

AD-A265 934



2

OFFICE OF NAVAL RESEARCH

Contract No. N00014-91-J-1409

Technical Report No. 136

Surface-Enhanced Raman Spectroscopy of
Electroactive Films of C_{60} and an Ir- C_{60} Complex on Gold:
Symmetry Lowering, Electron Localization, and Counteraction Effects

by

Yun Zhang, Yuhua Du, John R. Shapley, and Michael J. Weaver

Prepared for Publication

in

Chemical Physical Letters

Department of Chemistry

Purdue University

West Lafayette, IN 47907-1393

DTIC
ELECTE
JUN 17 1993
S B D

April 1993

Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

* This document has been approved for public release and sale; its distribution is unlimited.

93-13650



93 6 1 0 9

Abstract

Surface-enhanced Raman (SER) spectra are reported for thin films of C_{60} and $(\eta^5-C_9H_7)Ir(CO)(\eta^2-C_{60})$ 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_g 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_g pentagonal pinch mode, indicating that electron addition to the latter is fullerene localized. These spectral shifts are sensitive to the nature of the counteraction.

DTIC QUALITY INSPECTED 1

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Among the numerous chemical and physical properties of buckminsterfullerene, C_{60} , 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 C_{60} 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 C_{60} 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 C_{60} 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- C_{60} complex, consisting of a $(\eta^5-C_9H_7)Ir(CO)$ moiety bound to C_{60} in an η^2 fashion[10]. Moreover, the stepwise two-electron reduction of the complex in solution appears to be primarily C_{60} -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 consequences of electroreduction of these films as a function of the supporting electrolyte cation (and hence the fulleride counteranion) 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 counteranion 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 sequences 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 CaH_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_4AsCl , 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 ($\text{Fc}^{+/0}$). The frequency range shown, ca $200\text{--}1600\text{ cm}^{-1}$, 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_{60} films, most prominently the environment-sensitive "pentagonal pinch" A_g mode, do not differ greatly from those observed in the normal Raman spectra for bulk-phase C_{60} . This indicates that the chemical interaction of C_{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_{60} spectrum, however, is clearly very different. Most obviously, many more intense bands are apparent for Ir- C_{60} in comparison with C_{60} . A partial assignment of these features can be made by comparison with the published normal Raman spectra for η^2 complexes of Pt and Pd with C_{60} [8]. Interestingly, the band frequencies for Ir- C_{60} generally match closely those observed for the Pt- and Pd- C_{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_{60} molecular symmetry from I_h to C_s . Thus the H_g modes, which are fivefold degenerate in free C_{60} and thereby yield only single SERS bands for the C_{60} films, are split into several distinguishable features in the corresponding Ir- C_{60} spectrum. This is most clearly evident for the H_g mode appearing at 774 cm^{-1} for C_{60} , in that four additional bands appear for Ir- C_{60} in the frequency range $744\text{--}790\text{ cm}^{-1}$ (Table I).

Some other bands are apparent in the Ir- C_{60} SER spectra, for example those at 950 and 965 cm^{-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-C₆₀ are not evident in the corresponding C₆₀ SER spectra. A SERS study of ultrathin ($\leq$ few monolayer) C₆₀ 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 C₆₀ 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 C₆₀-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 C₆₀ and the more dramatic effects of symmetry lowering as found for metal-C₆₀ 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 C₆₀ 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 C₆₀ 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 0.1 M TBAP) to ca -1.2 V vs. $\text{Fc}^{+/0}$, 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_g mode is seen to be downshifted significantly, from 1461 to 1443 cm^{-1} , and the H_g 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 g_g/h_g orbital[22,23], thereby accounting at least qualitatively for the "symmetry-lowering" effect observed for the H_g 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 $\text{Fc}^{+/0}$. 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. $\text{Fc}^{+/0}$, albeit with some intensity loss due probably to partial film dissolution.

Broadly speaking, electroreduction of Ir-C₆₀ 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_g mode which, as expected, appears as a single band in Ir-C₆₀ as well as for C₆₀. Significantly, this band undergoes a similar downshift, from 1459 to 1442 cm⁻¹, upon electroreduction of Ir-C₆₀ as noted above for C₆₀ (Table I). This finding is consistent with the one-electron reduction of Ir-C₆₀ being localized chiefly on the fullerene ligand. As mentioned above, the same conclusion was reached for the solution-phase electroreduction of Ir-C₆₀ on the basis of the relatively small (12 cm⁻¹) downshift observed for the carbonyl (ν_{CO}) stretching band. Indeed, the present SER spectra for Ir-C₆₀ exhibit a weak ν_{CO} feature at 1993 cm⁻¹, which is downshifted only slightly (≤ 5 cm⁻¹) upon film electroreduction.

Attempts were made to characterize the spectral consequences of the second reduction step for the Ir-C₆₀ 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 C₆₀[9]).

Potential-dependent SER spectra encompassing the first electroreduction step were also obtained for C₆₀ and Ir-C₆₀ films in acetonitrile containing supporting electrolytes other than TBAP in order to characterize the spectral consequences of altering the fulleride counteranion. Figure 3 shows SER spectra obtained in the 1100-1600 cm⁻¹ range for reduced C₆₀ at -1.2 V vs. Fc^{+/0} in 0.1 M salts of various cations, as indicated. (The bottom spectrum is for unreduced C₆₀.) The spectra for C₆₀⁻ are seen to be markedly sensitive to the counteranion, in particular the shape as well as the frequency of the pentagonal pinch A_g band. (The H_g 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 counteranion[4].

The frequency downshifts, $\Delta\nu(A_g)$, observed for the six supporting electrolyte cations examined here are summarized in Table II. The $\Delta\nu(A_g)$ values range from 6 cm^{-1} for the larger counteranion Ph_4As^+ (Ph = phenyl) to 30 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 $\Delta\nu(A_g)$ 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 $\Delta\nu(A_g)$ 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}^{3-}) 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 $\Delta\nu(A_g)$ values for Na_6C_{60} and K_6C_{60} that the 30 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 $\Delta\nu(A_g)$ values obtained in TBA^+ and TEA^+ (18 cm^{-1}) compared with Ph_4As^+ (6 cm^{-1}). These differences are consistent with the larger perturbation upon C_{60}^- anticipated for fulleride lattices containing the smaller tetraalkylammonium counteranions, of comparable size to C_{60} . Indeed, a similarly small (7 cm^{-1}) value of $\Delta\nu(A_g)$ to that observed here for the Ph_4As^+ 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_g mode to that shown for C_{60} in Figure 3 was also observed for $Ir-C_{60}$. This finding also indicates again that the reduction of $Ir-C_{60}$ 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

We are grateful to Prof. Bart Kahr for providing a sample of purified C_{60} , and to Dr. Xiaoping Gao for helpful discussions. This work is supported by the Office of Naval Research (to MJW) and the National Science Foundation (CHM 91-19510, to MJW and DMR 89-20538, at University of Illinois Materials Research Laboratory, to JRS).

References

- (1) For example: H.W. Kroto, A.W. Allaf, and S.P. Balm, *Chem. Rev.*, 91 (1991), 1213; R.F. Curl and R.E. Smalley, *Scientific American*, October 1991, p. 54.
- (2) See representative overviews in *Acc. Chem. Res.*, March issue, 1992.
- (3) D. Dubois, G. Moninot, W. Kutner, M.T. Jones, and K.M. Kadish, *J. Phys. Chem.*, 96 (1992), 7137.
- (4) C. Jehoulet, Y.S. Obeng, Y-T. Kim, F. Shou, and A.J. Bard, *J. Am. Chem. Soc.*, 114 (1992), 4237.
- (5) P-M. Allemand, K.C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Grüner, and J.D. Thompson, *Science*, 253 (1991), 301.
- (6) For a review, see R.C. Haddon, *Acc. Chem. Res.*, 25 (1992), 127.
- (7) P.J. Fajan, J.C. Calabrese, and B. Malone, *Acc. Chem. Res.*, 25 (1992), 134.
- (8) B. Chase and P.J. Fagan, *J. Am. Chem. Soc.*, 114 (1992), 2252.
- (9) Y. Zhang, G. Edens, and M.J. Weaver, *J. Am. Chem. Soc.*, 113 (1991), 9395.
- (10) R.S. Koeford, M.F. Hudgens, and J.R. Shapley, *J. Am. Chem. Soc.*, 113 (1991), 8957.
- (11) R.S. Koeford, C. Xu, W. Lu, J.R. Shapley, M.G. Hill, and K.R. Mann, *J. Phys. Chem.*, 96 (1992), 2930.
- (12) Y. Zhu, R.S. Koefod, C. Devadoss, J.R. Shapley, and G.B. Schuster, *Inorg. Chem.*, 31 (1992), 3505.
- (13) R.L. Garrell, T.M. Herne, C.A. Szafranski, F. Diederich, F. Ettl, and R.L. Whetten, *J. Am. Chem. Soc.*, 113 (1991), 6302.
- (14) K.L. Akers, L.M. Cousins, and M. Moskovits, *Chem. Phys. Lett.*, 190 (1992), 614.
- (15) S.J. Chase, W.S. Basca, M. G, L.J. Pelione, and J.S. Lannin, *Phys. Rev. B.*, 46 (1992), 7873.
- (16) T. Wilke, X. Gao, C.G. Takoudis, and M.J. Weaver, *J. Catal.*, 130 (1991), 62.
- (17) X. Gao, Y. Zhang, and M.J. Weaver, *Langmuir*, 8 (1992), 668.

- (18) P. Gao, D. Gosztola, L.-W. H. Leung, and M.J. Weaver, *J. Electroanal. Chem.*, 233 (1987), 211.
- (19) R.E. Haufler, J. Conceicao, L.P.F. Chibante, Y. Chai, N.E. Byrne, S. Flanagan, M.M. Haley, S.C. O'Brien, C. Pan, Z. Xiao, W.E. Billups, M.A. Cuifolina, R.H. Hauge, J.L. Margrave, L.J. Wilson, R.F. Curl, and R.E. Smalley, *J. Phys. Chem.*, 94 (1990), 8634.
- (20) For example, (a) M. Moskovits, D.P. DiLella, and K.J. Maynard, *Langmuir*, 4 (1988), 67; (b) J.K. Sass, H. Neff, M. Moskovits, and S. Holloway, *J. Phys. Chem.*, 85 (1981), 621; (c) M. Moskovitz, *Rev. Mod. Phys.*, 57 (1985), 783.
- (21) D.S. Bethune, G. Meijer, W.C. Tang, H.J. Rosen, W.G. Golden, H. Seki, C.A. Brown, and M.S. DeVries, *Chem. Phys. Lett.*, 179 (1991), 181.
- (22) T.J. Dennis, J.P. Hare, H.W. Kroto, R. Taylor, D.R.M. Walton, and P.J. Hendra, *Spectrochimica: Acta*, 47A (1991), 1289.
- (23) V. DeCoulon, J.L. Martins, and F. Reuse, *Phys. Rev. B.*, 45 (1992), 13671.
- (24) (a) R.C. Haddon, L.E. Brus, and K. Raghavachari, *Chem. Phys. Lett.*, 125 (1986), 459; (b) F. Negri, G. Orlandi, and F. Zerhetto, *Chem Phys. Lett.*, 144 (1988), 31.
- (25) S.J. Duclos, R.C. Haddon, S. Glarum, A.F. Hebard, and K.B. Lyons, *Science*, 254 (1991), 1625.
- (26) R.C. Haddon, A.F. Hebard, M.J. Rosscinsky, D.W. Murphy, S.J. Suclos, K.B. Lyons, B. Miller, J.M. Rosamilia, R.M. Fleming, A.R. Kortan, S.H. Glarum, A.V. Makhija, A.J. Muller, R.H. Eick, S.M. Zahurak, R. Tycko, G. Dabbagh, and F.A. Thiel, *Nature*, 350 (1991), 320.
- (27) T. Pilcher, M. Matus, J. Kürti, and H. Kuzman, *Phys. Rev. B.*, 45 (1992), 13844.
- (28) W. Koh, D. Dubois, W. Kutner, M.T. Jones, and K.M. Kadish, *J. Phys. Chem*, 96 (1992), 4163.
- (29) R.G. Compton, R.A. Spackman, R.G. Wellington, M.L.H. Green, and J. Turner, *J. Electroanal. Chem.*, 327 (1992), 337.
- (30) M.L. McClashen, M.E. Blackwood, Jr., and T.G. Spiro, submitted for publication.

TABLE I Observed SERS Bands for Films of Ir-Coordinated and Uncoordinated C_{60} on Gold in Acetonitrile with 0.1 M TBAP, in Neutral and Monoanion (i.e. Reduced) Forms.

$(\eta^5-C_9H_7)Ir(CO)(\eta^2-C_{60})^-$ freq, cm^{-1}	$(\eta^5-C_9H_7)Ir(CO)(\eta^2-C_{60})$ freq, cm^{-1}	C_{60} freq, cm^{-1}	C_{60}^- freq, cm^{-1}	Assignment
261 (m)	262 (m)			
267 (m)	267 (m)	273 (s) . .	270 (s)	H_g
288 (m)	287 (s)			
340 (m)	348 (m)			
377 (s)	375 (s)			
400 (w)	401 (w)			
430 (m)	430 (m)	426 (m) . .	420 (s)	H_g
444 (m)	445 (m)			
489 (m)	490 (m)	492 (s) . .	489 (s)	A_g
504 (m)	502 (m)			
527 (s)	525 (s)	523 (w) . .	520 (s)	T_{1u}
549 (s)	547 (s)			
	577 (s)	576 (w) . .	576 (w)	T_{1u}
580 (m)	580 (s)			
672 (m)	669 (m)			
709 (s)	709 (s)	712 (w) . .	712,700 (s)	H_g
721 (s)	719 (s)			
747 (s)	744 (s)	743 (w) . .	743 (m)	
760 (s)	757 (s)			
	772 (s)	774 (m) . .	770,760 (s)	H_g
794 (w)	790 (m)			
834 (w)	834 (w) ^a			
861 (w)	861 (w) ^a			
950 (w)	950 (w)			
965 (m)	965 (m)			
1083 (w)	1082 (m)			
1098 (w)	1102 (w)	1099 (w) . .	1100 (w)	H_g
	1179 (m)			
1185 (w)	1188 (m)	1183 (w) . .	1183 (w)	T_{1u}
1235 (w)	1238 (w) ^a			
	1254 (vw) ^a	1245 (w) . .	1245 (m)	H_g
1280 (vw)	1281 (m)			
1330 (vw)	1330 (w) ^a			
	1346 (w) ^a			
	1422 (s)	1422 (m) . .	1422 (m)	H_g, T_{1u}
1442 (s)	1459 (s)	1461 (s) . .	1443 (s)	A_g
	1479 (w) ^a			("pentagonal pinch")
	1552 (m)			
1563 (s)	1568 (s)	1566 (s) . .	1566 (s)	H_g

^a bands due to C_9H_7 ligand

TABLE II Frequency Downshift of the A_g Mode in C_{60}^- Compared to C_{60} Films as a Function of Counteranion

Cation	$A_g(C_{60}^-)^a$ (cm^{-1})	A_g shift ^a (cm^{-1})	A_g shift ^b (cm^{-1})
Li	1431	30	
Na	1445	16	24 (-VI) ^c
K	1446	15	12 (-III), 29 (-VI) ^c 22 (-III), 30 (-VI) ^d 12 (-III), 29 (-VI) ^e
TEA	1443	18	
TBA	1443	18	
Ph_4A_s	1456	6	6 (-I) ^d

^a Experimental data for C_{60}^- films on gold, obtained in this work.

^b Raman shifts obtained for solid-state cation-doped fullerenes, from references cited (values in parenthesis refer to fullerene 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 ($Fc^{+/0}$) (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. $Fc^{+/0}$ 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.

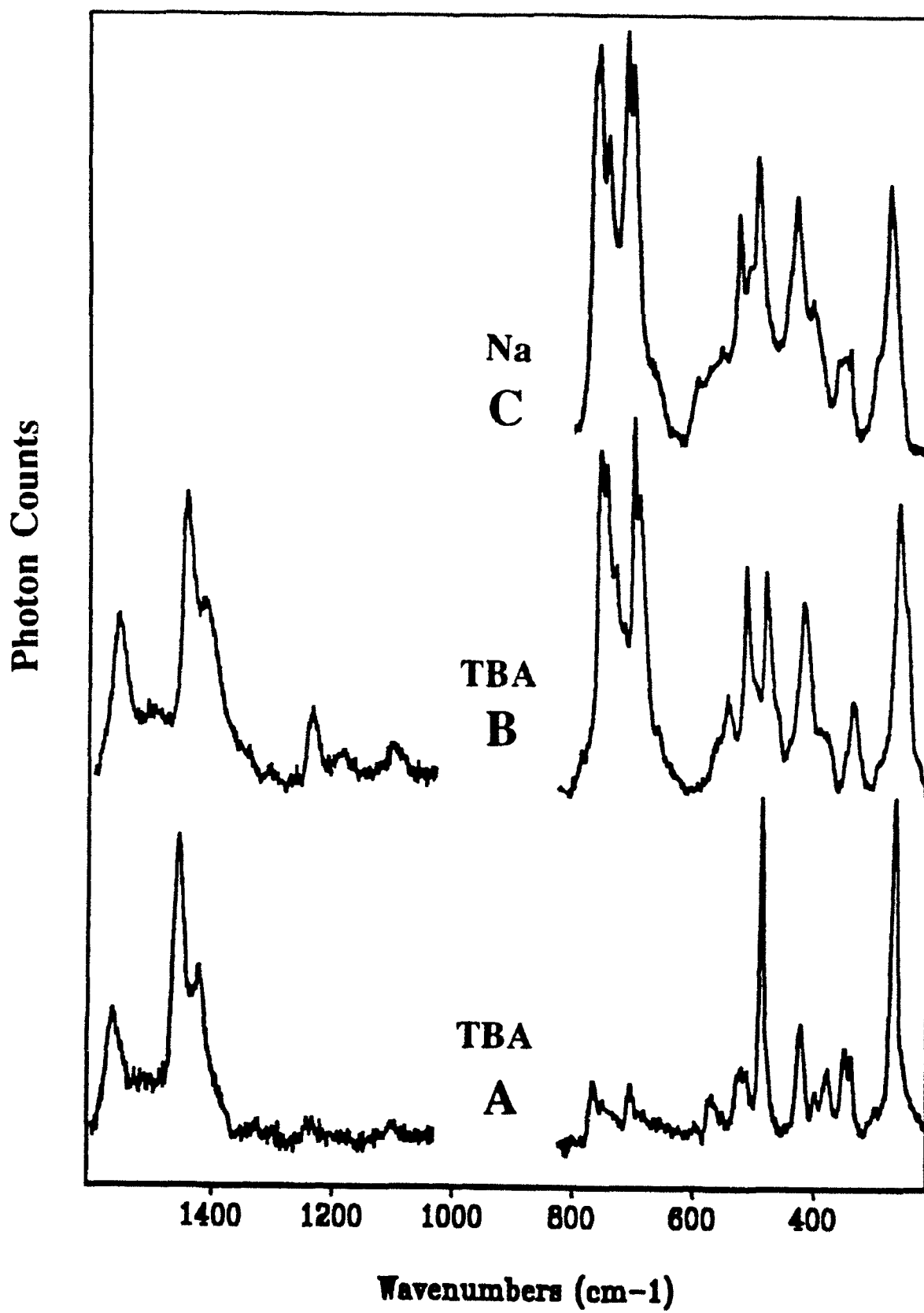


Fig.1

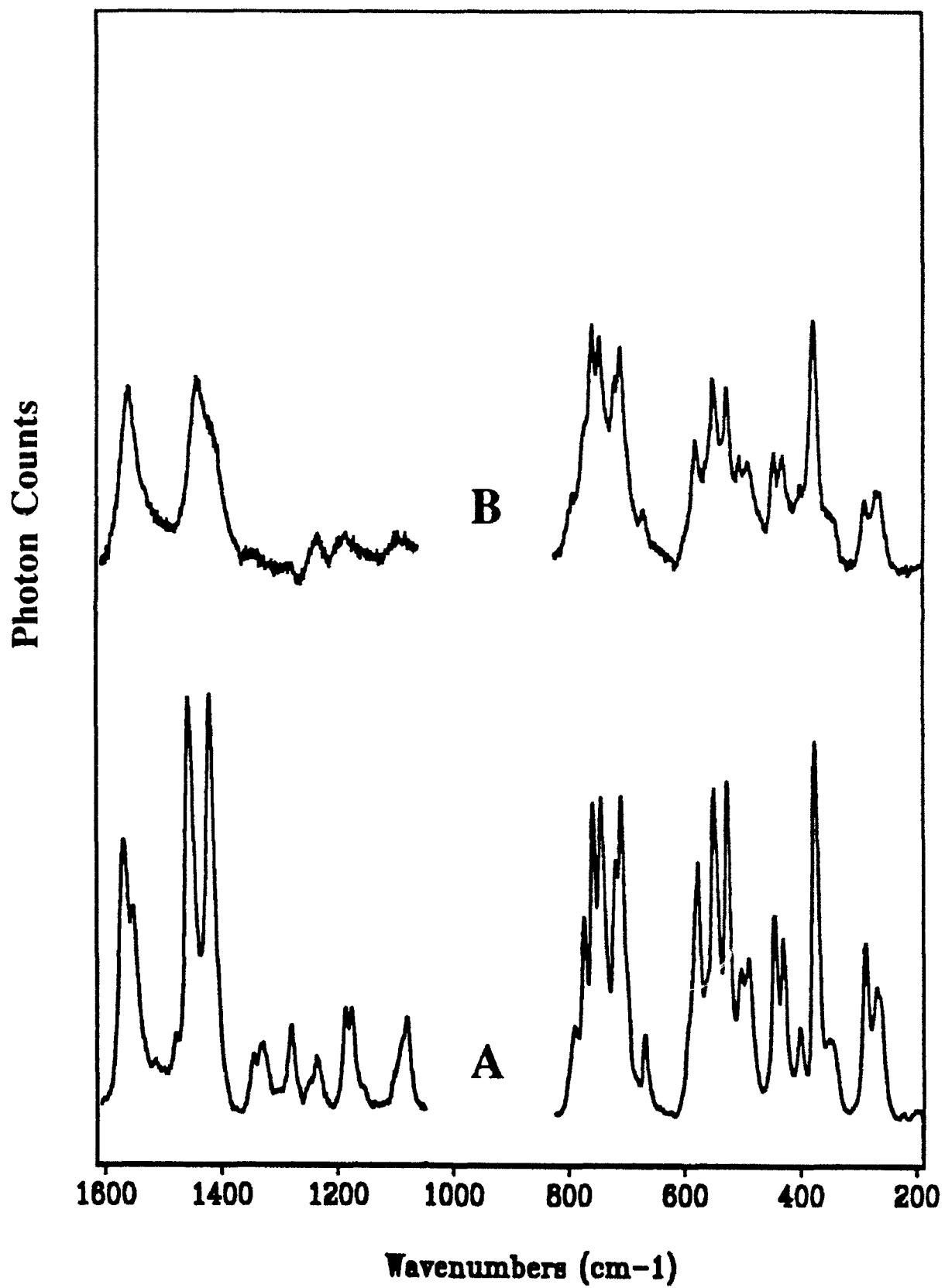


Fig.2

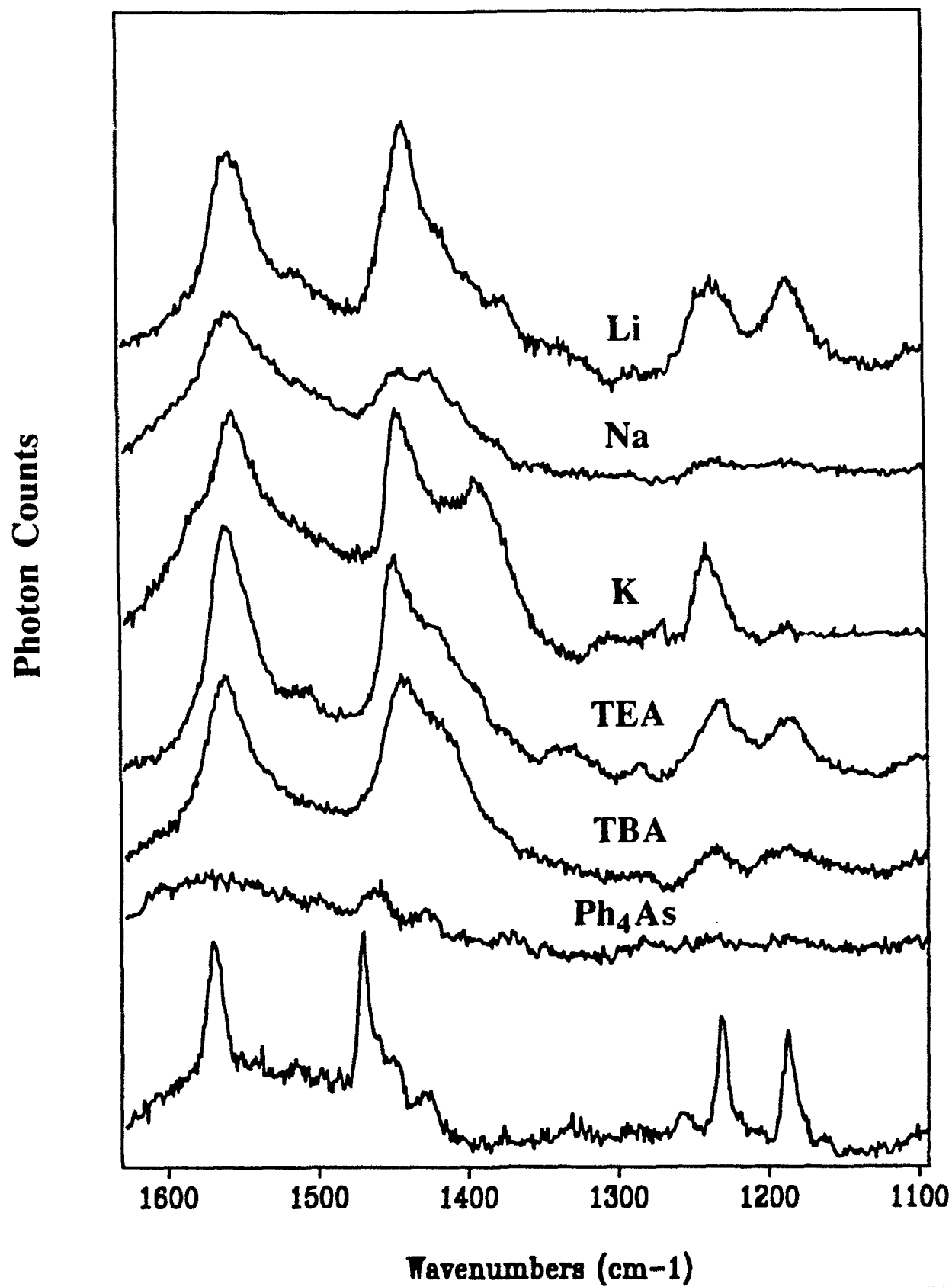


Fig.3