Discrete Fulleride Anions and Fullerenium Cations

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I. Introduction, Scope, and Nomenclature

The electron-accepting ability of C_{60}, the archetypal fullerene, is its most characteristic chemical property. It is a natural consequence of electronic structure and was anticipated in early molecular orbital calculations[1] which place a low-lying unoccupied t_{1u} level about 2 eV above the h_u HOMO:[2-4]

Early in the gas-phase investigations of fullerenes, the electron affinity of C_{60} was measured and found to be high (2.69 eV).[5-7] When the macroscopic era of C_{60} chemistry began in 1990, this property was soon found to translate into the solution phase.[8] In a rather remarkable cyclic voltammogram (see Figure 1), the reversible stepwise addition of up to six electrons was soon demonstrated electrochemically.[9,10]

Figure 1. Cathodic cyclic and differential pulse voltammograms of C_{60} in CH_3CN/toluene at -10 °C showing successive reversible reductions to C_{60}^{6-}. (Reprinted with permission from ref 9. Copyright 1992 American Chemical Society.)

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Robert Bolskar received his B.S. degree in Chemistry from Carroll College in Waukesha, WI, in 1992. He earned his Ph.D. degree at the University of Southern California in Los Angeles under the direction of Christopher Reed in 1997, investigating the synthetic redox chemistry of fullerene anions and cations. In 1998 he moved to the University of California, Riverside, as Managing Research Associate. He is currently Senior Chemist at TDA Research in Wheat Ridge, CO. His research interests include the chemistry and physics of fullerene compounds, supramolecular chemistry, strongly oxidizing systems, and electrophilic cations.

However, the best known demonstration of the electronegative nature of C_{60} is the solid-state intercalation of electropositive metals producing a large family of M_xC_{60} salts called fullerides. The most remarkable of these are the superconducting phases, A_3C_{60} (A = alkali metal cation).[11] The extended properties of these systems have been extensively reviewed elsewhere[12–15] but are part of this review when connections can be made to the discrete C_{60}^{n-} ions. Another early development was the discovery of a unique fulleride phase which displays ferromagnetism: [TDAE]-[C_{60}] (TDAE = tetrakis(dimethylamino)ethane).[16]

Solid-state superconductivity and ferromagnetism in [60]-fulleride materials arises from cooperative interactions between electrons on adjacent buckyballs. 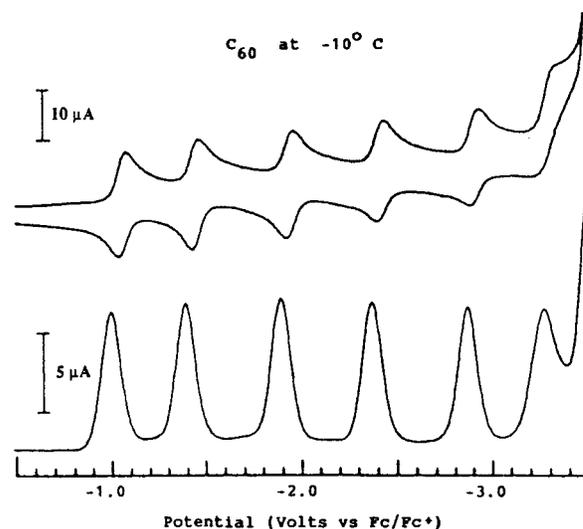The ball-to-ball contact is relatively meager, but tangential contact at near van der Waals separation is sufficient to develop the appropriate electronic band structures. Under these circumstances, the electronic properties of the individual ions must be largely retained, suggesting that the electronic structure of discrete fulleride ions is the preferred point of departure for understanding their extended properties.[17] This is one of the major reasons for studying isolated fulleride ions in detail.

An example of where discrete fulleride chemistry meets materials science is in the determination of an appropriate value for the Knight shift in A_3C_{60} metals. There are quite divergent opinions on how to partition the observed solid-state ^{13}C NMR shifts in A_3C_{60} compounds (185–196 ppm) into an intrinsic chemical shift and a Knight shift (i.e., the contribution of the conduction electrons relative to an insulating state). Knight shifts as high as 61 ppm[18] and as low as 6 ppm[19] have been suggested. The effect of unpaired electrons on the chemical shift in the C_{60}^{3-} ion, present in both the conducting and the insulating phases, has been largely neglected in the discussion. Determining the correct value has significant ramifications for the calculated density of states at the Fermi level, $N(E_F)$, in A_3C_{60} conductors.[20]

An unanticipated property of discrete C_{60}^{n-} fullerides is their propensity to disobey Hund's rule. For example, the 3-fold degeneracy of the t_{1u} LUMO leads to the expectation of a spin quartet ground state for C_{60}^{3-}:

$$\uparrow \quad \uparrow \quad \uparrow \qquad t_{1u}$$

This is, however, *not* observed. C_{60}^{3-} has a spin doublet ground state even though there is no requirement for a Jahn–Teller lowering of symmetry.[21] There is a similar counterintuitive result with C_{60}^{2-} whose electronic structure has been somewhat controversial. Resolving the conflicting interpretations of data and theory for this ion is one of the motiva-

tions for compiling this review. Another is to assess the current status of the long-standing problem regarding the origin of the extra signals seen in the EPR spectra of fullerides. Of the six explanations that have been offered to explain the origin of the sharp signal (or "spike") in the EPR spectrum of C_{60}^-, only two remain viable. Much of the early work is open to reinterpretation, and we now conclude that C−C bonded dimers of fullerides ($C_{120}O^{n-}$ or C_{120}^{n-}) offer the most compelling explanation for the extra signals. Dimeric[22] and polymeric[23] AC_{60} phases containing C−C bonded fullerides have become quite well characterized in recent years.

Related to the idea of C−C bonded dimers is the very recent finding that the newly recognized class of low HOMO−LUMO gap fullerenes (C_{74}, C_{80}, etc.), trapped in fullerene soot because of polymerization, can be solubilized by reduction to discrete anions.[24] There is also the relationship of fullerides to endohedral metallofullerenes, $M@C_{2n}$. The electropositive nature of the metals that form endohedral fullerenes means that their carbon frameworks must have a high degree of fulleride character.[25−28] Although they are not yet available in large quantities, there are indications that much of their chemistry can be understood in terms of what we are learning about fullerides.

In contrast to their facile reduction, commonly available fullerenes are difficult to oxidize in condensed media. It was some years into the macroscopic era of fullerene chemistry before the reversible oxidation of C_{60} was demonstrated electrochemically and then only on the cyclic voltammetric time scale (a few seconds).[29] Recently, however, the first salts of fullerenium cations (C_{60}^+, C_{70}^+, and C_{76}^+) have been prepared,[30,31] so their study is included in this review.

The gas-phase chemistry of fullerene anions[32] and cations[33] is mentioned in this review when connections can be made to condensed-phase chemistry.

C_{60} has a place in history similar to that of ferrocene. Both were discovered somewhat serendipitously.[34] Both are redox-active chromophores which presented chemists with an entirely new type of bonding. Both led to Nobel Prizes.[35−39] The earliest investigations concentrated on understanding the novel bonding, investigating the redox properties, and exploring the scope of the structural motif, particularly by involving a variety of metals.[40] Somewhat later, an extensive organic functionalization chemistry developed.[41−44] Both chromophores have been tagged to polymers, surfaces, electrodes, etc., and applied to problems from material science[45] to biochemistry.[46,47] The fullerene applications are, of course, at an earlier stage of development, but it is clear that the redox states of fullerenes will play an important role in these applications, just as the ferrocene/ferrocenium cation couple does. Presently, however, the reaction chemistry of fullerides and fullerenium cations is rather poorly developed and in need of further exploration. Given the longevity of ferrocene as a broadly useful redox-active chromophore, a sustained interest in C_{60} chemistry can be predicted. This review is written to serve the need

for continued comprehensive development of fullerene chemistry with an emphasis on the charged redox states of these novel curved-carbon structures. Donor−acceptor properties of fullerene and fulleride materials have recently been reviewed.[48]

The literature on fullerenes is widely spread across the disciplines of material science, physics, and chemistry in all its branches, adding to the challenge of writing a review that is both critical and comprehensive. Compounding this is the proliferation of publications associated with conferences which, apart from sometimes undesirable duplication, may introduce data and interpretations that have not had the benefit of thorough peer review. We take such data *cum grano salis*[49] and make no claims of being comprehensive in the coverage of conference-related literature.

As its point of departure, the recommended nomenclature for fullerenes[50] seems to have adopted the dubious assumption that fullerenes are dehydrogenated hydrocarbons rather than a unique class of molecules in their own right. As a result, the naming of derivatives is, in our opinion, heading toward obfuscation rather than clarity. For instance, instead of naming $1,2\text{-}(CH_3)_2C_{60}$ simply as 1,2-dimethyl[60]-fullerene, it is recommended that 1,2-dimethyl-1,2-dihydro[60]fullerene be used. This substitutive nomenclature contradicts the otherwise sensible recommendation that groups attached to fullerenes should be referred to as addends, not substituents (being formed by addition not substitution). Further complications arise when charges are introduced. For example, it has been suggested that the HC_{60}^- ion should be called the 1,2-dihydro[60]fulleren-1-ide ion (loss of H^+ from position 1) or the 2-hyrido[60]-fullerene-1-uide ion (addition of H^- to position 2, negative charge at position 1) depending on how it is made. In our view, neither can compete with the more straightforward hydrido[60]fulleride ion (formal H^- addition, no assumption about charge location). Similarly, it has been suggested that the C_{60}^- ion should be named the [60]fulleren-1-elide ion rather than the more straightforward [60]fulleride(−1) ion. The problem becomes more bizarre when the more highly charged states of fullerenes are considered. For example, siding for the moment with the school of thought that a name should reflect how something is made (rather than what it is), the C_{60}^{2-} ion might be called the 1,2-dihydro[60]fulleren-1,2-dielide ion (two H^+ loss from $1,2\text{-}H_2C_{60}$). Given the fact that the C_{60}^{2-} ion is simply a dianion with delocalized charges, an unassuming designation as the [60]fulleride(−2) ion would seem highly preferable. In this review, we use "fulleride" as a generic term for any negatively charged fullerene, with the charge indicated in parentheses if necessary (as would be used, for example, in C_x^{n-} carbide chemistry). For cations, there is too little chemistry known for strong recommendations on nomenclature to be made. We use the generic term "fullerenium" for electron-deficient, positively charged species derived from fullerenes.

Table 1. Redox Parameters (CV unless Otherwise Noted) of the Fullerenes C_{60}, C_{70}, C_{76}, $C_{2v}-C_{78}$, D_3-C_{78}, C_2-C_{82}, C_{84}, and C_{86}

fullerene	solvent[a]	$E_1^{Red\ b}$	$E_2^{Red\ b}$	$E_3^{Red\ b}$	$E_4^{Red\ b}$	$E_5^{Red\ b}$	$E_6^{Red\ b}$	$E_1^{Ox\ b}$	$E_2^{Ox\ b}$	ref
C_{60}	PhMe/MeCN[c,d]	−0.98	−1.37	−1.87	−2.35	−2.85	−3.26			9
	TCE[e]	−1.06						+1.26		29
C_{70}	PhMe/MeCN[c,d]	−0.97	−1.34	−1.78	−2.21	−2.70	−3.07			9
	TCE[e]	−1.02						+1.20	+1.75[f,g]	29
C_{76}	PhMe/MeCN[h]	−0.83	−1.17	−1.68	−2.10	−2.61	−3.04[i]			63
	TCE[e,f]	−0.83	−1.12					+0.81	+1.30[g]	57
$C_{2v}-C_{78}$	PhMe/MeCN[h,j]	−0.72	−1.08	−1.79	−2.16	−2.45	−2.73[k]			63
	TCE[e,f]	−0.77	−1.08					+0.95	+1.43[g]	57
D_3-C_{78}	CH_2Cl_2	−0.64	−0.94	−1.70	−2.05[l]					59
	TCE[e,f]	−0.77	−1.08					+0.70	+1.17[g]	57
C_2-C_{82}	ODCB[m]	−0.69	−1.04	−1.58	−1.94			+0.72		65, 205
C_{84}[n]	TCE[e,f]	−0.67	−0.96	−1.27				+0.93		57
C_{86}[o]	ODCB[m]	−0.58	−0.85	−1.60	−1.96			+0.73		65

[a] + 0.1 M Bu_4NPF_6. [b] V vs Fc/Fc^+. [c] At −10 °C. [d] 5.4:1 PhMe:MeCN. [e] TCE = 1,1′,2,2′-tetrachloroethane. [f] Osteryoung square wave voltammetry (OSWV). [g] Irreversible. [h] 8:2 PhMe:MeCN. [i] Differential pulse voltammetry (DPV) at −15 °C, possibly irreversible, see ref 63. [j] At −15 °C. [k] Speculated assignment, see ref 63. [l] Approximate potential, see ref 59. [m] ODCB = o-dichlorobenzene. [n] Isomer(s) not resolved—data is available vs SCE for isomers of C_{84} in various solvents, see refs 64, 66, and 67. [o] Major isomer.

II. Electrochemistry

A. Reductive Voltammetry

One of the very first experiments performed on C_{60} once it became available in macroscopic quantities was reductive electrochemistry.[8,51−53] Upon optimization of the electrochemical conditions, fifth and sixth reduction waves could be observed on the cyclic voltammetry time scale (see Figure 1).[9,10,54] The relatively even spacing of ca. 0.45 V for the successive reductions is striking. It is a particular feature of fullerenes as a class of molecules, reflecting their delocalized LUMOs, and is observed in C_{70}, C_{76}, C_{78}, and C_{84}.[9,51,55−59] It has also been calculated using density functional theory.[60] Table 1 lists representative redox data for the more commonly known fullerenes. Data in this table have been selected according to solvent (toluene/acetonitrile or chlorocarbon) and reference (ferrocene) so that valid comparisons can be made.

The ease of reduction of C_{60} is reflected in the value of the first reduction potential, only ca. −1.0 V vs ferrocene/ferrocenium (ca. −0.35 V vs Ag/AgCl or ca. −0.45 V vs SCE). Somewhat unexpectedly, C_{70} has an essentially identical value, prompting speculation about the underlying reasons.[51,61] Some of the higher fullerenes (e.g., C_{76}, the D_3 isomer of C_{78}, C_{82}, and all three isolated isomers of C_{84}) are as much as 450 mV easier to reduce to the (−1) state, but inspection of Table 1 shows that there is no strict correlation with size.[57−59,62−67] For the newly discovered class of small HOMO−LUMO gap fullerenes (e.g., C_{74}) reduction is even easier, occurring in the range from −0.2 to −0.5 V vs Fc/Fc^+.[24] For a number of fullerenes, there is a good correlation between the calculated HOMO−LUMO gap and the "electrochemical gap", i.e., the difference between the first reduction potential and the first oxidation potential.[57]

The effect of the medium on the redox potentials of C_{60} has been studied by a number of groups. Independent studies by Fawcett,[68] Kadish,[69,70] Bard,[71] and Compton[72] reveal a significant influence of the cation on the kinetics and, to a lesser extent, the thermodynamics of the first electron transfer to C_{60}.

Ion pairing with C_{60}^-, possibly to two cations,[68] is clearly important in chlorocarbon and nitrile solvents and in solid films,[72−76] slowing diffusion rates and influencing C_{60}/C_{60}^- potentials. A correlation of potential with R_4N^+ cation size has been reported,[69,77] but its statistical validity has been questioned.[78] Cation variation for the more highly charged redox couples is much less significant.[69,78]

The effect of solvent on the redox potentials of C_{60} is more substantial than the effect of electrolyte. Early indications of a correlation of the first reduction potential with solvent donicity[51,69] (e.g., Gutmann donor number) have held up to more detailed analysis,[78] but the interpretation of experimental data has turned out to be less straightforward than originally believed. The basic problem lies in obtaining statistically significant data that are not compromised by the solvent dependence of the reference couple used. For this reason, Lay and co-workers[78] have used the decamethylferrocene/decamethylferrocenium couple rather than the ferrocene/ferrocenium (Fc/Fc^+) couple as a reference, reinterpreting the data of Kadish and co-workers[69] to produce statistically valid analyses. Data are listed in Table 2. The formal potentials for the first four reduction steps vary by ca. 300−400 mV over a range of 16 solvents.[78] This indicates that a large change in solvation occurs with each change of charge. The major solvent-stabilizing effect for fulleride ions comes from H-bonding acidity and from polarity. This is readily understood in terms of negative charges on the fulleride ions. The lack of a correlation between the first reduction potential and functions involving the dielectric constant is taken as evidence for a substantial reorganization of charge between C_{60} and C_{60}^-. This is in accord with calculations and X-ray data that suggest a nonspherical concentration of electron density in fullerides in an equatorial belt (see section VI). An unexpected correlation of the first reduction potential with a solvent *basicity* parameter can be explained in terms of influences on ion pairing with cations.[78] There is some dependence of redox potential on solvent polarizability but only for the first reduction. This is explained in terms of $\pi-\pi$ solvent−solute interac-

Table 2. Formal Reduction Potentials of $C_{60}^{n-/(n+1)-}$ Couples Referenced to the Reduction Potential of the $Me_{10}Fc^{+/0}$ Couple in 0.1 M TBAClO$_4$[78]

solvent	$C_{60}^{0/1-}$	$C_{60}^{1-/2-}$	$C_{60}^{2-/3-}$	$C_{60}^{3-/4-}$
acetonitrile[a]		−735	−1225	−1685
dimethylformamide[a]	−312	−772	−1362	−1902
pyridine[a]	−343	−763	−1283	−1813
aniline[b]	−396	−693	−1158	−1626
benzonitrile[a]	−397	−817	−1297	−1807
nitrobenzene[a]	−406			
N-methylaniline[b]	−442	−782		
1,2-dichloroethane[a]	−448	−848	−1298	
benzyl alcohol[b]	−443	−817		
dichloromethane[a]	−468	−858	−1308	−1758
tetrahydrofuran[a]	−473	−1063	−1633	−2133
1,2-dichlorobenzene[b]	−535	−907	−1360	−1841
N,N-dimethylaniline[b]	−547			
chloroform[b]	−554	−908		
chlorobenzene[a]	−573	−953	−1438	
bromobenzene[b]	−587			

[a] From refs 69 and 70. Data recorrected to the $Me_{10}Fc^{+/0}$ couple. [b] Data from ref 78.

tions, important for neutral C_{60} but not for the charged fullerides. Again, this is consistent with X-ray structural data where the $\pi-\pi$ stacking interactions that are commonly observed in C_{60} solvates are frequently seen to switch to C−H dipole interactions in fullerides. Substantial negative shifts in redox potentials can be observed when C_{60} is complexed by calixarenes, presumably because fulleride-stabilizing solvent dipoles are excluded from the immediate solvation sphere.[79]

Reductive electrochemistry is frequently reported as part of the routine characterization of *derivatized* fullerenes. In an early systematic study, Suzuki and co-workers[80] showed that the usual effect of derivatization is to make the fullerene somewhat more difficult to reduce (0.1−0.3 V), although some electropositive addenda such as silyl groups, quaternary nitrogen centers,[81] or organocynanides[82] can move the redox in a positive direction. The origin of these effects seems to lie in the loss of delocalization and in the inductive effect of the substituents. In most cases, successive reductions of derivatized fullerenes cause loss of addenda. Comprehensive coverage of the literature on derivatized fullerenes is outside the scope of this review. The electrochemistry of derivatized fullerenes is part of a recent brief review,[83] and derivatized higher fullerenes are now receiving attention.[59] As discussed in section X.A, electrochemical formation of derivatized fullerides is being used to synthetic advantage. A number of reports on the electrochemistry of endohedral fullerenes have also appeared.[24,62,65,84,85]

B. Oxidative Voltammetry

At first, a four-electron *irreversible* oxidation of C_{60} was reported at a threshold potential of ca. 1.3 V vs Fc/Fc$^+$ in benzonitrile.[54] Presumably, C_{60}^+ was formed but it reacted with solvent nucleophiles and was further oxidized. *Reversible* anodic waves were first reported by Heinz and co-workers in dichloromethane/dimethylamine at low temperatures,[86] but the currents were believed to be indicative of two-electron waves. Dimethylamine is likely to have reacted with

any cations formed in this system. The electrochemical identification of C_{60}^+ was put on a firm footing by Echegoyen and co-workers in 1993 using scrupulously dried tetrachloroethane as solvent and lowered temperatures.[29] A reversible cyclic voltammetry wave was observed at 1.26 V for C_{60} and at 1.20 V for C_{70} (vs Fc/Fc$^+$), and the one-electron nature of the process was established by comparison of currents to the well-established C_{60}/C_{60}^- wave. A second, irreversible process was observed with C_{70}, presumably corresponding to the transient formation of C_{70}^{2+}.

Higher fullerenes are easier to oxidize than C_{60} or C_{70} (see Table 1). Although initially believed to form at an unusually low potential,[87] C_{76}^+ is now known to form reversibly at 0.81 V.[57] The C_{2v} and D_3 isomers of C_{78} oxidize at 0.95 and 0.70 V, respectively.[57] C_{84} has a number of isomers, all of which oxidize around 0.9 V.[57,59] A short review on the redox potentials of the higher fullerenes has appeared.[88] In keeping with their delocalized charges, the first oxidation potentials of C_{60}, C_{70}, C_{76}, and C_{78} follow the same trend as their first ionization potentials (7.61, 7.58, 7.10, and 7.05 eV, respectively).[89,90]

In contrast to reduction, the oxidation of fullerenes typically becomes easier upon derivatization,[59,80,91,92] particularly with bis(silyl) derivatization,[93] but no cations have been characterized.

III. Synthesis

The reduction potentials of fullerenes discussed above (Table 1) indicate what potential must be used to electrochemically prepare solutions of any particular fulleride via bulk electrolysis. They also dictate which reducing and oxidizing agents are useful for chemically adding or subtracting electrons from fullerenes. The observation of six reversible reduction waves and one reversible oxidation wave for C_{60} on the cyclic voltammetry time scale (a few seconds) indicates that eight different "oxidation states" of C_{60} should ultimately be accessible to solution-phase preparative chemistry. Further extremes in negative oxidation states (so-called "superfullerides") can be achieved by taking advantage of solid-state effects[94−97] and the special properties of lithium (e.g., in $Li_{12}C_{60}$).[98−100]

A. Chemical Reduction of Fullerenes to Fullerides

The nearly 0.5 V separation between the successive reduction steps of the common fullerenes means that it is relatively easy to find chemical reducing agents that are specific for a particular reduction state. Alternatively, careful stoichiometric control of strong reducing agents can be employed, particularly if the solubility characteristics of reactants and products are manipulated to synthetic advantage. This is possible because solvents that dissolve fullerenes[101−103] frequently do not dissolve fullerides. In fact, low solubility can be a problem in fullerene synthetic chemistry regardless of oxidation state. One exception is the relatively high solubility of alkali metal fullerides in tetrahydrofuran (THF). Fullerides are generally air sensitive, requiring manipulation and storage under an oxygen-free atmosphere, although

the aerobic oxidation of uninegative fullerides can be fairly slow. As a result, some fulleride(−1) solids are air stable and solutions can be "buffered" with excess reducing agent for brief aerobic exposure. Water is of little consequence in the synthesis of fulleride-(−1) salts because the basicity of uninegative fullerides is low (see section X.B). However, as the charge increases, fullerides become increasingly sensitive to both oxygen and water. Increasing attention must be paid to solvent purity. Glovebox, Schlenk, or vacuum line techniques (O_2, H_2O < 1 ppm) are necessary to isolate discrete salts.

Synthetic methods can be classified according to the type of reducing agent used: (i) metals, (ii) coordination/organometallic compounds, and (iii) organic/other. In the following sections, the major advances in methodology are highlighted and their utilities identified. Many methods are available to generate solutions of fullerides for the purpose of making physical measurements, but rather few fulleride salts of rigorously established analytical purity have been isolated.

i. Metals as Reducing Agents

The alkali metals (Li, Na, K, Rb, Cs) are powerful reducing agents with a remarkable ability to intercalate as vapors into solid fullerenes.[104] They have also been used successfully in solution, typically in an ether (e.g., tetrahydrofuran, dimethoxyethane)[105−109] or liquid ammonia.[110,111] C_{60}^{n-} fullerides up to $n = 5$ have been produced in this manner. Sonication with excess Li[112] or the use of sodium or potassium naphthalide[113,114] is reported to give rise to the $n = 6$ state.

The chief difficulty of using alkali metal for reduction is controlling the stoichiometry. In situ monitoring of the reduction state is generally required to halt reduction at the desired level, although in one case tetramethylethylenediamine as solvent along with sonication is reported to be specific for the −3 state of C_{60} with excess potassium.[115] This difficulty was overcome by Reed and co-workers who added stoichiometric amounts of complexants such as crown ethers or cryptands. Unlike alkali metals, complexants are easily weighed and manipulated in the small quantities needed. The lower solubilities of the complexed alkali metal salts allow crystallization of the desired products and separation from excess alkali metal before further reduction takes place. In this manner, Na(dibenzo-18-crown-6)$^+$ salts of C_{60}^{n-} for $n = 1$, 2, and 3 were isolated from THF solution.[21,116−118] To isolate a C_{60}^{4-} salt, a less base-sensitive complexant, 2.2.2-cryptand, was necessary.[119] This is the highest charged discrete fulleride salt yet isolated. Cryptands can also be used to isolate salts of lower charge.[120] Complexation of Li$^+$ with N-methylimidazole leads to isolable discrete salts of C_{60}^{n-} for $n = 1$ and 2.[121]

An alternative solution to the problem of controlling alkali metal reduction would be to use an electron carrier to mediate electron transfer.[122] In principle, the redox potential of the added carrier molecule rather than that of the alkali metal determines the level of reduction. As with the complexant

method, products must be separated from excess alkali metal in a timely manner to avoid over-reduction. This method remains to be fully exploited, but Huang and co-workers have used 1-methylnaphthalene as an electron carrier in conjunction with stoichiometric control of alkali metal to prepare C_{60}^{n-} salts for $n = 1$, 2, and 3.[123−126] Corranulene has been used as an electron carrier with excess Li in THF to produce diamagnetic fulleride ions from C_{60} and C_{70} without the need for sonication.[127] These are believed to be (−6) ions.

Other "dissolving metal" reductions can be used to produce fullerides in solution. The choice of metal, added ligand, and solvent allows some selectivity in the stoichiometry of reduction. Alkaline earth metals (Mg, Ca, Ba) have been used in THF,[106,128] N-methylimidazole,[121] mercury amalgam/toluene,[128] or liquid ammonia,[129] in the last case leading to isolable species for X-ray structural characterization.[129] Rare earth metals (Eu),[130] Hg,[131−133] Sn, Al−Ni alloy with varying conditions to get (−1) to (−3) selectivity,[134,135] and various transition metals (Mn, Fe, Cu, Zn)[121,134] have been utilized. The use of mercury provides a particularly versatile method of producing fulleride-(−1) salts with a wide variety of cations when combined with the addition of tetraalkylammonium, alkylpyridinium and tetrasubstituted arsonium bromides.[131−133] The method exploits the insolubility of Hg_2Br_2 which can be filtered off prior to evaporation of the solvent.

Cation metathesis has been achieved in many other systems by exploiting solubility differences. The large cation PPN$^+$ (bis(triphenylphosphine)iminium) forms low-solubility salts with C_{60}^{n-} for $n = 1$, 2, and 3,[21,118,136] and successful metathesis reactions have been reported with Me$_4$N$^+$.[137] Ion exchange of K$_2$C$_{60}$ in liquid ammonia has been very useful for producing M(NH$_3$)$_6^{2+}$ salts for X-ray crystallographic characterization (M = Ni, Mn, Cd).[129,138]

ii. Coordination and Organometallic Compounds as Reducing Agents

Coordination and organometallic compounds can have precisely defined redox potentials and are therefore well suited as selective reducing agents for fullerenes.[122] The first to be used were Cr(TPP) (TPP = tetraphenylporphyrinato) and cobaltocene, and their chemistry illustrates the principles involved.

Treatment of C_{60} with Cr^{II}(TPP) in toluene/THF solvent mixture gives the well-defined (−1) salt [Cr-(TPP)(THF)$_2$][C$_{60}$].[139] Interestingly, there is no reaction between C_{60} and Cr^{II}(TPP) in neat toluene and the electron transfer reaction can be reversed simply by dissolving [Cr(TPP)(THF)$_2$][C$_{60}$] in toluene. This means that C_{60}^- is too poor a ligand to stabilize Cr-(III). The presence of THF is required to shift the Cr$^{II/III}$ redox potential into the appropriate range, which it does by stabilization of Cr(III) via coordination. Sn(II) porphyrins and Al(III) porphyrin radical anions are also mentioned as suitable reductants for C_{60}.[116,117,139] Ru(bipy)$_3^{2+}$ has been employed as a counterion to prepare an isolable C_{60}^- salt.[140]

Cobaltocene has a reduction potential very close to the second reduction potential of C_{60}. Thus, if not

used in large excess, it is suitable for generating well-defined salts of the (−1) ion, [Co(Cp)$_2$][C$_{60}$].[40,116,117] A very recent application of this reducing agent with a 3-aminophenyl-methano-fullerene[60] derivative has produced a new ferromagnetic material.[141,142] Methylation of a cyclopentadienyl ligand makes a metallocene more reducing, and the use of different metals adds further versatility to the organometallic reduction method.[122] Thus, permethylated cobaltocene, Co-(Cp*)$_2$, can be used to form C$_{60}^{n-}$ salts for $n = 1$, 2, and 3 by control of stoichiometry, although it is most useful for $n = 2$.[118] In parallel work, the strongly reducing "electron reservoir" compound Fe^I(Cp)(C$_6$-Me$_6$) has been used to prepare isolable C$_{60}^{n-}$ salts for $n = 1$, 2, and 3.[143] Ni(Cp*)$_2$ is selective for a salt of C$_{60}^-$ suitable for X-ray crystallography.[144] Mn(Cp*)$_2$[121] and Cr(benzene)$_2$[145] are also suitable for the synthesis of (−1) salts. Reduced metallocene salts such as [Na]-[Mn(Cp*)$_2$] have been used to synthesize THF-solvated alkali metal salts of [60]fullerides in the (−1)[146] and (−3)[147] states. The strongly reducing metal carbonyl complexes Co(CO)$_4^-$ and Fe(CO)$_4^-$ have also been used to reduce C$_{60}$[148,149] whereas Mn(CO)$_5^-$ forms an η^2-C$_{60}$ complex.[150] It is believed that there is considerable unexplored potential for new materials with interesting electrical, magnetic, or photonic properties using metal complexes as counterions to fullerides.[48,151]

iii. Organic/Other Reducing Agents

Amines, thiols, *p*-benzoquinone, aldehydes, hydrosulfite ion, and the tetraphenylborate ion have been successfully used as selective reducing agents for fullerenes in solution. In addition, a variety of methods have been developed for photoproduction of fulleride(−1) ions, usually as transients.[152−156] These often rely on the high electron affinity of ^{3}C$_{60}$, readily produced by photoexcitation of ground-state C$_{60}$ (see section X.D).

The most interesting application of amines as reducing agents is the use of tetrakis(dimethylamino)ethane to produce an apparently ferromagnetic phase of formula [TDAE][C$_{60}$].[16] The reaction is relatively clean in neat amine.[157] A second, nonferromagnetic phase can be crystallized out by lowering the temperature of the crystallizing solution.[158,159] This simple redox reaction of TDAE and certain other amines[160] with fullerenes contrasts with that of most other amines where covalent addition chemistry frequently follows initial electron transfer.[161−163] The low solubility of the electron transfer product is probably the key to obtaining fulleride salts rather than addition compounds. Another ferromagnetic fulleride phase was believed to have formed with C$_{60}$ and the strongly reducing 1,1′,3,3′-tetramethyl-Δ2,2′-bi(imidazolidine),[164] but this was later shown to a be diamagnetic material, possibly containing a mixture of C$_{60}^-$ and C$_{60}^{2-}$ ions.[165] Primary amines such as 1-amino-3-propanol and 1,5-diaminopentane are reported to give (−1) and (−2) ions of C$_{60}$ and C$_{70}$.[166,167] Pyridine is a useful extractant for liberating endohedral fullerenes from metallofullerene soot.[168,169] An unrecognized chemical origin of this process may be the ability of pyridine to act as a reducing agent,

labilizing inter-fullerene C−C bonds in the polymerized soot.

Propanethiol in base has been used to reduce C$_{60}$.[170] Depending on the solvent conditions, the reaction can be made selective for the (−1) or (−2) ions. *p*-Benzoquinone and sterically hindered "active aldehydes" have been used similarly.[171,172] The tetraphenylborate ion, as an alkali metal salt, is a mild reducing agent capable of producing C$_{60}^-$ from C$_{60}$ in THF.[173,174] The rate of production of C$_{60}^-$ can be enhanced by intentional photolysis, proceeding via triplet ^{3}C$_{60}$.[156] Sodium hydrosulfite in base is also effective.[134,175] The carbon radical, crystal violet (tri-(*p*-dimethylaminophenyl)methyl radical), is a useful one-electron reducing agent for C$_{60}$ leading to an isolable trityl salt.[176] The same salt has been produced by electrocrystallization techniques.[177]

B. Electrosynthesis of Fullerides

Given the well-defined, distinct reduction potentials of fullerenes, it is only natural that controlled-potential, bulk electrolysis of fullerenes has been widely used to prepare solutions of specific fullerides. A variety of solvent systems have been introduced including toluene/dichloromethane,[178] dichloromethane, pyridine, benzonitrile, THF,[53,179−182] and water/γ-cyclodextrin.[183] From a synthetic point of view, however, electrochemical methods tend to work only when practical current densities can be achieved and when the products separate easily from the electrolyte solution. This usually requires the product to crystallize quickly and fall away from the electrode. It is a particular challenge in fullerene chemistry where the polar solvents needed for ion solubility and good electrochemistry are typically incompatible with high concentrations of neutral fullerenes. Electrocrystallization on the electrode surface can also be contemplated and when successful can lead to single crystals suitable for X-ray diffraction. However, such experiments are usually performed at constant applied current, leading to overpotentials that can cause unwanted electrochemistry of the solvent or nonstoichiometric reduction.

An early and successful application of electrosynthesis exploited the low solubility of tetraphenylphosphonium and tetraphenylarsonium double salts. Wudl and collaborators prepared [Ph$_4$P]$_2$[C$_{60}$]Cl as a well characterized [60]fulleride(−1) double salt in 1991.[184] Since then, single crystals of a number of closely related compounds containing C$_{60}^-$ and C$_{70}^-$ have been obtained by electrocrystallization.[185−190] These are discussed in section VI with regard to their X-ray structures. In another development, solid-to-solid electrochemistry of C$_{60}$ to produce a Bu$_4$N$^+$ fulleride has been shown to give a microcrystalline phase as opposed to a film.[191]

C. Chemical Oxidation of Fullerenes to Fullerenium Cations

The difficulty of oxidizing fullerenes to fullerenium radical cations has been discussed in section II.B above. At 1.26 V versus Fc/Fc$^+$, the first oxidation potential of C$_{60}$ is at least 0.5 V above the redox

potentials of commonly available strong oxidants such as tris(*p*-bromophenyl)aminium or phenoxathiin radical cations.[122] Transient production of fullerene radical cations has been achieved with a variety of photooxidants.[90,153,154,192–205] EPR signals in so-called pristine C_{60} powder have been assigned to trapped C_{60}^+,[206,207] but given its extremely high reactivity (see section X.G), other more chemically reasonable explanations should be considered.

Oxidizing superacid media,[105,112,208–212] chlorine dioxide,[213] and zeolites[214–216] have been employed in attempts to prepare stable cations of fullerenes, but even in the best of cases, success has been limited to the unquantified detection of C_{60}^+ by NIR and/or EPR spectroscopies (see sections IV.D and IX.G). The problem seems to be that cations of C_{60} (e.g., C_{60}^+, HC_{60}^+, or C_{60}^{2+}) are susceptible to oxidative degradation and nucleophilic attack by the anions of superacids (HSO_4^-, $SbCl_6^-$, SbF_6^-, etc. or halides therefrom).

The first successful synthesis of a fullerenium radical cation required the development of a new oxidant, one that was strong enough for the task but which did not bring along a reacting nucleophile.[30] A suitable oxidant was found in the radical cation of tris(2,4-dibromophenyl)amine ($E° = 1.16$ V). A suitable anion was the carborane $CB_{11}H_6Br_6^-$, one of the most useful members of a newly recognized class of exceptionally inert anions with extremely low nucleophilicity.[217] The byproduct of oxidation reactions using an aminium reagent such as $[Ar_3N^{•+}]$- $[CB_{11}H_6Br_6^-]$, i.e., the triarylamine, is a very poor nucleophile because electronic and steric effects make it nearly planar at the N atom. Although the redox potential of this reagent is insufficient to oxidize C_{60} or C_{70}, it has more than enough driving force to oxidize C_{76} to C_{76}^+ ($E° = 0.81$ V). Stoichiometric reaction occurs in *o*-dichlorobenzene or 1,1′,2,2′-tetrachloroethane to give an excellent yield of dark brown $[C_{76}^{•+}][CB_{11}H_6Br_6^-]$ (eq 1).

$$C_{76} + [Ar_3N^{•+}][CB_{11}H_6Br_6^-] \rightarrow$$
$$[C_{76}^{•+}][CB_{11}H_6Br_6^-] + Ar_3N \quad (1)$$
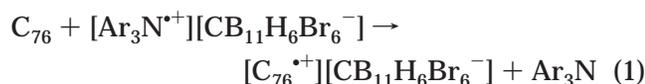
The development of an even stronger oxidant, one capable of oxidizing C_{60} to C_{60}^+, has recently been announced.[31] The oxidant is the radical cation of a hexabrominated phenylcarbazole, and the anion is the carborane $CB_{11}H_6Cl_6^-$. $[C_{60}^{•+}][CB_{11}H_6Cl_6^-]$ has been characterized by IR, NIR ($\lambda_{max} = 980$ nm), and EPR ($g = 2.002$, $\Delta H_{pp} = 3–8$ G depending on conditions) spectroscopies.[218]

Fullerenium radical cations are the first all-carbon carbocations and therefore represent a new class of ions. It remains to be seen whether a (+2) fullerenium ion can be prepared and whether it will be a diamagnetic singlet or a paramagnetic triplet. The preparation of two cations of derivatized fullerenes, $C_{60}Ph_5^+$ and $C_{60}R^+$, is discussed in section X.G.

IV. Electronic (NIR) Spectroscopy

A. Introduction

Fullerenes, fullerides, and fullerenium cations have electronic absorptions throughout the visible and ultraviolet spectral regions, but it is the near-infrared region (NIR) that has proved to be the most useful and informative for reduced and oxidized fullerenes. The $t_{1u}–t_{1g}$ gap of C_{60} is of NIR energy (ca. 1 eV) and is an allowed electronic transition in C_{60}^{n-} fullerides. Because of the delocalized nature of the added or removed electrons, the energy gaps of the parent fullerene are not drastically altered by redox. Nevertheless, each redox state has distinctive λ_{max} values in the 700–1200 nm region, and these have been usefully diagnostic of the charge state. Analysis of the accompanying weaker bands hints at a complex vibronic structure for each of the differently charged states, giving clues to the nature of Jahn–Teller distortions.

B. C_{60}^{n-} Fullerides

As reported by Lawson et al.,[182] Heath and co-workers,[110,181] and Baumgarten and co-workers,[107] each of the C_{60}^{n-} fullerides for $n = 1–5$ has a distinctive NIR spectrum. Selected spectra are reproduced in Figures 2–6. As the following tables
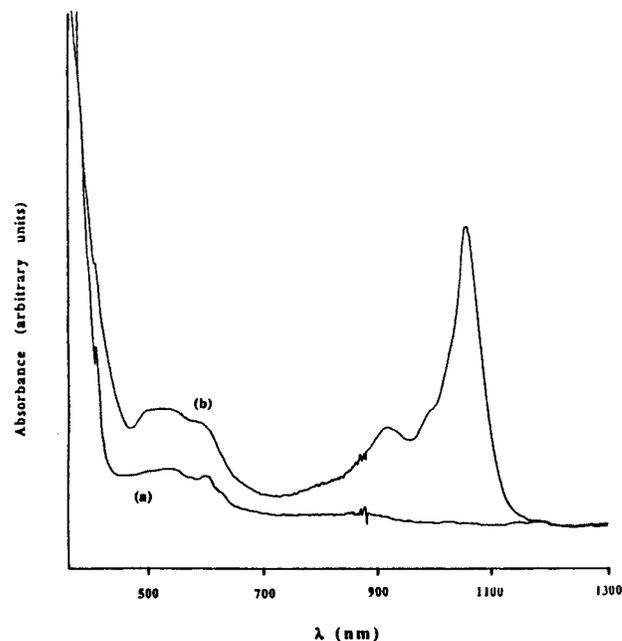

Figure 2. Visible–near-infrared spectrum of (a) C_{60} and (b) C_{60}^- in dichloromethane/toluene. (Reprinted with permission from ref 178. Copyright 1991 American Chemical Society.)

reveal, there is some solvatochromism in the fulleride spectra but the same essential features are found regardless of solvent or cation.

Table 3 lists representative λ_{max} values for C_{60}^- under a variety of conditions. There is consensus for a dominant transition at ca. 1075 nm ($\epsilon \cong 15000–20000$ M^{-1} cm^{-1}) accompanied by a progression of weaker bands to higher energy. In its simplest interpretation, the major band is assigned to the allowed $t_{1u} \rightarrow t_{1g}$ transition and the weaker bands to vibrational fine structure.[153,178,180–182] The energy is consistent with SCF-Xα-SW theory based on the HOMO–LUMO gap of C_{60}, acknowledging the simplification of I_h symmetry.[181] An alternative assign-
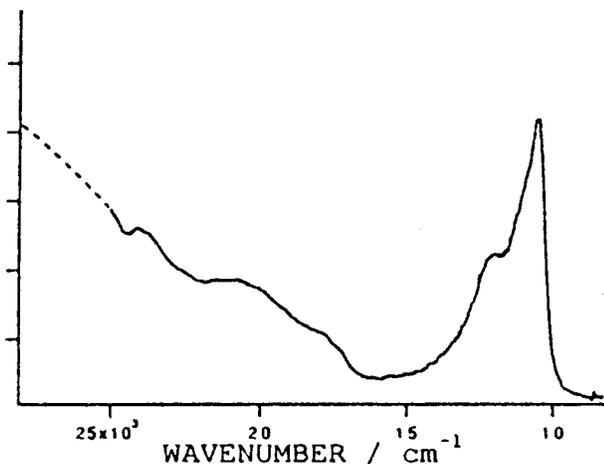
Figure 3. Near-infrared spectrum of C_{60}^{2-} in dichloromethane. (Reprinted with permission from ref 221. Copyright 1993 Gordon and Breach Publishers.)
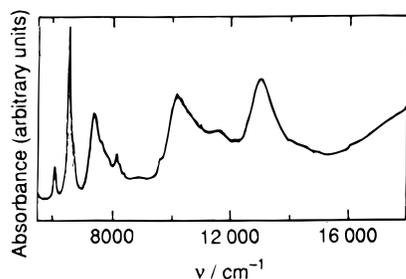

Figure 4. Near-infrared spectrum of C_{60}^{3-} in liquid ammonia at -40 °C. Bands below ca. 7000 cm^{-1} are due to the solvent. (Reprinted with permission from ref 110. Copyright 1993 Royal Society of Chemistry.)
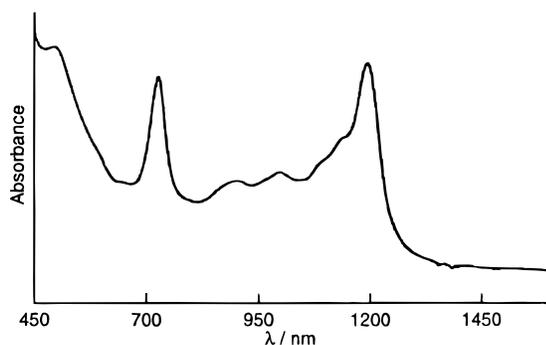

Figure 5. Visible−near-infrared spectrum of C_{60}^{4-} in dimethyl sulfoxide. (Reprinted with permission from ref 119. Copyright 1997 Royal Society of Chemistry.)

ment for the major transition is put forward on the basis of theory using a Hubbard interaction term for electron−electron repulsion.[219] It predicts the first allowed transition in the IR region (ca. 0.7 eV) and assigns the 1075 nm band to the second allowed transition. Experimental support for this alternate assignment is lacking. Symmetry lowering from I_h to D_{5d} was introduced by Lawson et al. to accommodate the intuitive necessity of Jahn−Teller splitting of the $^2T_{1u}$ state into $^2A_{1u}$ and $^2E_{1u}$ states.[182] A second allowed electronic transition was postulated to occur near 925 nm, but emission data argue for a single transition.[220,221] In the most thorough study to date, the low-temperature analysis of Shida and co-workers requires a lowering of the symmetry to D_{2h}
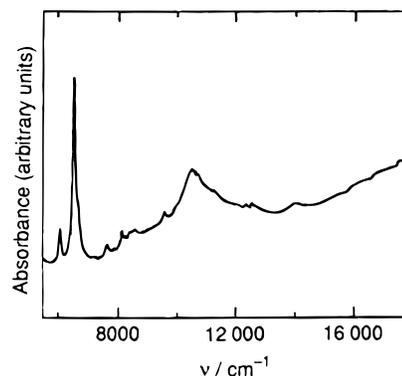

Figure 6. Near-infrared spectrum of C_{60}^{5-} in liquid ammonia at -40 °C. Bands below ca. 7000 cm^{-1} are due to the solvent. (Reprinted with permission from ref 110. Copyright 1993 Royal Society of Chemistry.)
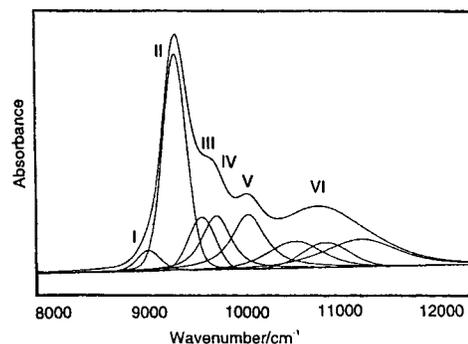

Figure 7. Deconvolution of the NIR of C_{60}^{-} in benzonitrile. (Reprinted with permission from ref 224. Copyright 1995 Elsevier Science.)

in polar media although in nonpolar media D_{5d} or D_{3d} symmetry is adequate to rationalize the spectra.[222] CNDO/S calculations were used to support assignments. Low-temperature MCD spectra in an argon matrix corroborate the assignments and reveal further complexity in the low-energy region.[223] A careful deconvolution of the room-temperature spectrum has revealed a previously unnoticed shoulder to the low-energy side of the principal band (see Figure 7).[224] This is believed to be a "hot band" having its origin in the thermal occupation of the first low-lying electronic level of C_{60}^{-}, a potentially important indicator of the magnitude of Jahn−Teller splitting.

Although D_{5d}, D_{3d}, or D_{2h} symmetry is adequate to rationalize the observed electronic structure of C_{60}^{1-}, it is possible that the true extent of symmetry lowering remains hidden to electronic spectroscopy. The spectrum may be a composite of Jahn−Teller-distorted structures, and the limitations of energy resolution may lead to a higher *effective* symmetry. On the other hand, the indication that polar solvents can lower the symmetry more than nonpolar ones suggests that fullerides are truly dynamic Jahn−Teller systems,[225] capable of being trapped in static structures by the environment.[226] Preferred locations for solvent interactions can, in principle, lead to a variety of different molecular symmetries.[116] In most cases, electronic structure calculations in the absence of a perturbing environment favor a D_{5d} energy minimum but pseudorotation barriers and other minima are less than 1 kcal/mol higher in energy.[227]

Table 3. Near-Infrared Data for C_{60}^-

λ_{max} (nm)	reductant or discrete salt	solvent/conditions	extinction coefficient ϵ (M^{-1} cm^{-1})	ref
1076	λ-irradiation	MeTHF, 77 K	30000 ± 10000	153
927				
1064	electrochemical	CH_2Cl_2/PhMe	12000	178
995			5100	
917			4600	
1073	electrochemical	CH_2Cl_2	15500	180, 221
930				
1078	electrochemical	PhCN	12000	182
1075	electrochemical	CH_2Cl_2, 213 K	12000	181
932			3560	
1075	K or Ca metal	THF	20000	106
1072	K mirror	THF		107
1036				
992				
934				
1087−1074	[CoCp_2][C_{60}]	9 different		224
1055−1043		solvents		
1035−1029				
1006−992				
970−891				
1087−1074	[Na(crown)][C_{60}]	9 different		224
1056−1042		solvents		
1041−1026				
1005−995				
968−888				
1075	electrochemical	PhMe/MeCN		347
1095	[Ph_4P]_2Cl[C_{60}]	solid state		189
1059				
1016				
965				
1101	[Ph_4P]_2I[C_{60}]	KBr matrix		261
1050				
1015				
953				
1075	electrochemical	PhMe/THF	18000	108

The observation of extensive vibrational fine structure in the electronic spectrum of a molecule in condensed media is rare. It is usually hidden in the broadness of the electronic bands. The approach taken to assigning the vibronic spectrum of C_{60}^- has been to inspect the H_g and A_g Raman fundamentals of C_{60} for coincidence with energy summation to the electronic transitions. The reasonable assumption is made that the vibrational fundamentals of C_{60}^- will not be very different from those of C_{60}. It is widely believed that the centrosymmetric $H_g(1)$ vibrational mode (264 cm^{-1} in C_{60}) couples to the principal transition at 1075 nm giving rise to the first of the secondary bands (band III in Figure 7).[106,178,180,222,224] A caveat is raised by the analysis of Bolskar et al., which suggests that a forbidden electronic transition may also contribute intensity at about the same wavelength.[224] It is likely that the $H_g(2)$ mode of C_{60} at 430 cm^{-1} and $H_g(4)$ mode at 771 cm^{-1}, presumably combined with other modes,[110,196] contribute to the subsequent progression of vibronic bands to higher energy. The band(s) labeled VI in Figure 7 are insufficiently resolved at room temperature for a confident deconvolution. At liquid helium temperatures in a neon matrix, the spectrum is very rich in resolved bands. Vibronic assignments have been made under the assumption of D_{5d} symmetry.[196]

The photoemission spectrum of C_{60}^- has been obtained and compared to detailed calculations of the vibronic structure.[228] The similarity to the absorption spectrum is striking. All eight H_g modes and two A_g modes are calculated to contribute to the phonon satellites (vibrational structure). This paper is the first to use the spectral analysis of a fulleride to develop estimates for electron−phonon coupling constants, a necessary component for developing an understanding of the mechanism of superconductivity in A_3C_{60} compounds. Higher resolution photoelectron spectra of C_{60}^- have recently been reported.[7]

Table 4. Near-Infrared Data for C_{60}^{2-}

λ_{max} (nm)	reductant or discrete salt	solvent/ conditions	extinction coefficient ϵ (M^{-1} cm^{-1})	ref
952	electrochemical	PhCN	16000	182
830			7000	
952	electrochemical	CH_2Cl_2, 213 K	10500	181
840			11900	
950	electrochemical	CH_2Cl_2	20900	221
840				
943	Rb metal	NH_3, 233 K	5600	110
813			2500	
1305	K mirror	THF		107
947				
829				
957	[PPN]_2[C_{60}]	MeCN		118
810				
950	electrochemical	PhMe/MeCN	18500	299, 347
840				
947	electrochemical	PhMe/THF	15000	108
840				

Resonance Raman spectroscopy could profitably be applied to C_{60}^- to further the understanding of its vibronic structure, but to date there has been only one brief report.[229]

Table 4 lists representative λ_{max} values for C_{60}^{2-} under a variety of conditions. There is consensus for two dominant bands at ca. 950 and 830 nm. Various

Table 5. Near-Infrared Data for C_{60}^{3-}

λ_{max} (nm)	reductant or discrete salt	solvent / conditions	extinction coefficient ϵ (M^{-1} cm^{-1})	ref
1367	electrochemical	PhCN	6000	182
956			9000	
878			7000	
788			14000	
1351	electrochemical	CH$_2$Cl$_2$, 213 K	6700	181
990			8000	
877			8000	
775			11250	
1357	Rb metal	NH$_3$, 233 K	5200[a]	110
985			6300	
866			4200	
769			7400	
694			3400	
1336−1344	K mirror	THF		107
957−990				
772				
1370	[PPN]$_3$[C$_{60}$]	pyridine DMSO		21
995				
860				
775				
1400	electrochemical	PhMe/MeCN		347
720−880				

^{a} Listed as "52,000" in the original ref 110.

Table 6. Near-Infrared Data for C_{60}^{4-} and C_{60}^{5-}

λ_{max} (nm)	reductant or discrete salt	solvent/ conditions	extinction coefficient ϵ (M^{-1} cm^{-1})	ref
		C_{60}^{4-}		
1209	electrochemical	PhCN	6000	182
728			4000	
1177	Rb metal	NH$_3$, 233 K	5500	110
714			6000	
1195	[Na(crypt)]$_4$[C$_{60}$]	DMSO		119, 324
1000				
904				
728				
934 (br)	K mirror	THF		107
		C_{60}^{5-}		
952	rubidium metal	NH$_3$, 233 K	7180	110

Table 5 lists representative λ_{max} values for C_{60}^{3-} under a variety of conditions. There is consensus for three dominant bands at ca. 1350, 960, and 770 nm, each with one or more vibronic transitions to the high-energy side.[110] A deeper investigation of this spectrum would be useful to look for connections to an electron−phonon mechanism for superconductivity in A$_3$C$_{60}$ compounds and to improve our understanding of why C_{60}^{3-} has a doublet rather than quartet ground state.

Table 6 lists representative λ_{max} values reported for C_{60}^{4-} and C_{60}^{5-} under a variety of conditions. For C_{60}^{4-}, there is near consensus for two dominant bands at ca. 1200 and 730 nm, each with multiple weaker vibronic transitions to the high-energy side. The report of a single band at 934 nm[107] appears to be in error and may be due to over-reduction to C_{60}^{5-}. The C_{60}^{5-} spectrum of the rubidium salt in liquid ammonia is reported to have its dominant band at 952 nm.[110] There is some similarity of the C_{60}^{5-} spectrum to that of C_{60}^{-}, of which it is the electron hole equivalent. This lends credence to the C_{60}^{5-} spectrum being assigned to the proper charge state. There is one report of a NIR spectrum for the C_{60}^{6-} ion.[107]

Many organic derivatives of C_{60} have been reduced to fullerides and their NIR spectra recorded.[108,212,230−239] For monoadducts of the type 1,2-R$_2$C$_{60}^{-}$, there is a reasonable similarity to C_{60}^{-} except that the dominant band is blue-shifted by ca. 70 nm. The same is true for 1,4 adducts, but the details of the spectra are usefully different from 1,2 adducts.[235] These findings are consistent with a HOMO/LUMO structure for derivatized fullerenes that is not greatly perturbed from that of the parent fullerene but one that reflects some loss of delocalization.

C. C_{70} and Higher Fullerenes

Like C_{60}, the fullerides of C_{70} and higher fullerenes have characteristic absorptions in the NIR. Table 7 lists representative λ_{max} values for C_{70}^{-} and C_{70}^{2-}

assignments for these bands, made prior to the knowledge that C_{60}^{2-} has a singlet ground state and a thermally accessible triplet, await revisiting.

Table 7. Near-Infrared Data (λ_{max} in nm) for C_{70}^{n-}

system	C_{70}^{-} (ϵ = M^{-1} cm^{-1})	C_{70}^{2-} (ϵ = M^{-1} cm^{-1})	C_{70}^{3-}	C_{70}^{4-}	ref
electrochemical in PhCN	1368 (4000)	1170 (7200)	1170	1170	242
		670 (4600)	670	670	
MeCyclohexane	1386				a
MeTHF (77 K γ irrad)	1377	1184			a
VUV irrad (5 K Ne matrix)	1363				195
K/THF	1369	1165	1070		234
K/THF	1369	1165	"none measurable"	1048	212
dissolution in 1-amino-2-propanol	1372	1172			167
dissolution in 1,5-diaminopentane	1370	1176			167
[Ph$_4$P]$_2$I[C$_{70}$]	1380				190
K/THF	1370	1171			108
[Ph$_4$P]$_2$Br[C$_{60}$]	NIR not detected				241
Na/PhCN	1374	1182	1172		243
		670	759		
			675		
K/PhCN	1373	1182	1171	1160	243
		670	759	759	
			670	674	
TDAE/PhCN	1379				243
chemical reduction	1370	1170	1178		135
(various methods)	791		759		

^{a} Hase, H.; Miyatake, Y. *Chem. Phys. Lett.* **1993**, 141−143.

under a variety of conditions. There is essential consensus for a dominant band at ca. 1370 nm for C_{70}^{-} which moves to higher energy as the charge is increased. Resonance-enhanced multiphoton electron detachment (REMPED) spectra favor a $^2E_1''$ ground state for C_{70}^{-}.[240] The conclusion that C_{70}^{-} in [PPh$_4$]$_2$-[Br][C$_{70}$] has no NIR spectrum[241] seems to be in error. There is insufficient consensus in the spectral observations attributed to C_{70}^{3-} and C_{70}^{4-} for a confident description of their spectra.[135,212,242,243] NIR spectra for electrogenerated C_{76}^{-} and C_{76}^{2-} have recently been reported, clarifying earlier tentative assignments.[244]

D. Fullerenium Cations

Table 8 lists λ_{max} values ascribed to C_{60}^{+} under a variety of conditions. There is consensus for a dominant NIR band at ca. 980 nm, and sometimes a band to higher energy is reported. Much of the data have been obtained on transients under conditions of unknown purity of the chromophore. Thus, the spectrum very recently obtained from an isolable salt of C_{60}^{+} (Figure 8) should probably be considered
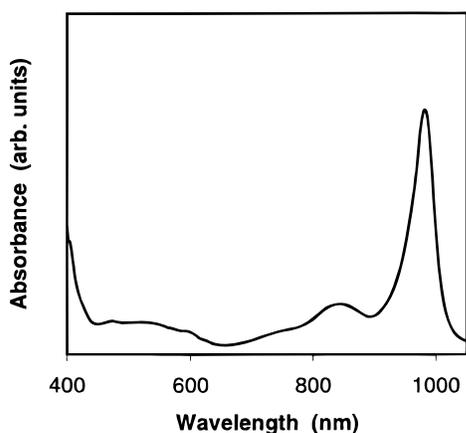

Figure 8. Near-infrared spectrum of C_{60}^{+} in 1,1′,2,2′-tetrachloroethane.[218]

definitive. In tetrachloroethane, the strong absorption at 980 nm is accompanied by a weaker, broad band at 850 nm.[218] These energies are consistent with an INDO calculation for allowed transitions from a ^2H_u ground state to ^2H_g and ^2G_g excited states under I_h

symmetry.[245] Allowing for a Jahn–Teller distortion, breaking of symmetry to a dynamic D_{5d} state is favored.[245] At liquid helium temperatures in a neon matrix, the C_{60}^{+} spectrum shows enough vibronic structure that symmetry lowering to D_{5d} can be justified and vibrational assignments have been made for the progression of higher energy bands.[196] The MCD spectrum corroborates the main assignment[193] and reveals low-lying excited states that are thermally accessible even at liquid helium temperatures.[223] A transition from paramagnetism to diamagnetism at very low temperatures, as predicted by theory for the mono*anion*,[246] is implied by the MCD data on C_{60}^{+}.[223]

The NIR spectrum of C_{70}^{+} is unexpectedly featureless at room temperature. A synthetically produced sample shows only a weak absorption near 780 nm.[218] This is consistent with a λ_{max} value of 798 nm reported for low-temperature transient production of C_{70}^{+} in a neon matrix.[195] However, the low extinction coefficient means the spectrum is not always observable[153] and is subject to masking by other chromophores. This may be the case in recent studies that ascribe bands at ca. 930 and 830 nm to C_{70}^{+}.[200,202] Theory suggests additional bands in the NIR and IR regions,[153,195] and one attempt at a vibronic assignment has been made.[195]

Because it is one of the easiest commercially available fullerenes to oxidize, C_{76}^{+} was in fact the first fully characterized fullerenium ion.[30] The NIR spectrum of [C$_{76}$][CB$_{11}$H$_6$Br$_6$] in tetrachloroethane contains several bands (1040, 980, 830, 780, 710 nm) consistent with the creation of an electron hole in the series of closely spaced electronic energy levels calculated for C_{76}.[247] More recent spectral measurements on transiently produced C_{76}^{+} are in general agreement with those from the synthetic sample.[90,202] Fullerenium ions of other higher fullerenes (C_{78}^{+}, C_{84}^{+}, etc.) are expected to have similar identifying NIR absorbances.[90,248]

E. Diffuse Interstellar Bands

There has been considerable speculation that fullerenes contribute to the diffuse interstellar bands (DIBs), the more than 150 unassigned absorptions in the visible and NIR spectral regions seen in the line-of-sight of many galactic and extra-galactic

Table 8. Near-Infrared Data Reported for C_{60}^{+}

oxidizing system	solvent/conditions	λ_{max} (nm)	ref
γ-ray irradiation	freon matrix (77 K)	980	153
"25% magic acid"	4:1 FSO$_3$H:SbF$_5$	818, 766	208
"100% magic acid"	1:1 FSO$_3$H:SbF$_5$	742	208
photoinduced electron transfer	CH$_2$Cl$_2$	980	192, 194
photoionization	Ar or CCl$_4$ matrix (11 K)	973	193
NeI irradiation or mass-selected C_{60}^{+} deposition	Ne matrix (5 K)	965, 958	196
pulse radiolysis	1,2-dichloroethane, CH$_2$Cl$_2$	980	a, 197
fuming sulfuric acid	(immediate)	929, 824	210
CF$_3$SO$_3$H/K$_2$S$_2$O$_8$	(20 h)	965 (weak)	211
SbCl$_5$	CH$_2$Cl$_2$	983	108
NAr$_3^+$	[C$_{60}$][CB$_{11}$H$_6$Cl$_6$] in TCE, CH$_2$Cl$_2$, or ODCB	980, 850	218
SbF$_5$	TCE	980, 850	218
photoinduced electron transfer	ODCB	930, 1050	203

^{a} Guldi, D. M.; Hungerbuhler, H.; Janata, E.; Asmus, K.-D. *J. Chem. Soc., Chem. Commun.* **1993**, 84−86.

objects.[36,249,250] Indeed, it was the desire to create in the laboratory carbon chains as possible candidates for the origin of some of these bands that led to the discovery of C_{60}.[34,249,250]

There is general agreement that carbon-containing species contribute to the DIBs,[249,251] but neutral fullerenes themselves are not considered to be likely candidates.[252,253] The spectral features of C_{60} do not coincide with any of the DIBs. However, diffuse interstellar bands at 958 and 965 nm are tantalizingly close to the NIR bands observed for C_{60}^+ in a neon matrix.[196] If the assignment of DIBs to C_{60}^+ can be confirmed, and there is good reason for doubt when considering the IR region,[37,196] C_{60} would be the largest molecule ever detected in the interstellar medium. This should motivate continued earth-bound studies of fullerene cations including fullerenium ions, protonated fullerenes, and endohedral fullerenes, all of which are candidates for interstellar molecules.

V. Vibrational Spectroscopy

A. Infrared Spectroscopy

Due to its very high symmetry, C_{60} has only four infrared-active fundamental vibrational modes.[254-258] These are the $T_u(1-4)$ modes at 527, 576, 1183, and 1429 cm^{-1}. The response of these frequencies to the addition of charge and Jahn–Teller lowering of symmetry are of considerable interest.

The effect of charge in intercalated A_xC_{60} fullerides is most pronounced in the $T_u(4)$ mode.[259] As can be seen in Table 9, the frequency decreases steadily with increasing charge from 1429 cm^{-1} in C_{60} to 1340 cm^{-1} in A_6C_{60}.[260] There is a similar but much less pronounced trend in the $T_u(2)$ mode. The $T_u(3)$ mode at 1183 cm^{-1} does not appear to be very sensitive to charge, and there are too few data to be certain of a trend in the $T_u(1)$ mode.

In discrete C_{60}^{n-} fulleride salts, data have been reported only for $n = 1$ and the frequencies are the essentially the same as those in intercalated AC_{60} compounds. The $T_u(4)$ mode shows a 34 cm^{-1} decrease relative to C_{60}, while the other frequencies are essentially unchanged. These general characteristics must now be considered diagnostic of the C_{60}^- ion regardless of environment. A 5-fold broadening of the

1394 cm^{-1} band relative to C_{60} has been reported in phosphonium salts of C_{60}^-.[261] Broadening, as opposed to distinctive frequency shifts, suggests that the effects of site symmetry differences and Jahn–Teller distortions are small. A recent temperature-dependent analysis of the lower frequency modes in $[PPh_4]_2I[C_{60}]$ reveals 2–7 cm^{-1} splittings indicative of symmetry lowering to D_{5d} or D_{3d} symmetry (but *not* D_{2h}).[262] This paper contains a particularly lucid analysis of the problem of distinguishing dynamic from static Jahn–Teller distortions in the C_{60}^- ion.

The symmetry-lowering effect of C–C bond formation in dimer and polymer phases of RbC_{60} has been studied for the two highest frequency modes.[263,264] The splittings and shifts should be useful for detecting possible dimer formation in discrete fullerides.[265]

The first fullerenium ion salt to be characterized by infrared spectroscopy was $[C_{76}^+][CB_{11}H_6Br_6^-]$.[30] The D_2 symmetry neutral fullerene has about 20 observable bands,[266] but because of masking absorptions of the anion, the shifts of only seven of these bands can be followed upon oxidation. All remain essentially unchanged except the highest frequency band at 1440 cm^{-1} which increases by 16 cm^{-1} to 1456 cm^{-1}.

Infrared measurements on matrix-isolated C_{60}^+ are complicated by remnant C_{60} and by the coproduction of C_{60}^-, but candidate frequencies have been proposed at 1332 and 1406 cm^{-1}.[196]

In conjunction with theory, there is a need for more extensive infrared studies on discrete fullerides and fullerenium cations.

B. Raman Spectroscopy

Neutral C_{60} has 10 allowed Raman modes.[255,257,258,267,268] These have been intensively studied in A_xC_{60} intercalated compounds because of interest in their involvement in an electron–phonon coupling mechanism for superconductivity in A_3C_{60}.[269,270] It was quickly discovered that the A_g "pentagonal pinch" mode at 1467 cm^{-1} was a good indicator of charge state in intercalated compounds. It decreases monotonically by ca. 6 cm^{-1} for each added negative charge.[104,269-271] The same appears to

Table 9. Infrared Absorbances of C_{60}, A_xC_{60}, and C_{60}^{n-} Compounds (cm^{-1})

compound	$T_u(1)$	$T_u(2)$	$T_u(3)$	$T_u(4)$	ref
C_{60}	527	576	1183	1429	254–258
RbC_{60}	525	574	1182	1392	259
K_3C_{60}		572		1363	259
K_4C_{60}		568		1352	259
K_6C_{60}	467	564	1183	1341	259
Cs_6C_{60}	(decreases)	566	1183	1340	260
RbC_{60} monomer	526	573	1181	1391	264
RbC_{60} dimer	526	575	1178	1410	264
RbC_{60} polymer	527	571	1198	1388	264
$[Ph_4P]_2X[C_{60}]$ X = Cl, Br, I	527	576	1179	1394 (broad)	261
$[Ph_4P]_2I[C_{60}]$			~1178	1394	263
$[Ph_4P]_2I[C_{60}]$	525 (doublet)	576 (doublet)			262
$[Ph_4P]_2Cl[C_{60}]$	(526)	576	(1177)	1392	189
$[Na(crown)(THF)_2^+][C_{60}^-]\cdot THF$	526	576		1395	116
$[Sn(TpTP)(N\text{-}MeIm)_2^{2+}][(C_{60}^-)_2]$	526	576	1182	1395	116

be true for the discrete C_{60}^- fulleride ion. Solid-state measurements on an isolated phosphonium salt[104] as well as solution measurements on an electrochemically generated sample[272] both find a diagnostic 6 cm^{-1} decrease in the 1467 cm^{-1} band. To our knowledge there are no reports of Raman spectra for more highly charged discrete C_{60}^{n-} salts, for discrete fullerides of the higher fullerenes, or for fullerenium cations. As with infrared spectroscopy, there is considerable opportunity for further experiments in Raman spectroscopy.

VI. X-ray Crystallography

A. Introduction

Single-crystal X-ray structure determination is possibly the most definitive experimental technique for investigating the important question of Jahn–Teller distortions in fullerides. All C_{60}^{n-} fullerides for $n = 1-5$ (including C_{60}^{3-} which unexpectedly is low spin rather than high spin) have electronically degenerate $(t_{1u})^n$ configurations under I_h symmetry and are therefore required by the Jahn–Teller theorem to undergo centrosymmetric distortion to lower the symmetry and remove the degeneracy. The nature, extent, and time scale of the distortions are of primary interest.

X-ray crystallography can also be helpful in establishing the composition of fulleride salts. A number of fulleride salts, particularly those of THF-solvated alkali metal cations, have uncertain degrees of solvation, and elemental analysis has not been a reliable guide to proper formulation. In addition, X-ray crystallography can reveal the nature of weak interion or ion–molecule interactions, giving indications of the way fullerides may be ion-paired and solvated in solution. Ball-to-ball contacts in the solid state are of particular interest because phenomena such as superconductivity and ferromagnetism in extended systems are the cooperative result of interacting perturbations in the repeating molecular entity. Establishing the presence of ball-to-ball contact is important for the interpretation of magnetic and conductivity data in salts that do not contain completely isolated, discrete ions.

Progress in using X-ray crystallography to address these questions has been slow, however. Single crystals have been hard to obtain in many systems and when formed are frequently small, twinned, and/or disordered. The biggest problem with C_{60} fulleride structures is orientational disorder of the sphere-like anions. The distortions of fullerides from I_h symmetry are small and can be lost in X-ray crystallography in a smear of electron density.

The first crystallographically ordered structure of a discrete fulleride contained the C_{60}^{2-} ion with PPN$^+$ cations (PPN$^+$ = bis(triphenylphosphine)iminium).[136] With large spectator cations, it is a structure that must reflect a close approach to the intrinsic relaxed dimensions of a discrete fulleride ion. It remains one of the most precisely determined fulleride structures, providing a convenient early benchmark against which subsequent structures can be compared. We therefore treat it and other C_{60}^{2-} structures first.

B. [PPN]$_2$[C$_{60}$] and Related C_{60}^{2-} Structures

[PPN$^+$]$_2$[C$_{60}^{2-}$] crystallizes in an unsolvated lattice with well-separated C_{60}^{2-} ions at C_i symmetry sites.[136] The only crystallographically required symmetry element of this fulleride ion is i, leading to a convenient description of the distortion from I_h in terms of radial distances of the 30 distinct carbon atoms from the inversion center. This is shown as a bar graph along with a color visualization of the distortion in Figure 9. Overall, there is an axial
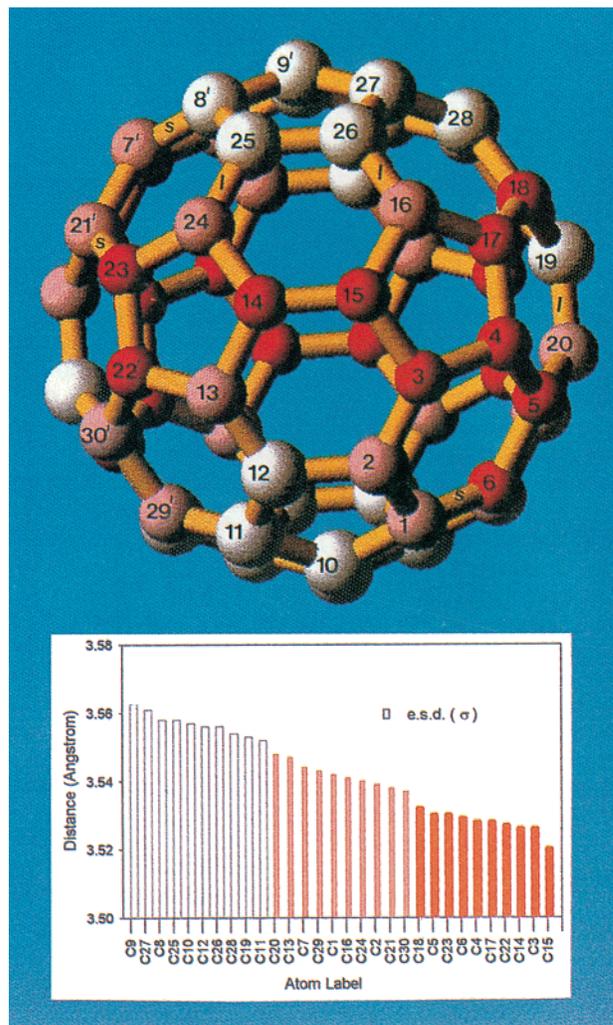

Figure 9. Size and color visualization of the distortion in the C_{60}^{2-} ion in the X-ray structure of [PPN]$_2$[C$_{60}$]. Carbons atoms are color coded according to their radii from the center of symmetry as indicated in the bar graph. The three longest 6:6 ring juncture bonds are labeled *l*, the three shortest *s*. (Reprinted with permission from ref 136. Copyright 1994 American Chemical Society.)

elongation and a rhombic squash that gives the ion an irregular prolate ellipsoidal shape. The structure is ordered apparently because of the "caliper effect" of symmetry related pairs of C–H bonds from phenyl groups on the cations interacting with the centers of fulleride hexagonal rings (see Figure 10). These interactions can be understood in terms of the electrostatic attraction of aryl $C^{\delta-}$–$H^{\delta+}$ bonds to electron-rich hexagons. They were subsequently seen in a highly ordered structure of neutral C_{60}, cocrystallized with five SbPh$_3$ molecules.[273] That these C–H
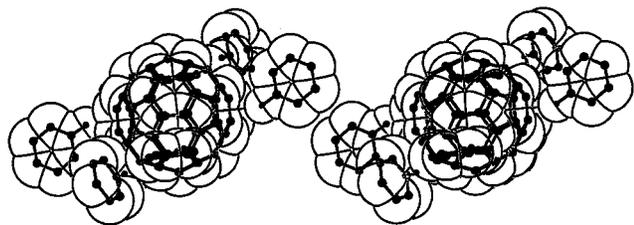
Figure 10. Stereoview showing how C−H bonds from phenyl groups of the PPN$^+$ cations act like calipers toward the six-membered rings of C$_{60}^{2-}$ in the crystal structure of [PPN]$_2$[C$_{60}$]. For clarity, only C$_6$H units of the phenyl groups are shown. (Reprinted with from ref 136. Copyright 1994 American Chemical Society.)

interactions cluster around the equator of the ellipsoidal C$_{60}^{2-}$ ion in [PPN]$_2$[C$_{60}$] is consistent with theory that localizes t_{1u} electron density in the equatorial belt relative to the polar regions.[60,274] There is no obvious relationship between the specific distortion of the C$_{60}^{2-}$ ion and the C−H interactions, suggesting that the influences of the surrounding environment are small.

Relative to neutral C$_{60}$,[273,275,276] the mean 6:6 ring juncture bond length has increased from 1.383(4)[273] to 1.399(2) Å. The mean 5:6 ring juncture bond has decreased from 1.453(5)[273] to 1.446(2) Å. These changes are consistent with the nature of the t_{1u} LUMO of C$_{60}$ which, in general, is antibonding with respect to 6:6 bonds and bonding with respect to 5:6 bonds (see Figure 11).[270,274] The calculated values in
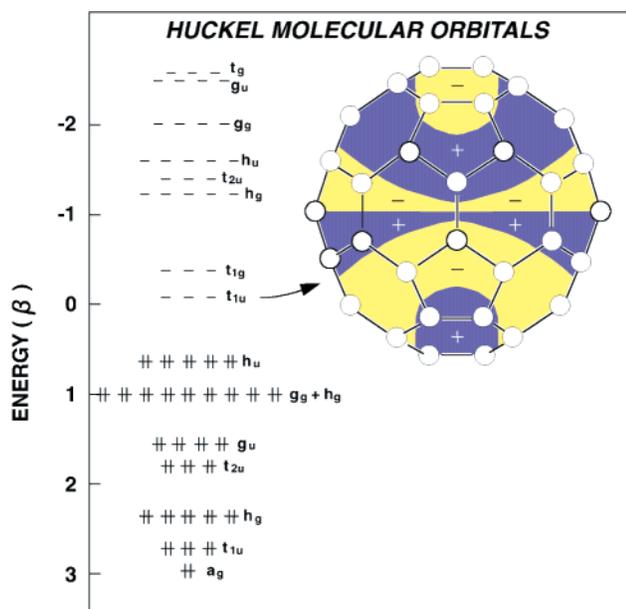

Figure 11. Color representation of one component of the t_{1u} LUMO of C$_{60}$. Blue and yellow are used to represent the phases of the orbital. Nodes appear mostly on the 6:6 ring juncture bonds indicating predominant antibonding character. By contrast, this orbital is predominantly bonding at the 5:6 ring juncture bonds. Figure supplied by Robert C. Haddon, adapted from black and white original. (Reprinted with permission from ref 270. Copyright 1992 American Chemical Society.)

vacuo using high-level density functional theory[60] are 1.404 and 1.443 Å, respectively. This agreement is remarkable, suggesting that the theory is excellent in this regard and that the large PPN$^+$ cations have

an insignificant effect on the average electron density in the condensed-phase structure. The calculated symmetry is D_{2h} for a singlet ground state and D_{3d} for a triplet.[60] The experimental symmetry is C_i although it closely approximates C_{2h}.

Does this C$_{60}^{2-}$ structure reflect the intrinsic Jahn−Teller distortion of the ion? At the beginning of the experimental exploration of the Jahn−Teller effect on any molecule, there is always a valid "chicken and egg" argument. Is the molecule distorted because it crystallizes in a low-symmetry environment or does it crystallize in a low-symmetry environment because it is intrinsically distorted? Or is it some of both? Only after a fairly large number of structures have been determined and a prevalent distortion identified can an intrinsic origin be ascribed.

For the C$_{60}^{2-}$ ion, Himmel and Jansen have published five ordered structures of sufficient resolution that comparisons can be made to [PPN]$_2$[C$_{60}$]: the triclinic [BzNMe$_2$]$_2$[C$_{60}$]·3NH$_3$,[277] three triclinic [M(NH$_3$)$_6$][C$_{60}$]·6NH$_3$ complexes (M = Ni, Mn, Cd),[129,138] and the rhombohedral [Ba(NH$_3$)$_7$][C$_{60}$]·NH$_3$.[278] Interactions of ammonia N−H dipoles with the fulleride anions appear to be responsible for the orientational order in these structures, a feature which bears a close conceptual relationship to the C−H effect observed in [PPN]$_2$[C$_{60}$]. The influence of N−H dipoles on the structure of the C$_{60}^{2-}$ ion may be greater than that of C−H dipoles because of their larger dipole and the greater proximity of the positive and negative charge centers. In the first structure, with benzyldimethylammonium cations, the C$_{60}^{2-}$ ion sits on C_i symmetry sites, like [PPN]$_2$[C$_{60}$]. A more precise description of the distortion, however, is not given. In the three triclinic hexammine structures, there is a similar type of distortion to that in [PPN]$_2$-[C$_{60}$], although the extent decreases in the order PPN$^+$ > Ni^{2+} > Mn^{2+} > Cd^{2+}. The Cd compound has much the same distortion as that seen in cubic C$_{60}$ itself, leading the authors to ascribe symmetry lowering in all C$_{60}^{2-}$ structures to interactions from the cations rather than to an intrinsic Jahn−Teller effect. The basis for this is not clear since direct relationships between the N−H (or C−H) interactions and the distortions are not established. In the fifth structure, the authors find that the C$_{60}^{2-}$ ion sits on a C_{3v} symmetry site and they conclude that "within the accuracy of our calculations and experimental data ... ideal I_h symmetry is retained". Caution in accepting this conclusion is warranted because, apart from the fact that the crystal suffers from twinning, the reported range of C−C distances at the 6:6 ring junctures [1.396(6)−1.415(5) Å] is just as large as in [PPN]$_2$[C$_{60}$] [1.395(5)−1.412(5) Å]. Overall, the similarities within the five structures are greater than their differences, which favors the predominance of intrinsic distortion over an environmentally imposed one. There is one other X-ray structure of a discrete of C$_{60}^{2-}$ salt, [K([2.2.2]crypt)]$_2$[C$_{60}$]·4toluene.[120] The C$_{60}^{2-}$ ions are quite well ordered, apparently because of C−H interactions with the toluene solvate molecules and the cryptand cations, but the C−C distances are insufficiently precise to show more than,

on average, a lengthening at the 6:6 ring junctures and a shortening at the 6:5 ring junctures. At this stage, it is apparent that the C_{60}^{2-} ion undergoes an intrinsic ellipsoidal Jahn−Teller distortion from I_h symmetry, at least to D_{5d} symmetry. In a nonperturbing environment, this distortion can be dynamic (pseudorotation), giving the appearance of I_h symmetry. However, it is easily trapped in condensed phases, with the precise final symmetry probably being dictated by the environment. Group theory prescribes which distortions are allowed,[226] and electronic structure calculations indicate which distortions are the lowest in energy.[227] For the C_{60}^{2-} ion, there is probably near equivalence of energy in a variety of symmetries from D_{5d} to C_i as well as low barriers for transformations between them. A similar situation was predicted for the C_{60}^{-} ion in the early calculations of Koga and Morokuma.[274]

Powder diffraction data on $[Na(ND_3)_4]_2[C_{60}]$ show a layered structure with interlayer fulleride contacts.[279] Surprisingly, the bond lengths are unchanged from C_{60}. This is discussed in section VI.E below. Powder diffraction data have also been reported on the structure of $[NMe_4]_2[C_{60}]$, and the cell parameters suggest that the fulleride ions are in van der Waals contact.[137]

C. C_{60}^{-} Structures

There are more reports of single-crystal structures for the C_{60}^{-} ion than for the C_{60}^{2-} ion, but because of disorder, much less progress has been made in determining the effects of charge and the nature of the Jahn−Teller distortion. In fact, there is only one ordered structure, $[Ni(Cp^*)_2][C_{60}]\cdot PhCN$.[144] In this structure, however, the cation/anion interactions may be so strong that the C_{60}^{-} ion is not in its intrinsic geometry.

Electrocrystallization with a tetraphenylphosphonium cation was the first technique to produce single crystals, giving rise to a double salt formulated as a $[Ph_4P]_2[C_{60}][I_{<1}]$.[185] The iodide deficiency was later reinterpreted in terms of unnoticed chloride substitution, presumably arising from electrodecomposition of the dichloromethane solvent.[186] There is no good evidence for nonstoichiometric salts of discrete fullerides. Indeed, tetraphenylphosphonium and tetraphenylarsonium cations give rise to some of the better characterized stoichiometric C_{60}^{-} salts.[184,186−189] All are double salts with 1 equiv of halide in a tetragonally distorted CsCl type lattice of space group $I_{4/m}$ (see Figure 12). The C_{60}^{-} ions occupy sites of 4-fold symmetry and thus have to be treated as 2-fold disordered psuedo-I_h entities. Bond length and distortion information is therefore unavailable. Nevertheless, these structures establish the bona fide salt character of these materials and prove that the C_{60}^{-} ions are well isolated from each other (>2 Å van der Waals separation). The phenyl groups of the cations interact with C_{60}^{-} mostly via weak $\pi−\pi$ contacts in the range 3.5−4.0 Å, but there are also edge-to-face interactions. Scudder and Dance[280] have analyzed the cation interactions in terms of 4-fold phenyl 'embraces' propagating into a high-symmetry two-
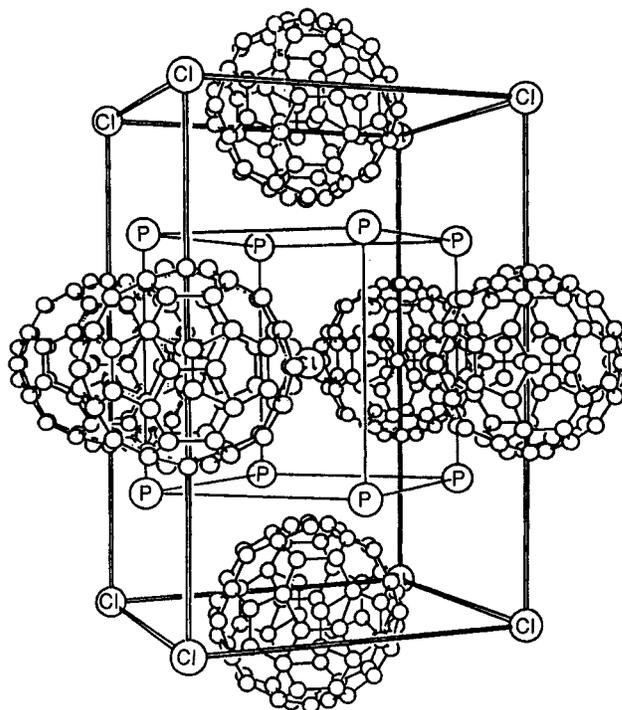

Figure 12. Unit cell of $[PPh_4]_2Cl[C_{60}]$ with the pseudocubic sublattice of phosphorus atoms indicated. Phenyl rings of the cations are omitted for clarity. (Reprinted with permission from ref 188. Copyright 1994 Royal Society of Chemistry.)

dimensional network. There is one report of single crystals of a tetraphenylphosphonium C_{70}^{-} double salt but it suffers the same disorder problems as its C_{60} counterparts.[190]

A preliminary report of single crystals of $[PPN][C_{60}]\cdot C_6H_5Cl$ has appeared,[281] and $[Co(Cp)_2][C_{60}]\cdot CS_2$ is known to form a disordered structure.[40] Single crystals of $[Na$ or $K_x(THF)_y][C_{60}]$ have been reported,[173,282] but the diffraction data have yet to yield accurate compositional or structural information. They are particularly intriguing because of the possibility of a new metallic phase[282] or, as postulated in section IX.B.vii, the possibility of a $(C_{60})_2^{-}$ dimer structure. Powder diffraction data on $[NMe_4][C_{60}]\cdot 1.5THF$ suggest van der Waals contact of the C_{60}^{-} ions in three dimensions.[137]

In 1995, Broderick and co-workers reported the first highly ordered structure of monoanionic $[C_{60}]$-fullerene in $[Ni(Cp^*)_2][C_{60}]\cdot PhCN$.[144] The order is believed to arise from C−H interactions of the permethylated cyclopentadienyl ligand of the cation with the hexagonal rings of C_{60}^{-}. A staggered $\pi−\pi$ interaction of the five-membered rings of the cation with pentagonal faces of the fulleride must also contribute to the rotational ordering (see Figure 13).

The anion is axially sandwiched between cations and sits on a C_{2h} symmetry site. This gives C_{60}^{-} an inversion center and a mirror plane passing through the midpoint of a 6:6 C−C bond. Unexpectedly, the anion is axially compressed into an oblate ellipsoid. This is opposite to the prolate ellipsoid (i.e., axial elongation) found in C_{60}^{2-} and is contrary to theoretical predictions for C_{60}^{-}.[60,274] Given the very close $\pi−\pi$ approach of the cations to the poles of the anion (3.17
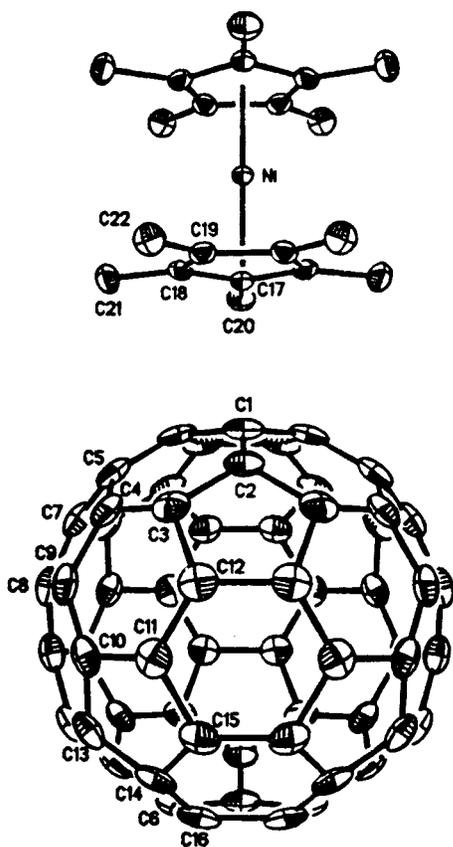
Figure 13. ORTEP drawing showing the close approach of a $Ni(Cp^*)_2^+$ cation to an ellipsoidally squashed C_{60}^- anion in $[Ni(Cp^*)_2^+][C_{60}]\cdot CS_2$. There is an identical interaction at the opposite pole. (Reprinted with permission from ref 144. Copyright 1995 American Chemical Society.)

Å), it is entirely possible that the sandwich effect of the cations is strongly influencing the nature of the distortion. However, even though the *type* of distortion is the opposite of that expected, the *degree* of distortion, as measured by the lengthening of the 6:6 C−C bonds and the weakening of the 5:6 C−C bonds, is entirely in accord with expectations of $(t_{1u})^1$ occupation and a Jahn−Teller distortion. Compared to neutral C_{60} and to C_{60}^{2-} in $[PPN]_2[C_{60}]$, the mean bond distances of C_{60}^- fall in between, although they are closer to C_{60}^{2-} (see Table 10). The average 6:6 bond distance is 1.389(3) Å compared to 1.400 Å from density functional calculations.[60] The average 5:6

bond distance is 1.449(3) Å compared to the calculated value of 1.444 Å. The degree of distortion, as measured by the range of symmetry related diameters, is similar to C_{60}^{2-} and in fact slightly larger [0.098(6) vs 0.086(5) Å]. While further structures are necessary for a confident assessment, these comparisons suggest that the Jahn−Teller effect in C_{60}^- ions is real and will, like C_{60}^{2-}, typically amount to ca. 1% distortion from I_h symmetry along centrosymmetric vibrational modes. Of greater certainty is that C−C bond distances respond to $(t_{1u})^n$ occupation in a fairly predictable way, requiring a low-symmetry, ellipsoidal-type distortion of discrete C_{60}^{n-} ions. The environment, particularly the cations, can probably localize this electron density in different regions of the ball, thereby altering the precise shape and point symmetry of the distortion. In the absence of perturbing environment, most electronic structure calculations favor a D_{5d} distortion but D_{3d} is close in energy.

The crystal structure of a nonferromagnetic phase of $[TDAE][C_{60}]$ has recently been determined at very low temperature (7 K) to minimize disorder.[283] The average bond lengths are close to those found for C_{60} in $C_{60}\cdot 2$ferrocene and for C_{60}^- in $[NiCp^*_2][C_{60}]\cdot CS_2$ (see Table 10). Inter-fulleride C⋯C distances as short at 3.08 Å are noted in this structure. They presumably contribute to the antiferromagnetic coupling observed in this phase.

D. C_{60}^{3-} Structures

There is one reported single-crystal structure of a discrete C_{60}^{3-} salt, $[K_3(THF)_{14}][C_{60}]$.[115] The closest anion/cation approaches are fulleride 6:6 C−C bonds to THF-solvated potassium ions (K⋯C = 3.29−3.44 Å) in a linear chain (see Figure 14). Although the C_{60}^{3-} ions are apparently ordered, there is sufficient disorder in the THF molecules that distortion and bond length information on the fulleride ion are unavailable.

E. Comparison of Discrete and Extended Structures

One of the most interesting questions in fulleride structural chemistry concerns the extent to which the low-symmetry structure of a discrete ion is preserved

Table 10. Comparison of C_{60} and C_{60}^{n-} Structural Data

compound	C_{60} site symmetry	average C−C (Å) (6:6 ring junctions)	average C−C (Å) (6:5 ring junctions)	average C−C diameter (Å)	ref
$C_{60}\cdot 6SbPh_3$	S_6	1.383(4)	1.453(5)	7.074(3)	273
$C_{60}\cdot 2$ferrocene	C_i	1.387(6)	1.450(6)	7.074(7)	276
C_{60}	S_6	1.391(8)	1.455(8)		275
C_{60} (gas phase)		1.401(10)	1.458(6)	7.133(10)	a
$[TDAE^+][C_{60}^-]$		1.389(5)	1.453(5)		283
$[NiCp^*_2^+][C_{60}^-]\cdot CS_2$	C_{2h}	1.389(3)	1.449(3)	7.072(5)	144
$[PPN^+]_2[C_{60}^{2-}]$	C_i	1.399(2)	1.446(2)	7.084(2)	136
$[Na(ND_3)_4^+]_2[C_{60}^{2-}]^b$	D_{3d}	1.388(6)	1.456(8)	7.092(10)	279
$K_3C_{60}^b$	O_h	1.400(4)	1.452(13)	7.104(9)	291
$Na_2CsC_{60}^b$	S_6	1.43(1)	1.43(1)		289
$Ba_2CsC_{60}^b$		1.422(11)	1.440(8)		290
$K_6C_{60}^b$	O_h	1.455(3)	1.432(10)	7.120(8)	291

a Hedberg, K.; Hedberg, L.; Bethune, D. S.; Brown, C. A.; Dorn, H. C.; Johnson, R. D.; de Vries, M. *Science* **1991**, *254*, 410−412. b Powder neutron diffraction data.
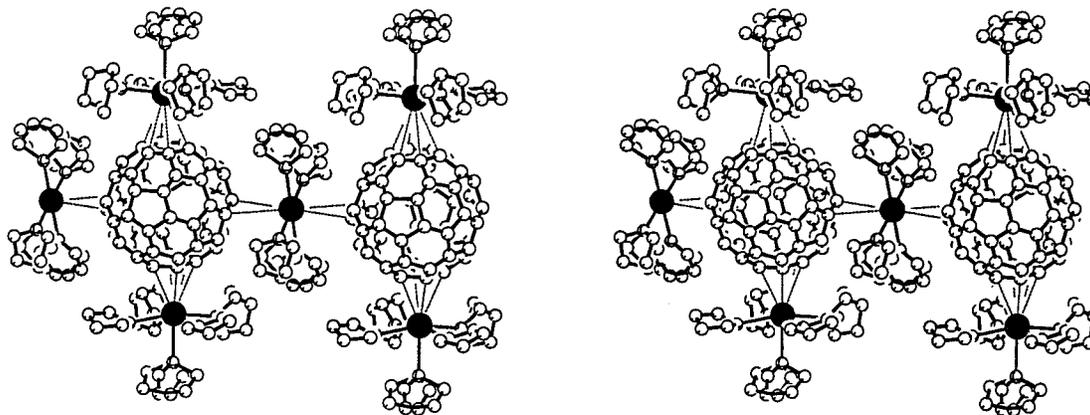
Figure 14. Stereoview of a section of the chain structure of $[K_3(THF)_{14}][C_{60}]$. (Reprinted with permission from ref 115. Copyright 1996 Elsevier Science.)

in the higher symmetry environment of metal-intercalated C_{60}. Are there distortions of comparable magnitude? If so, are they static or dynamic? How are they masked by the inevitable disorder of higher symmetry sites? A close relationship between orientational disorder and superconductivity is proposed in A_3C_{60}.[17,284−288] Are the mean C−C bond lengths comparable in discrete vs extended fullerides or do strong A^+ cation interactions override intrinsic geometries? What are the structural consequences of ball-to-ball contact of the anions?

The detailed structure of fulleride anions in alkali metal intercalated phases of C_{60} has been unavailable until recently because single-crystal data are unknown and interpreting X-ray powder patterns requires constraining the bond lengths and angles close to assumed values. A frequent problem lies in merohedral disorder[157] that allows C_{60} to occupy sites of higher symmetry than its molecular structure can properly sustain. There has been recent progress in dealing with this problem by the use of neutron diffraction. Powder data are taken at liquid helium temperatures to minimize thermal effects, but available high-resolution structures are too few at this point in time to more than begin to answer all the questions raised above. Some comparisons can be made, however. Selected data are collected in Table 10. The most interesting outcome from the point of view of discrete fullerides is the near equalization of 6:6 and 5:6 bond lengths believed to occur in the C_{60}^{3-} ion of Na_2CsC_{60}[289] and in the C_{60}^{5-} ion of Ba_2CsC_{60}[290] and the *reversal* of relative lengths (6:6 > 5:6) reported in K_6C_{60}.[291] For the discrete C_{60}^{6-} ion, the calculated bond lengths retain the usual order, 6:6 (1.429 Å) < 5:6 (1.445 Å), although they have moved considerably toward equalization.[60] The effects of the intercalated cations seem to be quite large. The opposite effect is apparent in $[Na(ND_3)_4]_2[C_{60}]$ where, unexpectedly, the C−C distances are essentially unchanged from those of C_{60}.[279] On the other hand, the expected gradual increase in size of C_{60}^{n-} with increasing charge[227,292] is borne out by the average C···C diameter data listed in Table 10. There is a considerable need for more data and calculation in this area.

VII. Magnetic Susceptibility and Spin States

Magnetic susceptibility measurements have played an important role in defining the spin states and the spin-coupling interactions of fullerides, but a number of limitations have arisen which prevent a fully quantitative utilization of the technique. One problem intrinsic to discrete fulleride salts is their low spin density. Molecular weights are necessarily high on a per-spin basis because of 60 carbon atoms and large cations. Also, C_{60}^{n-} with $n = 2$, 3, and 4 show an unanticipated tendency to be low spin. In addition, the bulk purity of materials has frequently proved to be difficult to establish. Problems of chemical and phase purity and the presence of trace ferromagnetic impurities have been encountered. This has restricted investigations to questions of paramagnetism arising from unpaired electrons and has so far prevented an exploration of the changes in diamagnetism expected when the charge on a fullerene is altered.[293] This question has, however, been approached by NMR spectroscopy (see section VIII).

The susceptibility characteristics of magnetically isolated fulleride spins are important as the point of departure for understanding inter-fulleride spin-coupling phenomena, the most interesting cases occurring in $[TDAE][C_{60}]$ and $[Co(Cp)_2][3-NH_2−C_6H_4−CH−C_{60}]$, which show ferromagnetic behavior below 16 and 19 K, respectively.[16,141,142] There is disagreement over whether the ferromagnetism is solely a property of the fulleride interactions in the TDAE complex,[294,295] but the diamagnetism of the cobaltocenium cations in $[Co(Cp)_2][3-NH_2−C_6H_4−CH−C_{60}]$ indicates it is a possibility. Whatever the mechanism, an understanding of spin coupling in fullerides can only be gained when a detailed knowledge of structure is in hand. Unfortunately, it is rare that single-crystal X-ray structures are known for those fullerides with the most interesting spin-coupling properties. This review concentrates on the more magnetically isolated systems, particularly those with some degree of structural characterization.

Variable-temperature magnetic susceptibility measurements have been reported on a variety of C_{60}^- salts. For a magnetically dilute $S = 1/2$ system, Curie−Weiss law behavior and a room-temperature magnetic moment of 1.73 μ_B is expected. This has not

been observed as commonly as might be anticipated.[143] It is approached in $[PPN][C_{60}] \cdot PhCN$[21] and is implied by the data on $[Cr(TPP)(THF)_2][C_{60}] \cdot THF$ where the paramagnetic cation is noninteracting.[139] Early data on phosphonium salts, known to be magnetically dilute from X-ray data, unexpectedly showed excess spin[184] or non-Curie–Weiss behavior.[185,296] Later measurements on both C_{60}^- and C_{70}^- salts are, however, in accord with an $S = 1/2$ system and Curie–Weiss behavior.[186,190] Ferromagnetic impurities are believed to have been the source of some of the misleading data in the earlier measurements.[190] A tetramethylammonium salt of C_{60}^- has small enough cations that complex magnetic behavior occurs.[137] Ball-to-ball spin coupling within layers is observed, leading to metallic-like behavior, and there is a dramatic drop in susceptibility near 200 K with the onset of a different magnetic behavior. Somewhat similar results are observed in $Na(THF)_5C_{60}$.[146] Preliminary reports of susceptibility data on other materials have appeared.[143,148,297,298]

The C_{60}^{2-} ion in $[PPN]_2[C_{60}]$, known from X-ray crystallography to be magnetically isolated,[136] displays considerable paramagnetism at room temperature (ca. 2.0 μ_B).[21,118] This value is considerably short of the 2.8 μ_B value expected for a high-spin $S = 1$ system, and an extrapolation of the high-temperature data also falls short of the value expected for a spin triplet. The low-temperature moment decreases with decreasing temperature but does not reach that of a diamagnetic species, probably because of ferromagnetic impurities. These data provided the first experimental evidence for a singlet ground state with a small singlet–triplet gap in the C_{60}^{2-} ion. This spin state is counterintuitive for a $(t_{1u})^2$ ground-state configuration even if an expected Jahn–Teller splitting is taken into account. The ion disobeys Hund's rule, suggesting that the two added electrons are sufficiently spatially separated that the usual orthogonal exchange interactions between them are minimal. Measurements on a $K(cryptand)^+$ salt of the C_{60}^{2-} ion whose crystal structure shows separated anions (13.77 Å center-to-center)[120] shows qualitatively similar data but with fewer magnetic impurities. In neither case did the temperature-dependent data lend themselves to a good determination of the energy of the singlet–triplet gap. Temperature-dependent EPR data[299] suggest a value of 600 cm^{-1}, which is roughly consistent with the room-temperature magnetic moment of the $K(cryptand)^+$ salt but is smaller than the gap indicated by ^{13}C NMR spectroscopy (see section VIII.C). All three techniques are consistent, however, with the *qualitative* picture of a singlet ground state and a low-lying triplet state, leading to significant paramagnetism at room temperature. By and large, this picture is supported by theory. Calculations which include configuration interaction typically find the singlet state lower or equal in energy to the triplet state.[60,300–304]

The magnetic susceptibility data for $[PPN]_3[C_{60}]$ (see Figure 15),[21] a necessarily magnetically dilute system because of the three large cations, and for $[Fe(C_5H_5)(C_6Me_6)]_3[C_{60}]$[143] are consistent with an isolated $S = 1/2$ system, not the $S = 3/2$ quartet expected from

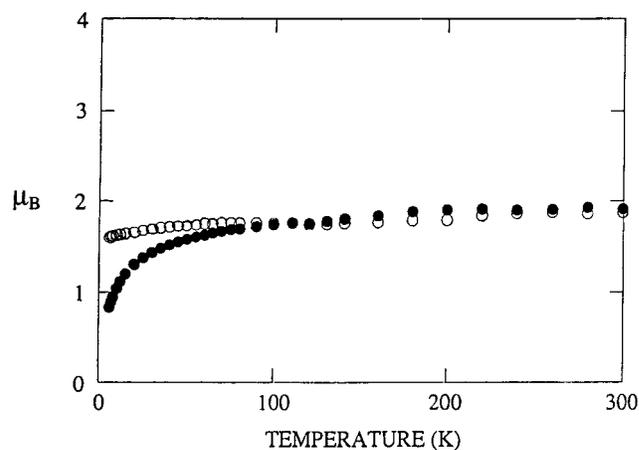**Figure 15.** Comparison of plots of magnetic moment versus temperature for a [60]fulleride(−1) salt, $[PPN][C_{60}] \cdot PhCN \cdot THF$ (●), and a [60]fulleride(−3) salt, $[PPN]_3[C_{60}] \cdot 2CH_3CN$ (○). (Reprinted with permission from ref 21. Copyright 1993 American Chemical Society.)

a Hund's rule $(t_{1u})^3$ configuration. This is perhaps the most unexpected result that has arisen from the study of the spin states of discrete fulleride ions. It was not anticipated by early theory[305] and, by ca. 1 kcal, is not the ground state in more recent density functional calculations.[60] The magnetic susceptibility data are, however, fully consistent with EPR studies (see section IX.D). Evidently the three electrons in the orthogonal t_{1u} orbitals are, on average, sufficiently remote from each other that typical Hund's rule exchange interactions are overridden by spin-pairing (and presumably symmetry lowering) effects. Theory can rationalize this phenomenon in terms of vibronic coupling and configuration interaction with the higher energy t_{1g} orbitals,[300–303,305–312] sometimes referred to as a pseudo-Jahn–Teller effect.[313]

VIII. NMR Spectroscopy

A. Introduction

In the early stage of the macroscopic fullerene era, carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR) played a crucial role in establishing the structure and integrity of C_{60}. A single, sharp ^{13}C NMR resonance was observed in solution near 143 ppm.[314–316] The magnetic equivalence of all 60 carbon atoms, in conjunction with the observation of only four infrared absorptions, allowed the confident conclusion that C_{60} had the spheroidal geometry and icosahedral symmetry originally proposed by Kroto, Heath, O'Brien, Curl, and Smalley.[317] The observation of five lines in the ^{13}C NMR spectrum of C_{70} established its D_{5h} structure.[314,318]

Solid-state ^{13}C NMR spectroscopy quickly became a significant tool for investigating the wide variety of charge states and electronic properties of metal-intercalated C_{60} fullerides.[318–321] Despite this demonstrated utility, it was a number of years before ^{13}C NMR spectroscopy was applied to the investigation of discrete fullerides. A sharp signal at 156.7 ppm was detected in a lithium-sonicated tetrahydrofuran solution of C_{60}, and this was tentatively ascribed to diamagnetic Li_6C_{60}.[112] A ^{13}C NMR signal from the

C_{60}^- radical anion was reported to be undetectable in solution,[322] perhaps anticipating the line-broadening effects of paramagnetism but more likely reflecting the experimental difficulties of maintaining sufficient concentration of an air-sensitive material during the long periods required for data acquisition of broad signals.

Solution data are more likely to reflect the intrinsic properties of noninteracting discrete ions. We therefore treat them first.

B. ^{13}C NMR Data in Solution

With the development of synthetic methods for producing analytically pure salts of discrete C_{60}^{n-} fullerides, it became possible to detect ^{13}C NMR signals of these paramagnetic entities. High-sensitivity instrumentation, long acquisition times, scrupulously oxygen-free conditions and practical concentrations are required to detect resonances with acceptable signal-to-noise ratios. For the more highly reduced fullerides, scrupulously water-free conditions are also required. Close attention to sample integrity is also necessary, not only because oxidative decay of samples can be difficult to avoid, but because signal averaging between fullerenes of different charge states can be anticipated via fast electron exchange. Pre- and post-measurement integrity checks using NIR spectroscopy on the actual NMR sample are highly desirable.

Solution data for C_{60}^{n-} fullerides were first obtained for $n = 1-4$ by Reed and co-workers.[118,119] Sufficient solubility of alkali metal crown ether or cryptand salts was found in dimethyl sulfoxide (DMSO), a good solvent for fullerides although a poor solvent for neutral fullerenes. Nitrile solvents, particularly propionitrile for subambient temperature work, and tetrahydrofuran (THF) have also been used successfully.

The reported ^{13}C chemical shifts of fulleride salts at ambient temperatures in solution are listed in Table 11. All signals are downfield of neutral C_{60}. The signals for the $n = 1-4$ C_{60}^{n-} fullerides are all broad, particularly that from C_{60}^{3-}, and are all about 40-50 ppm downfield of C_{60}. A first-order rationale for these data is that they arise from C_{60}^{n-} species all having a similar shift arising from similar average distributions of unpaired electron density. This contribution from the paramagnetism of the electronic states of the fullerides should not be confused with the shift contributions from the so-called "paramagnetic term"—a descriptor from modern NMR terminology used to separate ground state ("diamagnetic") from excited state ("paramagnetic") contributions to the chemical shifts of diamagnetic molecules. Likewise, the contribution of molecular paramagnetism to chemical shifts should not to be confused with now ancient usage where *upfield* shifts were referred to as "paramagnetic" and *downfield* shifts as "diamagnetic". This terminology disappeared from the chemical literature some time ago but unfortunately persists in modern physics journals. A more detailed interpretation of the chemical shifts is given in a following section.

The data in Table 11 do not indicate any particularly significant influence of the cation or the solvent. This is not too surprising given the delocalized nature of the electron density on the anions and the large size of the cations that are typically employed (metallocenium ions, complexed or THF-solvated alkali metals, etc.).

It has been reported that mixtures of differently charged fullerides give averaged chemical shifts in room-temperature solution spectra. For example, mixtures of C_{60}^{2-} and C_{60}^{3-} in DMSO-d_6 show shifts intermediate between the values for the pure ions, 184 and 197 ppm, respectively.[118] Similarly, mixtures of C_{60} and C_{60}^- in pyridine-d_5 show shifts between 143 and 184 ppm.[323] This shows that electron exchange between fullerides is fast on the NMR time scale. ^{13}C NMR spectroscopy is therefore not expected to be able to detect mixtures of C_{60}^{1-} and C_{60}^{2-} at room temperature. Their chemical shifts are accidentally near-coincident, and thus, NMR cannot be used as a criterion of purity for these two ions.

There are no widely disseminated reports on the temperature dependence of the chemical shifts of C_{60}^{n-} fullerides in solution, but preliminary data are available in a Ph.D. thesis.[324] These are summarized in Figure 16. It is notable that within experimental error the chemical shifts of the C_{60}^{1-} and C_{60}^{3-} ions both increase linearly with decreasing temperature (in accordance with Curie law behavior) while those for the C_{60}^{2-} ion have the opposite slope. This strongly supports the interpretation that the C_{60}^{1-} and C_{60}^{3-} ions are normal paramagnets with S = 1/2 paramag-

Table 11. Isotropic ^{13}C NMR Chemical Shifts in Solution

| compound	δ (ppm rel. TMS)	line width (at half height, ppm)	solvent	temp (°C)	ref
C_{60}	142.7	sharp	d_6-benzene	RT	314
C_{60}	142.5	sharp	CCl_4	RT	315
$[Na(crown)(THF)_2^+][C_{60}^-]$	186	3	d_6-DMSO	RT	118
$[Na(THF/H_2O)_x^+][C_{60}^-]$	188	3	THF/D_2O	RT	134
$[K(crown)^+][C_{60}^-]$	188	2	d_8-THF/THF	RT	19, 126
$[Na(crown)(THF)_2^+]_2[C_{60}^{2-}]$	184	2	d_6-DMSO	RT	118
$[Na(crown)(THF)_2^+]_3[C_{60}^{3-}]$	197	6	d_6-DMSO	RT	118
$[Na(crypt)^+]_4[C_{60}^{4-}]$	185	2	d_6-DMSO	RT	119
Li_6C_{60}	156.7	sharp	d_8-THF	RT	112
C_{70}	150.7, 148.1, 147.4, 145.4, 130.9	sharp	d_6-benzene	RT	314
Li_6C_{70}	158.3, 152.3, 149.6, 137.9, 133.7	sharp	d_8-THF	−80°	112
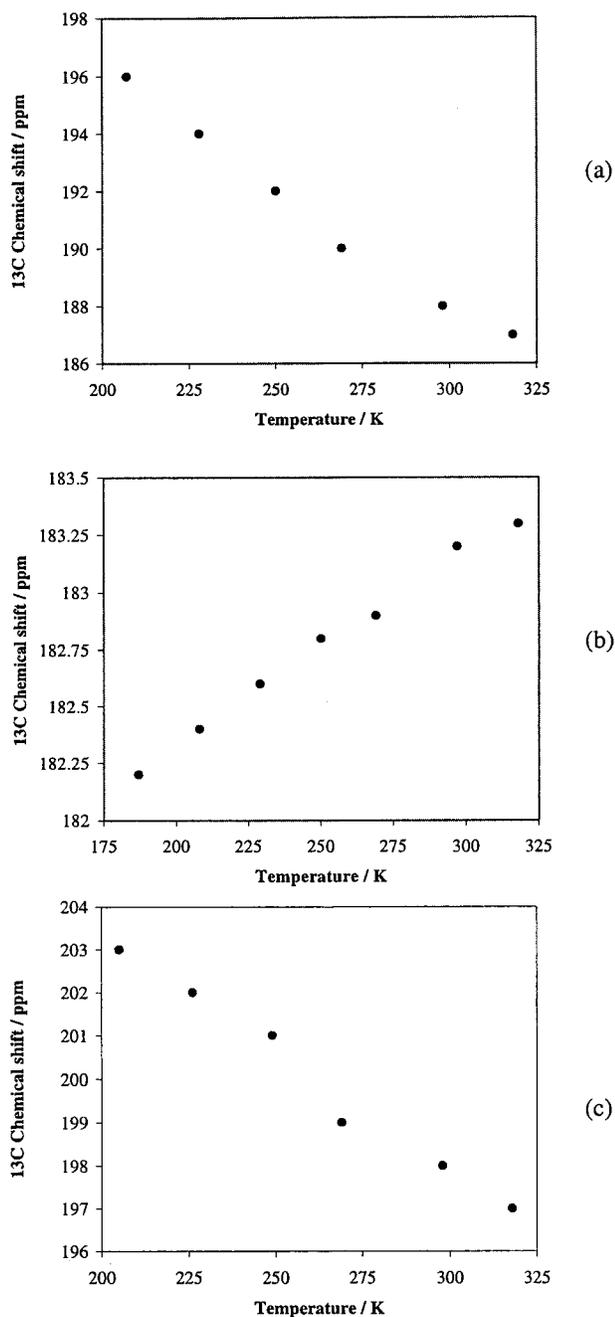
Figure 16. Plots of the temperature dependencies of the ^{13}C chemical shifts for the (a) C_{60}^-, (b) C_{60}^{2-}, and (c) C_{60}^{3-} ions in CH_3CH_2CN (propionitrile) solution.[324]

netic ground states but that C_{60}^{2-} has a diamagnetic ground state with a low-lying S =1 paramagnetic excited state which is significantly occupied at room temperature.[118]

There are no reports of ^{13}C NMR spectra for paramagnetic C_{70}^{n-} fullerides. There is no reason they should be unobservable but, compared to C_{60}, the signals will probably be an order of magnitude more difficult to detect because of dispersal of the resonances into five separate signals spread over a range of ca. 20 ppm. This problem could be readily overcome via ^{13}C enrichment of C_{70}.

Overall, one can be fairly confident that the data in Table 11 reflect intrinsic properties of discrete fullerides. Neither the thermodynamics of redox

disproportionation nor the dynamic effects of Jahn–Teller distortions should be of significant concern.

C. Interpretation of Solution NMR Data

As can be seen from the data in Table 11, there is no simple relationship between charge and chemical shift in C_{60}^{n-} fullerides. This arises because of the overlay of the effects of paramagnetism onto a trend arising from increasing charge. Each ion must therefore be considered in terms of both its charge and the particulars of its paramagnetic electronic state.

London theory has been applied to C_{60} and C_{60}^{6-} to explain their magnetic ring current susceptibilities.[325] By separating the ring currents inside and outside of the buckyball and assuming that fulleride formation progressively displaces the negatively charged π clouds to the outside, a downfield chemical shift for C_{60}^{6-} has been qualitatively rationalized. A downfield shift is counterintuitive with respect to carbanion chemistry where significant *de*shielding of ^{13}C nuclei might be expected and upfield shifts are typically observed. However, the asymmetry between the inner and outer ring currents is believed to override this effect.

This theory lends credence to the proposal that the sharp signal ascribed to Li_6C_{60} at 156.7 ppm,[112] i.e., about 14 ppm downfield of C_{60}, is correctly assigned. The C_{60}^{6-} ion is expected to be diamagnetic with a $(t_{1u})^6$ configuration, so the sharpness of the NMR signal is rationalized. There are no comparable solution NMR studies on other M_6C_{60} salts so the extent to which the lithium cation might influence the chemical shift of the C_{60}^{6-} ion is unknown. ^7Li NMR studies do indicate that there are ion-pairing effects in Li_6C_{60}[112] and, since lithium is a small, polarizing cation that can give covalence to its interactions with carbon, some influence on the ^{13}C shifts is possible. However, solid-state magic angle spinning experiments on intercalated A_6C_{60} species (A = K, Rb, Cs) reveal isotropic ^{13}C shifts for most other alkali metals at about the same value (154–159 ppm).[326] It is therefore reasonable to ascribe the ca. 14 ppm downfield shift to the effect of added charge in C_{60}^{6-}. It seems logical to expect smaller "charge-only" shifts for C_{60}^{n-} fullerides of lower charge (n = 1–5). Perhaps the value should be about 2 ppm downfield per anionic charge,[327] but there is yet no theoretical or experimental basis for this assumption. Data on the presumably analogous C_{70} compound,[112] Li_6C_{70}, also show mostly downfield shifts but the magnitudes are lower than in Li_6C_{60}. The charge states in these compounds have yet to be confirmed.

It is clear then that by far the largest portion of the downfield shifts of the n = 1–4 fullerides must be ascribed to the effects of paramagnetic electronic states. In C_{60}^- the ca. 43 ppm downfield shift relative to C_{60} is mostly due to its S = 1/2 ground spin state. The C_{60}^{3-} ion also has an S = 1/2 ground state. Its shift is somewhat further downfield (54 ppm from C_{60}), consistent with additivity of a larger "charge-only" effect together with a similar effect of paramagnetism from an S = 1/2 ground state. The observed shift is actually somewhat greater than

might be expected on the basis of simple additivity of the two effects, however. Possibly there is some thermal population of a low-lying $S = 3/2$ excited-state contributing to a greater effect from paramagnetism. This might also explain the greater line width of the C_{60}^{3-} ion (6 ppm) compared to that of the C_{60}^- ion (1−2 ppm).

The case of the electronically related C_{60}^{2-} and C_{60}^{4-} ions, both with ca. 40 ppm downfield shifts relative to C_{60}, is more complicated. Both are believed to have diamagnetic ground states with close-lying (<600 cm^{-1}) $S = 1$ excited states. Significant thermal population of these $S = 1$ states would give rise to paramagnetic shifts in the ^{13}C NMR spectra at accessible temperatures. By coincidence, the effect at room temperature is apparently very similar to that arising from the $S = 1/2$ state of the C_{60}^- ion. In contrast to the C_{60}^- ion, however, the chemical shift of the C_{60}^{2-} ion decreases with decreasing temperature (Figure 16).[324] This is consistent with thermal depopulation of the paramagnetic $S = 1$ excited state as the temperature is lowered.

The rationalization of ^{13}C NMR chemical shifts is a potentially fruitful area for theoretical exploration. In addition, experimental data on a C_{60}^{5-} salt in solution would be interesting. The C_{60}^{5-} ion must have an $S = 1/2$ ground state arising from a $(t_{1u})^5$ configuration, so a downfield shift of ca. 50 ppm relative to C_{60} (ca. 12 ppm from the effect of charge and ca. 40 ppm from the effect of paramagnetism) might be predicted.

D. ^{13}C NMR Data in the Solid State

The large amount of solid-state ^{13}C NMR chemical shift data available on metal-intercalated fullerides, M_xC_{60}, must be compared to that from discrete fullerides with caution because of the potential complication of contributions from the conduction electrons (the Knight shift) and magnetic coupling phenomena. There are also possible effects from the cations and from incomplete electron transfer. Nevertheless, the partial listing of room-temperature isotropic shifts for various alkali metal fullerides in Table 12 indicates a number of quite close correspondences between extended and discrete systems of comparable C_{60}^{n-} oxidation state. This suggests that much of the intrinsic nature of the fulleride ions is retained in extended systems, although a more stringent test of similarity would be to compare the details of the temperature-dependent data. Solution data are rather limited in this regard because of the small liquid ranges of the solvents required to dissolve fulleride salts at subambient temperatures. Solid-state data must be chosen carefully, with an eye on structure, because of the potential complications arising from intermolecular effects. Some salts have large cations (tetraphenylphosphonium, K(crown ether)$^+$, etc.) where lattice separations may be sufficient to produce reliably discrete ions. Others have smaller cations (tetramethylammonium, NH$_3$- or THF-solvated alkali metal ions, etc.) where complicating ball-to-ball magnetic interactions may be present. Unfortunately, in most cases where NMR data have been determined, the structures are un-

Table 12. Isotropic ^{13}C NMR Chemical Shifts in the Solid State at Room Temperature

fulleride	system	δ (ppm)	ref
C_{60}^-	NaC$_{60}$(THF)$_5$	188	146
	KC$_{60}$(THF)	187	123
	KC$_{60}$(THF)$_x$	187, 162	322
	NaC$_{60}$(THF)$_3$	187	125
	Na$_x$C$_{60}$(THF)$_y$	158	282, 173
	[NMe$_4$]C$_{60}$ 1.5THF	185	137
	K(crown)C$_{60}$	188	126
	RbC$_{60}$(fcc)	179	329
$(C_{60}^-)_2$	RbC$_{60}$(dimer)	146	328, 329
C_{60}^{2-}	K$_2$C$_{60}$(THF)$_2$	183	124
	[NMe$_4$]$_2$C$_{60}$	180	137
	Na$_2$(NH$_3$)$_8$C$_{60}$ (rh)	180	279
	Na$_2$(NH$_3$)$_{5.3}$C$_{60}$ (bcc)	184	279
	Na$_2$C$_{60}$	172	a
C_{60}^{3-}	[NMe$_4$]$_3$C$_{60}$	200	137
	K$_3$C$_{60}$(THF)$_3$	180	19, 124
	A$_3$C$_{60}$	180−195	b, 327, 331
	K$_3$C$_{60}$(NH$_3$)$_{0.67-1.14}$	191−196	c
C_{60}^{4-}	Rb$_4$C$_{60}$	180−182	b, 327, 330
	K$_4$C$_{60}$	180−182	327, 335
C_{60}^{6-}	K$_6$C$_{60}$	156	327, 326
	Rb$_6$C$_{60}$	156	327, 326

^{a} Rachdi, F.; Hajji, L.; Galtier, M.; Yildirim, T.; Fischer, J. E.; Goze, C.; Mehring, M. *Phys. Rev. B* **1997**, *56*, 7831−7834. ^{b} Tycko, R.; Dabbagh, G.; Rosseinsky, M. J.; Murphy, D. W.; Ramirez, A. P.; Fleming, R. M. *Phys. Rev. Lett.* **1992**, *68*, 1912−1915. ^{c} Maniwa, Y.; Sugiura, D.; Kume, K.; Kikuchi, K.; Suzuko, S.; Achiba, Y.; Hirosawa, I.; Tanigaki, K.; Shimoda, H.; Iwasa, Y. *Phys. Rev. B* **1996**, *54*, R6861−R6864.

known. Furthermore, a number of the reported salts have poorly defined composition. There is often variability in the number of THF solvent molecules associated with the cation in Na(THF)$_x^+$ or K(THF)$_x^+$ salts. The solid materials may therefore be physical mixtures of different phases. In addition, the stoichiometry of some salts is not always established with sufficient certainty to be fully confident of a homogeneous $n-$ charge state for the fulleride.

Reported data are listed in Table 12. The first report was by Green and co-workers in 1994 on the C_{60}^- ion in a THF-solvated sodium salt, given the formulation NaC$_{60}$·5THF.[146] Subsequent results on a salt formulated as NaC$_{60}$·3THF are essentially the same.[125] A relatively sharp peak at ca. 188 ppm was observed at room temperature without sample spinning, indicating rapid rotation of the buckyball anions on the ^{13}C NMR time scale.[146] The peak width at half-height (v) was 2000 Hz (40 ppm) at an operating frequency of 50 MHz, narrowing to <200 Hz (<2 ppm) at an operating frequency of 200 MHz. The signal broadened as the temperature was lowered, consistent with slower rates of rotation and the onset of chemical shift anisotropy. The signal moved downfield with decreasing temperature in accordance with the behavior expected of a species with a paramagnetic ground state. Overall similar results were later reported for a tetramethylammonium salt of formula [Me$_4$N][C$_{60}$]·1.5THF.[137] In this case the crystal structure was determined and the presence of ball-to-ball interactions within layers established in low-temperature magnetic measurements. The increasing downfield shift with decreasing temperature was found to respond to an abrupt change in the magnetic state of the material. Nonzero inter-

cepts in the Curie law behavior of the data were noted. This seems to be a common feature of the fullerides measured to date. There is a qualitative congruence of the shift data in these compounds to those obtained for the C_{60}^- ion in solution (see Figure 16 above), suggesting that even with some extended interactions, much of the intrinsic nature of the discrete C_{60}^- ion is conserved in these materials.

Contrasting studies, however, are provided by the work of Huang and co-workers[322] who studied a closely related potassium salt of approximate composition $KC_{60} \cdot x$THF $(0 < x < 1)$. They identified two ^{13}C NMR signals assignable to C_{60} fullerides. The dominant signal (187 ppm, $T_1 = 15.9$ ms, $v = 1220$ Hz) is comparable to the sodium salt discussed above and showed a similar temperature dependence. A second signal at 162 ppm ($T_1 = 134$ ms, $v = 769$ Hz), which could be enhanced at the expense of the 187 ppm signal by removing THF from the sample, is unusual because of its unique chemical shift and because it shows considerably less temperature dependence. The authors assigned the two signals to differently ion-paired forms of C_{60}^- in different electronic ground states. The 187 ppm signal was proposed to arise from a loosely ion-paired form of C_{60}^- in a ^2A state, the expected ground state of Jahn–Teller-induced symmetry lowering from the degenerate $(t_{1u})^1$ configuration. The 162 ppm signal was proposed to arise from a ^2E electronic state originating from a tight $K^+ \cdots C_{60}^-$ ion-pairing distortion of the anion. Corroborating evidence was offered in the form of dual signals (broad and narrow line widths) in EPR studies, but no explanation was offered for the lack of a temperature dependence in the 162 ppm chemical shift. The lack of normal paramagnetic behavior suggests that a different explanation must be found.

It is possible that the 162 ppm shift arises from the "mixed valence" $(C_{60})_2^-$ ion, a C–C bonded species with one unpaired electron per C_{60} dimer that may be present in other fulleride samples (see section IX.B.vii). Partial aerobic oxidation of C_{60}^- may have occurred during the hexane washing and vacuum treatment used to produce "$KC_{60} \cdot x$THF $(0 < x < 1)$" from $KC_{60} \cdot$THF.[322] Elemental analyses of the material were not reported. The solid state could assist in holding together a labile dimeric unit that might otherwise be expected to dissociate. The 162 ppm chemical shift is close to the average of C_{60} (143 ppm) [or $(C_{60})_2^{2-}$ (ca. 148 ppm)[328,329]] and authentic C_{60}^- (ca. 187 ppm), consistent with delocalization of one unpaired electron over the two halves of the dimer or more likely, rapid oscillation between them. The line width of the signal accommodates the range of chemical shifts expected of a covalently bonded dimer, and the sp^3 carbon signals would be lost in the noise due to the effects of paramagnetic broadening, just as they are in the ^{13}C NMR of the radical anion of a derivatized [60]fulleropyrrolidine.[231] The narrowness of the solid-state NMR signal requires rapid motional tumbling of the C_{60} moieties. This is a reasonable expectation for a dumbbell-shaped $(C_{60})_2^-$ ion inasmuch as intramolecular spinning around a single weak C–C σ bond should be facile.

It is even possible that the σ bond is sufficiently labile that it "walks" around the sphere via 1,2 shifts, thereby allowing the balls to spin randomly. This would average the ^{13}C resonances and give a narrow line if the process was fast on the NMR time scale. The lack of a marked temperature dependence of the signal, compared to a normal paramagnet, might be a special feature of a mixed-valence dimer.

Possible corroboration of this idea comes from preliminary work by Moriyama et al.[173,282] on a salt formulated as the half-reduced species Na_xC_{60}(THF)$_y$ ($x = 0.4–0.5$, $y = 2–6$) on the basis of elemental analyses. Notably, the ^{13}C chemical shift of this material at room temperature is 158 ppm, close to the 162 ppm value discussed above. Further characterization of this material is highly desirable.

There are three reports of solid-state ^{13}C NMR data for C_{60}^{2-} salts where the ions may be approaching the discrete ideal. For a potassium salt formulated as $K_2C_{60} \cdot 2$THF, Huang and co-workers[124] found a room-temperature shift of 183 ppm, essentially identical to the 184 ppm value reported earlier in DMSO solution.[118] Ammoniated phases of Na_2C_{60}, which have some ball-to-ball contact between layered structures, have similar shift values (180 and 184 ppm, see Table 12) as does a tetramethylammonium salt.[137] This suggests that the C_{60}^{2-} ions in these phases have properties approaching those of discrete ions. The contrast with Na_2C_{60} (172 ppm) is notable, and an explanation for this difference must lie in the subtleties of its weakly extended electronic structure.

Unlike a C_{60}^{1-} salt, the resonance for the C_{60}^{2-} ion in solid $K_2C_{60} \cdot 2$THF moves *upfield* as the temperature is lowered, to 172 ppm at 150 K.[124] This mirrors the solution data discussed earlier (Figure 16), and we ascribe this to predominant occupation of an S = 0 ground state as the temperature is lowered. It would be very interesting to follow or extrapolate this shift to even lower temperatures where approach to a diamagnetic "charge-only" fulleride shift for the (−2) ion in the range 148–158 ppm might be predicted.

With respect to data on possibly discrete salts of the C_{60}^{3-} ion, there is a preliminary report of a peak at ca. 200 ppm for a compound of possible composition $[NMe_4]_3[C_{60}]$.[137] This is close to the value observed in solution (197 ppm) and in ammoniated K_3C_{60} phases (190–196 ppm). Huang and co-workers have reported solid-state ^{13}C NMR shift data for the C_{60}^{3-} ion in a compound formulated as $K_3C_{60} \cdot 3$THF.[124] At room temperature the shift is ca. 180 ppm and there is virtually no temperature dependence down to 145 K. This is quite unexpected since the C_{60}^{3-} ion is an S = 1/2 paramagnet. Like the C_{60}^{1-} ion, the discrete C_{60}^{3-} ion would be expected to show increasing downfield shift with decreasing temperature in accordance with the Curie law. Perhaps there are ball-to-ball interactions in this nominally 3THF-solvated salt such that it is more like unsolvated K_3C_{60}. Complementary X-ray diffraction data would be useful to determine whether this material is a discrete and different phase. The possibility that the sample is a mixture of C_{60}^{3-} and C_{60}^{2-} ions, with electron exchange occurring rapidly on the NMR time

scale, also needs to be ruled out by independent experiment. An averaged $C_{60}^{3-/2-}$ chemical shift would be difficult to distinguish from that of authentic C_{60}^{3-} and could accidentally give rise to the unexpected lack of temperature dependence. Data on a C_{60}^{3-} salt with large cations and proven chemical purity would be very useful in understanding the published data on C_{60}^{3-} salts.

The solid-state ^{13}C NMR of the C_{60}^{4-} ion in Rb_4C_{60} has been studied allowing a singlet–triplet energy gap of 907 cm^{-1} (113 meV) to be extracted from the variable-temperature data.[330] The influence of ball-to-ball contact on this splitting is unknown, but the magnitude is not unlike that expected for the discrete C_{60}^{4-} ion.

Finally, there is a very puzzling report of a massive *upfield* ^{13}C shift (ca. -182 ppm) for the low-temperature (190 K) solid-state ^{13}C NMR spectrum of a fulleride formulated as [K(dibenzo-18-crown-6)$^+$]- [C_{60}^-].[126] This is ascribed to an effect of magnetic ordering in a phase having interactions between C_{60}^- and the arene rings of the crown ether. The data must be viewed with considerable skepticism until independent corroboration is available.

E. Knight Shift in A_3C_{60}

There is disagreement in the literature over the contribution of conduction electrons to the ^{13}C shift (i.e., the Knight shift) of metallic A_3C_{60} fullerides. Observed shifts in conductors are typically partitioned into two contributions, a chemical shift and a Knight shift, by comparing the metallic state with an appropriate insulating state. The problem has been in deciding which nonmetallic state to use for the reference chemical shift.[20]

The first estimate for K_3C_{60}, whose observed chemical shift at room temperature is at 186 ppm, was made by Tycko et al.[331] They took neutral C_{60} (143 ppm) as the chemical shift reference and ascribed the total downfield shift (43 ppm) to a Knight shift. Holczer et al.,[332] Kerkoud et al.,[18] Reichenbach et al.,[327] and Chen et al.[19] all recognized that the effect of the -3 negative charge had been neglected in this estimate but they differed markedly on how to compensate for it. Kerkoud et al. used pressure-dependent data to extrapolate a value of 61 ppm for the Knight shift. This implied that the addition of three negative charges to C_{60} would result in an 18 ppm *upfield* (so-called "diamagnetic") shift in a nonmetallic phase, in contradiction to existing theory[325] and later experiments.[19,118,327] Reichenbach et al. used the chemical shift of A_6C_{60} compounds (ca. 156 ppm) and proposed an approximate 2 ppm progression per charge from C_{60} (143 ppm). This would place C_{60}^{3-} at ca. 149 ppm and lead to a proposed Knight shift of 37 ppm. Chen et al. took the 180 ppm value of a presumed nonmetallic salt formulated as $K_3C_{60}\cdot3THF$ as the appropriate reference and nominated 6 ppm as the Knight shift. Despite the wide range of values proposed for the Knight shift in K_3C_{60} (6–61 ppm), each found some corroboration in existing experimental data or theory.

Missing from this discussion has been any consideration of the effect of unpaired electrons on ^{13}C shifts

in nonmetallic states of C_{60}^{3-} salts. In other words, all the unpaired electron spin density in A_3C_{60} metals has been ascribed to conduction electrons. We now know, however, that the discrete C_{60}^{3-} ion is an $S = 1/2$ paramagnet and that in solution, an obviously nonmetallic state, the chemical shift is ca. 197 ppm.[118] A value of 196 ppm is found in $K_3C_{60}\cdot1.14NH_3$ (see Table 12). The use of these values as a reference for the Knight shift would lead to a *negative* Knight shift in K_3C_{60} of ca. -10 ppm! This brings sharp attention to the lack of consensus over the magnitude of the Knight shift in A_3C_{60} metals. Experiments are needed which give a sensible partitioning of the total unpaired spin density into that localized on a fulleride ion and that delocalized in the conduction bands. Perhaps this even raises a definitional problem for the Knight shift in conducting fullerides. In the most recent review on this matter, Pennington and Stenger[320] acknowledge that the ^{13}C hyperfine coupling to electron spin density "is a complex affair" and that theory still falls short of rationalizing the "small magnitude" of the Knight shift.

What does seem clear is that ^{13}C shifts, even in interacting A_xC_{60} systems, are not so much indicators of metallic behavior or delocalized electrons but more a reflection of the electronic states of the individual fulleride ions and the spin-coupling interactions between them. A deeper understanding of the relationship between ^{13}C shifts and conductivity (and superconductivity) is coming from the analysis of temperature-dependent data.[333,334]

The modest temperature dependence of the ca. 180 ppm shifts for A_4C_{60} (A = K, Rb)[330,335] (decreasing to 177 at 4 K) is particularly intriguing because these materials are not metals and yet the shifts are considerably downfield of the values that might be expected for a C_{60}^{4-} ion with an $S = 0$ ground electronic state (ca. 151 ppm). There are no solid-state data available on a discrete C_{60}^{4-} salt to establish a baseline for comparison, but these data may be providing the best available clue about how ball-to-ball cooperative effects can influence electronic structure and ^{13}C shifts.

F. ^3He NMR of Endohedral Fullerides

Saunders and co-workers have established ^3He NMR as a highly sensitive probe of the interior magnetic properties of fullerenes and derivatized fullerenes.[336] Helium is trapped inside C_{60} by high-pressure treatment at 650 °C, and although the incorporation level is only ca. 0.1%, the high sensitivity of ^3He NMR yields a unique chemical shift marker for every fullerene derivative. The resonance of $^3He@C_{60}$ appears at -6.3 ppm (relative to free ^3He dissolved in the solvent), while that of $^3He@C_{70}$ appears at -28.8 ppm. The only results published to date on fullerides are for the diamagnetic lithium salts of $^3He@C_{60}^{6-}$ and $^3He@C_{70}^{6-}$.[127] The observed upfield shift of -48.7 ppm for the C_{60} polyanion is consistent with increased aromaticity, while the downfield shift of 8.3 ppm observed for the C_{70} polyanion is consistent with decreased aromaticity.

The ^3He NMR resonances for the C_{60}^{n-} ($n = 1-5$) fullerides and for C_{60}^+, although broadened by effects

of paramagnetism, should be observable. They are presently unreported but are expected to be distinctive markers of oxidation state and informative with respect to electronic structure. The ^{3}He NMR resonance has been measured for the $C_{60}(4\text{-}F\text{-}C_6H_4)_5^+$ cation.[337]

G. ^{13}C NMR of Derivatized Fullerenes

There is one report of the ^{13}C NMR spectrum of a fulleride of a derivatized fullerene, the radical anion of *N*-methylfullero[60]pyrrolidine.[231]
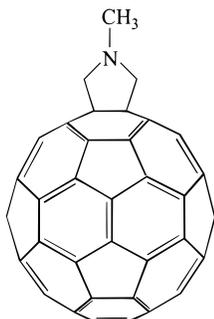
The effect of the unpaired electron is to broaden the C_{60} resonances into a 10 ppm wide envelope centered at 187 ppm. The close similarity of this shift to unfunctionalized C_{60}^- is notable. It indicates that the unpaired electron is delocalized over the ball in much the same way.

H. ^{13}C NMR of Fullerenium Cations

Sharp EPR signals tend to correlate with broad NMR signals. Thus, it is not too surprising that authenticated ^{13}C NMR signals from fullerene radical cations have yet to be reported. The EPR spectra of C_{60}^+ and C_{76}^+ show narrower line widths than their corresponding fullerides (see section IX) so very broad NMR signals can be expected.

There are two reports on the use of ^{13}C NMR to monitor fullerene chemistry under superacid conditions where cations might be expected to form. Miller and co-workers detected a single, sharp signal at 246 ppm when C_{60} was treated with 1:1 FSO_3H/SbF_5.[208] This could only arise from a diamagnetic species. The same solution exhibited a sharp EPR signal, ascribable to C_{60}^+, so superacid chemistry must lead to at least two nonexchanging products. Olah, Prakash, and co-workers have reported "extremely broad ^{13}C NMR spectra... (−80 °C to room temperature)" assigned to unidentified "radical cations".[112]

This is a fruitful area for further investigation, by both ^{13}C and ^{3}He NMR spectroscopy, but special attention will have to be paid to sample integrity and identification.

IX. EPR Spectroscopy

A. Introduction

A comprehensive and succinct review on the EPR of C_{60}^{n-} fullerides was published by Eaton and Eaton[338] in 1996. The reader is referred to Table 1 of the Eaton and Eaton review for specific g values and line width data under a wide variety of experimental

conditions. It surveys the literature through 1995 and is particularly useful in its tabulation of parameters and its analysis of instrumental limitations and data reliability. Apart from bringing this review up to date, our treatment differs in a number of ways. We place greater emphasis on the development of the historical record, preserving the original chronology of key papers. More integrated into our review are critical observations from complementary techniques (e.g., ^{13}C NMR spectroscopy, X-ray structure determination, etc.), allowing us to be more conclusive about the interpretation of conflicting data. Also, we give much greater weight to spectra derived from well-characterized, isolated samples of fulleride salts. A number of these salts have sample characterization criteria which exceed those for samples prepared by quantitative electrochemical techniques. The latter techniques are most reliable when accompanied by a quantitative NIR spectroscopic assessment of sample purity and identity. In our view, much of the complexity and confusion in this field has arisen from problems of sample purity and from a lack of complementary quantitative characterization of samples. The in situ generation of fullerides for EPR analysis has been promoted over ex situ methodology by some workers,[232] but our analysis suggests the reverse priority is preferable.

The major unsolved problem in C_{60}^{n-} fulleride EPR spectroscopy is the chemical identity of species giving rise to narrow line width signals. We conclude that the most logical explanation lies in the presence of dimeric structures, $C_{120}O^{n-}$ or $(C_{60})_2^{n-}$.

B. Features of the C_{60}^- Spectrum

There are three proven intrinsic features of the EPR spectrum of the C_{60}^- ion: (i) a low g value, (ii) an unusually broad signal at room temperature whose line width decreases markedly with decreasing temperature down to about 70 K, and (iii) observable anisotropy at low temperatures. A fourth distinctive feature, which has been the subject of extensive but inconclusive discussion, is the frequent observation of superimposed narrow line width signal(s). When observed, these sharp signals are usually minor components, although there are conditions where these are apparently the only observable signals. ^{13}C satellites are also sometimes observed[339,340] and have been rationalized by the effects of strong ion pairing.[341]

The first report of the EPR spectrum of the C_{60}^- ion (see Figure 17) remains one of the most definitive because it was made on a well defined, air stable, magnetically dilute salt, $[PPh_4]_2Cl[C_{60}]$.[184] Subsequent X-ray crystal structure analysis[188] confirmed the formulation and showed that the C_{60}^- ions are discrete and well separated (>2.5 Å from van der Waals contact). The g value was 1.9991, significantly lower than the free electron value of 2.0023 and the values observed for most organic radicals. The room-temperature signal was broad with a peak-to-peak line width (ΔH_{pp}) of ca. 45 G, decreasing dramatically to ca. 7 G at 80 K (see Figure 17). A superimposed sharp signal was *not* observed. The third distinctive feature of the EPR spectrum of the C_{60}^- ion, anisot-
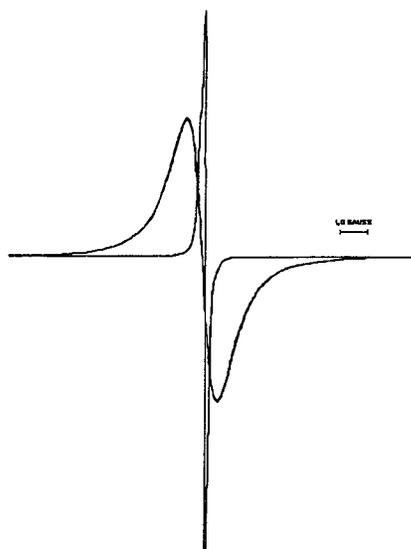
Figure 17. Solid-state EPR spectrum of C_{60}^- in $[PPh_4]_2$-Cl$[C_{60}]$ at 300 K (broad line, ΔH_{pp} ca. 45 G) and 80 K (narrow line). The scale bar is 40 G. The narrow line is *not* 'the spike' referred to in section IX.B.iv. (Reprinted with permission from ref 184. Copyright 1991 American Chemical Society.)

ropy, was first seen when frozen solution spectra were run below liquid nitrogen temperatures.[139] Again, these measurements are considered definitive because they were made on a well characterized salt, $[Cr(TPP)(THF)_2][C_{60}]$, dissolved in scrupulously deoxygenated THF solvent to attain magnetic dilution. We treat these three features in turn and then address the problem of sharp signals.

i. The Low g Value

There is universal agreement that the broad signal of C_{60}^- has a low g value, close to 1.999.[338] It is does not change significantly with temperature, and the range of reported values (1.994−2.001, see ref 338) probably has as much to do with calibration error limits as environmental sensitivity. The unusually low value is attributed to spin−orbit coupling effects from unquenched angular momentum in Jahn−Teller-distorted states of the $(t_{1u})^1$ configuration.[178,180,184] It has been treated[180,342] and defended[220] theoretically by Kato et al.

ii. Temperature Dependence of the Line Width (ΔH_{pp})

From liquid nitrogen temperatures up to room temperature, ΔH_{pp} increases from ca. 5 G up to ca. 60 G (see Figure 17).[53,106,116,117,123,125,132,146,179,183−185,343−349] The most extensive investigations have been made by Eaton and co-workers, and the following general features have been identified.[338] Below about 80 K, there is no longer a substantial temperature dependence. In solution, the temperature dependence of ΔH_{pp} begins to level off above the melting point of the solvent but the magnitudes vary with solvent. In solid samples, the line widths are usually still increasing above room temperature. The variation with cation is substantial. Room-temperature line widths have been reported in the range 10−54 G.[133] These features have led Eaton et al. to conclude that

electron−spin relaxation rates are the main determinant of the line width variation, but the whole problem of line width variation is made complex by the presence of low-lying excited states,[179] motional effects,[106,220] and environmentally induced distortions.[346] A more quantitative understanding of the broad, temperature-dependent signal is coming from pulsed EPR measurements of the traverse and longitudinal relaxation times of C_{60}^- in a tetraphenylphosphonium salt.[350] Its origin clearly lies in the dynamic nature of the small Jahn−Teller distortion associated with degeneracy of the $(t_{1u})^1$ ground state. This gives rise to a ^2A ground state and a close lying ^2E excited state[179] which can give rise to signal broadening by an Orbach relaxation process. However, the total picture is more complex and no single process can explain the leveling off of ΔH at high temperatures.[351]

iii. Anisotropy

Below about liquid nitrogen temperatures, the isotropic EPR signal of the C_{60}^- ion becomes anisotropic.[106,116,117,139,220,347,348] Under the best conditions, classical "axial" features are seen. As shown in Figure 18, the spectrum of the Na(crown)$^+$ salt at 4.5 K in
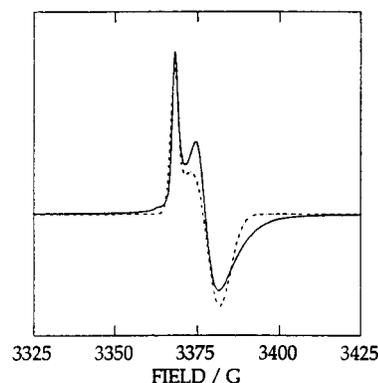

Figure 18. Anisotropy of the EPR signal of the C_{60}^- ion in frozen 2-methyltetrahydrofuran solution at 4.5 K (solid line) and simulation with $g_\perp = 1.9968$ and $g_\parallel = 2.0023$ (dotted line). (Reprinted with permission from ref 116. Copyright 1993 American Chemical Society.)

frozen 2-methyl tetrahydrofuran, a good glassing solvent, has been fit with $g_\perp = 1.9968$ and $g_\parallel = 2.0023$.[116,117] The imperfect fit to the Lorentzian simulation probably arises from so-called g strain, the signal broadening effect that arises from a distribution of slightly different structures induced by microscopically different sites in the frozen/solvent matrix.[116,117]

The anisotropic nature of the spectrum is prima facie evidence for a static C_{60}^{1-} distortion from icosahedral symmetry in the C_{60}^- ion.[116,117,220] Early UHF 3-21G calculations by Koga and Morokuma[274] concluded that C_{60}^- would adopt an axially elongated ellipsoidal structure with the unpaired electron density concentrated in a delocalized belt around the equator. Under three imposed symmetries, D_{5d}, D_{3d}, and D_{2h}, the energies and distortions were found to be very similar. Thus, the axial EPR spectrum is readily rationalized. Nevertheless, it must be pointed out that these calculations have been somewhat

overinterpreted. The symmetries are *imposed* symmetries, to simplify the calculations, and the axially symmetric nature of the distortion is therefore a foregone conclusion. The actual geometry of the C_{60}^- ion in a frozen matrix may be lower than D_{5d}, D_{3d}, or D_{2h} and, if static, could give rise to a set of rhombic EPR signals. This has yet to be observed. Dynamical behavior and the limitations of time and energy resolution in EPR (and NIR)[224] spectroscopy may only reveal *effective* symmetry. More recent, higher level ab initio calculations at the 6-31G* level have concluded that the lowest energy geometry of C_{60}^- has C_i symmetry.[352]

Recently, single-crystal EPR spectra have been obtained for a C_{60}^- salt.[352,353] The observation of two precisely defined g values gives more insight into the nature of the Jahn−Teller-distorted ground state in this environment. The rationalization of the results requires a molecular symmetry of C_{2h} or lower.[352]

As the temperature is raised toward liquid nitrogen temperatures, $g_\perp$ moves toward $g_\parallel$ and the anisotropy collapses. This is readily ascribed to dynamic averaging of ellipsoidal structures to give effective icosahedral symmetry (so-called pseudorotation).[116,117,347,352,353] It finds a counterpart in the dynamic collapse of anisotropy in the EPR spectrum of triplet state C_{60} which occurs over a similar temperature regime.[354] Phase memory relaxation rates acquired by electron spin−echo techniques are faster in the high-field tail of the C_{60}^- spectrum than in the central portion.[347] This has been interpreted in terms of time-dependent interconversions between "distortomers" and is supported by the wide distribution of T_1 values at each position in the spectrum.[347,348]

iv. Problem of the Sharp Signals

The history of the "spike" in the EPR spectrum of the C_{60}^- ion is an interesting illustration of the way scientific understanding can develop. Each new explanation stimulated new experiments until six different theories had been forwarded in as little as four years. After a detailed analysis of all of the data, we conclude that only two remain viable.

Not always seen, the sharp signal can have an elusive quality. Typically the minor component of a mixture, and possibly the disfavored part of a labile equilibrium, it presents a classic problem for analytical chemistry. Detected by a very sensitive technique, but one that does not lend itself to easy molar quantification, it has yet to yield satisfactory characterization by complementary spectroscopic methods. In what follows, we recount the development of explanations for narrow line width EPR signals, accompanied by a critical analysis of their applicability. Ironically, the superposition of a narrow "impurity phase" signal on a broad conduction−electron spectrum is also observed for the A_3C_{60} superconductors.[355] Perhaps there is a commonality to their chemical origin.

The first report of an EPR spectrum for C_{60}^- showing both broad and sharp signals remains typical (see Figure 19).[178] It has been widely observed that the two signals have different saturation characteristics with applied microwave power. This in-
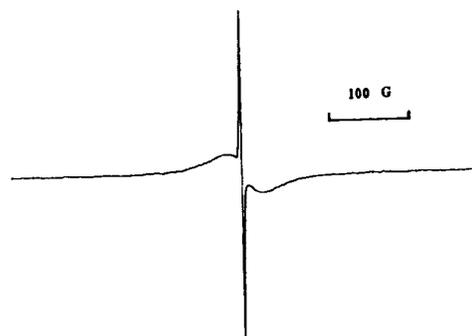

Figure 19. Representative EPR spectrum of C_{60}^- (major, broad signal) containing the minor, narrow signal or 'spike'. (Reprinted with permission from ref 178. Copyright 1991 American Chemical Society.)

dicates they arise from separate chemical entities. The consensus characteristics of the sharp signal, derived either from quantitative electrolysis of solutions of C_{60} or from redissolution of synthetic salts, are as follows. (a) It represents no more than a few percent of the sample, although precise quantification is difficult. (b) The g value (ca. 2.000) is somewhat greater than that of the broad signal but remains distinctively below the free electron value. This has been widely accepted as evidence for a fulleride origin. This is confirmed by signal broadening of the narrow signal upon ^{13}C enrichment.[356] (c) The ΔH_{pp} line width is typically in the range 1−3 G, although considerably smaller values have been reported under very specific conditions. This line width remains somewhat large for a typical organic radical, again consistent with fulleride origin. Unlike the broad signal of C_{60}^-, however, the line width of the sharp signal is not particularly temperature sensitive. Under one set of conditions, ΔH_{pp} is reported to decrease from 0.9 G at room temperature to 0.25 G at 180 K.[356] This means that the electronic features giving rise to the broad signal (the t_{1u} degeneracy) are removed in the species giving rise to the sharp signal. At 100 K or below, the signal becomes noticably anisotropic and can be fit to an axial spectrum with $g_\perp = 2.0002$ and $g_\parallel = 1.9994$.[356] Since the onset of observable anisotropy occurs at a higher temperature than with the broad signal, the species giving rise to the sharp signal must have a greater deviation from icosahedral symmetry. This is an important clue to the origin of the sharp signal.

Greany and Gorun proposed that the sharp signal arose from C_{60}^- and that C_{60}/C_{60}^- electron exchange in an ion pair gave rise to the broad signal.[178] This is inconsistent with the observation of the sharp signal in frozen solutions of stoichiometric C_{60}^- salts.[116,117,179]

Jones, Kadish, and co-workers proposed that the sharp signal was due to a small amount of C_{60}^{2-} arising from redox disproportionation.[179] This is inconsistent with Nernst equation quantitation and the persistence of the sharp signal in the presence of a large excess of C_{60}.[116,117] It is now recognized that C_{60}^{2-} is EPR silent at low temperatures, and the inapplicability of the disproportionation proposal has been accepted by its proposers.[171]

Reed and co-workers proposed that the sharp signal arose from thermal population of a low-lying

excited state.[116,117] The spike seems to disappear as the temperature is lowered, but this may be due to unavoidable signal distortion when spectra are recorded by standard CW techniques at liquid helium temperatures.[338,348] There is also masking by the broad signal as it becomes anisotropic. The existence of low-lying states has been verified for C_{60}^- [224,350] and C_{60}^{2-} by EPR spectroscopy,[118,299,357] but it is doubtful this is the correct explanation for the spike. Rather, low-lying states contribute to the line width of the broad signal via Orbach relaxation.[350]

In 1995, Huang and co-workers made a related proposal that C_{60}^- could exist in two different ground states depending on ion-pairing effects.[322] They observed that the relative intensity of the sharp versus broad signal in $KC_{60} \cdot THF$ increased as the solvent was removed under vacuum. A concomitant change in the ^{13}C NMR spectrum was also observed. An unusual resonance grew in at 162 ppm at the expense of the normal C_{60}^- resonance at 187 ppm. We have argued in section VIII.D that a simple change in ground state is difficult to reconcile with the chemical shift and temperature characteristics of the 162 ppm signal, making this proposal untenable.

By 1994, it was becoming clear that an explanation for the two EPR signals might not lie in the intrinsic properties of the discrete C_{60}^- ion. Papers by Green and co-workers[146,358] and Eaton and co-workers[347] put forward ideas that extrinsic factors such as decomposition, impurities, or dimerization might be responsible for the sharp signal. Confirming data has been difficult to obtain, but circumstantial evidence is mounting in support of the essential correctness of these ideas. At the same time, Stasko and co-workers added to the puzzle by finding conditions where apparently *only* sharp signals are observed.[356,359] Furthermore, they assigned the two types of signals in exactly the opposite way to that of the prevailing wisdom, the narrow line to discrete C_{60}^- and the broad line to the product of subsequent chemistry. We reinterpret this opposing view after reviewing the evidence in favor of the impurity and dimerization proposals. A theoretical justification for both the narrow and broad signals being intrinsic to C_{60}^- has been offered recently[360] but the circumstances are too hypothetical to apply to the experimental observations.

v. Origins of Sharp Signals

Since the broad signals are associated with the high symmetry of C_{60}, the $(t_{1u})^1$ degeneracy of C_{60}^-, and its Jahn–Teller distortion, a chemical process which destroys this degeneracy is a likely origin of narrow signals.[131] Stasko and co-workers proposed that strong solvation might be sufficient to lift the $(t_{1u})^1$ degeneracy,[361] and Jones, Kadish, and co-workers have tended toward this view.[133,171] However, it is inconsistent with the large body of data on the broad signal discussed above. There is no convincing evidence that environmental influences or supramolecular interactions can bring about such a dramatic change in signal characteristics. Studies with calixarenes show that complexation of C_{60}^- leads to a loss of the broad signal[362] and some of the sharp signal,[79]

but this is most easily explained by the effects of spin coupling in noncovalent aggregates.

The removal of the $(t_{1u})^1$ degeneracy of C_{60}^-, sufficient to change the broad signal into a sharp signal, can be accomplished by the formation of a persistent covalent bond to one or more carbon atoms. The EPR spectra of a number of derivatized fullerides illustrate this.

Extensive studies by Krusic, Morton, and co-workers on neutral radicals of the type $RC_{60}{}^\bullet$ have established g values in the range 2.0023−2.0025, line widths of 1.5−2.8 G, and ^{13}C hyperfine splitting as characteristic properties.[363,364] While the line widths are compatible with the sharp signal of C_{60}^-, the high g values and observed hyperfine splittings are not. The special case of $HC_{60}{}^\bullet$ must be considered because of the possibility that protonation of C_{60}^- by water could be the source of the sharp signals. However, $HC_{60}{}^\bullet$ has $g = 2.0022$ and shows H hyperfine[363] so it is readily ruled out. In addition, the electrochemistry of the C_{60}/C_{60}^- couple is not sensitive to the presence of weak acids.[365] Water has been reported to be of little consequence in the synthesis of C_{60}^- salts,[134] and EPR studies with purposeful addition of water show only minor effects.[175,299,357,362] Covalently bonded dioxygen adducts of C_{60}^- have been recently proposed as the source of sharp signals.[366] To be a serious contender, this proposal needs a much firmer chemical precedent. It is contrary to reports that simple oxidation back to neutral C_{60} is the major consequence of exposure of C_{60}^- to air,[116,117] although polyoxygenated fullerenes have been reported under aerobic electrolysis conditions at the C_{60}^{2-} level.[367]

Studies on fullerene derivatives of the type $R_2C_{60}^-$ are more appropriate models for the sharp signal in C_{60}^-. Signals ascribable to such species have been reported to have g values close to 2.000 and line widths of 1−2 G.[108,132,230,232,368−370] In temperature-dependent studies on the well characterized anion of *N*-methyl[60]fulleropyrrollidine, the g value was 2.0006 and the line width was 3 G at room temperature. It decreased to about 1 G at liquid helium temperatures with the onset of noticeable anisotropy.[231] These characteristics are essentially indistinguishable from those of the sharp signal for C_{60}^-. They are consistent with PM3 calculations which show a high degree of delocalization of spin density over the fullerene cage atoms, preserving low g values.[231] At the same time, functionalization has sufficiently perturbed the $(t_{1u})^1$ degeneracy that the line width is neither particularly broad nor temperature dependent. Bis-functionalized fulleride anions $(R_4C_{60}^-)$ show much narrower lines.[371]

These studies support the idea that the presence of some sort of a functionalized fulleride could be the source of sharp signals. The C_{60}^- ion is not a particularly reactive species toward electrophiles, and the use of high-purity solvents under strictly anaerobic conditions argues against the formation of derivatives during the preparation of samples. If involved, they must be already present in the C_{60} sample. If C_{60}^- reacted with impurities in a solvent, conditions would probably have been found by now where a dilute solution of a pure salt gave the sharp signal

as the major or only observable EPR signal. A recent study reports that increased levels of sharp signals appear when low-purity toluene solvent was used, and this was taken as evidence for the formation of σ-bonded adducts by reaction with impurities.[79] However, there are alternate explanations. For example, the impurities could change solubilities leading to precipitates with different EPR properties. Cloudy solutions are mentioned in these mixed toluene/acetonitrile studies.

There is a remote possibility that nonicosahedral isomers of C_{60} are "impurities" in regular C_{60} samples and that their fullerides could give rise to narrower EPR signals than I_h–C_{60} fullerides. However, in the absence of any proof of their existence,[372] we consider this explanation most unlikely.

vi. The $C_{120}O$ Impurity Postulate

In a very recent development, it has been shown that $C_{120}O$
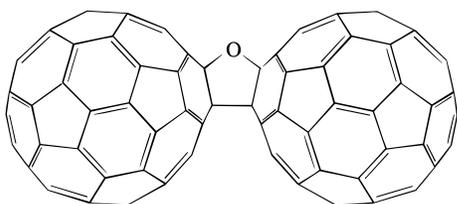
is a common impurity in solid C_{60} samples that have been exposed to air and light.[373] It is assumed to arise from the reaction of the epoxide $C_{60}O$ with C_{60} and is estimated to be present in up to 1% in typical samples of C_{60}. The epoxide has long been recognized as a common impurity in C_{60}, but its reversion to a fullerene upon reduction[374] removed $C_{60}O^{n-}$ from serious consideration as a source of the spike. It is surprising that it has taken so long to recognize the presence of the $C_{120}O$ impurity but it does explain why $(C_{120}O)^{n-}$ has not been a prime suspect in the search for an explanation for the minor EPR-active components in fulleride preparations. We now consider it the most likely explanation.

Some of the EPR characteristics for $[C_{120}O]^{n-}$ have been reported. Upon reduction at a potential known to produce bulk $[C_{120}O]^{2-}$, an EPR spectrum noted to have "a marked similarity to spectrum observed for C_{60}^{2-}" was recorded.[375] The main feature at 77 K (see Figure 20) was a narrow line doublet-type signal at $g = 2.0016$ with $\Delta H_{pp} = 1.1$ G. The signal was assigned to $[C_{120}O]^{2-}$ but, in the absence of quantification, this doublet-type signal could have arisen from an odd-electron species, $[C_{120}O]^-$ or $[C_{120}O]^{3-}$. It is possible that all even-numbered n in $[C_{120}O]^{n-}$ have only weak triplet-type signals or are EPR silent at low temperature. Since $C_{120}O$ is somewhat easier to reduce than C_{60}, a narrow EPR signal arising from $[C_{120}O]^-$ impurity should be present in under-reduced samples of C_{60} in accord with experiment.[116,117] At slight (one-electron) *over*-reduction of C_{60} samples, a new spike due to $[C_{120}O]^{3-}$ would be expected to replace that from the $[C_{120}O]^-$ ion. The signals from these two species could be sufficiently similar that their distinction might pass unnoticed or be ascribed
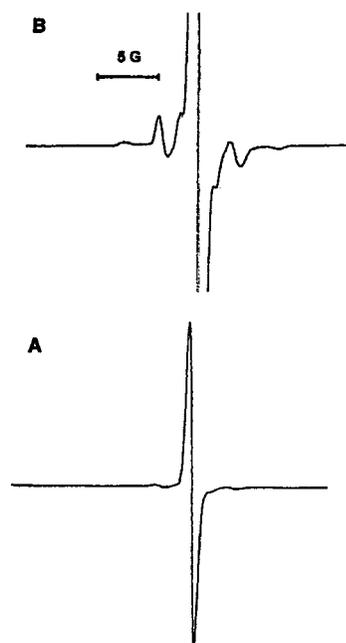
Figure 20. EPR spectrum of a sample of $C_{120}O$ reduced to the (−2) level (frozen *o*-dichlorobenzene at 77 K): (A) entire spectrum; (B) expansion magnifying the flanking triplet features. (Reprinted with permission from ref 375. Copyright 1996 American Chemical Society.)

to experimental error. The dominant feature of the EPR spectrum of the species reported after the bulk four-electron reduction of $C_{120}O$ is a new doublet-like signal at $g = 2.0025$ and $\Delta H_{pp} = 1.3$ G.[375] Instead of assigning this to the even-electron species $[C_{120}O]^{4-}$, it could arise from either $[C_{120}O]^{3-}$ or $[C_{120}O]^{5-}$. Since C_{60}^{2-} is EPR silent at low temperatures, a narrow signal from traces of $[C_{120}O]^{3-}$ or $[C_{120}O]^{5-}$ would become the major observable in solutions of C_{60}^{2-} which contained the impurity. Again, this is in accord with experiment (see Figure 22).[118] Sharp signals with $g = 2.0000-2.0020$ and $\Delta H_{pp} = 1-4$ G are observed for "C_{60}^{2-}".[338] The same logic can be applied to the C_{60}^{3-} ion. A spike is observed along with the broad signal and can be assigned to $[C_{120}O]^{5-}$ or $[C_{120}O]^{7-}$.

We have carried out preliminary experiments on $C_{120}O$ which support the above hypothesis.[376] The EPR spectrum of C_{60}^-, produced by reduction of C_{60} with cobaltocene or sodium/crown ether in the good glassing solvent 2-methyltetrahydrofuran, shows a minor narrow signal ($g = 2.0005$ (± 0.0002), $\Delta H_{pp} = 2$ G at 100 K) superimposed on the major signal of C_{60}^- ($g = 1.9977$ (± 0.0003), $\Delta H_{pp} = 30$ G at 100 K). Upon addition of $C_{120}O$, the only change is an increase in the relative intensity of the narrow signal. When pure $C_{120}O$ is independently reduced to $C_{120}O^-$ in an identical manner, the EPR spectrum shows *only* a narrow signal. Its g value and line width are *identical* to the narrow signal in reduced, off-the-shelf C_{60}. In addition, the characteristics of the signal in 2-methyltetrahydrofuran solvent lie comfortably in the range of g values and line widths reported for the sharp signal in C_{60}^- ($g = 1.9995-2.0012$, $\Delta H_{pp} = 0.10-3.5$ G).[338] This is compelling evidence that the "spike" in C_{60}^- is due to $C_{120}O$ impurity.

If $C_{120}O$ impurity, arising from the aerobic aging of C_{60} samples, is the source of spurious EPR signals in fullerides, then anaerobic experiments on freshly chromatographed samples of C_{60} should give rise to C_{60}^{n-} fullerides which are free of these signals. This seems to be the case in electrocrystallized phosphonium salts[184,185] and in $[CoCp_2][C_{60}]\cdot 2CS_2$,[40] where no spike is observed. The crystallization process may be assisting purity in these situations. We have only found one published solution spectrum that is apparently free of sharp signal, although it develops a spike immediately upon air exposure.[366] Indeed, it has been commonly observed that the sharp signal increases at the expense of the broad one upon standing.[133,345,366,377] This can be readily interpreted in terms of C_{60}^- being more easily oxidized than $C_{120}O^-$ to an EPR-silent species (C_{60}), even to the point that the spike is the only remaining trace signal after extensive aging in air.[345]

There are few data, if any, that cannot be explained by the $C_{120}O$ impurity hypothesis. Nevertheless, a cogent argument can be made that simple dimerization of C_{60} fullerides could give rise to the narrow EPR signals. Because it remains feasible and makes such an interesting intellectual exercise, we expound this theory in some detail in the following section, even though we favor the $C_{120}O$ impurity postulate in most, if not all, circumstances.

vii. The Dimer Postulate

The formation of C–C bonds in dimers or oligomers can be considered a special case of functionalization. The recent characterization of dimer and polymer phases of intercalated AC_{60} (A = alkali metal) and of neutral $(C_{60})_2$ itself has provided a sound basis for expectations of a related reactivity for discrete fullerides. In addition, $C_{59}N\cdot$ is isoelectronic with C_{60}^- and exists as the C–C bonded dimer $(C_{59}N)_2$.[378,379]

The rapid quench phases of KC_{60} and RbC_{60} contain $(C_{60})_2^{2-}$ ions with a single covalent bond like $(C_{59}N)_2$ (see Figure 21a).[22] The structural assignment is supported by vibrational[380] and ^{13}C NMR[328] spectroscopies and by theory.[381,382] On the other hand, the slow cooled phases of AC_{60} are polymeric and believed to have pairs of covalent bonds—the so-called [2+2] addition product.[23,157,383] Electrochemically produced LiC_{60} polymers are also believed to have this structure.[384] This linkage has been unambiguously established by Komatsu and co-workers for neutral $(C_{60})_2$ (see Figure 21b).[385] This remarkable dimer of C_{60} is quite stable at room temperature because of the high activation energy for making and breaking bonds in closed-shell molecules. By contrast, the making and breaking of bonds between C_{60}^- ions in AC_{60} compounds is facile. It is controlled by lattice energy effects and phase transformations which occur at temperatures as low as 220 K.[386] When $(C_{60})_2$ is electrochemically reduced, the voltammetric behavior is nearly indistinguishable from that of C_{60}.[385,387] This means that upon reduction, the dimer dissociates into monomers on the cyclic voltammetry time scale (seconds). Nevertheless, a small shoulder on the first reduction peak is consistent with $(C_{60})_2$ being slightly easier to reduce than C_{60} and/or with $(C_{60})_2^-$ having
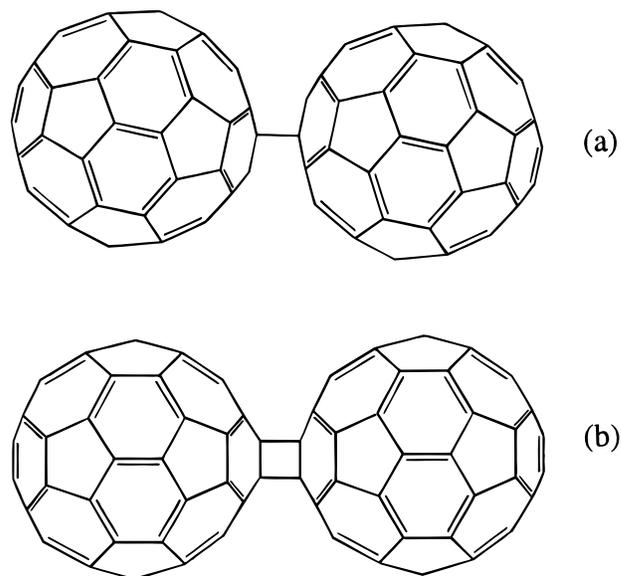
(a)

(b)

Figure 21. Structure of (a) the singly C–C bonded dimer of C_{60} in $(C_{60})_2^{n-}$ and (b) the [2+2] bonded dimer C_{120}.

a detectable lifetime. As outlined in the previous section, reduction of covalent dimers such as $C_{120}O$ can give rise to a sharp EPR signals of the type seen in C_{60}^- samples.

The above observations make a good case for proposing that discrete C_{60}^- ions could participate in a weak dimerization reaction (eq 2). Although the

$$2C_{60}^- \rightleftharpoons (C_{60})_2^{2-} \qquad (2)$$
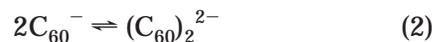
equilibrium is thermodynamically unfavorable, it should be established quickly at room temperature. This is supported by theory.[381,388] The dimeric dianion $(C_{60})_2^{2-}$ is diamagnetic in the rapid quench phases of RbC_{60} and KC_{60},[386,389] suggesting that it would also be diamagnetic and EPR silent as a discrete ion. Thus, the $(C_{60})_2^{2-}$ dimer itself is not considered a likely source of the sharp EPR signal. When an attempt was made to reconcile the concentrations of C_{60}^- solutions by EPR and NIR spectroscopies, there was always some deficit of spins in the EPR quantitation.[338] This is readily explained by the formation of significant amounts of the even-spin, EPR-silent dimer $(C_{60})_2^{2-}$.

The dimer proposal rests on the premise that sharp signals arise from dimers with an odd number of electrons. This could be the result of a small amount of disproportionation (eq 3) or, much more likely, imprecise stoichiometry of the reduction state. Under-

$$2(C_{60})_2^{2-} \rightleftharpoons (C_{60})_2^- + (C_{60})_2^{3-} \qquad (3)$$
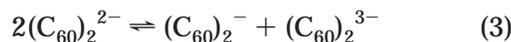
reduction of C_{60} would favor the presence of $(C_{60})_2^-$ (eq 4), and over-reduction would favor the presence of $(C_{60})_2^{3-}$ (eq 5), both of which are expected to have sharp EPR signals. C_{60} has been referred to as the

$$C_{60} + C_{60}^- \rightleftharpoons (C_{60})_2^- \qquad (4)$$

$$C_{60}^- + C_{60}^{2-} \rightleftharpoons (C_{60})_2^{3-} \qquad (5)$$
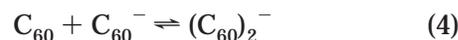
"electrophile par excellence".[162] With C_{60}^- as the

nucleophile, eq 4 is the natural combination of an electrophile and a nucleophile. Alternatively, the reaction can be viewed as C_{60} reacting with a radical. It is well-known as a radical scavenger.[390] Consideration of these equilibria explains why it would be so difficult to obtain samples that are free of the sharp signal. Nevertheless, one apparent case is with the electrodeposited salts [PPh$_4$]$_2$X[C$_{60}$] (X = Cl, I).[184,185] It is reasonable for a low-solubility lattice to be kinetically and thermodynamically selective for monomer. In solution, however, any reasonably finite value for the equilibrium constant of eq 2, coupled with Nernstian disproportionation and/or imprecise reduction stoichiometry (eqs 3, 4, and 5), would make the presence of some odd-electron dimer inevitable. The common observation that the sharp signal increases at the expense of the broad one upon standing could be explained in terms of preferential aerobic oxidation of the monomer and solid-state trapping of the dimer as EPR-active $(C_{60})_2{}^-$.
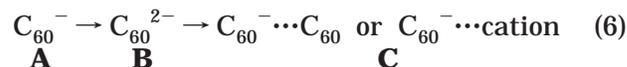
A number of workers have reported *two* sharp signals.[79,345,356,366] One explanation is a slight difference in the g values of solid and solution forms of $(C_{60})_2{}^-$ ions. Notably, two persistent sharp signals have yet to be reported in studies involving dilute solutions at equilibrium. The common use of toluene as a cosolvent in electrochemical studies, chosen to assist dissolving C_{60} prior to reduction, is not conducive to maintaining ions in solution. A second explanation is that the second sharp signal could arise from trapping of further reduction product, $(C_{60})_2{}^{3-}$. It is even conceivable that both $(C_{60})_2{}^-$ *and* $C_{120}O^-$ could be present, i.e., both the dimer postulate and the impurity postulate are invoked.

If dimerization of $C_{60}{}^-$ is facile in solution and only slightly thermodynamically unfavorable, it would be reasonable to expect that, on occasion, lattice energy would shift eqs 2 or 4 to the right-hand side and trap the dimer as the major or sole species in the solid state. This occurs in the rapid-quench, intercalated phases of AC_{60} but has yet to be established in discrete fulleride salts. Nevertheless, there are many observations that could be interpreted in these terms. Compton et al. have reported electrochemical data which indicates the formation of a salt of stoichiometry [NBu$_4{}^+$][C$_{60}$][C$_{60}{}^-$].[72,358] This could equally well be formulated as [NBu$_4{}^+$][(C$_{60}$)$_2{}^-$]. Selegue and coworkers have preliminary data that suggest a similar stoichiometry for decamethylmanganocenium salts.[121] Only a sharp signal EPR is reported in the solid state for a material of approximate composition [Mn(Cp*)$_2$]-[C$_{60}$][C$_{60}{}^-$]. Moriyama et al. have reported obtaining single crystals of a compound formulated as [Na-(THF)$_y{}^+$][(C$_{60}$)$_2{}^-$] but a detailed molecular structure has not been forthcoming.[173] Nevertheless, the lattice spacing of 9.93 Å is smaller than the fulleride van der Waals diameter (ca. 10.1 Å) so that C–C bonding is a possibility. The same authors have reported a related lithium salt whose EPR evolves anaerobically from a broad signal into two sharp signals.[174] The ^{13}C NMR spectrum shows a resonance with the unusual chemical shift of 162 ppm which we have suggested in Section VII.D might arise from the $(C_{60})_2{}^-$ ion. Preliminary results from Jones and Kad-

ish[133] suggest that with one particular tetraalkylammonium cation (hexyl), broad versus sharp EPR signals in isolated salts are dependent on the solvent used. Possibly, one form crystallizes in the $(C_{60})_2{}^{2-}$ ion and the EPR signal arises from some $(C_{60})_2{}^-$ ion.
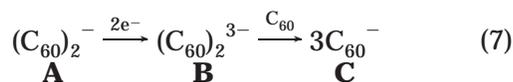
These indications of dimeric structure show the need for definitive characterization of materials by single-crystal X-ray diffraction. Elemental analysis alone has been unsuccessful in defining composition or assessing phase purity, at least in part because fullerenes and fullerides occlude solvents and organic impurities so readily, but the problem could be exacerbated if the facile equilibria of eqs 3–5 exist.

There are no sharp signals from well-characterized $C_{60}{}^-$ materials that cannot be rationalized by the dimer postulate *or* the $C_{120}O$ postulate. The most serious challenge comes from the work of Stasko and co-workers,[356,359,361,391] but even these data are readily re-interpreted in terms of either postulate. The time evolution of EPR signals from in situ reduction of C_{60} by a variety of methods is reported to give exclusively a narrow line width signal **A** ($g = 2.0000$, $\Delta H_{pp} = 0.9$ G). Upon further exposure to reducing agent, this transforms in seconds to an even narrower signal **B** at slightly higher g value ($g = 2.0006$, $\Delta H_{pp} = 0.35$ G) before giving rise to the familiar broad signal **C** ($g < 2.0000$, $\Delta H_{pp} > 30$ G). These signals have been assigned as follows:

$$C_{60}{}^- \rightarrow C_{60}{}^{2-} \rightarrow C_{60}{}^- \cdots C_{60} \text{ or } C_{60}{}^- \cdots \text{cation} \quad (6)$$
$$\;\;\textbf{A} \quad\quad\; \textbf{B} \quad\quad\quad\quad\; \textbf{C}$$

There are several reasons to suggest different assignments, not the least of which is that $C_{60}{}^{2-}$ is known to be EPR silent (except for an unrelated weak thermally populated triplet signal, see section IX.C).

Let us begin by reconsidering these results in terms of the dimer postulate where the following assignments could be made

$$(C_{60})_2{}^- \xrightarrow{2e^-} (C_{60})_2{}^{3-} \xrightarrow{C_{60}} 3C_{60}{}^- \quad (7)$$
$$\;\;\textbf{A} \quad\quad\quad\; \textbf{B} \quad\quad\quad\; \textbf{C}$$

The first point to note is that the room temperature data were gathered under conditions of relatively high signal-to-noise where the broad signal would be difficult to observe at low concentrations. This is also true for other studies which claim that only a sharp signal is observable.[340,392] Indeed, if the temperature is lowered, the superimposed broad signal **C** does become visible.[359] This is consistent with better signal-to-noise at low temperatures and possibly a slowing of the dimerization rate (eq 4). Stasko et al. note that the NIR spectrum of $C_{60}{}^-$ ($\lambda_{max} = 1075$ nm) appears simultaneously with EPR signal **A**, but there is no quantitative correspondence in the time evolution of the two measurements.[356,359] This again suggests that $C_{60}{}^-$ is present but undetected by EPR. Polar solvents such as acetonitrile or methanol are found to favor the formation of **A** over **C** but the lifetime of **A** becomes shorter. Polar solvents encourage aggregation or even precipitation of neutral C_{60} but facilitate the dissolution and dissociation of ions. $(C_{60})_2{}^-$ would be more easily formed initially as the

major observable but would dissociate faster. In pure toluene, where C_{60} is more likely to be truly dilute, the broad signal **C** is seen immediately.

Signal **B** could logically be ascribed to the *tri*anionic dimer $(C_{60})_2^{3-}$ since the *di*anionic form, $(C_{60})_2^{2-}$, is expected to be diamagnetic and therefore EPR silent. Signal **B** is a proven consecutive product of **A** and is favored by increasing exposure to reducing agent. The reducing agents used ($TiO_2/h\nu$, amperometric electrolysis and $Et_3N/h\nu/^3C_{60}$) are all strong enough to cause this three-electron reduction. The trianionic dimer would be a transient species because, upon diffusion, it would equilibrate with unreduced C_{60} and dissociate to give 3 equiv of C_{60}^- (signal **C**). The total yield of radicals **A** and **B** is estimated to be only ca. 5% of available C_{60}.

The other evidence suggesting that signal **B** could be ascribed to $(C_{60})_2^{3-}$ comes from a consideration of g values, line widths, and anisotropies. **B** has the same characteristics as the doublet signal seen as a minor component in samples of C_{60}^{2-}. In the framework of the dimer hypothesis, it too is logically ascribed to slight over-reduction and dimerization forming $(C_{60})_2^{3-}$. Compared to the "spike" in C_{60}^- samples, the sharp signal in C_{60}^{2-} has a higher g value and smaller line width,[118] just like **B** when compared to **A** under comparable conditions. Anisotropy, not unlike that seen in derivatized fullerides,[231] is observable in these signals at low temperatures.

The results of Stasko et al. can equally well be reinterpreted in terms of the $C_{120}O$ hypothesis. Species **A** is ascribed to $C_{120}O^-$ and species **B** to $C_{120}O^{3-}$. They are seen in the early stages of the reaction because $C_{120}O$ is easier to reduce than C_{60} and because their sharp signals have better signal-to-noise than the broad signal of C_{60}^-. Given the simplicity of this explanation, we prefer it to the dimer explanation. Either way, ascribing the narrow signal to C_{60}^- is untenable.

The dimer and $C_{120}O$ postulates also suggest a reexamination of the rather speculative proposal that triplet C_{60} disproportionates in toluene solution to C_{60}^+ and C_{60}^-. Yang and Huang recently studied the irradiation of C_{60} in the presence and absence of $[PPh_4^+][BPh_4^-]$ and observed persistent broad and sharp EPR signals following the production of transient $^3C_{60}$.[393] These were ascribed to C_{60}^- and C_{60}^+, respectively. The features of the sharp signal ($g = 2.0006$, $\Delta H_{pp} = 1.25$ G) are entirely consistent with $(C_{60})_2^-$ or $C_{120}O^-$ formation and, in fact, are rather different from those of C_{60}^+ (see section IX.G). This assignment also makes better chemical sense. Tetraphenylborate ion is a good electron donor,[173] and C_{60}^+ would not be a persistent species in its presence. Earlier studies, even in the absence of a added electron donor, found no evidence for C_{60}^+.[394]

Finally, it should be mentioned that dimerization (and oligomerization) might explain why, in general, endohedral metallofullerenes are so insoluble and so intractable. Since the metals that form endohedrals are electropositive, the carbon cages in $M@C_{2n}$ must have strong fulleride character. With the additional consideration of the internal effects of the metal cations, the tendency to form intermolecular C−C

bonds may be significantly greater than in metal-free fullerides. This seems to be the case for the insoluble endohedral fullerenes $Gd@C_{60}$ and $Gd@C_{74}$ which can be solubilized by reduction to anions.[24] Curiously, $M@C_{82}$ endohedrals are significantly more soluble and isolable than other $M@C_{2n}$. The answer to the intriguing question "Why?" may lie in a deeper understanding of dimerization and oligomerization in higher fullerides. This is one of the reasons for keeping the dimer postulate alive even though the $C_{120}O$ impurity postulate offers a more straightforward explanation for the spurious EPR signals of fullerides.

C. Features of the C_{60}^{2-} EPR Spectrum

There has been considerable controversy over the interpretation of the EPR signals found in samples containing the C_{60}^{2-} ion. With the benefit of hindsight, several factors can be seen to have contributed to this. The first was a counterintuitive ground state. Hund's rule leads to the expectation of a spin triplet ground state from the $(t_{1u})^2$ configuration, with or without a Jahn−Teller distortion, and the early observation of triplet EPR features cemented this incorrect impression. The second was an early lack of good quantitation of spin. It was some time before the observed signals were recognized to arise from just a small percentage of the sample. The third was confusion over the use of the words "paramagnetic" and "diamagnetic ground state". These were taken by some authors to be mutually exclusive terms. In fact, a molecule with a singlet ground state and a close-lying triplet excited state will have significantly detectable paramagnetism at ambient temperatures. This is the case with the C_{60}^{2-} ion.

The first report of EPR signals from C_{60}^{2-} was by Jones, Kadish, and co-workers for electrochemically generated material in benzonitrile.[53,179] Triplet features ($g = 2.001$, $2D \approx 28$ G) and doublet features ($g = 2.000$, $\Delta H_{pp} \approx 3$ G) were identified, suggesting a triplet ground state for C_{60}^{2-}, but these were otherwise not amenable to straightforward interpretation. Partly this was due to an accidental coincidence of the parallel portion of the triplet with the perpendicular portion of a second triplet identified later by Boyd, Reed, and co-workers[118] and partly it was the "problem of the spike". Figure 22 is representative of the signals observed in samples containing the C_{60}^{2-} ion.[107,118,179,347] The three signals are referred to as (a) the central line ($g \sim 2.001$, $\Delta H_{pp} = 1$−3 G), (b) the low-temperature triplet ($g \approx 2.0015$, $2D = 19$−29 G), and (c) the high-temperature triplet ($g \approx 2.001$, $2D = 58$−60 G). It is worth noting that half-field resonances, expected features of triplet state spectra,[179] have yet to be observed in any C_{60}^{2-} spectra.

Early spin density measurements by EPR[343,395] and magnetic susceptibility[21] indicated that the C_{60}^{2-} ion had a diamagnetic ground state, and this was confirmed by careful EPR quantitation.[347] Thus, the signals seen in samples of the C_{60}^{2-} ion arise from only a few percent of the sample.

The high-temperature triplet (c) is the only signal that can be ascribed to the discrete C_{60}^{2-} ion. Following the suggestion of Boyd, Reed, and co-work-
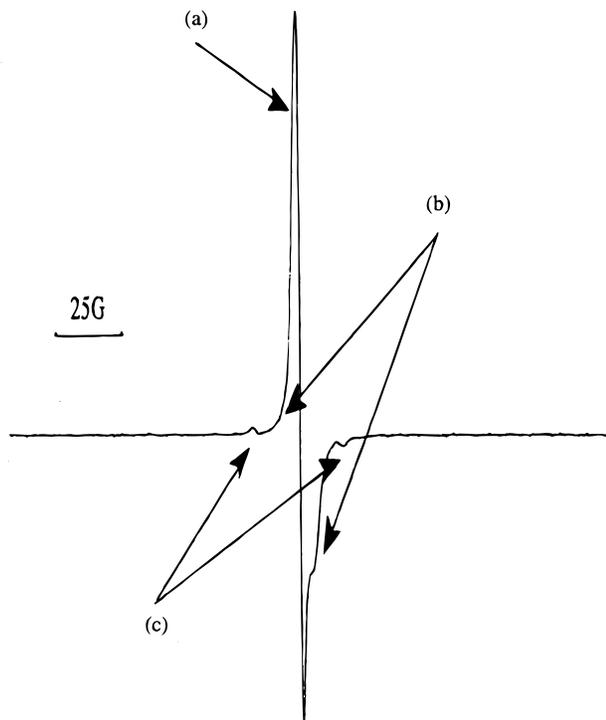
Figure 22. Representative EPR spectrum of signals seen in samples of C_{60} reduced to the (-2) level (frozen benzonitrile at 85 K): (a) central line; (b) low-temperature triplet; (c) high-temperature triplet. (Reprinted with permission from ref 118. Copyright 1995 American Chemical Society.)

ers,[118] Eaton[299] and Jones[357] independently showed that this signal is consistent with thermal occupation of an S = 1 state about 600 cm^{-1} above the ground state. This magnitude of the singlet−triplet separation is somewhat at odds with indications from magnetic susceptibility[21] and ^{13}C NMR spectroscopy.[118] A smaller gap, giving rise to more paramagnetism at ambient temperatures, is indicated by these complementary probes. Nevertheless, there is general agreement for the qualitative description of the discrete C_{60}^{2-} ion having a singlet ground state with one or more thermally accessible triplets. According to conditions, dynamic effects appear to collapse the triplet features of signal (c) at high temperatures to give a "doublet" Lorentzian-type line shape with $\Delta H_{pp} \approx 30$ G.[299]

The central line (a) is a doublet-type signal assignable to an S = 1/2 ground-state species.[299] It has variously been ascribed to C_{60}^-,[107,179] impurities or oligomers,[347] or a triplet with very small zero-field splitting.[118] It is now most logically assigned to $C_{120}O^{3-}$ or $C_{120}O^{5-}$ impurity. Alternatively, the formation of dimeric species is possible. These would be the $(C_{60})_2^{3-}$ ion in under-reduced samples and the $(C_{60})_2^{5-}$ ion in over-reduced samples. The g values and line widths are entirely consistent with those discussed above in section IX.B.vi for these species.

The origin of the low-temperature triplet, signal b, is most readily ascribed to an even-spin triplet state of $C_{120}O^{2-}$ or $C_{120}O^{4-}$, particularly because the smaller splitting compared to signal (c) is strongly suggestive of a species with its spin-parallel electrons more widely separated than in C_{60}^{2-}. The essential coin-

cidence of signal (b) with signals in electrochemically reduced samples of $C_{120}O$ ($g = 2.0037$, $2D \approx 18$ G)[375] lends further support to the $C_{120}O$ postulate.

D. Features of the C_{60}^{3-} EPR Spectrum

The similarities between the EPR spectra of the discrete C_{60}^- and C_{60}^{3-} ions are so strong that they could nearly be mistaken for each other. The physical and chemical interpretations are therefore the same. The signals differ only in g value (for example, 2.0025 for the C_{60}^{3-} ion compared to 1.9963 for C_{60}^- in DMSO)[118] and in the details of the temperature dependence of the broad signal line width.

Like C_{60}^-, the spectrum of C_{60}^{3-} shows a broad temperature-dependent signal with a superimposed "spike".[21,107,115,179,347] The broad signal is the major component and is ascribed to discrete C_{60}^{3-} ions having an S = 1/2 ground state. This state is counterintuitive for a $(t_{1u})^3$ configuration and was not anticipated from alkali metal doping studies. It is consistent with magnetic susceptibility measurements on isolated salts with large cations (see section VII).[21] The broad signal has been observed to become anisotropic at low temperatures, consistent with the freezing out of static Jahn−Teller-distorted structures.[347] It is said to be rhombic[338] as predicted by theory[226] but a detailed fit has not been presented. The details of the temperature dependence of the line width are consistent with the dynamic effects seen in C_{60}^-.[338,348]

By analogy to C_{60}^-, the minor sharp signal is assigned to $C_{120}O^{5-}$ in under-reduced samples or $C_{120}O^{7-}$ in over-reduced samples. Due to Coulombic considerations, with the large buildup of charge, the dimer postulate becomes increasingly less attractive. Nevertheless, polymer phases of A_3C_{60} (and A_4C_{60}) have been proposed.[396−398]

E. Features of C_{60}^{4-} and C_{60}^{5-} EPR Spectra

With its $(t_{1u})^4$ configuration, the C_{60}^{4-} ion is the "hole equivalent" of the C_{60}^{2-} ion. As such, it is expected to have a diamagnetic ground state and be EPR silent at low temperatures. This appears to be the case.[119] Like C_{60}^{2-}, however, minor sharp signals are observable. The dominant one can be ascribed to the $C_{120}O^{7-}$ ion. Also like C_{60}^{2-}, ^{13}C NMR spectroscopy indicates that C_{60}^{4-} has significant paramagnetism at room temperature.[119] This suggests the presence of a low-lying S = 1 excited state which might be EPR detectable.

There are no definitive reports on the EPR spectrum of the discrete C_{60}^{5-} ion. Close similarity with C_{60}^- can be expected because of the electron hole analogy to the $(t_{1u})^5$ configuration.

F. EPR Spectra of Higher Fullerides

The EPR study of the radical anions of higher fullerenes has received very little attention. This is beginning to change now that preparative amounts of C_{70}, C_{76}, C_{78}, C_{84}, and others are now commercially available.

The EPR spectrum of C_{70}^- [53,108,167,190,399] has remarkable line width features. In a well characterized

tetraphenylphosphonium double salt, $[PPh_4]_2[C_{70}][I]$, ΔH_{pp} is ca. 600 G at room temperature, reducing by orders of magnitude to ca. 2 G at liquid helium temperatures.[190] No theoretical analysis of this phenomenon is presently available but it does suggest that the features giving rise to the temperature-dependent line width of C_{60}^- are not only present in C_{70}^- but are amplified. This strongly implicates the importance of low-lying excited states. Electronically, C_{70} can perhaps be usefully viewed as a "permanently distorted" analogue of a Jahn−Teller-distorted C_{60}, with close-lying ^2A and ^2E states. Single-crystal EPR detects anisotropy with $g_\perp = 1.9996$ and $g_\| = 2.0150$ ($g_{av} = 2.0047$).[190]

C_{76}^- has a relatively narrow signal (0.5−3 G) with a g value very close to the free electron value (2.0023).[58] This is consistent with the low symmetry of this fulleride since the low g values of C_{60} fullerides are associated with spin−orbit coupling in the degenerate ground states.

C_{78} exists in two isomers whose monoanions are distinguishable by EPR spectroscopy. In frozen tetrachloroethane solution, the C_{2v} isomer has $g = 2.0021$ and $\Delta H_{pp} = 2.5$ G.[58] The D_3 isomer has $g = 2.0045$ and $\Delta H_{pp} = 2.9$ G.[58]

C_{84} also exists in two isomers which, when reduced to anions under selected solvent conditions, can be distinguished by EPR spectroscopy.[64] The most easily reduced isomer has D_{2d} symmetry, and the monoanion is characterized in frozen pyridine solution by a doublet-type signal with $g = 2.002$ and $\Delta H_{pp} = 2.3$ G. The dianion is believed to behave like C_{60}^{2-} with a singlet ground state and a thermally accessible triplet excited state. The triplet features ($2D = 26$ G) increase in intensity with temperature, consistent with a singlet−triplet gap of 0.022 eV (180 cm^{-1}). The trianion has doublet-type features with $g = 2.003$ and $\Delta H_{pp} = 3.9$ G. The EPR characteristics for all reduction states are consistent with a doubly degenerate ground state for the D_{2d} isomer of C_{84}.

The D_2 isomer of C_{84} has lower symmetry and a singly degenerate ground state. Consistent with this, the D_2 monoanion and trianion show narrower line width signals ($\Delta H_{pp} < 2$ G) than the D_{2d} isomer and the dianion is EPR silent.[64] The signals saturate more easily with microwave power, again consistent with lower electronic degeneracy.

One caveat is given with respect to the EPR spectra of reduced higher fullerenes. Higher fullerenes are typically more air sensitive than C_{60},[400] so the presence of impurities analogous to $C_{120}O$ is more likely. The possibility of spurious signals may be correspondingly higher when aged samples are used.

G. EPR Spectra of Fullerenium Cations

The extreme difficulty of generating fullerene cations as stable entities in condensed media has apparently made them inaccessible to even the highly adaptable technique of spectroelectrochemistry[401] and, until very recently, to synthetic methods as well. Nevertheless, there have been many reports of EPR signals ascribable to C_{60}^+. Most spectra arise from chemical or photochemical treatment of C_{60} under conditions where strongly oxidative chemistry is

Table 13. Reported EPR Data for C_{60} Radical Cations

generation method	g-value	line width (G)	ref
concentrated H_2SO_4	2.0030	2.5	105
fuming H_2SO_4	2.0030	0.2	105
FSO_3H/SbF_5	(not given)	7	208
HY zeolite	2.0033−2.0047	3−11	215
$C_{60}/h\nu$/solvent	2.0024	0.75	393
$C_{60}/h\nu/PPh_4^+BPh_4^-$/solvent	2.0006	1.25	393
$SbCl_5/CH_2Cl_2$	2.0030	1.5	108
Fe^{3+}/zeolite	2.0027	12	216
Ar_3N^+ synthesis: solid $[C_{60}][CB_{11}H_6Cl_6]$	2.0022	3	218
frozen ODCB solution of $[C_{60}][CB_{11}H_6Cl_6]$	2.002	8	218
photoinduced electron transfer	2.0021	0.8	203
fuming H_2SO_4 with 5% SO_2FCl (100 K)	(not given)	triplet species	209

reasonably proposed. The sensitivity of C_{60}^+ to subsequent reaction with nucleophiles can, however, leave doubt about whether the primary oxidation product has always been observed.

Table 13 summarizes the reports of EPR spectra ascribed to C_{60}^+. Data obtained on a preparative-scale sample in the form of the salt $[C_{60}^{\bullet+}]$-$[CB_{11}H_6Cl_6^-]$ suggest that those reports with g values in the range 2.0016−2.0033 and line widths of a few gauss are correctly assigned. Similar values are obtained for a well characterized salt of C_{76}^+ ($g = 2.0030$, $\Delta H_{pp} = 0.5$ G in frozen solution; $g = 2.0042$, $\Delta H_{pp} = 2.7$ G in the solid state).[30] Despite the existence of low-lying excited states and the requirement of a Jahn−Teller distortion, these parameters have none of the complexity seen of the EPR spectra of fulleride anions. With g values close to the free-electron value, they are not unlike the spectra of typical arene radical cations. EPR spectra are observed when C_{70} is treated with sulfuric acid. They have been assigned to C_{70}^+ and C_{140}^+ (two isomers), but in the absence of corroborating data these assignments must be considered very speculative.[402]

Besides doublet-like EPR spectra ascribable to C_{60}^+, there is one report of a triplet spectrum arising from C_{60} in fuming sulfuric acid.[209] This transient is presumed to arise from C_{60}^{2+} but corroborating evidence is lacking. Doublet and triplet spectra have also been obtained by dissolution of C_{120} and $C_{120}O$ in fuming sulfuric acid.[403]

X. Chemical Reactivity

A. Introduction

The reactivity of fulleride ions has four potential elements: (a) Brønsted basicity, (b) Lewis basicity or nucleophilicity, (c) electron transfer, and (d) radical reactivity. These terms can used to describe the overall stoichiometric result of a reaction and may not imply mechanism. In particular, fulleride reactivity can give the appearance of nucleophilic attack but may involve electron transfer steps. Indeed, given the facile stepwise redox behavior and, more importantly, the delocalized electronic structure of fullerides, one-

electron chemistry can be expected to predominate over nucleophilic chemistry. At a more intimate level of mechanism, the distinction between electron transfer and nucleophilic attack in the actual encounter event of a fulleride ion with an electrophile may become impossible. Nevertheless, useful reactivity classifications are becoming apparent for fullerides and for fullerenium cations.

The promise of fullerides for synthesis lies in their potential for selective functionalization in high yield. Functionalization reactions of fullerenes rarely proceed in better than 50% yield, and many addition reactions give a mixture of multiple addition products because different equivalent sites can react more or less independently. A redox reaction is typically quantitative, i.e., 100% yield, so charged fullerenes, particularly those with (−2) or (+2) charges, have the capacity for selective *mono*addition reactivity in high yield.

Any such functionalization with fullerides must be done with relatively strongly binding addends because, as a general observation, adducts of fullerenes are labilized by reduction. Metal−fullerene complexes tend to dissociate upon reduction.[40] This same property in methanofullerenes (the so-called retro-Bingel reaction) has been turned to advantage in the preparation of enantiomerically pure C_{76}[404] and isomerically pure C_{84}.[66] In certain cases, the addenda in bismethano[60]fullerenes "walk" around the sphere while in their fulleride form.[405] Interconversion of [5,6]-open fulleroids to [6,6]-closed methanofullerenes is promoted by fulleride formation.[406,407]

B. Fulleride Basicity

The basicity of the C_{60}^- and C_{60}^{2-} ions have been established by electrochemical methods in *o*-dichlorobenzene[365] and DMSO.[408] Contrary to the early indications,[367] the monoanion is a very weak base. In *o*-dichlorobenzene, the acidity of $C_{60}H^\bullet$ approaches that of dilute triflic acid. In DMSO, the pK_a of $C_{60}H^\bullet$ is estimated to be ca. 9, making it a slightly weaker acid than *p*-nitrobenzoic acid. When encapsulated in γ-cyclodextrin, the pK_a is about 4.5 in H_2O/propan-2-ol.[409] These measurements are consistent with reports that the synthesis[134] and EPR spectrum[175,299,362] of C_{60}^- are relatively insensitive to the presence of water. The weak basicity of C_{60}^- is probably best understood in terms of delocalization of electronic charge.[365] The formation of $C_{60}H^\bullet$ formally produces a carbon radical α to the site of protonation, and the energetic cost of this localization is high. There is no electrochemical evidence for the reasonable expectation of dimerization of $C_{60}H^\bullet$ radicals.[365]

With its additional charge, C_{60}^{2-} is a very strong base. The first and second pK_a values for its conjugate acid, H_2C_{60}, have been estimated at 4.7 and 16, respectively, in DMSO, making C_{60}^{2-} a 10^7 stronger base than C_{60}^-.[408] In *o*-dichlorobenzene, the estimate is lower, comparable to the benzoate ion,[365] but because of solvation energy differences and the unknown influence of traces of water, a detailed comparison of data is not warranted.

Strong acids reversibly protonate C_{60}^{2-} to give brown solutions of HC_{60}^-,[408] a species that can also be prepared by H^- addition to C_{60} using Li[Et$_3$BH].[163,410] Further protonation to give H_2C_{60} occurs to some extent, but the reactivity of the H_2C_{60}/HC_{60}^-/C_{60}^{2-} system is complex and accounts for the difficulty of isolating H_2C_{60} in bulk.[411]

Carbon-based acids can be deprotonated with C_{60}^{n-} ions (n = 1, 2, and 3 depending on C−H bond acidity)[412] (see section E below), and water is apparently a strong enough acid to protonate the C_{60}^{4-} ion, leading to oxidation of the fulleride.[119] The suggestion that C_{60}^{n-} with n > 6 are stable in DMSO solution[413] does not seem chemically reasonable. The basicity of highly charged fullerides (and hydrofulleride anions) underlies the success of acidic "dissolving metal" methods for synthesizing an extensive array of hydrofullerenes, from H_2C_{60} up to $H_{36}C_{60}$.[411]

C. Fulleride Nucleophilicity/Electron Transfer

An early report of unselective polymethylation of C_{60} with methyl iodide and lithium metal were suggestive of nucleophilic behavior of fullerides,[112] although alkylation might equally well have occurred via a series of methyl radical additions. Fullerenes are well recognized as excellent radical scavengers.[390] A report on the use of C_{60}^{n-} for the electrocatalytic debromination of alkyl bromides[414] indicated good electron transfer reactivity of fulleride ions and hinted at alkylation utility. The dimethylation of C_{60} to form 1,2- and 1,4-dimethyl[60]fullerene in 44% overall yield was first achieved by Jones, Kadish, and co-workers.[415] The reaction of methyl iodide proceeds via the C_{60}^{2-} ion, not the C_{60}^- ion. Fukuzumi et al.[416] have shown that the first step in the alkylation of C_{60}^{2-} with methyl iodide (and a variety of other alkyl halides) proceeds via electron transfer followed by fast radical trapping (eq 8). This step in the mecha-

$$C_{60}^{2-} + RX \rightarrow [C_{60}^- \cdots R^\bullet \cdots X^-] \rightarrow RC_{60}^- + X^- \quad (8)$$

nism is consistent with rate studies that show little dependence on the steric effect of R and correlate with known electron transfer rates to RX. The second step, however, appears to be a nucleophilic attack since the rate is highly sensitive to increasing steric effects and rates correlate with other S_N2 reactions (eq 9). Unlike C_{60}^{2-} with its delocalized charge, the

$$RC_{60}^- + RX \rightarrow R_2C_{60} + X^- \quad (9)$$

alkylated fullerene RC_{60}^- can behave as a nucleophile because alkylation localizes the negative at the 2 (and 4) carbon atoms.[171] For bulky R (e.g., benzyl, *tert*-butyl), the alkylated fullerene can be intercepted with a different alkyl halide or an acid to prepare unsymmetrical $RR'C_{60}$ and RHC_{60} derivatives.[416,417] Other methods involving solid-state Zn/C_{60}/RBr mixtures[418] or Na$_2$[Fe(CO)$_4$][149] have also been developed. The 1,4 isomer appears to be the thermodynamic product, and a crystal structure of the dibenzyl adduct of C_{60} has been determined.[171] A useful variant of this reaction is the synthesis of methanofullerenes from α,α-dibromides and diiodides.[419] Similarly, α,ω-diiodides form 1,2-cycloalkane adducts.[420] Reaction of uninegative C_{60}^- is reported to occur with a highly

electron-deficient dibromide such as 1,2-dibromotetrachloroethane.[414] The trinegative C_{60}^{3-} is reported to activate aryl halides[421] and form adducts with 1,3 and 1,5 α,ω-dibromides.[422,423] Tetrasubstituted derivatives of the type R_4C_{60} are accessible upon further reduction.[235] Further studies are discussed below with respect to electrocatalytic uses of fullerides. From a study of their electron transfer rates, C_{60}^- and C_{60}^{2-} have been usefully compared to the *p*-benzoquinone/semiquinone one-electron couple.[424] Electron self-exchange rates in fullerides are fast because the t_{1u} electrons are delocalized and accessible and because nuclear reorganization is small.[199]

In summary, because of delocalized charge there is little evidence for classical nucleophilic behavior of fullerides, although this does not thwart the addition of electrophiles via electron transfer pathways. Only when carbanion character is concentrated at a particular carbon atom via monofunctionalization is nucleophilic character manifest. Two more interesting examples of this are the postulated role of $C_{60}(CN)^-$ adding to C_{60} en route to C_{120}[385] and HC_{60}^- adding to cationic alkene transition metal complexes to form σ-bonded fulleroalkylmetal complexes.[410] An alternative mechanism for the formation of C_{120} from C_{60} in the presence of CN^- is the direct reaction of C_{60}^- with C_{60}.[425] This reactivity finds C_{60}^- expressing simultaneous nucleophile/radical addition behavior, brought about by pressure in the solid state. Another interesting observation is that electroreduction of fullerene epoxides such as $C_{60}O$ leads to redox-active polymers that adhere to a variety of electrode surfaces.[374,426] The chemistry is believed to involve $C_{60}O^{2-}$ attack on the carbon framework of neighboring $C_{60}O$ molecules.

The reaction of dioxygen with fullerides has not received much study. Typically, the uninegative C_{60}^- ion is simply oxidized back to C_{60}. The mechanism is believed to involve initial electron transfer to form superoxide ion (eq 10) because the rate is qualitatively dependent on the ability of the solvent and counterion to stabilize the charge on the O_2^- ion [Cr-(TPP)$^+$ > H$^+$ > Na$^+$ > Co(Cp)$_2^+$].[116,117] Equation 10

$$C_{60}^- + O_2 \rightarrow C_{60} + O_2^- \qquad (10)$$
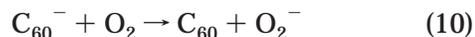
is thermodynamically disfavored by ca. 0.4 V in low dielectric media but may become favored in highly protic media.[409] Equation 10 will only proceed if superoxide is irreversibly removed from the system, presumably via proton or metal ion catalyzed disproportionation to peroxide and dioxygen. It has been proposed that O_2 can add to C_{60}^- to form stable adducts.[366] This seems doubtful in the light of the above studies and the observation that $C_{60}O^-$ rapidly deoxygenates to give C_{60}.[374] It is possible, however, that peroxide is formed as a byproduct of simple reduction and this could attack C_{60} to form oxygenated products such as fullerene epoxides or fullerenols.

Reaction of oxygen with C_{60}^{2-} is reported to give oxygenated products with mass spectrometrically identified formulas $C_{60}O_x$ ($x = 1-4$)[367] and NIR bands between 900 and 1000 nm[243] but other studies report

simple oxidation.[175] By contrast, aerobic exposure of C_{70}^{2-} is reported to give $C_{70}(OH)_2$.[135] Electroreduction of C_{60} to the (−2) level in the presence of oxygen gives a conducting polymeric film.[427] Evidence has also been found for substantial degradation of the C_{60} framework when prolonged electrolysis was carried out in the presence of O_2.[367]

This area is in need of further study, particularly since neutral C_{60} has very recently been found to react with O_2 to form $C_{120}O$.[375] Such studies are also relevant to the effects of oxygen on the photoconductivity of fullerene films[428] and the reactivity of O_2 with fullerenes in general.[429,430]

D. Fullerides as Intermediates

Fulleride(−1) ions are putative or proven intermediates in a variety of addition reactions of fullerenes. These can be thermal or photochemical. Involvement in thermal reactions occurs because fullerenes are easily reduced. Involvement in photochemical reactions occurs because the triplet states of fullerenes are even stronger reducing agents, $^3C_{60}$ exceeding the reduction potential of C_{60} by 1.5 V.[431] The intermediacy of fulleride(−1) ions are often inferred from comparative kinetic data since the characteristics of an electron transfer reaction are readily recognized. In other cases fullerides can be detected spectroscopically. However, these studies typically tell us more about the reactivity of $^3C_{60}$ than of C_{60}^- because, apart from final product analysis, subsequent reactivity of the intermediate is usually less accessible to kinetic or spectroscopic detection. Nevertheless, there are good indications that C_{60}^- acts as a base and a radical. Some examples of these reactivities follow.

A typical thermal reaction believed to proceed via C_{60}^- is the addition of a primary amine to C_{60} (eq 11).[161−163,431,432] Simple monoaddition is rare. The

$$C_{60} + H_2NR \rightarrow [C_{60}{}^{\bullet-}\cdots H_2NR^{\bullet+}] \rightarrow$$
$$1,2\text{-}H(NHR)C_{60} \quad (11)$$
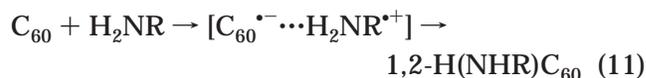
reaction typically continues until six amines have been added, presumably via the same mechanism. Collapse of the radical ion pair intermediate is presumed to involve radical coupling reactivity but probably also involves a component of Brønsted acid/base chemistry. Additions of less reactive tertiary amines can be photochemically promoted via the triplet state of C_{60}, but the same radical ion pair is believed to be an intermediate.[433] With triethylamine, a C−C bonded adduct can be trapped via subsequent intramolecular reactivity.[434]

The photoinduced addition of ketene silyl acetals to $^3C_{60}$ has been shown to proceed via C_{60}^- formation.[435] Subsequent radical coupling of the ion pair is believed to lead to C−C bond formation (Scheme 1), and similar reactivity is reported with allylic stannanes to add allylic groups to C_{60}.[436]

Similar chemistry with aryl thiols invokes both basicity and radical coupling reactivities for C_{60}^- (Scheme 2).[437]

Scheme 1. Proposed Mechanism for the Photoinduced Addition of Ketene Silyl Acetals to $^3C_{60}$ via C_{60}^- Formation[435]
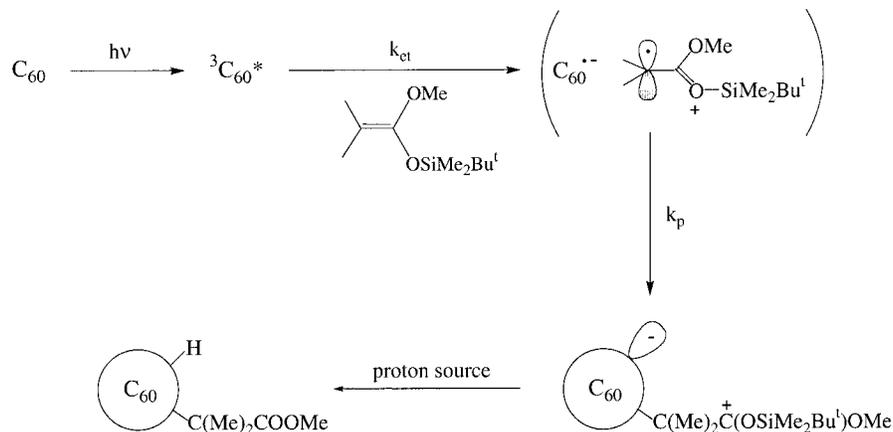
Scheme 2. Proposed Mechanism for the Photoinduced Addition of p-Aminophenyl Thiol to C_{60} via C_{60}^- [437]
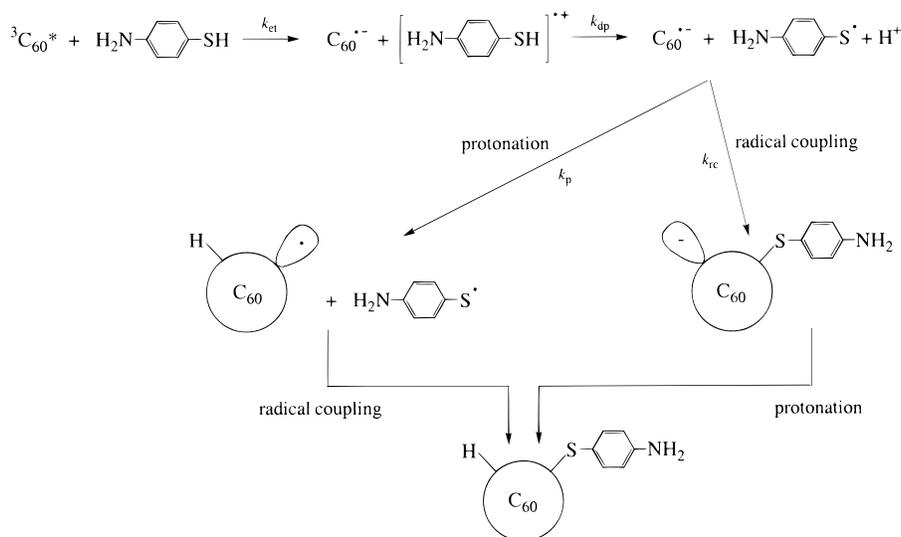
Triplet C_{70} shows greater efficiency than triplet C_{60} in photoinduced electron transfer reactivity.[438]

E. Fullerides as Catalysts

Closely related to the formation of adducts via fulleride formation is the use of fullerides as electroreduction catalysts. Early electron transfer studies of fullerides and alkyl bromides[414] suggested that the charge on the fulleride has the effect of tuning the reductant to suit its substrate. Preparative-scale studies have been carried out with *vic*-dihalides, reducing them to olefins.[439] The catalysts are C_{60}^{2-} or C_{60}^{3-} depending on the reduction potential of the substrate. Similar analytical-scale studies with α,ω-dihaloalkanes produce alkanes, alkenes, and monohaloalkanes with C_{60} fullerides[422] being more active and less prone to adduct formation than those of C_{70}.[423,440] While electroreduction activity has concentrated on alkyl halides, there is one report of C_{60}^{3-} mediating the formation of biphenyl from benzene.[441] Further study of these types of reactions could be illuminating with regard to the interplay of basicity, electron transfer, and radical behavior of fullerides as catalysts.

The basicity of fullerides has been exploited to promote base-catalyzed nucleophilic addition reac-

tions.[412] Electrogenerated C_{60}^- deprotonates ethyl nitroacetate and promotes double addition to ethyl acrylate and acetonitrile. The more basic C_{60}^{2-} ion deprotonates nitromethane, diethyl malonate, and octane thiol to promote a variety of addition reactions. The highly basic C_{60}^{3-} ion promotes the addition of pyrrole to acrylonitrile and the reaction of diethyl benzylphosphonate with benzaldehyde.

F. Fullerides as Ligands

There are a large number of fullerene complexes of low-valent transition metals.[40] Although the fullerene is acting as an acceptor in these complexes, bonding is best viewed in terms of π-back-donation into olefinic bonds of the neutral fullerene rather than coordination of a fulleride. Nevertheless, electroreduction of fullerene complexes typically allows the observation of radical anion complexes, at least on the time scale of cyclic voltammetry.[442,443] Because three reduction waves can frequently be observed, equally spaced but displaced by ca. 0.2 V from those of C_{60}, the added electron can safely be assumed to reside predominantly on the fullerene. Thus, these species are formally fulleride complexes. In most cases the fulleride anion dissociates readily, particularly as successive reductions take place, but ex-

Scheme 3. Reaction Products from the Photoinduced Electron Transfer Reaction of C_{60} with Aldehydes, Ethers, and Primary Alcohols Believed To Proceed via H-Atom Abstraction by C_{60}^+ [447]
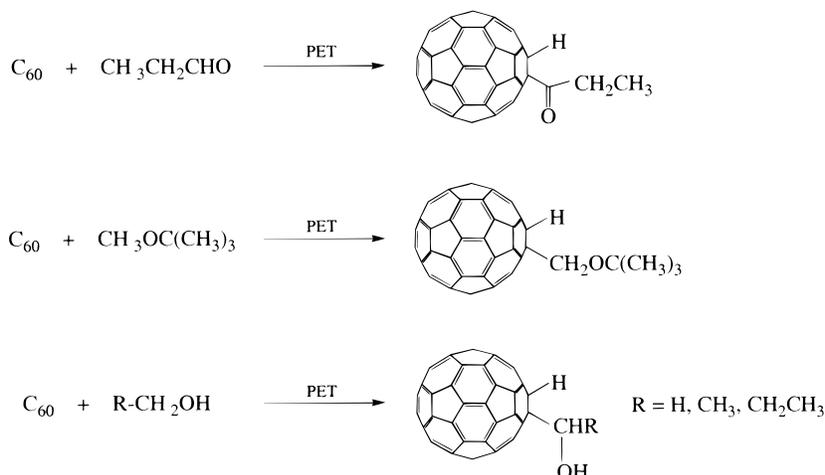
amples of relatively stable radical anion complexes such as $[W(C_{60}{}^{\bullet})(CO)_3(diphos)]^-$ have been reported.[444,445]

Electrochemical reduction of $Pd(PHCN)_2Cl_2/C_{60}$ in toluene/acetonitrile produces black polymeric films which are believed to have the composition $C_{60}Pd_x$.[446] Related chemistry occurs with low-valent Rh and Ir complexes. These films are conducting in the potential range of their preparation, indicating they are capable of supporting fulleride character and electron transfer activity.

G. Fullerenium Cations

The very high oxidation potential of the C_{60}/C_{60}^+ couple makes C_{60}^+ an extremely strong one-electron oxidant and a potentially very strong electrophile. However, the best established reaction pathway for $C_{60}{}^{\bullet+}$ in solution is H-atom abstraction. Using photooxidant methodology presumed to generate transient C_{60}^+, reactions with ethers, aldehydes, and alcohols have been shown to produce $1,2\text{-}H(R)C_{60}$ derivatives in modest isolated yields (Scheme 3).[447]

These results are consistent with earlier analytical-scale studies by Schuster and Wilson on the addition of hydrocarbons to a derivatized C_{60} cation, detected by mass spectrometry.[448] Similar multiple addition products with alcohols were originally interpreted as O-bonded adducts arising from nucleophilic addition[448] but have since been recognized as C-bonded species.[449] Mattay and co-workers have recently extended their PET studies of Scheme 3 to include H-atom abstraction from dimethylformamide, propionic acid, methylformate, ethylene glycol, and further ethers and alcohols.[450] In each case, 1-hydro-2-(C-bonded addend)fullerenes are formed, in 2−30% isolated yields. The formation of carbon-bonded adducts rather than the anticipated O-bonded products of nucleophilic addition in Scheme 3 is mechanistically significant. It suggests H-atom abstraction followed by rapid radical trapping. This reactivity is somewhat reminiscent of the $HO^{\bullet}$ radical but $C_{60}{}^{\bullet+}$ must be less reactive than the hydroxyl radical because $C_{60}{}^{\bullet+}$ can be isolated as a stable salt (see section III.C). Mattay and co-workers propose the

Scheme 4. Proposed Mechanism for the Photoinduced Electron Transfer Reaction of C_{60} with H-Atom Donor Organic Molecules[450]
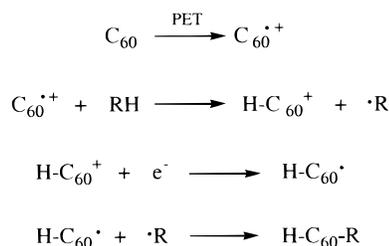
mechanism outlined in Scheme 4.[450] Evidence suggests that H abstraction (step 2) occurs from O−H bonds rather than C−H bonds, even though the latter are weaker. The association of the substrate with $C_{60}{}^{\bullet+}$ in the activated complex apparently favors separation of an O-centered radical $R^{\bullet}$ which rearranges to a C-centered radical before recombination with $^{\bullet}C_{60}H$ in step 4. There is some evidence from pulse radiolytic generation that C_{60}^+ can react with C_{60} to form the dimer $(C_{60})_2{}^+$.[197]

While the solution-phase chemistry of C_{60}^+ is poorly developed, its gas-phase chemistry has received considerable attention.[33] Adduct formation with strongly basic amines, $[C_{60} \leftarrow NR_3]^{\bullet+}{}_{(g)}$ gives manifestation of electrophilic character.[451] Polyunsaturated hydrocarbons react to give carbon-bonded radical cation adducts,[452] but on the whole, $C_{60}^+{}_{(g)}$ is not considered a particularly reactive species.

The irreversibility of the second oxidation wave of in the solution voltammetry of C_{60} indicates that $C_{60}{}^{2+}$ is an exceedingly reactive species. Solvents and electrolytes with sufficiently low nucleophilicity and oxidation resistance and dry enough to be unreactive toward $C_{60}{}^{2+}$ have yet to be found. On the other hand, the gas-phase chemistry of $C_{60}{}^{2+}$ and even more highly charged fullerenium ions has been well developed.[33] Acid/base chemistry typical of a strongly electrophilic behavior is observed in the formation of $[C_{60} \leftarrow Donor]^{2+}{}_{(g)}$ adducts with a wide variety N- and O-atom donors.[453] Electron transfer begins to compete with adduct formation in reactions with unsaturated hydrocarbons and $C_{60}{}^{2+}$ has also been shown to be a

gas-phase initiator of ethylene oxide polymerization.[454]

There is a fairly extensive electrophilic addition chemistry of fullerenes,[455] some of which may proceed through (a) fullerene radical cation intermediates or (b) cationic fullerene adducts formed by addition of an electrophile (e.g., Br^+ etc.). Mechanisms of the former type have been proposed to account for the formation of alkoxylated and phenylated C_{60} derivatives when alcohols and benzene are added, respectively, to C_{60} in oxidizing superacid media (HF/ SbF_5).[208] However, the process could equally well be a Brønsted[456] or Lewis[455] acid catalyzed process. Sulfur trioxide is believed to add successively to C_{60} via radical cations to give a polysultonated product.[210] Nitronium ion (NO_2^+) has been proposed to add to C_{60} to give cationic intermediates that can be quenched with water to give fullerenols,[457] but the process could equally well in involve $NO_2^•$ radicals.[458] This work highlights the difficulty of separating redox processes from acid-catalyzed processes (Brønsted *or* Lewis) in oxidizing superacid media.

The first definitive characterization of a cationic fullerene with formal addition of an electrophile has very recently been reported with chloroalkyl ions of the type RC_{60}^+ (R = $-CHCl_2$, $-CCl_2CH_2Cl$).[459] They were formed by the treatment of hydroxy chloroalkane adducts $(OH)(R)C_{60}$ with triflic acid and are presumptive intermediates in the $AlCl_3$ catalyzed addition of chloroalkanes to C_{60}. This work presages the isolation of further RC_{60}^+ cations and their use in chemical synthesis. Radical cations of hexachlorinated [60]fullerene[460] and spin-paired carbocations of pentaphenylated [60]fullerene[461] add to the growing dimension of cationic fullerene chemistry.

XI. Conclusions and Future Directions

Nine years into the macroscopic exploration of fullerene chemistry, much has been learned about the fundamental chemistry of fulleride anions. Reactivity patterns are emerging but have yet to be widely exploited. By contrast, condensed-phase fullerenium cation chemistry is at a very primitive level of development. Overall, perhaps it is fair to say that most of the easy experiments have been done. However, because of the subtlety of Jahn−Teller effects and impurity effects, unsolved problems and limits to our knowledge are revealed in almost every aspect of the physical characterization of discrete fullerene ions.

By reviewing and analyzing the entire literature on the EPR spectra of fullerides, we have come up with a new explanation for the mysterious sharp signals seen as minor components in most spectra (section IX.B.vi). If this "$C_{120}O$ impurity postulate" holds up to more detailed experimental verification, the warning issued by Taylor regarding fullerene purity should be taken seriously in future fullerene research.[400]

We began this review with the thesis that the electronic structure of discrete fulleride ions ought to be the preferred point of departure for understanding the extended properties of metal-intercalated fullerides. Since metallic and superconducting behavior is a property highly specific for A_3C_{60} fullerides of precise stoichiometry[14,462] (it is not observed in A_2C_{60} or A_4C_{60} compounds), an explanation in terms of the electronic properties of the individual C_{60}^{n-} ions would seem to be demanded. The breakdown of simple band theory in the extended systems of A_xC_{60} fullerides must surely be related to the "memory" that individual C_{60}^{n-} ions retain of their discrete ion character. It is probably no accident that K_4C_{60} is a semiconductor with a band gap of ca. $450 \, cm^{-1}$ (50 meV)[463] and the discrete C_{60}^{4-} ion is a Jahn−Teller-distorted ion with a likely similar singlet−triplet gap.[119] The distinguishing feature of the all-important C_{60}^{3-} ion in discrete form is a *pseudo*-Jahn−Teller distortion and a likely small *doublet−quartet* gap. We are unaware of any explanation for superconductivity that makes an explicit connection between such vibronically induced on-ball spin pairing and inter-ball Cooper pairing. We hope that this review will stimulate further experimental and theoretical exploration along these lines.

In the gas phase, odd-electron fullerene ions must be truly dynamic Jahn−Teller systems, undergoing essentially barrierless fluxionality between symmetry-equivalent distorted structures (pseudorotation). How much of this behavior is maintained in condensed media and whether the predominant distortion in the various ions has D_{5d}, D_{3d}, D_{2h}, or lower symmetry remains to be established.[262] Condensed media can trap "snapshots" of these distortions in discrete fulleride ions revealing intrinsic ellipsoidal excursions from pseudo-O_h symmetry, but the observed environmental variations suggest there are many wells on a shallow potential energy surface. The accumulation of more data is necessary to map out this surface. Theory challenges experiment in this area,[226,227,246,464,465] and the simultaneous application of a variety of complementary physical probes on well characterized compounds will be necessary to resolve ambiguities and avoid overgeneralizations. This need is well illustrated by considering the history of C_{60}^{2-} whose electronic structure could not be understood until a wide diversity of measurements (EPR, magnetic susceptibility, X-ray, NMR, etc.) were made on well characterized samples.

Heterofullerenes [e.g., $(C_{59}N)_2$],[378,379] endohedral fullerenes[466,467] (particularly the long sought $M@C_{60}$), organofunctionalized fullerenes, and solubilized single-walled nanotubes[468] are likely growth areas for creative synthetic chemistry. All will have extensive redox chemistries with similarities to and differences from familiar fullerenes. Fullerides have higher second-order hyperpolarizabilities than fullerenes, making them superior candidates for nonlinear optical materials.[469−471] Enhanced photoluminescence from fullerides[472] is another property, among many,[45,151,473] that can be envisioned to lead to material science applications.[48] After a period of very intense publication activity, fullerene research can now profit from a period of less frenetic exploration, confident that there are decades worth of interesting phenomena and applications to be discovered. The model of ferrocene as a redox-active chromophore with a 48-year history of sustained interest and more

than 35 years before commercial use (glucose electrodes[474] and cationic group 4 metallocene catalysts for alkene polymerization[475]) should be remembered. The 1985 disclosure that a new form of elemental carbon was always there, waiting to be unearthed by curious researchers, only underscores the potential of discoveries yet to be made.

XII. Acknowledgments

XIII. References

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