution as the system moves on the potential energy surface. The reaction path on the excited surface immediately after vertical excitation will be determined by behavior of the vertical S_1 state (a $^1(\pi\pi^*)$ state best described as partly Rydberg ionic C$^+$–C$^-$). After adiabatic geometrical relaxation, the system enters a region where S_1 is a covalent excited state (essentially doubly excited with respect to S_0). The only features of the covalent region of S_1 that we have been able to locate are the three conical intersections just discussed (i.e., the *minima* on the covalent excited-state surface are conical intersections). Thus our theoretical characterization of the Born–Oppenheimer violation region in the region of **3** shows that there is a point where fully efficient decay from the excited-state surface is possible *avoiding* the 1,4-diradicaloid region **2** and that the subsequent ground-state reaction path leads directly to the 1,3-diradicaloid **3**. Thus a concerted path for the *model* singlet di-π-methane reaction exists. The higher energy conical intersection points can lead back to reactants, to [2 + 2] cycloaddition, or to **2**. The triplet reaction is well known in more rigid systems and probably proceeds by a different mechanism,[3] such as that studied in ref 4.

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Resonance Raman Spectroelectrochemistry of the C_{60} Radical Anion

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We report the first resonance Raman spectrum of the C_{60} monoanion in solution. This spectrum resolves a significant issue regarding the extent of electron transfer during fullerene doping with alkali metals. When C_{60} films are doped with alkali metals, they show conducting and superconducting[1] behavior. These electronic effects are associated with the partial filling of the degenerate LUMO orbitals by electrons transferred from the alkali metal ions. The resulting decrease in average bond order can be monitored via vibrational spectroscopy. In particular, the totally symmetric "pentagonal pinch" mode of C_{60}, which appears as a strong band in the Raman spectrum,[1,2] shifts to lower frequencies when C_{60} is doped. The band has been found by Haddon and co-workers[1,8] to be at 1467 cm^{-1} in an undoped film, but at 1445

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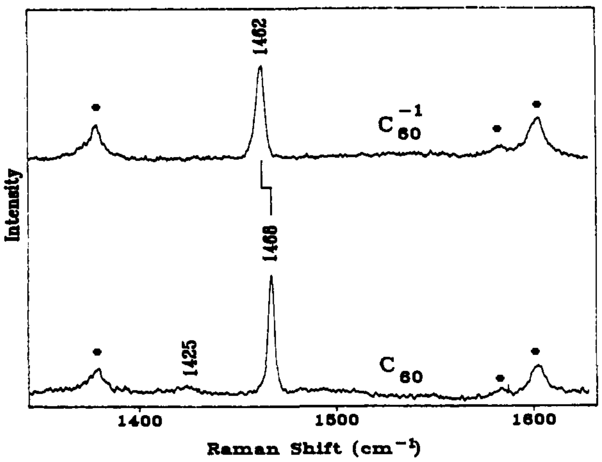

Figure 1. Resonance Raman spectra of C_{60} and C_{60}^- in oxygen-free (70%/30%) toluene/acetonitrile solvent. Spectra were recorded using 20-mW 356.4-nm (Kr$^+$) excitation. The sample was stirred continuously in a cell designed for simultaneous Raman/absorption measurements.[6] Asterisks (*) designate solvent modes.

cm^{-1} in a film of composition K_3C_{60}, which is highly conducting, and becomes superconducting below 18 K.[1] At the composition K_6C_{60}, the film is an insulator, reflecting the complete filling of the t_{1u} LUMO, and the vibrational frequency is 1430 cm^{-1}. These numbers indicate a frequency shift of 6–7 cm^{-1} per added electron, and indeed a C_{60}^- salt, [(Ph$_4$As$^+$C$_{60}^-$)·2(Ph$_4$As$^+$Cl$^-$)], was found to show a 6-cm^{-1} shift of the pentagonal pinch mode relative to the undoped C_{60} film.[1]

In contrast, surface enhanced Raman scattering (SERS) studies of C_{60} deposited on gold and silver surfaces show variable results depending upon the metal substrate and the counterion employed.[3-5,10] Garrell and co-workers[3] observed a shift in the pentagonal pinch mode at a gold electrode in KCl electrolyte from 1452 to 1444 cm^{-1} upon changing the electrode potential from 0.0 to −0.6 V vs SCE. Weaver and co-workers[4] report a shift in the same mode at a gold electrode in tetrabutylammonium perchlorate electrolyte from 1461 to 1443 cm^{-1} at an applied potential of −1.0 V (vs Fc$^+$/Fc), where voltammetry shows reduction of C_{60} to the monanion. This shift is 3 times as large as expected on the basis of the film doping data. If addition of an electron shifts the pentagonal pinch frequency by as much as 18 cm^{-1}, then the degree of electron transfer to C_{60} in doped films would appear to be much less than one per potassium atom. An alternative interpretation of the discrepancy, however, is that the larger SERS shift is due to perturbation of the C_{60} monoanion by interactions at the gold surface or to counterion effects in the C_{60} film. (We have recently learned[10] that the downshift to the pentagonal pinch SERS band upon reduction of C_{60} surface films is highly sensitive to the countercation in the supporting electrolyte.)

To resolve this issue we undertook to determine the shift in the pentagonal pinch frequency upon controlled potential generation of the C_{60} monoanion in dilute solution (ca. 1 mM), using resonance Raman (RR) spectroscopy to provide the needed sensitivity. C_{60} (Texas Fullerenes Corporation) solutions were prepared in 70%/30% toluene/acetonitrile which was 0.1 M in electrochemical grade Bu_4NPF_6 (Fluka) supporting electrolyte. C_{60} monoanions were generated by controlled-potential electrolysis at −1.0 V vs a platinum wire pseudo-reference electrode inside a glovebox in a conventional three-electrode electrochemical cell.[6] Near-infrared measurements confirmed the electrochemical reduction of C_{60} to the monoanion. The near-infrared spectra of the monoanioon were essentially identical to those found in the literature.[7] All Raman measurements were made using 20-mW 356.4-nm Kr$^+$ (Coherent Innova, Model I-100) excitation, near the absorption maximum (339 nm) of C_{60}^- in the near UV.[6] Raman scattered radiation was dispersed using a 1.25-m single spectrograph equipped with a 3600-groove/mm holographic grating and an intensified diode array detector. All Raman spectra were recorded at 3-cm^{-1} resolution.

RR spectra are compared in Figure 1 for the neutral and monoanion species. The pentagonal pinch mode is strongly enhanced and shifts down by 6 cm^{-1} upon monoanion formation, a value exactly in accord with the doped film data, if electron transfer from potassium to C_{60} is complete.[8]

Since the C_{60} LUMOs are degenerate, the anion is subject to Jahn–Teller (J–T) distortion.[9] The previously reported SERS spectra contain prominent bands at the positions of non-totally symmetric modes, some of which show evidence of splittings. These effects were suggested to arise from symmetry lowering due to surface interactions and the field gradient, as well as to J–T distortions.[3-5] A non-totally symmetric Hg mode at 1424 cm^{-1}[2] is seen weakly in our neutral C_{60} spectrum, but not in the C_{60}^- spectrum (Figure 1). No band is seen in either spectrum near 1560 cm^{-1}, where a strong SERS band appears.[3-5] We have also examined the 700–800-cm^{-1} region, where band splittings are reported in the C_{60}^- SERS spectrum,[4] but have seen no features in the C_{60} or C_{60}^- RR spectra. Although additional data at higher sensitivity are needed to evaluate the issue quantitatively, it is apparent that the J–T effect does not provide significant RR enhancement, at least with 356.4-nm excitation. Instead the RR enhancement is mainly restricted to the totally symmetric pentagonal pinch mode, consistent with Franck–Condon scattering from an allowed excited state which is mainly displaced along the pentagonal pinch coordinate. RR enhancement is weaker for C_{60}^- than for C_{60}, as judged by the relative intensities of the solvent bands, consistent with the broader electronic absorption band observed for the anion.[6]

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Oxygen-Atom Transfer from Nitrous Oxide to a Nickel Metallacycle. Synthesis, Structure, and Reactions of (2,2′-Bipyridine)$\overline{\mathrm{Ni(OCH_2CH_2CH_2CH_2}}$)

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Nitrous oxide (N═N═O) is one of the most thermodynamically potent oxygen-transfer reagents,[1] comparable in oxidizing power to hydrogen peroxide or perbromate, yet it is kinetically inert toward most organic substrates in the absence of a suitable activating agent. These facts have led us to investigate its use as an oxidant in organometallic systems in which transition-metal centers serve to activate N_2O. Our previous studies have centered on early transition-metal (Ti, Zr, Hf) systems in which the inherent strength of the M–O bonds that are formed place limits on potential applications of the reactions of N_2O that we have discovered (precluding, for example, catalytic cycles that might require reductive elimination involving the M–O linkage).[2-5] We have

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