Surface-Enhanced Raman Spectroscopy of
Electroactive Films of C₆₀ and an Ir-C₆₀ Complex on Gold:
Symmetry Lowering, Electron Localization, and Countercation Effects

by

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Abstract

Surface-enhanced Raman (SER) spectra are reported for thin films of C_{60} and (η^5-C_5H_7)Ir(CO)(η^2-C_60) on gold electrodes in acetonitrile. The latter spectra display the hallmarks of vibrational symmetry lowering for C_{60} arising from metal coordination, involving splitting of the normally degenerate H_6 modes and the appearance of vibrationally forbidden bands. Only a milder selection rule relaxation is observed for SERS of uncoordinated C_{60}. Electroreduction of both C_{60} and the Ir-C_{60} complex yielded similar frequency downshifts in the A_2 pentagonal pinch mode, indicating that electron addition to the latter is fullerene localized. These spectral shifts are sensitive to the nature of the countercation.
Among the numerous chemical and physical properties of buckminsterfullerene, C₆₀, that have come under recent scrutiny[1,2], those associated with electron addition have attracted particular interest. The various reduced states thus formed have been characterized in solution[3], as electroactive films[4], and as solid-state charge-transfer salts displaying ferromagnetic[5] and also superconducting[6] behavior. Allied with these activities have been the syntheses of C₆₀ coordination compounds, enabling the electronic and other consequences of metal attachment to be explored[7].

Vibrational spectroscopies provide a powerful means of examining the electronic and structural perturbations thereby induced upon the fullerene cage. For example, transition-metal binding yields dramatic changes in the normal Raman spectra arising from symmetry lowering[8]. Significant Raman band splittings as well as frequency downshifts are observed upon electroreducing thin C₆₀ films on gold, consistent with a diminution of molecular symmetry caused by electron addition[9]. Of general significance in this context is the sensitivity of the C₆₀ vibrational properties to environmental perturbations, either separately or together, brought about by metal coordination and electron addition. The Illinois group has recently characterized a particularly stable metal-C₆₀ complex, consisting of a (η⁵-C₆H₇)Ir(CO) moiety bound to C₆₀ in an η² fashion[10]. Moreover, the stepwise two-electron reduction of the complex in solution appears to be primarily C₆₀-localized on the basis of the relatively small downshift in the carbonyl stretching frequency observed by infrared spectroelectrochemistry[11,12].

As demonstrated in several recent reports[9,13-15], surface-enhanced Raman scattering (SERS) provides a useful means by which fullerene vibrational spectra can be obtained with high sensitivity. Furthermore, time-resolved SERS in electrochemical environments offers the opportunity of preparing reduced
fullerene films in a uniquely controllable fashion[9]. We report herein SER spectra obtained for \( C_{60} \) in comparison with \( (\eta^5-C_9H_7)Ir(CO)(\eta^2-C_{60}) \) as insoluble thin films on gold in acetonitrile. The observed spectral differences enable a distinction to be drawn between the relaxation of the usual Raman selection rules (i.e. appearance of Raman-forbidden bands) commonly observed in SERS and the symmetry lowering arising from metal coordination. The spectral consequencies of electroreduction of these films as a function of the supporting electrolyte cation (and hence the fulleride countercation) are also presented. Acetonitrile solvent was chosen partly because of its large polarizable potential range, enabling the fullerene films to readily be electroreduced. Besides confirming the fullerene-localized nature of electron addition in the above \( Ir-C_{60} \) complex, the findings provide an assessment of the combined effects of molecular asymmetry and the countercation upon the fulleride vibrational properties.

**Experimental**

Most details of the Raman spectroscopy arrangement, consisting of a SPEX Model 1877 spectrometer coupled to a Photometrics PM 512 CCD detector, are given in refs. 16 and 17. Laser excitation was a Kr\(^+\) laser operated at 647 nm with ca 20 mW power on the sample. The acquisition time for each spectrum was typically 8s; spectral sequencies were also obtained during voltammetric potential excursions where appropriate. The gold electrode, 4 mm in diameter sheathed in Teflon, was rendered SERS-active by means of the oxidation-reduction procedure described in ref. 18.

The solid \( C_{60} \) and \( (\eta^5-C_9H_7)Ir(CO)(\eta^2-C_{60}) \) complex (hereafter referred to as "\( Ir-C_{60} \)") were prepared and purified according to procedures given in ref. 19 and 10 respectively. Acetonitrile was distilled over \( CaI_2 \) prior to use. The \( LiClO_4, NaClO_4, \) and \( KPF_6 \) were recrystallized from water and stored in a desiccator while
not in use. Tetraethylammonium and Tetrabutylammonium perchlorates (TEAP, TBAP) were recrystallized twice from ethanol and water, respectively. Tetraphenylarsonium chloride (Ph$_4$AsCl, Eastern Chemical Corporation) was used as received. The C$_{60}$ and Ir-C$_{60}$ films on gold were prepared as in ref. 9. The average film thickness ranged typically from 2 to 10 equivalent monolayers, so that SERS provides the overwhelming contribution to the observed Raman spectra.

**Results and Discussion**

As already noted, Raman-forbidden bands are often observed for adsorbed symmetric molecules in SERS[20]. The mechanisms responsible for this "selection-rule relaxation" may well originate from effects other than the well-known "symmetry lowering", i.e. reduction in the molecular point-group symmetry, which may be anticipated if the adsorbate is bound rigidly to the metal surface[20]. A clearcut experimental differentiation between these two alternatives is not often forthcoming. However, the comparison of SER spectra for C$_{60}$ and the Ir-C$_{60}$ complex provides an unusual opportunity to test this distinction since only the latter system would necessarily be expected to exhibit the hallmarks of symmetry lowering.

Figures 1A and 2A display typical SER spectra obtained for films of C$_{60}$ and Ir-C$_{60}$, respectively, on gold in acetonitrile at 0 V vs. ferrocenium-ferrocene (Fc$^+$/0). The frequency range shown, ca 200-1600 cm$^{-1}$, is divided into two segments since the spectra recorded using the multichannel CCD detector were limited to increments of ca 600 cm$^{-1}$ in order to obtain satisfactory frequency resolution. Two of us have previously reported spectra similar to Figure 1A[9], although the present data exhibit higher signal-to-noise. The various band frequencies obtained for such spectra are summarized in Table I, along with the band assignments. The latter are obtained for C$_{60}$ by comparison with published normal Raman spectra[21,22].
Several features of these spectra are noteworthy here. As reported earlier[9], the SER frequencies and relative intensities seen for the C\textsubscript{60} films, most prominently the environment-sensitive "pentagonal pinch" A\textsubscript{g} mode, do not differ greatly from those observed in the normal Raman spectra for bulk-phase C\textsubscript{60}. This indicates that the chemical interaction of C\textsubscript{60} with the gold surface encountered here is relatively weak. Nevertheless, in addition to the 10 Raman-active modes, the four normally Raman-forbidden yet infrared-active modes are also observed in the SER spectra. Such selection-rule relaxation is, as already mentioned, a common feature of SER spectra.

The form of the corresponding Ir-C\textsubscript{60} spectrum, however, is clearly very different. Most obviously, many more intense bands are apparent for Ir-C\textsubscript{60} in comparison with C\textsubscript{60}. A partial assignment of these features can be made by comparison with the published normal Raman spectra for \eta\textsuperscript{2} complexes of Pt and Pd with C\textsubscript{60}[8]. Interestingly, the band frequencies for Ir-C\textsubscript{60} generally match closely those observed for the Pt- and Pd-C\textsubscript{60} complexes. Most of the additional Raman bands arising in the latter systems can be ascribed clearly to loss of vibrational degeneracy associated with a lowering of the C\textsubscript{60} molecular symmetry from I\textsubscript{h} to C\textsubscript{2}. Thus the H\textsubscript{g} modes, which are fivefold degenerate in free C\textsubscript{60} and thereby yield only single SERS bands for the C\textsubscript{60} films, are split into several distinguishable features in the corresponding Ir-C\textsubscript{60} spectrum. This is most clearly evident for the H\textsubscript{g} mode appearing at 774 cm\textsuperscript{-1} for C\textsubscript{60}, in that four additional bands appear for Ir-C\textsubscript{60} in the frequency range 744-790 cm\textsuperscript{-1} (Table I).

Some other bands are apparent in the Ir-C\textsubscript{60} SER spectra, for example those at 950 and 965 cm\textsuperscript{-1}, which are unlikely to be assignable to such split degenerate modes. By comparison with the spectra reported in ref. 9, these features can be attributed to normally forbidden modes which also become Raman-active by virtue of symmetry lowering. As for the split-degeneracy bands, these additional
features present for Ir-C$_{60}$ are not evident in the corresponding C$_{60}$ SER spectra. A SERS study of ultrathin (≤ few monolayer) C$_{60}$ films on gold, copper, and silver in vacuum[15] as well as a related study on silver[14] report substantial (up to 28 cm$^{-1}$) downshifts of the A$_g$ frequency from the bulk-phase value, 1467 cm$^{-1}$. This contrasts the small (6 cm$^{-1}$) downshift observed for the present C$_{60}$ films (Table I), and suggests that the fullerene films in refs. 14 and 15 experience more pronounced interaction with the metal surface. Consistent with this, a pair of seemingly Raman-forbidden bands at 948 and 971 cm$^{-1}$ are also reported in ref. 14. Apparently, then, such stronger C$_{60}$-metal surface interactions can also result in symmetry lowering.

Nevertheless, the present results allow a unusually clearcut distinction to be made between the milder selection-rule relaxation observed here for SERS of C$_{60}$ and the more dramatic effects of symmetry lowering as found for metal-C$_{60}$ complexes. The former is limited to the appearance of otherwise only infrared-active features in the Raman spectra, no loss of degeneracy of either the Raman or infrared-active modes being obtained. Coordination of C$_{60}$ to a metal atom, however, yields both strong satellite bands from the loss of degeneracy and the appearance of "vibrationally silent" modes, consistent with full-fledged symmetry lowering. These effects are observed similarly in both the bulk-phase (normal Raman)[8] or interfacial (SERS) environments. The present observations for C$_{60}$ are in harmony with the arguments of Moskovits and coworkers, who note that otherwise Raman-inactive bands can appear in SER spectra as a consequence of the inhomogeneity of the electromagnetic field near the metal surface[19]. Significantly, this effect does not require that the adsorbate interact significantly with the metal, and can therefore account for the appearance of additional modes without significant frequency shifts or loss of vibrational degeneracy. An additional source of selection rule relaxation may arise from the
large (and variable) static electric field present at the metal–electrolyte interface, which can act to create a significant dipole moment in highly polarizable molecules such as $C_{60}$.

As noted in ref. 9, sweeping the potential (at 10 mV s$^{-1}$) of the gold electrode in acetonitrile (containing 0.1M TBAP) to ca. -1.2 V vs. $Fc^+/0$, corresponding to the first voltammetric reduction wave where $C_{60}$ is formed[4], yields noticeable changes in the SER spectra of $C_{60}$ films. Figure 1B shows a typical SER spectrum obtained in this manner, at -1.2 V; the peak frequencies are listed in the far right-hand column in Table I. In particular, the pentagonal pinch $A_5$ mode is seen to be downshifted significantly, from 1461 to 1443 cm$^{-1}$, and the $H_6$ bands appearing at 712 and 774 cm$^{-1}$ for $C_{60}$ are both markedly intensified and split into two components upon reduction to form $C_{60}$. The latter effect can be understood in terms of Jahn–Teller distortions in the monoanion. Thus theoretical calculations predict that addition of one electron into the empty $t_{1u}$ orbital to form $C_{60}$ splits the degeneracy of the filled $e_g/h_g$ orbital[22,23], thereby accounting at least qualitatively for the "symmetry-lowering" effect observed for the $H_6$ vibrations.

The SER spectra for the Ir–$C_{60}$ films are also affected by sweeping the electrode potential to more negative values, again in acetonitrile containing 0.1 M TBAP. Voltammograms obtained simultaneously show a clearcut reduction wave, also at about -1.2 V vs $Fc^+/0$. The SER spectra exhibit significant changes by this point; a typical spectrum for reduced Ir–$C_{60}$ thus obtained is shown in Figure 2B for comparison with that for the unreduced film in Figure 2A. The band frequencies for the former are listed in the far left-hand column of Table I. Similarly to $C_{60}$[9], the latter spectrum can be regenerated by returning the electrode potential to 0 V vs. $Fc^+/0$, albeit with some intensity loss due probably to partial film dissolution.
Broadly speaking, electroreduction of \( \text{Ir-C}_60 \) is seen to yield significant broadening of most of the SER features. Interpretation of these effects, however, is not straightforward. Of interest here is the behavior of the pentagonal pinch \( A_5 \) mode which, as expected, appears as a single band in \( \text{Ir-C}_60 \) as well as for \( C_60 \). Significantly, this band undergoes a similar downshift, from 1459 to 1442 cm\(^{-1}\), upon electroreduction of \( \text{Ir-C}_60 \) as noted above for \( C_60 \) (Table I). This finding is consistent with the one-electron reduction of \( \text{Ir-C}_60 \) being localized chiefly on the fullerene ligand. As mentioned above, the same conclusion was reached for the solution-phase electroreduction of \( \text{Ir-C}_60 \) on the basis of the relatively small (12 cm\(^{-1}\)) downshift observed for the carbonyl (\( \nu_{\text{co}} \)) stretching band. Indeed, the present SER spectra for \( \text{Ir-C}_60 \) exhibit a weak \( \nu_{\text{co}} \) feature at 1993 cm\(^{-1}\), which is downshifted only slightly (\( \leq 5 \) cm\(^{-1}\)) upon film electroreduction.

Attempts were made to characterize the spectral consequencies of the second reduction step for the \( \text{Ir-C}_60 \) film anticipated on the basis of the solution-phase behavior. However, only ill-defined and highly irreversible voltammetric waves, (at ca -1.5 V) were obtained, along with broad and weak spectral features (cf behavior of \( C_60 \)[9]).

Potential-dependent SER spectra encompassing the first electroreduction step were also obtained for \( C_60 \) and \( \text{Ir-C}_60 \) films in acetonitrile containing supporting electrolytes other than TBAP in order to characterize the spectral consequencies of altering the fulleride countercation. Figure 3 shows SER spectra obtained in the 1100-1600 cm\(^{-1}\) range for reduced \( C_60 \) at -1.2 V vs. \( \text{Fe}^{+7/0} \) in 0.1 M salts of various cations, as indicated. (The bottom spectrum is for unreduced \( C_60 \).) The spectra for \( C_60^- \) are seen to be markedly sensitive to the countercation, in particular the shape as well as the frequency of the pentagonal pinch \( A_5 \) band. (The \( H_5 \) modes, especially those at lower frequencies, are
affected less by the nature of the electrolyte. This point can be discerned by comparing the spectra for $C_{60}$ in Fig. 1B and C, obtained in 0.1 M TBAP and 0.1 M NaClO$_4$, respectively.) The voltammograms for film reduction and reoxidation obtained under these NaClO$_4$ conditions are strongly dependent upon the electrolyte counterion[4].

The frequency downshifts, $\Delta \nu(A_8)$, observed for the six supporting electrolyte cations examined here are summarized in Table II. The $\Delta \nu(A_8)$ values range from $6 \text{ cm}^{-1}$ for the larger counterion Ph$_4$As$^+$ (Ph = phenyl) to $30 \text{ cm}^{-1}$ for Li$. The films formed in tetraalkylammonium electrolytes, such as TBAP considered above, are known to consist of $C_{60}[28,29]$. However, alkali metal-doped fullerides exhibit different stoichiometries, corresponding to fulleride oxidation states from $-1$ to $-6$. Also included in Table II are Raman $\Delta \nu(A_8)$ values reported for corresponding bulk-phase fullerides of known stoichiometry (the Roman numerals given in parenthesis refer to the fulleride oxidation state).

Comparing the latter $\Delta \nu(A_8)$ values with those obtained here provides information on the likely stoichiometry of our fulleride films. Thus it appears that $K_3C_{60}$ (i.e. $C_{60}^2$) is being formed electrochemically in acetonitrile in the presence of 0.1 M KPF$_6$. Although bulk-phase lithium fullerides have yet to be characterized by Raman spectroscopy, we infer by comparison with $\Delta \nu(A_8)$ values for Na$_6C_{60}$ and K$_6C_{60}$ that the $30 \text{ cm}^{-1}$ downshift observed here in the presence of 0.1 M LiClO$_4$ signals the formation of Li$_6C_{60}$. Also of interest are the larger $\Delta \nu(A_8)$ values obtained in TBA$^+$ and TEA$^+$ ($18 \text{ cm}^{-1}$) compared with Ph$_4$As$^+$ ($6 \text{ cm}^{-1}$). These differences are consistent with the larger perturbation upon $C_{60}$ anticipated for fulleride lattices containing the smaller tetraalkylammonium counterions, of comparable size to $C_{60}$. Indeed, a similarly small ($7 \text{ cm}^{-1}$) value of $\Delta \nu(A_8)$ to that observed here for the Ph$_4$As$^+$ fulleride has been observed recently for $C_{60}$ in toluene/acetonitrile solution containing TBA$^+$[30], supporting the
expectation that the effect of the solid-state countercation will be minimized by employing large cations. A comparable cation-dependent behavior of the $A_1$ mode to that shown for $C_{60}$ in Figure 3 was also observed for $\text{Ir-C}_{60}$. This finding also indicates again that the reduction of $\text{Ir-C}_{60}$ is largely fullerene-localized.

The present results demonstrate the virtues of SERS for exploring the vibrational properties of fullerenes and their derivatives. They also further illustrate the value of surface electrochemistry in providing a controllable route for both the preparation and the characterization of fullerene derivatives in the solid state.
Acknowledgments

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References


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(30) M.L. McGlashen, M.E. Blackwood, Jr., and T.G. Spiro, submitted for publication.
**TABLE I** Observed SERS Bands for Films of Ir-Coordinated and Uncoordinated C₆₀ on Gold in Acetonitrile with 0.1 M TBAP, in Neutral and Monoanion (i.e. Reduced) Forms.

<table>
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<tr>
<th>(n²-C₉H₇)Ir(CO)(n²-C₆₀⁻)</th>
<th>freq, cm⁻¹</th>
<th>C₆₀⁻</th>
<th>freq, cm⁻¹</th>
<th>Assignment</th>
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<td>freq, cm⁻¹</td>
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<td>261 (m)</td>
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<td>267 (m)</td>
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<td>288 (m)</td>
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<td>340 (m)</td>
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<td>377 (s)</td>
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<td>400 (w)</td>
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<td>1563 (s)</td>
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*a bands due to C₉H₇ ligand.
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<tr>
<th>Cation</th>
<th>$A_g(C_{60})^a$ (cm$^{-1}$)</th>
<th>$A_g$ shift$^a$ (cm$^{-1}$)</th>
<th>$A_g$ shift$^b$ (cm$^{-1}$)</th>
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<td>1431</td>
<td>30</td>
<td>24 (-VI)$^c$</td>
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<tr>
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<td>15</td>
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<td>12 (-III), 29 (-VI)$^e$</td>
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<td>Ph$_4$A$_8$</td>
<td>1456</td>
<td>6</td>
<td>6 (-I)$^d$</td>
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$^a$ Experimental data for $C_{60}^{-}$ films on gold, obtained in this work.

$^b$ Raman shifts obtained for solid-state cation-doped fullerides, from references cited (values in parenthesis refer to fulleride oxidation state).

$^c$ Ref. 25

$^d$ Ref. 26

$^e$ Ref. 27
Figure Captions

Figure 1

SER spectra of $C_{60}$ film on gold in acetonitrile. (A) For neutral $C_{60}$, in 0.1 M TBAP at 0.0 V vs ferrocenium/ferrocene (Fc$^{+}$/Fc). (B) For $C_{60}$ monoanion in 0.1 M TBAP, at -1.2 V. (C) For $C_{60}$ monoanion in 0.1 M NaClO$_4$, at -1.2 V.

Figure 2

As for Figure 1 A and B, but for Ir-$C_{60}$.

Figure 3

SER spectra of reduced $C_{60}$ films obtained at -1.2 V vs. Fc$^{+}$/Fc on gold in acetonitrile with different 0.1 M electrolytes, containing cations as indicated. The bottom spectrum refers to unreduced $C_{60}$ obtained at 0.0 V.
Fig. 1

Wavenumbers (cm$^{-1}$)

Photon Counts

Na
C
TBA B
TBA A

1400 1200 1000 800 600 400
Fig. 2
Figure 3 shows spectra labeled with different materials: Li, Na, K, TEA, TBA, and Ph₄As, across wavenumbers (cm⁻¹). The X-axis represents wavenumbers from 1100 to 1600 cm⁻¹, while the Y-axis seems to denote photon counts.