



2

OFFICE OF NAVAL RESEARCH

Contract N00014-90-J-1159
R&T Code 413n007

Technical Report No. 8

**Absorption Spectra and Electronic Properties
of Alkali Metal Doped C₆₀**

by

**V.I. Srdanov, A.P. Saab, D. Margolese, E. Poolman, K.C. Khemani,
A. Koch, F. Wudl, B. Kirtman, and G.D. Stucky**

Prepared for Publication in
Chemical Physics Letters

May 15, 1992

**DTIC
ELECTE
MAY 29 1992
S B D**

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

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

This statement should also appear in Item 12 of the Report Documentation Page, Standard Form 298. Your contract number and R&T Code should be reported in Item 5 of Standard Form 298. Copies of the form are available from your cognizant grant or contract administrator.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

The reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 05-15-92	3. REPORT TYPE AND DATES COVERED Technical 06-01-91 to 05-31-92	
4. TITLE AND SUBTITLE Absorption Spectra and Electronic Properties of Alkali Metal Doped C ₆₀			5. FUNDING NUMBERS N00014-90-J-1159	
6. AUTHOR(S) V.I. Srdanov, A.P. Saab, D. Margolese, E. Poolman, K.C. Khemani, A. Koch, F. Wudl, B. Kirtman, and G.D. Stucky				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of California Department of Chemistry Santa Barbara, CA 93106			8. PERFORMING ORGANIZATION REPORT NUMBER T8	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Chemistry Program 800 N. Quincy Street Alexandria, VA 22217			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Prepared for Publication in Chemical Physics Letters				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Changes in optical absorption spectra of ~500 Å thick films of C ₆₀ during doping with alkali metals (A = Li, Na, K and Rb) were recorded. The stoichiometry of the potassium-doped C ₆₀ films was monitored by simultaneous <i>in situ</i> measurements of electrical conductivity. The spectral changes indicate that the molecular solid behavior of C ₆₀ bulk is preserved in the A ₆ C ₆₀ phase. Assignments for the C ₆₀ and K ₆ C ₆₀ absorption spectra based on molecular orbitals of C ₆₀ are discussed.				
14. SUBJECT TERMS			15. NUMBER OF PAGES 20	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

Absorption Spectra and Electronic Properties of Alkali Metal Doped C_{60}

V.I. Srdanov^{(b)*}, A.P. Saab^(a), D. Margolese^(a),
E. Poolman^(b), K.C. Khemani^(a), A. Koch^(a), F. Wudl^(a),
B. Kirtman^(a) and G. D. Stucky^{(a,b)*}

*Department of Chemistry^(a) and the Center for Quantized Electronic
Structures^(b), University of California Santa Barbara, CA 93106.*

Abstract: Changes in optical absorption spectra of ~500 Å thick films of C_{60} during doping with alkali metals (A=Li,Na,K, and Rb) were recorded. The stoichiometry of the potassium-doped C_{60} films was monitored by simultaneous *in situ* measurements of electrical conductivity. The spectral changes indicate that the molecular solid behavior of C_{60} bulk is preserved in the A_6C_{60} phase. Assignments for the C_{60} and K_6C_{60} absorption spectra based on molecular orbitals of C_{60} are discussed.



Recent discoveries of metallic conductivity in alkali metal doped C_{60} [1] and superconductivity in K_3C_{60} [2] ($T_c = 19$ K) as well as Rb_3C_{60} [3] ($T_c = 28$ K) have increased interest in the electronic and structural properties of these materials. Upon exposure to alkali vapor the conductivity of alkali metal (A) doped C_{60} first increases, then decreases [1]. The conductivity increase has been explained in terms of electron transfer to the empty three-fold degenerate $2t_{1u}$ LUMO [4] of C_{60} leading to a maximum conductivity ascribed to an A_3C_{60} phase with a half filled $2t_{1u}$ orbital. In the fully doped insulating A_6C_{60} phase the $2t_{1u}$ orbital is fully occupied. Photoemission studies [5,6,7] confirm that the HOMO of K_6C_{60} is derived from the LUMO of C_{60} . Doping with alkali metals induces a phase transition after half of the $2t_{1u}$ orbital is filled, as tentatively indicated in the photoemission study of Wertheim et al. [5] It was found later [8] that, upon alkali doping, a face centered cubic (fcc) lattice of C_{60} transforms into a body centered cubic lattice (bcc) capable of accommodating six alkali metal atoms per C_{60} molecule.

The changes in electronic structure of C_{60} induced by doping with alkali metals have been investigated by several different techniques. These include PES [5,6,7], IPES and XPS [9], and EELS [10] studies of potassium-doped C_{60} . To the best of our knowledge there have been no reports yet on optical spectroscopy of the alkali metal-doped C_{60} systems. Here we present our observed changes in absorption spectra of potassium-doped C_{60} in the $220 \text{ nm} < \lambda < 2.1 \text{ } \mu\text{m}$ region, and Li, Na, and Rb doped C_{60} in the $220 \text{ nm} < \lambda < 800 \text{ nm}$ region.

Based upon the changes in the electronic spectra of K-doped C_{60} , the assignment of the electronic states involved in the optical transitions of the C_{60} and K_6C_{60} phases is proposed and compared with existing data in the literature.

C_{60} was synthesized using a simple benchtop reactor [11] and purified by liquid phase chromatography [12]. A few milligrams of C_{60} were sublimed from a quartz crucible, heated to 450°C at a pressure of 5×10^{-6} Torr, onto $1" \times 1"$ fused silica plates to produce films with thicknesses between 300 and 600 Å as determined from absorbance measurements. Raman spectroscopy indicated that the films contained less than 4% C_{70} . For the simultaneous absorbance/resistivity measurements that were performed on the K_xC_{60} samples, a pair of thin gold pads was deposited on the quartz plate prior to the C_{60} deposition. Simple two probe resistivity measurements were carried out using a laboratory Fluke-25 multimeter with lowest readout corresponding to 1 nS. No attempt to estimate specific resistance was made since our goal was a simple correlation of the absorption spectra with change in conductivity.

The vacuum chamber originally used to study reactions of alkali metals with zeolites [13] was adapted for this experiment as shown in Fig. 1. Absorption spectra in the region between $220 < \lambda < 800$ nm were collected using a commercial HP 8452A UV-VIS spectrophotometer whose optical cavity was modified to provide a double pass of the UV-VIS light through the sample. Due to the considerable optical losses in the far-UV region the measurements were restricted to $\lambda > 220$ nm. Commercial SAES-

COPY
100-100000

For	
☒	
☐	
☐	
/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Getters alkali sources were powered using a dc current stabilized power supply. Prior to deposition, the alkali metal flux was adjusted using the feed-back from a quadrupole mass-spectrometer (UTI 100C) placed in line of sight with the alkali source. The fused silica plate containing the C_{60} film was attached to the end of a metal rod and vacuum sealed by an Ultratorr fitting. Using such an arrangement the sample plate could be rotated and translated in the direction perpendicular to the optical axis. Successive alkali metal deposition intervals followed by quick absorbance measurements were achieved by a simple 90° rotation of the sample. The HP spectrometer equipped with a diode array detector provided 2 nm spectral resolution with an integration time of 5 s. The spectra were corrected for the absorption of the fused silica plate. The IR spectrum of the K_6C_{60} phase in the $0.85\text{ }\mu\text{m} < \lambda < 2.1\text{ }\mu\text{m}$ region was recorded with a Cary-14 digital spectrophotometer modified in such a way as to include the vacuum chamber with doped sample inside its optical path.

The change in the K_xC_{60} resistivity with deposition time is plotted in Fig 2. For every experimental point in this figure the absorption spectrum of the K_xC_{60} film was recorded in the manner described above. For the sake of clarity a few of the recorded spectra, which correspond in time to the filled circles on the conductivity curve, are shown in Fig. 3.

Given the film thickness of $\sim 450\text{ }\text{\AA}$ and the deposition time of 73 minutes required to form the insulating K_6C_{60} phase, the potassium flux in our experiment was estimated to be on the order of $5 \times 10^{13}\text{ atoms}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$. In a series of experiments with up to four times higher deposition rates, we obtained essentially identical

spectral/conductivity behavior as presented in Figs. 2 and 3. This suggests high potassium diffusion rates through thin films of A_xC_{60} which is in agreement with recent observations [9,14,15].

Owing to the exceptional stability of the alkali source one may attempt to associate deposition time with the predominant K_xC_{60} stoichiometry. This requires that the sticking coefficient of the alkali metal remains unchanged and that the potassium diffusion rate through the sample is much greater than the deposition rate. While the latter requirement appears to be met, the most recent studies indicate certain nonlinearities in the sticking coefficient of potassium on C_{60} films [9]. Therefore, direct correlation between the observed spectra and K_xC_{60} stoichiometry using the deposition time is strictly correct only for $x=0$ and $x=6$ while intermediate concentrations should be regarded as approximate. Deviation of the resistivity curve in Fig. 2 from the Gaussian shape could be a consequence of both the change in the sticking coefficient and/or the sign of an onset of the phase transition expected to take place after half of the doping is completed.

Among the spectroscopic studies of potassium-doped C_{60} the best comparison with our data can be made with the XPS [9] and EELS [10] spectra. While there is substantial agreement in the 0.6 - 4 eV region, our absorption spectra show more details in the 4-6 eV region. The reason is that the 216 nm and 264 nm bands [16], as well as the strong 6.4 eV plasmon band, of C_{60} [10] broaden in the EELS and XPS spectrum to the point where no individual transitions can be recognized (for comparison see Fig 3. in ref [9]).

Starting from the high energy end of the spectrum in Fig. 3, we can clearly follow in time a slowly increasing red shift of the 216 nm band of C_{60} . The intensity does not change significantly with doping and the shift appears to be almost completed at half the deposition time. The $\lambda_{\max}$ of this band was found at 225 nm in the K_6C_{60} spectrum. The strongest UV band of C_{60} , at 264 nm, broadens in the initial doping stages although its maximum can be clearly followed through all of the intermediate spectra. The band appears to be only slightly red shifted with $\lambda_{\max}$ found at ~ 267 nm in the K_6C_{60} spectrum. The maximum intensity of this band in the K_6C_{60} spectrum is slightly less than the band at 225 nm. The first new feature that appears in the K_6C_{60} spectrum is the band at 302 nm. It is difficult to say from our data whether or not this band evolves from a splitting of the strong 264 nm band of C_{60} . In any case, its maximum gains in intensity beyond the half doping point but does not significantly shift.

The 339 nm absorption band of C_{60} shows rather different behavior from the bands described above. As can be seen in Fig. 3, the intensity of this band rapidly decreases with doping so that it can not longer be recognized in spectra taken past the half-doping point. A weak absorption plateau in the C_{60} spectrum in the $420 < \lambda < 500$ nm region vanishes at a rate similar to the 339 nm band. Disappearance of the 339 nm band is followed by appearance of two new absorption features: a broad (~ 1 eV FWHM) asymmetric band in the visible with $\lambda_{\max}$ at ~ 425 nm and an additional band in the near IR with $\lambda_{\max}$ at ~ 1100 nm (see Fig. 4c). Both of these new bands continuously grow with alkali

deposition to reach maximum intensity at the end of the doping cycle. The broad and asymmetric shape of the 425 nm band indicates that it may consist of more than one optical transition. Even though the two absorption maxima at 1.1 μm (1.1 eV) and 425 nm (2.9 eV) nm measured in the absorption spectrum of K_6C_{60} differ slightly from the peak energies in the EELS spectrum [10], it appears that the same transitions were recorded in both experiments.

While no definite assignment exists for the 216 nm band of C_{60} , the strongest UV 264 nm band has been tentatively attributed to the $1h_u \rightarrow 3h_g$ transition by Sochmen et al. [10]. They also attribute the C_{60} 339 nm band to the $1h_u \rightarrow 1t_{1g}$ transition in agreement with theoretical calculations based on the CNDO/S [17] method. However, another optically allowed [4] $2h_g \rightarrow 2t_{1u}$ transition is also predicted in the same energy region [17,18].

The two new bands which appear in the EELS spectrum of potassium-doped C_{60} [10] at 1.3 and 2.75 eV were attributed, respectively, to the $2t_{1u} \rightarrow 1t_{1g}$ and the $1h_u \rightarrow 1t_{1g}$ transitions of K_6C_{60} with the energy shifts from C_{60} to K_6C_{60} being considered a consequence of nonrigid behavior of the C_{60} π levels as a function of dopant concentration [10]. The relatively large ($3.66 - 2.75 = 0.91$ eV) energy shift of the $1h_u \rightarrow 1t_{1g}$ transition in the EELS spectrum was supported by the shifts of the $1s - \pi_1^*$ transitions in potassium doped C_{60} [10]. The largest shift was found for the $1s - \pi_2^*$ ($\pi_2^* = 1t_{1g}$) transition.

Based upon changes in the absorption spectra with doping and the following theoretical considerations, we offer an alternative spectral assignment, specifically for the 339 nm band

of C_{60} and the 425 nm band of K_6C_{60} . The transfer of electrons from alkali metal atoms into the empty $2t_{1u}$ LUMO of C_{60} is expected to strongly affect optical transitions which involve electronic states derived from this orbital. Thus, the $2h_g \rightarrow 2t_{1u}$ transition should lose its intensity as the $2t_{1u}$ orbital is filled with electrons to the point where it is completely extinct in the fully doped K_6C_{60} . In addition, the two lowest energy electric dipole allowed transitions originating from the newly occupied $2t_{1u}$ orbital should occur: $2t_{1u} \rightarrow 1t_{1g}$ and $2t_{1u} \rightarrow 3h_g$ [19]. These are expected to gain in intensity with doping since the population of the $2t_{1u}$ orbital increases from C_{60} to K_6C_{60} .

The above suggest that the 339 nm (3.66 eV) band of C_{60} should be assigned to the $2h_g \rightarrow 2t_{1u}$, rather than to the $1h_u \rightarrow 1t_{1g}$, transition. If $2h_g \rightarrow 2t_{1u}$ were the stronger of the two transitions, then the calculated 18:1 [18] ratio of oscillator strengths for these two transitions would be consistent with our analysis. Our analysis is also consistent with assigning the two absorption bands of K_6C_{60} occurring at 425 nm (2.92 eV) and 1.1 μm (1.1 eV) as due to excitation of an electron from the $2t_{1u}$ orbital to the $3h_g$ and the $1t_{1g}$ orbitals respectively. Again, if the $1h_u \rightarrow 1t_{1g}$ transition is weak it is possible that both our assignment and the previous one could be valid.

There is little doubt that the $2t_{1u} \rightarrow 1t_{1g}$ assignment of the 1.1 μm band in K_6C_{60} is correct. This transition was found at a similar energy in the XPS [9] study and in the absorption spectrum of the C_{60} - radical anion [20]. The LDA calculations of K_6C_{60} predict an indirect band gap at $E_g = 0.48$ eV and, from the

band diagram, it appears that the direct $\Delta k=0$ transition is just above the calculated band gap [21]. Although the true origin of the electric dipole allowed $2t_{1u} \rightarrow 1t_{1g}$ transition of K_6C_{60} is not known, we found the long wavelength onset of the absorption in this excitonic band at $\sim 2 \mu m$ (0.62 eV). One should be careful, however, about comparing this experimental result with band gap calculations [22].

Changes in the UV-VIS absorption spectra with doping were also recorded for Li, Na and Rb doped C_{60} films but no simultaneous conductivity measurements were made in these experiments. We find similar overall spectral behavior for all alkali metal doped C_{60} samples with some variations in the positions, splitting, and relative intensities of the absorption bands. These differences can be readily noticed in Fig. 4 where the spectra of the fully doped A_6C_{60} ($A=Na, K, Rb$) phases are compared. Changes in the spectrum of the Li doped C_{60} sample could only be monitored in the initial doping stages since continuous absorption due to the reaction of Li with the fused silica substrate eventually masks the spectrum. Up to the point where the spectral changes could no longer be followed ($\sim Li_3C_{60}$), the changes in the Li_xC_{60} spectrum were found to be similar to the rest of the alkali doped samples.

In an early study on alkali metal-doped C_{60} [8], performed under thermodynamic equilibrium, only the fcc phase of C_{60} and the bcc phase of A_6C_{60} ($A=K, Cs$) were found in the X-ray diffraction spectra. The existence of the stable fcc A_3C_{60} ($A_3=K_3, Rb_3, Rb_2Cs$) phases has since been documented [24]. In fact, X-ray photoelectron studies of C_{60}/A_xC_{60} ($A=K, Cs$)

heterostructures [14] indicate that the C_{60}/A_3C_{60} heterostructure is more stable than that of C_{60}/A_6C_{60} . Quite recently, a new K_4C_{60} phase with the body centered tetragonal (bct) lattice has also been identified [24].

We took advantage of our experimental set up to study the stability of the K_3C_{60} stoichiometry and its possible disproportionation to more stable C_{60} and K_6C_{60} phases [8]. A thin film of K_3C_{60} stoichiometry with the characteristic spectrum shown in Fig 3 ($t_d = 37$ min) was heated for 24h using collimated light from a 300 W xenon lamp and the spectrum remained unchanged. In addition, normalized absorption spectra of C_{60} and K_6C_{60} from Fig. 3 were averaged and upon comparing to the spectrum of K_3C_{60} some obvious differences were seen. Finally, we also found that all K_xC_{60} spectra in the $0 < x < 3$ region can be well reproduced by addition of appropriate intensity normalized spectra of the C_{60} and K_3C_{60} phases. This analysis excludes the possibility that disproportionation into C_{60} and K_6C_{60} took place during the experiment and supports the postulated[14] nonexistence of solid solutions of K_xC_{60} in the $0 < x < 3$ region. Similar modeling to the above, based on the K_3C_{60} and K_6C_{60} spectra, was not successful in the $3 < x < 6$ region.

In conclusion, we have introduced a simple experimental technique to monitor changes in the absorption spectra of thin films of solid C_{60} during doping with alkali metals. This technique can be easily extended to other heterostructures. The UV-VIS and near IR spectra of alkali metal ($A = \text{Li, Na, K, Rb}$) doped C_{60} molecules were investigated with simultaneous conductivity

measurements being used to monitor the K_xC_{60} stoichiometry. All investigated A_xC_{60} systems show similar spectral behavior with alkali doping, although the absorption spectrum of Na_6C_{60} is noticeably different from that of K_6C_{60} and Rb_6C_{60} . Based upon the changes in the absorption spectra induced by electron transfer from potassium atoms to the C_{60} molecule we propose alternative assignments of the 339 nm band of C_{60} and the 425 nm band of K_6C_{60} to those previously proposed. Annealing of the K_3C_{60} phase showed no signs of disproportionation, supporting higher stability with respect to the other phases. Analysis of the K_xC_{60} spectra in the $0 < x < 3$ region indicates the existence of a simple mixture of the C_{60} and the K_3C_{60} phases but the same cannot be said for the K_3C_{60} and K_6C_{60} phases in the $3 < x < 6$ region.

We are grateful to Prof. J. Weaver for a critical reading of the manuscript. We thank Prof. Z. Vardeny for testing the purity of the C_{60} samples by Raman spectroscopy, and to Prof. D.H Aue and Prof. J.T.C. Gerig for a generous loan of equipment. This research was supported by the NSF Quantized Electronic Structures Science and Technology Center (QUEST) at UCSB and by ONR.

References:

- [1] R.C. Haddon, et al., *Nature* **350** (1991) 320 .
- [2] A.F. Hebard, M.J. Rosseinsky, R.C. Haddon, D.W. Murphy, S.H. Glarum, T.T.M. Palstra, A.P. Ramirez and A.R. Kortan, *Nature* **350** (1991) 600 .
- [3] M.J. Rosseinsky, A.P. Ramirez, S.H. Glarum, D.W. Murphy, R.C. Haddon, A.F. Hebard, T.T.M. Palstra, A.R. Kortan, S.M. Zahurak, and A.V. Makhija, *Phys. Rev. Lett.* **66** (1991) 2830.
- [4] R.C. Haddon, L.E. Brus and K. Raghavachari, *Chem. Phys. Letters* **125** (1986) 459 .
- [5] G.K. Wertheim, J.E. Rowe, D.N.E. Buchanan, E.E. Chaban, A.F. Hebard, A.R. Kortan, A.V. Makhija and R.C. Haddon, *Science* **252** (1991) 1419 .
- [6] P.J. Benning, J.L. Martins, J.H. Weaver, L.P.F. Chibante and R.E. Smalley, *Science* **252** (1991) 1417.
- [7] C.T. Chen, L.H. Tjeng, P. Rudolf, G. Meigs, J.E. Rowe, J. Chen, J.P. McCauley Jr., A.B. Smith III, A.R. McGhie, W.J. Romanow and E.W. Plummer, *Nature* **352** (1991) 603.
- [8] O. Zhou, J.E. Fischer, N. Coustel, S. Kycia, Q. Zhu, A.R. McGhie, W.J. Romanow, J.P. McCauley Jr., A.B. Smith III, *Nature* **351** (1991) 462.
- [9] P.J. Benning, D.M. Poirier, T.R. Ohno, Y. Chen, M.B. Jost, F. Stepniak, G.H. Kroll, J.H. Weaver, J. Fure and R.E. Smalley, *Phys. Rev. B* (submitted).
- [10] E. Sohmen, J. Fink and W. Kratschmer, *Europhys. Lett.* (in press).
- [11] A. Koch, K.C. Khemani, and F. Wudl, *J. Org. Chem.* **56** (1991) 4543 .
- [12] R.D. Johnson, G. Meijer and D.S. Bethune, *J. Am. Chem. Soc.* **112** (1990) 8983.
- [13] V.I. Srdanov, K. Haug, H. Metiu and G. Stucky, *J. Phys. Chem.* (submitted).
- [14] D.M. Poirier, T.R. Ohno, G.H. Kroll, Y. Chen, P.J. Benning, J.H. Weaver, L.P.F. Chibante and R.E. Smalley, *Science* **253** (1991) 646 .
- [15] G.P. Kochanski, A.F. Hebard, R.C. Haddon and A.T. Fiory,

Science (submitted).

[16] W. Kratschmer, L.D. Lamb, K. Fostiropulos and D.R. Huffman, *Nature* **347** (1990) 354.

[17] S. Larsson, A. Volosov and A. Rosen, *Chem. Phys. Lett.* **137** (1987) 501 .

[18] I. Laszlo and L. Udvardi, *Chem. Phys. Lett.* **136** (1987) 418.

[19] For the icosahedral group $T_{1u} \times T_{1g} = A_u + T_{1u} + H_u$; see also ref. [17].

[20] T. Kato, T. Kodama, T. Shida, T. Nakagawa, Y. Matsui, S. Suzuki, H. Shiromaru, K. Yamauchi and Y. Achiba, *Chem. Phys. Lett.* **180** (1991) 446 .

[21] S.R. Erwin and M.R. Pederson, *Phys. Rev. Lett.* **67** (1991) 1610.

[22] M.B. Jost, N. Troullier, D.M. Poirier, J. L. Martins, J.H. Weaver, L.P.F. Chibante and R.E. Smalley, *Phys. Rev. B* **44** (1991) 1966.

[23] R.M. Fleming , A.P. Ramirez, M.J. Rosseinsky, D.W. Murphy, R.C. Haddon, S.M. Zahurak and A.V. Makhija, *Nature* **352** (1991) 787.

[24] R. M. Fleming, M.J. Rosseinsky, A.P. Ramirez, D.W. Murphy, J.C. Tully, R.C. Haddon, T. Siegrist, R. Tycko, S.H. Glarum, P. Marsh, G. Dabbagh, S.M. Zahurak, A.V. Makhija and C. Hampton, *Nature* **352** (1991) 701.

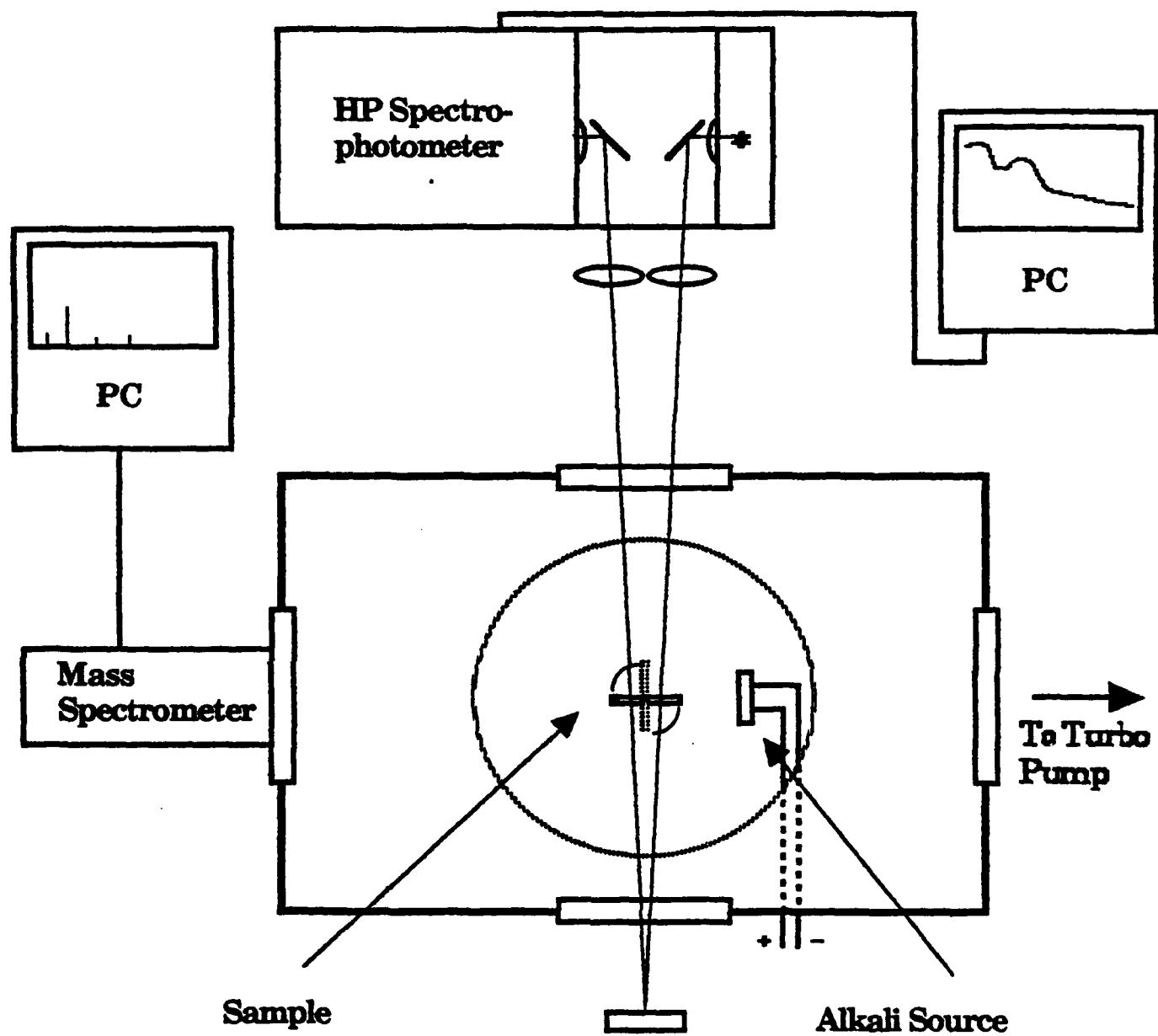
Figure captions:

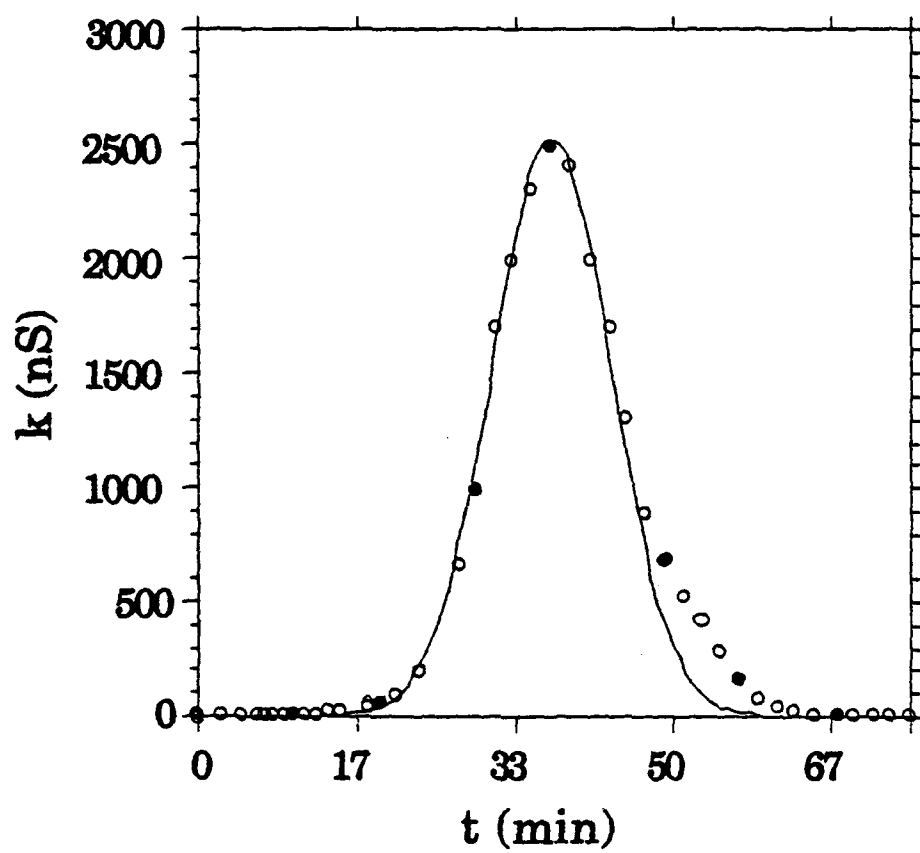
Fig.1. Experimental apparatus.

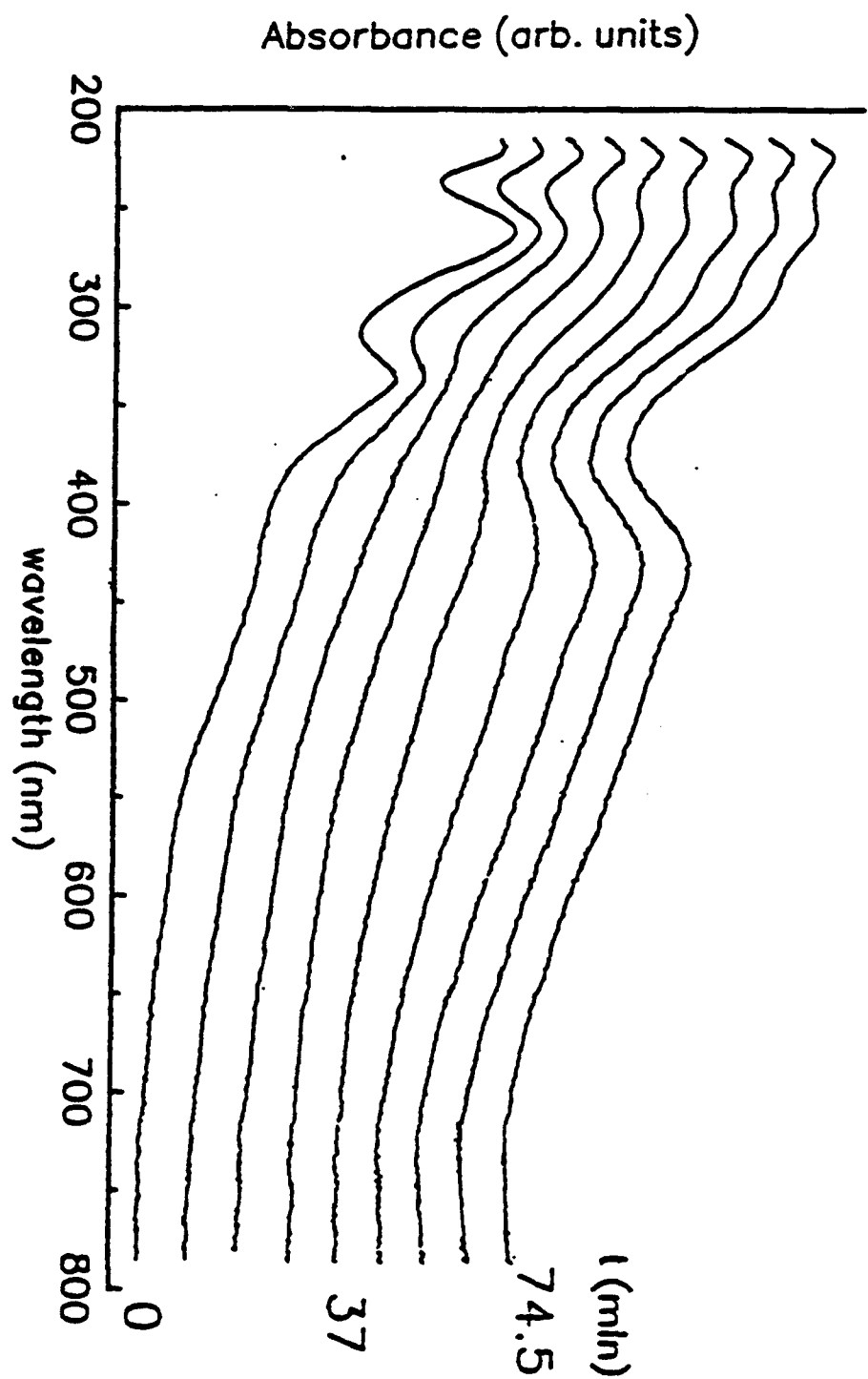
Fig.2. Two probe conductivity measurements of the ~ 450 Å potassium doped C_{60} film with electrode separation of ~ 1 ". Solid curve is a least squares fit to a Gaussian function using slightly more than the half experimental points in the region to the left of the maximum. Experimental points assigned by filled circles correlate to the spectra shown in Fig.3.

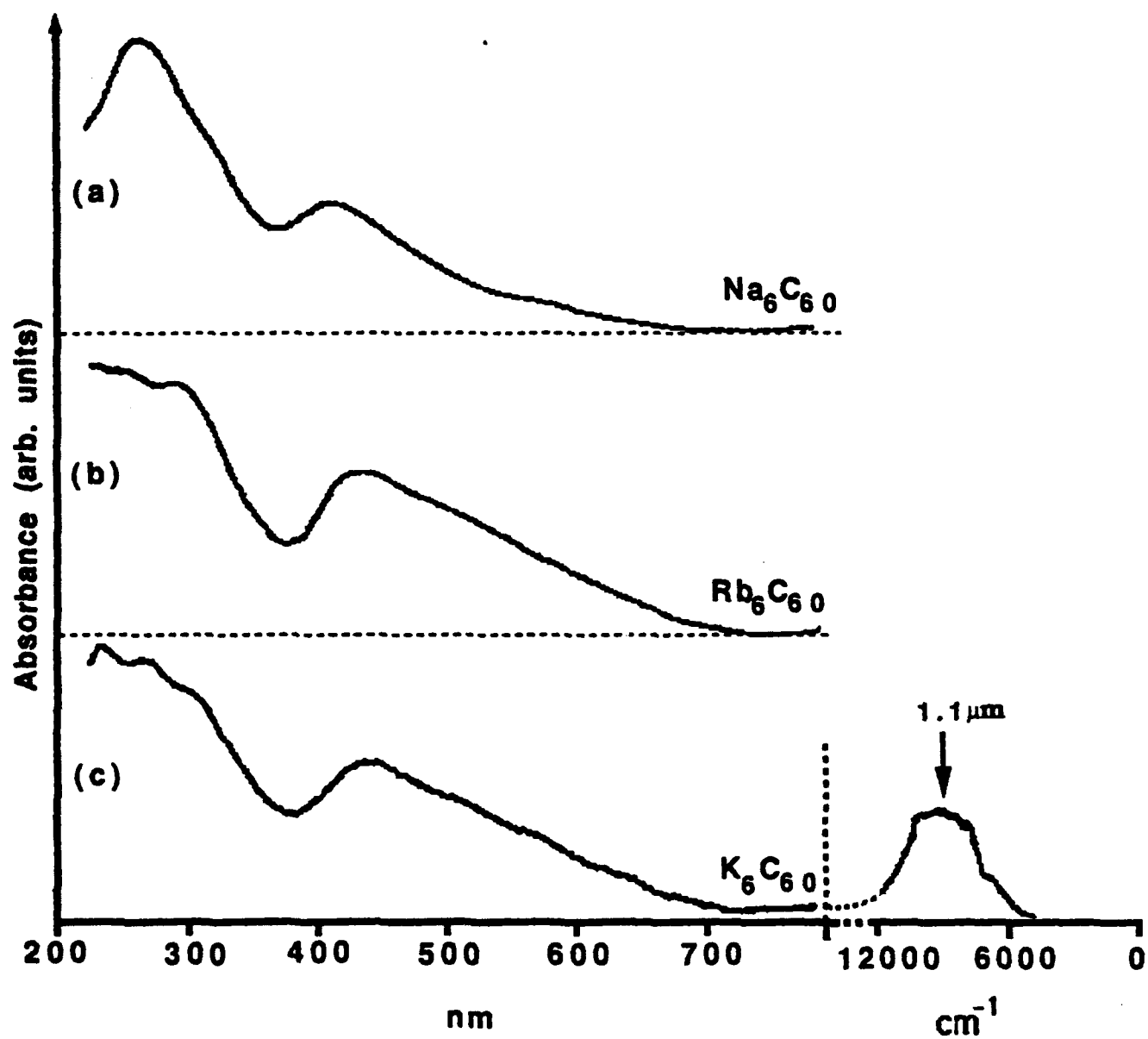
Fig 3. Change in the absorption spectrum of an ~ 450 Å C_{60} film deposited on the quartz substrate during doping with potassium. Absorption spectra taken after 0, 37 and 74.5 min correspond to the C_{60} , K_3C_{60} and K_6C_{60} samples respectively.

Fig 4. Absorption spectra of A_6C_{60} ($A=Na, K, Rb$).









TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)*
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Harold H. Singerman (1)
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Air Weapons Center
Weapons Division
China Lake, CA 93555-6001

Dr. Eugene C. Fischer (1)
Code 2840
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Elek Lindner (1)
Naval Command, Control and Ocean
Surveillance Center
RDT&E Division
San Diego, CA 92152-5000

Defense Technical Information
Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

Dr. Bernard E. Douda (1)
Crane Division
Naval Surface Warfare Center
Crane, Indiana 47522-5000

* Number of copies to forward