AD-A282 730

(1)

EDGEWOOD
RESEARCH, DEVELOPMENT & ENGINEERING CENTER
U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND

ERDEC-CR-086
(TCN 92431)

CHEMICAL PROPERTIES OF THE FULLERENES

DTIC
ELECTE
JUL 27 1994
S G D

Allan L. Smith

DREXEL UNIVERSITY
Philadelphia, PA 19104

November 1993

Approved for public release; distribution is unlimited.

Aberdeen Proving Ground, MD 21010-5423

94-23781

94 7 26 086

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public 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
1993 November

3. REPORT TYPE AND DATES COVERED
Final, 92 Jun - 92 Dec

4. TITLE AND SUBTITLE
Chemical Properties of the Fullerenes

5. FUNDING NUMBERS
C-DAAL03-91-C-0034
D.O.-477

6. AUTHOR(S)
Smith, Allan L.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Chemistry Department, Drexel University
32nd and Chestnut Sts
Philadelphia, PA 19104

8. PERFORMING ORGANIZATION REPORT NUMBER
ERDEC-CR-086
(TCN 92431)

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
ARO, P.O. Box 12211, Research Triangle Park, NC 27709

DIR, ERDEC,* ATTN: SCBRD-RT, APG, MD 21010-5423

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
COR: Patrick M. Nolan, SCBRD-RTM, (410) 671-3614.
Task was performed under a Scientific Service Agreement issued by Battelle, Research Triangle Park Office, 200 Park Drive, P.O. Box 12297, Research Triangle Park, NC 27709. (Continued on page 2)

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The UV-visible absorption spectra of pure C_{60}, C_{70}, and $C_{60}O$ dissolved in toluene were used to perform multicomponent analysis of graphitic soot extracts and to assess the purity of fullerene samples. Diffuse-reflectance FTIR spectroscopy of 1-2 mg solid C_{60} and C_{70} samples was used to determine the fraction of hydrocarbon impurities at the level of 0.01 atom fraction H. Vacuum sublimation is the only way to produce C_{60} and C_{70} samples free of hydrocarbon impurities. The solubility of C_{60} and C_{70} in toluene was measured as a function of temperature for $25\ °C < T < 80\ °C$, and for C_{60} in CS_2 for $25 < T < 45\ °C$. At 30 °C, C_{60} is three times as soluble as C_{70}, but both solubilities decrease with increasing temperature. This unusual temperature dependence, exhibited by virtually no other organic solids in organic solvents, is attributed to the formation of solvated fullerene solids. The heat of combustion of $C_{60}(cr)$ was determined with the NIST adiabatic bomb calorimeter, and used to determine the enthalpy of formation of C_{60}, 2193 ± 9.6 kJ/mol. The average strength of the carbon-carbon bonds in C_{60} is 453 kJ/mole. The absorption spectrum of C_{60} gas in equilibrium with the solid was recorded between 500 and 680 °C. From the slope of the $\ln(P_{vap})$ vs $1/T$ plot, an enthalpy of sublimation for C_{60} of 159 kJ/mol was determined.

14. SUBJECT TERMS

Solubility	Enthalpy of formation
Fullerenes	Ultraviolet gas phase absorption
C_{60}	C_{70}

15. NUMBER OF PAGES
45

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

11. SUPPLEMENTARY NOTES (Continued)

*When this study was conducted, ERDEC was known as the U.S. Army Chemical Research, Development and Engineering Center, and the Contracting Officer's Representative was assigned to the Research Directorate.

PREFACE

The work described in this report was authorized under Contract No. DAAL03-91-C-0034, Delivery Order No. 477. This work was started in June 1992 and completed in December 1992.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for release to the public. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

Accesion For
NTIS CRA&I ☒
DTIC TAB ☐
Unannounced ☐
Justification ....
By ....
Distribution /
Availability Codes
Dist | Avail and / or Special
A-1

Blank

CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. Introduction

The U.S. Army Chemical Research, Development and Engineering Center (CRDEC) sponsored this Short-Term Analytical Services contract with Dr. Smith and with his research group at Drexel University's Chemistry Department in order to investigate the chemical and physical properties of fullerenes[1] , a new form of elemental carbon. Fullerenes have potential application as novel sorbent materials to enhance the adsorption capabilities for detoxification of highly volatile chemical warfare vapors. Of interest is the ease with which fullerenes form strong intermolecular complexes and covalently bonded adducts with other compounds, since this chemical reactivity determines the usefulness of fullerenes as sorbents. At present, not enough is known about the chemical and physical properties of fullerenes to determine their usefulness for this application. The spectroscopic and thermodynamic properties determined in this STAS contract will be helpful in assessing the relative reactivity and stability of fullerenes with respect to other forms of carbon.

II. The Proposed Work (from the rfp)

(1) Measure and report the solubility of C_{60} and C_{70} in benzene, toluene, CS_2, and hexane at 25°C and in 10 °C increments to 65 °C. (At the beginning of this contract, no thermodynamic information had been published on the solubility and heats of solution of any of the fullerenes in any solvent.) The temperature dependence of the solubility will be obtained by UV/visible spectrophotometry in a temperature-regulated absorption cell. An analysis of this temperature dependence will give the heats of solution of C_{60} and C_{70} in these solvents. Using standard thermodynamic relationships for two-component systems [C_{60} - solvent] , we shall estimate the melting point of pure C_{60} and C_{70}, as well as the enthalpy of formation of C_{60} and C_{70} in these solvents

(2) Determine the heat of combustion of high-purity (a level of not greater than 0.1% of hydrocarbon impurities) C_{70} by employing calorimetry and calculate the heat of formation of the solid C_{70}. Samples will be characterized by one or more of the following methods: diffuse reflectance FT-IR, FT nuclear magnetic resonance, and mass spectrometry.

---

[1] *Fullerenes: Synthesis, Properties, and Chemistry of Large Carbon Clusters* ; Hammond, G. S., Kuck, V.S., Eds, ACS Symposium Series 481, 1992

(3) Measure and report the vapor phase UV/visible absorption spectrum of C_{60} and C_{70}. From the measured absorbance and a calculated relationship between solution-phase and gas-phase molar absorptivities, we will calculate the vapor pressure of C_{60} in equilibrium with its solid phase at temperatures between 500 and 700 °C. We will plot $\ln(P_{vapor})$ versus 1/T (absolute temperature) to obtain the heat of sublimation of C_{60}.

III. Preparation and Characterization of Highly Pure Fullerene Samples

Fullerene Sample Preparation

The measurements described above require pure, well characterized samples of C_{60} and C_{70}. For some time we have been using neutral alumina column chromatography for separating and purifying fullerenes from graphitic soot extract, following published methods[2]. C_{60} with less than 0.1% C_{70} was obtained from the extract by preparative chromatography on neutral alumina and characterized by HPLC, FT-IR, and multicomponent UV-visible absorption. We have also employed the separation method of Tour et al[3], using Norit A decolorizing carbon as the stationary phase and pure toluene as the mobile phase. However, we find the Tour method to be unsatisfactory for producing C_{70}, since all fullerenes other than C_{60} remain adsorbed on the column even after extensive elution and must be removed by Soxlet extraction. The chromatography of fullerenes on carbon substrates needs to be investigated further, since these substrates appear to be very promising stationary phases.

Characterization of fullerene sample purity

For some time we have been accumulating evidence (from FT-IR spectroscopy, analytical HPLC, proton nmr, and thermal gravimetric analysis) that these C_{60} samples contain trace quantities of hydrocarbon impurities not removed by chromatography. These impurities are not the

---

[2] Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M. ; Anz, S.; Sensharma, D.; Wudl, F.; Khemani, K. C. ; Koch, A., Science 1991 , 252, 548

[3] Scrivens, W. A.; Bedworth, P. V.; Tour, J. M., J. Am. Chem. Soc. 1992, *114* , 7919

solvents used in extraction and chromatography (toluene and hexane), but heavier, possibly polynuclear aromatic hydrocarbons which appear to be synthesized during the production of the graphitic soot itself. This observation is supported by Guiochon and coworkers[4], who developed a preparative chromatographic method using a C-18 column and a hexane mobile phase which effectively removes these hydrocarbon impurities. Hanna and Wilson[5] have used cross-polarization ^1H-^{13}C magnetic resonance techniques to characterize the toluene and aliphatic impurities in crude fullerene extract and their removal upon chromatography. Because the availability of fullerene samples free of hydrocarbons is essential in accomplishing our original thermodynamic measurement objectives, we have spent much time developing methods for assessing low levels of hydrocarbon impurities. We are presently investigating the purchase of a preparative C-18 column so that we can do this separation at Drexel.

UV-visible studies of fullerene-containing solutions

The molar absorptivities $\varepsilon[\lambda]$ of C_{60} ,C_{70}, and $C_{60}O$ in toluene ($300 < \lambda < 800$ nm) and of C_{60} in CS_2 ($390 < \lambda < 800$ nm).were determined by measuring absorbances of standard solutions (0.3 -3.0×10^{-4} M) on a Hewlett-Packard -8451 diode array spectrophotometer. These molar absorptivity spectra, shown in Figures 1-2 , agree within 10% with molar absorptivities of Wudl, Diederich et at selected wavelengths[6]. The molar absorptivities at 338 and 384 nm[7] for C_{60} and C_{70} in toluene were used in a two-component Lambert-Beer analysis to yield concentrations of C_{60} and C_{70} in the solution of extract from measured absorbances. The results were $[C_{60}] = 2.6 \times 10^{-3}$ and $[C_{70}] = 8.4 \times 10^{-4}$ M, a 76%/24% ratio of C_{60}/C_{70} as expected in extract.

Multilinear regression methods were also used to perform quantitative spectrophotometric analysis of solutions containing C_{60} and C_{70}[8]. The Lambert-Beer law for a 2-component mixture can be written as

$$\mathbf{A} = \mathbf{b}\,\boldsymbol{\varepsilon}\,\mathbf{c} \qquad [1]$$

where A is an m-component vector containing solution absorbances measured at m equally spaced wavelengths (obtained from the diode array spectrophotometer), ε is an m by 2 matrix containing molar absorptivities

---

[4] Diack, M.; Hettich, R. L.; Compton, R. N.; Guiochon, G., Anal. Chem. 1992, *64* , 2143

[5] Hanna., J.V.; Wilson, M. A.. J. Phys. Chem. 1992, *96*, 6518

[6] P. M. Allemand, A Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alverez, S. J. Anz, R. L. Whetten, J. Am. Chem. Soc. 1991, *113*, 1050, ref 3.

[7] For C_{60}, $\varepsilon[338] = 51{,}000$, $\varepsilon[384] = 7{,}860$; for C_{70}, $\varepsilon[338] = 27{,}100$, $\varepsilon[384] = 26{,}400$, all in units of $M^{-1}cm^{-1}$

[8] O'Haver, T. C. , Chemometrics and Intelligent Lab Systems 1989, 6, 95

of the two components, c is the two-component concentration vector, and b is the (scalar) path length. The least-squares solution for the concentration vector is then

$$c = b^{-1} [\varepsilon ' \varepsilon]^{-1} \varepsilon ' A \qquad [2]$$

where $\varepsilon '$ is the transpose of ε and $[]^{-1}$ represents the inverse. The necessary matrix computations were performed using the Matlab software package[9] on a Macintosh IIcx. The residual spectrum $A - b\, \varepsilon\, c$, with c determined from Eq. [2], is a sensitive probe of other absorbing impurities such as higher fullerenes. From these analyses, the mole fraction of C_{70} in all of the C_{60} samples used for solubility measurements was < 0.01. The mole fraction of C_{60} in the C_{70} sample was determined to be < 0.03.

FTIR studies of hydrocarbon impurities in C_{60}

The hydrogen-containing impurity content of C_{60} samples was determined by Fourier-transform infrared spectroscopy in the diffuse reflectance mode[10]. A 1 mg sample of C_{60} was ground with 15 mg KBr, and spectra with 2 cm^{-1} resolution were recorded with a Perkin-Elmer 1610 FT-IR (400 scans). Figure 3 shows spectra of several C_{60} samples. In addition to the four prominent vibrational fundamentals at 528, 578, 1183, and 1429 cm^{-1}, about 70 other much weaker bands are evident both in our spectra and in those of Chase et al [11]. These as yet unassigned bands, distributed between 600 and 2950 cm^{-1}, are probably due to combination bands built from the four observed IR fundamentals and the 42 other modes expected for C_{60}[12]. They are not due to impurities because they occur with the same relative intensities in every C_{60} spectrum we record, regardless of sample preparation. In the 2800-3100 cm^{-1} region, however, bands which can be assigned[13] to the carbon-hydrogen stretching frequencies of aliphatic and aromatic hydrocarbons appear, and their intensity relative to the C_{60} bands is a good measure of hydrocarbon impurity in fullerenes.

We define an intensity ratio $R = A(2760\ cm^{-1}$ to $3100\ cm^{-1})/(A(2620\ cm^{-1}$ to $2760\ cm^{-1})$, where the A's are integrated reflectance intensities between the given wavenumber limits. The spectral range of the denominator includes only C_{60} combination bands, with peaks at 2676 and 2737 cm^{-1}.

---

[9] Matlab, by The Mathworks, Inc., Natick, MA 01760-1415

[10] Griffiths, P. R.; deHaseth, J. A., Fourier Transform Infrared Spectrometry, 1986, Vol 83 in Chemical Analysis, ed P. J. Elving and J. D. Winefordner, Wiley-Interscience, , pp 194ff

[11] Chase, B.; Herron, N. ; Holler, E., J. Phys. Chem. 1992, *42* , 4262, Fig. 2

[12] Negri, F. ; Orlandi, G. ; and Zerbetto, F., Chem. Phys. Lett. 1988 , *144*, 31

[13] Lin-Vien, D.; Colthup, N. B.; Fately, W. G. ; Grasselli, J. G., 1991, The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press, ,Chaps 2 and 17

The range of the numerator includes both aromatic C-H stretches and aliphatic -CH_3 and -CH_2 stretches. Difference spectra of samples with and without hydrogen show peaks corresponding to methylene stretching vibrations (2848 cm^{-1} and 2919 cm^{-1}) indicating the presence of aliphatic hydrocarbon impurities. The ratio R varies from ca. 1.7 for a well purified, sublimed C_{60} sample to ca. 60 for a needle-like C_{60} sample crystallized slowly from toluene.

Diffuse reflectance FTIR spectra of samples with known atom fractions of hydrogen from neutron activation analysis and from Rutherford backscattering[14] were used to determine the hydrogen content of the samples under study here. The results are shown in Table 1.

Differential scanning calorimetry (DSC) studies of the first-order phase transition in C_{60} at 260 K[15] show that the phase transition temperature and the width of the DSC peak are very sensitive to sample purity. DSC measurements of most of the samples in Table 1, done by A. R. McGhie of the University of Pennsylvania, show that the sublimed samples have the sharpest DSC peaks and the highest transition temperature. These are also the samples which show the lowest C-H stretch/C_{60} band FT-IR intensity ratio R.

Hydrocarbon impurities in C_{70}

FT-IR specoscopy in combination with x-ray diffraction is also useful in characterizing hydrocarbon impurities in C_{70}[16]. For the first set of diffraction measurements, C_{70} samples were used which had been dried at 200°C for two hours under vacuum to remove residual hexane, the last solvent with which the sample had been washed. Evidence that this process did not remove toluene (another solvent used in the chromatographic separation) was obtained from a diffuse-reflectance infrared spectrum of the sample, shown in Figure 4 A. Previously identified[17] infrared bands of C_{70} were observed[18], but two additional bands at 694 cm^{-1} and 724 cm^{-1} can be attributed to the two strongest

---

[14] C. Kniaz and J. E. Fischer, Dept. of Materials Science, University of Pennsylvania, private communication

[15] Yannoni, C.S.; Wendt, H. R.; Siemens, R. L.; Salem, J. R.; Nguyen, D.
Lyeria, J.; Johnson, R. D.; Hoinkis, M.; de Vries, M. S.; Crowder, M. S.; Brown, C. A., Intl. Conf. on Synthetic Metals, Goteborg, Sweden, Aug 12-16, 1992, in press

[16] Vaughan, G. B. M. ; Heiney, P. A.; Fischer, J. E.; Luzzi, D. E.; Ricketts-Foot, D. A.; HcGhie, A. R. ; Hui, Y. W.; Smith, A. L.; Cox, D. E.; Romanow, W. J.; Allen, B. H.; Coustel, N.; McCauley, J. P.; Smith III, A. B. , Science 1991 , *254*, 1350

[17] Bethune, D. S. ; Meijer, G. ; Tang, W. C. ; Rosen, H. J.; Golden, W. G.; Seki, H. ; Brown, C. A.; de Vries, M. S., Chem. Phys. Leu 1991 , *179*, 181

[18] bands at 504, 534, 564, 578, 642, 674, 794, 1134, 1430 cm^{-1} (± 2 cm^{-})

infrared absorptions of toluene[19], corresponding to C-H out-of-plane bending modes. Additional bands between 1416 and 1566 cm^{-1} are less easily assigned, but are consistent with C=C stretching modes of the benzene ring in the toluene spectrum[3]. The methyl group bending modes observed in the 1350-1400 cm^{-1} spectrum of hexane[20] are absent.

The final step of sample preparation was changed. The C_{70} sample containing residual hexane was heated to 550°C under vacuum for 12 hours in a horizontal quartz tube with a cooled end. The sublimed film formed on the cool end of the tube was then scraped off; its FT-IR spectrum is shown in Figure 4b. Note the absence of bands due to toluene.

We conclude that vacuum sublimation is essential in preparing highly pure C_{60} and C_{70} samples suitable for thermodynamic measurements. It is not surprising that aromatic solvents are hard to remove from fullerenes. Each carbon in C_{60} has an unshared p-orbital normal to the surface of the icosahedron, and these orbitals should overlap with the pi-orbitals of the benzene ring to form a van der Waals pi complex. In addition, there are large voids in the C_{60} crystal structure due to the octahedral and tetrahedral holes in the fcc structure, and these voids could hold solvent if slightly expanded.

IV. Temperature Dependence of The Solubility of C_{60} and C_{70} in Toluene and Carbon Disulfide (manuscript in preparation)

Abstract

During the past year we have measured the solubility of C_{60} and C_{70} in toluene from 25 °C to 80°C and of C_{60} in CS_2 from 25 to 45 °C. The method has been to measure the concentration of saturated solutions of the fullerene using UV/visible absorption spectrophotometry. The most remarkable feature of these data is that as the temperature increases, the solubility of both C_{60} and C_{70} decrease. This is highly unusual for organic compounds in organic solvents - so much so, in fact, that despite my have done several literature searches, consulted databases of organic solubilities and current comprehensive literature[21], and asked experts on organic

---

[19] Sadtler Research Labs, Standard IR Spectra, #419, Philadelphia, PA 1962

[20] op. cit, #678

[21] Grant, D. W. J.; Higuchi, T., "Solubility Behavior of Organic Compounds", 1990, Vol XXI of Techniques of Chemistry, Wiley-Interscience

solubility[22], I have not been able to find any other organic compound which exhibits a negative temperature dependence of the solubility.

Introduction

One of the classical ways to study intermolecular interactions between two substances is to determine their mutual solubility [20, 23]. The notion of ideal and regular solutions evolved from thermodynamic and statistical mechanical investigations of solubility. In addition, the solubility of chemical substances plays a key role in their isolation and purification and the control of their chemical reactivity. Experimental study of the fullerenes[24] grew explosively after it was discovered by Krätchmer, Huffman, et al[25] that a component of the graphitic soot produced by electric arcs could be dissolved in benzene. Yet, aside from footnotes in the burgeoning fullerene research literature, the first quantitative study of the solubility of C_{60} in various organic solvents was only recently published. Mathews et al[26] measured solubilities of C_{60} in fifteen organic solvents at 303 K, and they explain the large variation (a factor of $\sim 10^3$) in terms of Hildebrand's theory of regular solutions. They suggest that C_{60} has a solubility parameter of ca. 18.5, closely matching that of toluene and benzene. Ruoff et al[27] report the temperature dependence of C_{60} solubility in hexane, toluene, and CS_2 over the temperature range 195 K to the normal boiling point of each solvent. The solubility/temperature curve displays a maximum at ca. 280 K. We have chosen toluene and CS_2 as solvents in this study because of their importance in both the extraction of the fullerenes from soot and their subsequent chromatographic purification.

Experimental method and results

For the initial studies[28] (February - April 1992), C_{60} and C_{70} were separated and purified from the extract of graphitic soot provided by W. A. Romanow of the University of Pennsylvania. Preparative

---

[22] telephone conversation with Dr. D. W. J. Grant, February 16, 1993

[23] Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. , 1970 , Regular and Related Solutions, Van Nostrand Reinhold

[24] Kroto, H. W. ; Allaf ,A. W. ; Balm, S. P., Chem. Rev. 1991, *91* , 1213

[25] W. Kratschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature 1990 , *347* , 354

[26] Sivaraman, N.; Dhamodaran, R.; Kaliappan, I.; Srinivasan, T. G.; Vasudeva Rao, P. R.; Mathews, C. K., J. Org. Chem. 1992, *57*, 6077

[27] Ruoff, R. S.; Malhotra, R.; Huestis, D. L.; Tse, D. S.; Lorents, D. C., "The Unusual Solubility Behavior of C_{60}", Nature 1993, *in press*

[28] A. L. Smith, Y. W. Hui, and D. Li, presentation at 186th Electrochemical Society meeting, St. Louis, MO, April 1992

chromatography as previous described was performed using neutral alumina (Fisher, Brockman Activity 1), and reagent grade hexanes and toluene. Solvents were removed with a rotary evaporator, and samples were dried in 1×10^{-4} torr vacuum at 200 °C for 6 hours and then characterized by diffuse reflectance FTIR and HPLC (Regis phenylglycine column with hexane as mobile phase). For later C_{60} solubility measurements in toluene and in CS_2, a sample obtained from Texas Fullerenes was used without further purification. The C_{60} and C_{70} content of the original extract and of the separated solutions was determined by quantitative UV/visible absorption with a HP 8451 diode array spectrophotometer, as described above.

For our first measurements on C_{60} in toluene (February-March, 1992) saturated solutions were prepared in a 1.0 cm path length quartz cell held in a stirred, thermostatted cell holder (± 0.1 °C) at temperatures of between 25 and 75 °C (measured with a calibrated thermocouple placed in the cell itself). After the stirrer was turned off, the solution was allowed to settle for 1-2 hours and the absorbance measured. These measurements showed clearly that the solubility of C_{60} decreased with increasing temperature, but the spectra also exhibited positive baseline shifts of up to 1.2 a.u. in the near infrared, which we attribute to optical scattering of undissolved, suspended C_{60} (the density of fullerenes is <2 g/cm^3, so material settles out of solution very slowly). Absorbances were too large to make good concentration measurements, so we shifted to 1.0 and 2.0 mm path length cells. The data sets of 4/21/92 and 6/16/92, taken after allowing shaken solutions to equilibrate and settle for an hour, showed residual absorption at 750 nm due to optical scattering of less than 5% of the absorbance at 590 nm. Absorbances between 500 and 600 nm (0.2 -0.8 a.u.) were corrected for this residual baseline, and C_{60} concentrations were then determined at 50 wavelengths and averaged to determine the concentration of the saturated solution. The data are plotted in Figure 5.

For the data sets of 7/20/92 and 7/24/92, stirred, saturated solutions were allowed to settle for an hour, then 30-40 µl was withdrawn into a glass syringe. A syringe filter was added between the syringe and the needle to remove suspended crystallites, and the solution was then expelled into the 1.0 mm path length cuvette and the cuvette was quickly capped. Even though the temperature of the saturated solution may well have dropped in the process, the inverse dependence of solubility on temperature assured that no solid precipitated out. The data (Figure 5) show solubilities from 10-30% lower than earlier (or later) measurements, which we attribute to slight absorption of C_{60} on the filter material.

The final data sets of Figure 5 (11/16 and 11/1792) were obtained from the Texas Fullerenes C_{60} sample, measured in a sealed 2.0 mm cell allowed to equilibrate for an hour.

The two data sets for C_{70} in toluene (Figure 6) were taken on 4/20/92 and 4/22/92, and agree well with one another. The two data sets for C_{60} in CS_2 (Figure 7) were taken in December 1992; particular care was taken to seal the 2.0 mm cuvette with Teflon tape so as to prevent CS_2 from evaporating and forming a supersaturated solution.

Discussion

Ruoff et al have recently reported that the solubility of C_{60} in toluene, CS_2, and hexane all shows negative temperature dependence for $T > 280$ K. From thermodynamics it can be shown that a negative temperature dependence of solubility implies an exothermic heat of solution, ΔH^{soln}. If we assume that the equilibrium

$$C_{60}(s,T) = C_{60}(\text{satd soln}, x_{C60}, T), \qquad [1]$$

$$(x_{C60} = \text{mole fraction of } C_{60} \text{ in the saturated solution})$$

is established, from the thermodynamics of solid solubility[29], the enthalpy of solution of C_{60} is given by

$$\Delta H^{soln} = \bar{H}_{C_{60}} - H^{s}_{C_{60}} = -R\left(\frac{\partial \ln x_{C_{60}}}{\partial (1/T)}\right)_{sat} \qquad [2]$$

The resulting enthalpies of solution vary from -10.7 kJ/mole to -18.1 kJ/mole for the various data sets of Figure 5, with a mean value of -13.6 ± 2.5 kJ/mole. This is in reasonable with agreement Ruoff et al's value of -11 ± 2 kJ/mole.

The negative heat of solution for the system C_{60}/toluene is hard to understand. The theory of regular solutions[20, 22], based on modifications of the theory of ideal solutions, is quite successful in correlating solubilities of organic compounds in organic solvents. For an ideal solution of two liquids, the enthalpy of mixing ΔH^{mix} is zero; for an ideal solution of a solid and a liquid, the enthalpy of solution is positive and equal to the enthalpy of fusion of the solid. Regular solutions show positive deviations from the ideal solution theory heats of solution. Polynuclear aromatic

---

[29] Ref 22, eqn 2.57, page 24

hydrocarbons form almost ideal solutions with benzene[30], and their solubilities increase with temperature, as shown in Figure 8.

The dissolution of solid C_{60} in toluene may be described as a two-step process:

$$C_{60}(\text{solid}, T) = C_{60}\ (\text{supercooled liquid}, T), \quad \Delta H = \Delta H^{fus} \qquad [3a]$$

$$C_{60}(\text{supercooled liquid}, T) + \text{toluene} = \text{saturated solution } (T) \quad \Delta H = \Delta H^{mix} \qquad [3b]$$

The enthalpy change for 3a is approximately the heat of fusion of C_{60} if one ignores the heat capacity differences between solid and supercooled liquid. Thus,

$$\Delta H^{soln} = \Delta H^{fus} + \Delta H^{mix}. \qquad [4]$$

Although ΔH^{fus} is not known (since the melting point T_m of the solid has not been observed and must be greater than 900 °C [31]), we can estimate it as follows. We assume that at the melting point, C_{60} molecules are freely rotating in the solid phase, as they are known to be at room temperature. Thus, the only contribution to the entropy of fusion $\Delta S^{fus} = \Delta H^{fus} / T_m$ of C_{60} comes from "positional melting". It is known that this contribution to ΔS^{fus} for rigid spherical molecules is about 10.5 J/mole[32]. Taking T_m = 1173 K, we obtain $\Delta H^{fus} \approx$ 12 kJ/mole. The enthalpy of sublimation of C_{60} is known to be 39 kJ/mole[33], so $\Delta H^{fus}/\Delta H^{subl} \approx 0.3$. This is a reasonable result, since other rigid, nearly spherical organic molecules have similar ratios[34]. Since the observed heat of solution of C_{60} in toluene, assuming the equilibrium in Eq. 1, is -13.6 kJ/mole kJ/mole, from Eq. [4] we obtain $\Delta H^{mix} \approx$ --25.6 kJ/mole.

We submit that such a large, negative heat of mixing is unrealistic. It implies very large negative departures from Raoult's law and solution ideality, yet there seems to be no plausible microscopic reason why so much energy is released when forming a solution between molecules whose

---

[30] D. S. Mishra and S. H. Yalkowski, Ind. Eng. Chem. Res. 1990, 29, 2278

[31] X-ray powder diffraction patterns of the solid are still observed at 900 °C (G. Vaughan and P. Heiney, private correspondence)

[32] Yalkowsky, S. H., Ind. Eng. Chem. Fundam. 1979, *18*, 108

[33] Mathews, C. K.; Baba, M. Sai; Lakshmi Narasimhan, T. S.; Balasubramanian, R.; Sivaraman, N.; Srinivasan, T. G.; Vasudea Rao, P. R., J. Phys. Chem. 1992, *96* , 3566

[34] For example, the ratio for adamantane is 0.22. (C. Kniaz, U. Pennsylvania, private communication)

electronic structure is similar (aromatic rings and pi electron density on the "surface" of each). Admittedly, the low-density, fcc structure[35] of C_{60} in the solid does not permit close contact between solute molecules, whereas the solute-solvent contact in the solution is more intimate and thus the van der Waals interactions are probably stronger. Yet it is very hard to believe that such effects could account for a heat of mixing of two liquids which is almost as large as the heat of sublimation of one of the corresponding solids.

We must thus seek another explanation for the negative temperature dependence of the solubility of C_{60} in toluene. Ruoff et al have proposed that the primary contribution to the negative temperature dependence is the formation of a solid solution of C_{60} and solvent, with increasing mole fraction of solvent at increasing temperatures. In equation [1] we assumed that the solid phase was pure C_{60}, yet evidence from crystallography and from vibrational spectroscopy shows that C_{60} indeed forms stable inclusion compounds with pentane[36] and a number of other organic solvents[37]. Thus, the formation of toluene inclusion compounds is likely.

As Grant and Higuchi prove, "A rule applying to solubility is that solid solvates are always less soluble in the solvent forming the solvate than is the original solid."[38] When C_{60} precipitates from a saturated solution in toluene, the resulting solid may not be a pure phase but a mixture of pure C_{60} and of toluene inclusion compounds, with ill-defined stoichiometry. This mixed phase solid will have a lower apparent "equilibrium solubility" than would pure C_{60}. The rate of formation of solvated solid phase probably depends upon the temperature, the degree of supersaturation, and the availability of nucleating crystallites. Thus, the longer we wait for equilibrium to occur, the more the solid material in equilibrium with the solvent changes its composition to solvated solid. This makes the determination of true equilibrium solubilities of unsolvated solid fullerenes more difficult. The non-reproducibility shown in Figure 5 for the "equilibrium solubility" of C_{60} in toluene at various temperatures may well be due to the formation of solid phases of variable solvent composition. We are investigating this possibility at present, using FTIR spectroscopy to determine the percentage of solvent trapped in the C_{60} crystal. Preliminary studies of the solid precipitating from saturated toluene at 50

---

[35] Fischer, J. E.; Heiney, P. A., Smith, A. B. III, Accts Chem. Res. 1992, *25*, 112

[36] Pekker, S.; Faigel, G.; Fodor-Csorba, K.; Granasy, L.; Jakab, E.;Tegze, M., SOlid State Comm. 1992, *83*, 423

[37] Kamaras, K.; Hadjiev, V. G.; Thomsen, C.; Pekker, S.; Fodor-Czorba, K.; Faigel, G.; Tegze, M., Intl. Conf. on Synthetic Metals, Goteborg, Sweden, Aug 12-16, 1992, in press

[38] Ref. 20, page 38

°C indicates that at early times the solid includes a good deal of toluene, whereas at later times the solid is pure C_{60}. Without a direct measurement of the percentage of solvent included in the precipitated solid in a solubility experiment, the "equilibrium" solubilities reported here or elsewhere cannot be accepted as the true thermodynamic solubilities.

Figure 6 implies that the heat of solution of C_{70} in toluene is also negative over the temperature range studied, and and fit of the data to $\ln[C_{70}]$ vs $1/T$ gives a heat of solution of -5.2 ± 0.7 kJ/mole. Since C_{70} shows two rotational disordering transition at 276 K and 337 K [15], Ruoff et al's observation that the maximum of the solubility vs temperature curve (280 K) for C_{60} is correlated with the occurrence of an order-disorder phase transition (260 K) does not hold in C_{70}.

A case can be made from the data in Figure 7 that the solubility of C_{60} in CS_2 is independent of temperature, although the scatter is rather large. This disagrees with the results of Ruoff et al, who found similar heats of solution of C_{60} in toluene and CS_2. Further work is needed to resolve this discrepancy.

In separating and purifying the fullerenes, we have noticed gradations of color of the deposit as the solvent is removed from the extract of the raw soot, suggesting that C_{60} and C_{70} are precipitating out under different conditions. A more systematic study of selective precipitation of C_{60} within a Soxhlet extractor has been reported by Coustel et al[39]. As the toluene solvent from soot extract with a 4:1 ratio of C_{60}:C_{70} is slowly allowed to evaporate within a Soxhet extractor, 98% pure C_{60} selectively precipitates in the solvent flask. This observation can be explained as follows. The extraction temperature T_1 in the thimble of a Soxhlet extractor is undoubtedly lower than the boiling point of the solvent, T_2, since no heat is applied to the extractor thimble. Thus, the solubility of fullerenes in the thimble exceeds the solubility in the solvent flask. Even though C_{60} is several times more soluble than C_{70}, as the extract at T_1 mixes with the solution at T_2 the solution becomes saturated first with respect to C_{60}, and C_{60} precipitates.

Clearly there is much to learn about the solute-solvent intermolecular interactions in fullerene/organic solvent systems which exhibit such unusual temperature dependencies. The fact that the solubilities of C_{60} and C_{70} are different and also show different temperature dependencies could form the

---

[39] Coustel, N. ; Bernier, P.; Aznar, R.; Zamed, A.; Lambert, J.-M.; Lyard, P. J. Chem. Soc. Chem. Comm. 1992, *19* , 1402

basis for a separation process which completely avoids chromatography and thus would be more amenable to large-scale industrial production.

The fact that van der Waals interactions between typical solvents and fullerenes are so strong has definite implications for the eventual use of fullerenes as adsorbents. By further understanding why these interactions are so large, we should put on a better basis the intermolecular interactions between carbonaceous solids and volatile materials, thus helping to understand why standard carbon materials are good adsorbents. It will be very important to characterize these strong interactions better by studying further the solubilities of fullerenes in other organic solvents , including those which more closely match the organic vapors whose removal from air is of interest to the Army.

The authors would like to thank Jack Fisher and the other members of the U. Penn buckyball research group for many useful discussions.

V. Experimental Heat of Formation and Average Carbon-Carbon Bond Energy in C_{60}, Buckminsterfullerene (manuscript in preparation)

D. A. Kirklin
Chemical Thermodynamics Division, Center for Chemical Physics,
National Institute of Standards and Technology, Gaithersburg, MD, 20899

A. L. Smith*, Y. W. Hui
Chemistry Department, Drexel University, Philadelphia, PA 19104

A. R. McGhie, W. A. Romanow
Laboratory for Research in the Structure of Matter, University of
Pennsylvania, Philadelphia, PA 19104

Abstract

Using the NIST aneroid adiabatic rotating calorimeter, we have measured the energy of combustion of a pure, well characterized sample of C_{60}. The standard molar enthalpy of combustion $\Delta_c H^0_m$ is -(25803.9 ± 5.6) kJ·mol^{-1}. The derived enthalpy of formation of C_{60}(c) is (2193.3 ± 9.6) kJ·mol^{-1}, somewhat lower than reported values of this quantity. Using the enthalpy of formation of C(gas) we calculate that the average carbon-carbon bond

energy in C_{60} is 453 kJ/mol, less than in graphite but more than in diamond.

Introduction

The strengths of the covalent bonds in organic compounds are of fundamental importance in understanding their structure and reactivity. It is well known[40] that thermochemical heats of formation may be combined to compute bond strengths. In this paper we report an experimental measurement of the heat of formation of solid C_{60}, Buckminsterfullerene, and we use this number to compute the average carbon-carbon bond energy in C_{60}.

By definition, the standard heat of formation of graphite, C(cr), at 298.15 K, 1 atm, is zero. When graphite is burned in oxygen,

$$C(graphite) + O_2(g) = CO_2(g) \qquad [1]$$

the standard heat of combustion of graphite is equal to the standard heat of formation of carbon dioxide, $\Delta_f H^0_m[CO_2(g)]$. The heat of combustion of graphite is measured to be -393.509 $kJ\cdot mol^{-1}$. Since C_{60} is less thermodynamically stable than graphite, its heat of combustion must be larger than that of graphite.

Newton and Stanton[41] first reported a quantum calculation of the heat of formation of C_{60}, based on the semi-empirical MNDO method. Their result is +14.5 kcal . mol^{-1} (per mole of C), or 3640 kJ . mol^{-1} (per mole of C_{60}). Another MNDO study of large carbon clusters[42] reports a value of 13 kcal . mol^{-1} (of C), or 3260 kJ . mol^{-1} (of C_{60}). Schulman and Disch[43] have used a 6-31G* SCF energy of C_{60} in combination with group equivalent methods to arrive at a value of 11.2 kcal . mol^{-1} (of C), or 2811 kJ . mol^{-1} (of C_{60}). These computations are all for gaseous C_{60}, but they can be corrected to the solid form by subtracting the heat of sublimation of C_{60}[32, 44,45].

Experimental Section

---

[40] Benson, S. J. Chem Ed 1965, *42*, 502
[41] Newton, M. D.; Stanton, R. E., J. Am. Chem. Soc. 1986, *108*, 2469
[42] Bakowies, D.; Thiel, W., J. Anm. Chem. Soc.. 1991, *113*, 3704
[43] J. M. Schulman and R. L. Disch, J. Chem. Soc. Chem. Comm. 1991, 411
[44] Pan, C.; Sampson, M. P., Hauge, R. H.; Margrave, J. L. J. Phys. Chem. 1991, *95*, 2944
[45] Tokmakoff, A.; Haynes, D. R.; George, S. M., Chem. Phys. Lett. 1991, *186*, 450

The soot from a graphite rod arc reactor was extracted with room temperature toluene, producing a fullerene mixture which by high-performance-liquid-chromatography on a Pirkle column contained about 75% C_{60}, 20% C_{70}, and 5% higher fullerenes. Neutral alumina column chromatography fractions, using 5% to 20% toluene in hexanes, were monitored with a diode-array UV-visible spectrophotometer to assay the fullerene composition in real time, and an early C_{60} fraction was selected which had no contamination from $C_{60}O$. Solvent was removed in a rotary evaporator at 80^{0}C, and the dried sample (finely divided brown powder) was washed three times with reagent grade hexane. The sample was redissolved in toluene, filtered to remove residual alumina, pumped to dryness in a rotary evaporator, washed with diethyl ether, then dried under vacuum (ca 1 Pa , or 10^{-3} torr) at 230 ^{0}C for 6 hours. The weight loss of the sample during drying was 3.2%. An electron-impact mass spectrum of the resulting dark brown sample showed only mass 720 and 721. The sample redissolved slowly in toluene, and its UV-visible spectrum was identical to that of other samples of >99.9% fullerene purity prepared at the University of Pennsylvania. Pirkle column hplc confirmed that the C_{70} content was less than 0.1%.

Because of the large effect of residual hydrocarbon impurities on the apparent heat of formation of C_{60} (0.1% of toluene by weight will increase $\Delta_f H^0_m[C_{60}(c)]$ by 1.1%), an effort was made to characterize the hydrogen content of the sample. Diffuse reflectance infrared spectroscopy of the sample (5% in KBr) showed weak C-H stretch bands in the 2900-3100 cm^{-1} region, but no C_{60} sample of known hydrocarbon content was used to quantify this residual hydrogenic impurity.

The NIST adiabatic bomb calorimeter was used for the heat of combustion measurements. It is a vacuum-jacketed, aneroid calorimeter with an adiabatic shield around the calorimeter. A calibrated capsule-type platinum resistance thermometer is located in the bomb wall. A constant current source was passed through the platinum resistance thermometer and a calibrated standard resistor. The resulting voltages were measured with a high precision nanovoltmeter. A more comprehensive description of the calorimeter system can be found in an earlier paper by Kirklin and Domalski.[46]

The calorimeter was calibrated by a series of combustion experiments using benzoic acid, NIST SRM 39i. The calorimeter is normally calibrated for a three- or one-degree temperature rise. Since the total C_{60} sample was

---

[46] Kirklin, D. R.; Domalski, E. S. J. Chem. Thermdynamics 1983, *15*, 941

only 100 mg, the calorimeter was calibrated for only 0.5 degree temperature rise. The C_{60} analysis samples were not large enough to produce a 0.5 degree temperature rise and therefore a small pellet of benzoic acid was used as an auxiliary substance. A mass of benzoic acid was chosen to produce half of the measured energy. A standard procedure for bomb calorimetric measurements was followed for these measurements.

The results of the set of calibration measurements and the C_{60} combustion measurements are presented in Table 2. All calculations were performed using a computer program originally written by C. H. Shomate[47] and later revised by G. T. Armstrong[48] according to the methods of Hubbard, Scott, and Waddington.[49] The calculations required several auxiliary values. Thermochemical quantities for $CO_2(g)$ and $O_2(g)$ were taken from Wagman et al [50] and CODATA.[51] The molar mass of C_{60} is 720.66 $g \cdot mol^{-1}$ and is based on the 1985 Table of International Atomic Weights.[52] The density and specific heat capacity of C_{60} were taken as 2.25 $g \cdot cm^{-3}$ and 0.397 $J \cdot K^{-1} \cdot g^{-1}$, respectively. The value of the gas constant used in the calculations is $R = 8.314510\ J \cdot K^{-1} \cdot mol^{-1}$.[53] The standard heat capacities used for CO_2 and O_2 were 37.11 and 29.355 $J \cdot K^{-1} \cdot mol^{-1}$, respectively. The $\Delta_f H^0_m$ for CO_2 is -393.509 $kJ \cdot mol^{-1}$ and was used to convert from $\Delta_c H^0_m$ to $\Delta_f H^0_m$.

The enthalpy of combustion was determined for the following chemical reaction:

$$C_{60}(cr) + 60\ O_2(g) = 60\ CO_2(g).$$

The combustion data were used to calculate the enthalpy of formation of crystalline C_{60} at 298.15 K by the following reaction:

$$60\ C(cr) = C_{60}(cr).$$

---

[47] (a) Shomate, C. H. U. S. Naval Ordnance Test Station Technical Report 327. August 1963, China Lake, CA. (b) Shomate, C. H. U. S. Naval Ordnance Test Station Technical Report 5052. January 1967, China Lake, CA.

[48] Armstrong, G. T. Nat. Bur. Stand. Report 9803, 1968, chap. 3.

[49] Hubbard, W. N. ; Scott, D. W.; Waddington, G. J. Phys. Chem. 1952, *58*, 152

[50] Wagman, D. D.; Evans, W. H.; Parker, V. B. ; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. J. Phys. Chem. Ref. Data 1982, *11*, Supplement no. 2

[51] CODATA recommended key values for thermodynamics 1977, CODATA Bulletin 28, April 1978

[52] Holden, N. E.; Martin, R. L. Pure Appl. Chem. 1986 , *58*, 1677

[53] CODATA 1986 recommended values of the fundamental physical constants. CODATA Newsletter 38. October 1986.

The calculated thermochemical results are presented in Table 3. The total uncertainty was calculated according to the guidelines presented by G. Olofsson[54]. The assigned uncertainty is equal to twice the overall standard deviation which includes components for sample measurements, calibration measurements, and benzoic acid certification measurements[55]. In addition, there are components for the auxiliary substance and estimated uncertainties of 0.01 percent each for sample impurities and systematic error. The uncertainty in the enthalpy of formation contains a component for the uncertainty in the enthalpy of formation of $CO_2(g)$.

Results and Discussion

There have been two other experimental determinations of the enthalpy of formation of C_{60}[56, 57]. The three sets of measurements are summarized in Table 4. Clearly there is disagreement within the stated experimental precision. We believe that this is due to inadequately characterized samples, particularly with respect to the hydrocarbon content. The work discussed in previous sections shows that it is very difficult to remove the last traces of solvent except by vacuum sublimation, and none of the three groups did this. We are working to produce the purest sample of C_{60} and C_{70} possible with present technology. When this becomes available, we will forward the samples to NIST for their calorimetric measurements.

In Figure 9 we present the enthalpy of formation of different allotropic forms of carbon, in kJ per mole of atoms. Our experimental result is in reasonable agreement with the calculations of Schulman and Disch. Notice that Buckminsterfullerene, C_{60}, is much less thermodynamically stable than either graphite or diamond. Of course this does not tell us how chemically stable C_{60} is with respect to degradation into graphite (or diamond, for that matter). Only further experimental work will elucidate the chemcial reactivity of this unusual all-carbon molecule.

Strengths of carbon-carbon bonds in carbon allotropes

---

[54] Olofsson, G. Combustion calorimetry. 1979, Sunner, S.l Mansson, M.: editors. Pergamon: New York, , chap. 6.

[55] Churney, K. L.; Armostrong, G. T. *J. Res. Nat. Bur. Stand.* *1968*, *72A*, 453.

[56] Beckhaus, H.-D; Ruchardt, C.; Kao, M.; Diederich, F.; Foote, C. S.. Angew. Chem. Int. Ed. Engl. 1992, *31*, 63

[57] Steele, W. V.; Chirico, R. D.; Smith, N. K.; Billups, W. E.; Elmore, P. R.; Wheeler, A. E.. J. Phys. Chem. 1992, *96*, 4731

By using thermochemical information on the carbon allotropes themselves, it is possible to calculate and compare the strength of the carbon-carbon bond in diamond, graphite, and Buckminsterfullerene without reference to any organic compound containing hydrogen, oxygen, or other elements.

The carbon-carbon single bond.

From the accepted heats of formation of diamond and gaseous atomic carbon[58], the molar enthalpy change for the atomization of diamond,

$$\text{C(diamond)} = \text{C(gas)} \qquad (1)$$

is 714.9 ± 0.5 kJ/mol. In the atomization process, two moles of C-C bonds are broken per mole of diamond atomized, so the carbon-carbon single bond strength in diamond is 357.5 ± 0.5 kJ/mol. This is lower than the accepted C-C bond strength in ethane, 376.1 ± 2.1 kJ/mol, but it is well known that varying the substituents on sp3 hybridized carbons affects the C-C bond energy by as much as 15-20 kJ/mol.

The carbon-carbon double bond.

An accurate experimental heat of formation of the gaseous carbon dimer, C_2, has recently been reported by Jackson and coworkers[59]: $\Delta_f H^0_m[C_2(g)] = 815.0 \pm 2.0$ kJ/mol. For the dissociation reaction

$$C_2(\text{gas}) = 2C(\text{gas}),$$

the standard enthalpy change is thus 618.3 ± 2.2 kJ/mol, which we take as the strength of a carbon-carbon double bond. This is again lower than the accepted value of the C=C bond energy in ethylene[60], 720 ± 8 kJ/mol. but well above the carbon-carbon double bond energy in C_2F_4, 319 kJ/mol[61]

The carbon-carbon bond in graphite

In graphite, the atoms within a sheet are bonded covalently whereas the interaction between sheets is intermolecular (Van der Waals bonding). A convenient reference state for atomization calculations is the infinite graphite sheet, whose enthalpy with respect to graphite has been calculated

---

[58] Cox, J. D.; Wagman, D. D.; Medvedev, V. A., *CODATA Key Values for Thermodynamics*, 1989, Hemisphere Publishing Company

[59] Urdahl, R. S.; Bao, Y.; Jackson, W. M., Chem. Phys. Lett. 1991, *178*, 425

[60] Value calculated using enthalpy data from Cox, J. D., and Pilcher, G., Thermochemistry of Organic and Organometallic Compounds, Academic Press, 1970, and Walsh, R., Accts. Chem. Res. 1981, *14*, 246

[61] Zmbov, K. F.; Uy, O.; Margrave, J. L., J. Am. Chem. Soc. 1968, *90*, 5090

by Girifalco[62] as 6.3 kJ/mol of carbon. Thus, the standard enthalpy change for the reaction

$$\text{C(infinite graphite sheet)} = \text{C(g)}, \quad \Delta H^0_m = 710.4 \text{ kJ/mol},$$

can be taken as a measure of the covalent carbon-carbon bond energy in graphite. In atomizing a mole of infinite graphite sheets we break 3/2 moles of C-C bonds. Thus, the carbon-carbon bond strength in graphite is 474 kJ/mol.

We can estimate the resonance stabilization energy of the covalent bonding in graphite as follows. If resonance stabilization played no role, the bond energy in graphite would be 1/3 C=C bond energy + 2/3 C-C bond energy, or 444 kJ/mol. Since the actual bond strength is 474 kJ/mol, the stabilization energy in graphite is 30 kJ/mol of carbon. The accepted value for the resonance stabilization energy of benzene is 138 ± 12 kJ/mol of C_6H_6, or 23 kJ/mol of carbon.

The carbon-carbon bond in C60.

The atomization energy of carbon in fullerene, C_{60}, can be calculated from the equation

$$C_{60}(\text{gas}) = 60\ \text{C(gas)}.$$

Using our value of 2193 kJ/mol for the heat of formation of C_{60}(solid), the heat of sublimation of C_{60}, and the heat of formation of C(gas) we calculate the total atomization energy of C_{60} to be 40769 kJ/mol C_{60}. There are 30 double bonds and 60 single bonds in most of the 12,500 Kekule structures[63] of C_{60}, so the average energy of one C-C bond in C_{60} is 40769/90 = 453 kJ/mol. Again, if resonance stabilization were inoperative in C_{60} the average carbon-carbon bond strength would be 444.4 kJ/mol as it is in graphite, which also has a 2/1 ratio of single to double bonds. Thus, the resonance stabilization energy of C_{60} is 9 kJ/mol of bonds, or 810 kJ/mol of C_{60}.

VI. Gas phase absorption spectrum of C_{60} (manuscript in preparation)

G. Zimmerman and A. L. Smith
Chemistry Department, Drexel University
Philadelphia, PA 19104

---

[62] Girifalco, L., J. Chem. Phys. 1956, *25* , 693

[63] Brendsdal, E.; Cyvin, S. J., J. Mol. Struct. 1989, *188* , 55-66

Introduction

Recent studies of Buckminsterfullerene, C_{60}, show that it sublimes at temperatures of above 400 °C. We decided to attempt a measurement of the gas phase absorption spectrum of C_{60}, in part to see if the material was stable enough at elevated temperatures to permit such a measurement, and in part to compare its gas phase electronic absorption spectrum with that of the solid and the solution phase.

Experimental Procedure

Approximately 1 mg samples of crystalline C_{60} purified by column chromatography as described above were placed into a 10 cm path length cylindrical quartz cell with suprasil windows, then baked in a high vacuum at 300 °C and sealed off. The cell was mounted at the center of a length of brass tubing which fitted inside a 25 cm long tube furnace. The cell windows were maintained at a temperature 7° to 10 ° higher than the center of the cell by means of two identical auxiliary heating coils built into the brass mounting, adjacent and just outside of the windows. Immediately beyond the heating coils were two additional suprasil windows. The whole assembly was symmetrical about the center with the lowest cell temperature at the center; this temperature was measured with a thermocouple in contact with the cell wall, and when constant is presumed to be the equilibrium temperature of the C_{60} in the cell. By using the auxiliary heating current as a fine adjustment, it was possible manually to hold the temperature to within ± 1 °C.

The radiation source was a deuterium lamp providing a continuum from 180 nm up to the visible range. By monitoring the observed intensity at the wavelength of the minimum absorption, it was possible to correct for slow drifts of the lamp intensity over observation times of hours. The transmitted radiation was measured in two ways:

(a) Using quartz lenses to collimate the radiation and focus it on the entrance slit of a McPherson grating monochromator from which the radiation was detected and recorded with a standard photomultiplier-picoammeter-computer combination. The lenses were not made of suprasil quartz, and so, below 200 nm, the intensity at the entrance slit was too small to give reliable absorbances.

(b) The same as (a), except than no lenses were used. The monochromator and , as much as possible, the spaces between the cource, cell and monochromator slit with flushed with N_2 or Ar. The effectiveness of flushing was demonstrated by showing that the absorption of the Schumann-Runge absorption bands of O_2 could be reduced to a few percent of their intensity in air and kept constant with time. Thus, reliable absorbances could be obtained between 180 and 220 nm. The resolution of the monochromator, as used, was estimated to be 0.2 nm by scanning the Hg emission lines at 313 nm.

Results

Figure 10 shows the ultraviolet absorbance of C_{60} gas at three temperatures: 500 °C, 550 °C, and 600°C, taken with modification (a) above. These spectra are quite reproducible from day to day. After over a month of recording high temperature absorption spectra similar to these, the cell was opened and the contents dissolved readily in toluene, giving the characteristic C_{60} absorption spectrum. From this observation we conclude that, in the absence of oxygen, C_{60} retains its chemical identity for days even up to 600 °C.

Figure 11 shows one of the spectra recorded with the nitrogen-flushed optical path (modification (b), which permits absorbance measurements down to 180 nm. The most notable feature of this spectrum , taken at 650 °C, is the relative intensities of the three peaks at 210, 258, and 332 nm. The 210 nm is almost 40% more intense than the peak at 258 nm; in contrast, the intensity of the 212 nm absorption peak of C_{60} in hexane is 30 percent less than that of the 258 nm peak.

In Figure 12 we show a plot of C_{60} vapor pressure versus temperature, computed from our data under the assumption that the molar absorptivities of C_{60} in the vapor are the same as in hexane solution. Also shown are recent determinations of the vapor pressure/temperature curve by Balooch et al[64] and by Mathews et al[32]. While the slope of the ln (P_{vapor}) vs 1/T plot give a heat of sublimation of 159 ± 12 kJ/mole from our data, in good agreement with the data of Mathews et al, the assumption of equivalent molar absorptivities of C_{60} in gas and in solution must be in error, since our vapor pressure curve is a factor of 1.5-3 higher than that of the other two measurements.

We are investigating further these subtle differences between the gas phase and solution phase spectra of C_{60}, and are in the process of making a detailed comparison of gas phase and solution phase molar absorptivities for C_{60}.

---

[64] Abrefah, J.; Olander, D. R.; Balooch, M.; Siekhaus, W. J., Appl. Phys. Lett. 1992, *60*, 1313

VII. Some thoughts on the implications of these results for CRDEC.

The fullerenes may well provide a new route to interesting and novel new adsorbent materials. The fact that fullerenes are far more reactive than originally thought is borne out by the difficulty we are having in obtaining pure samples, as well as the ease with which C_{60} is functionalized. For example, L. Chiang[65] at Exxon has succeeded in functionalizing fullerenes with hydroxyl groups, producing a compound of formula $C_{60}(OH)_{24}$. This material becomes extremely hydroscopic! The hydroxyls can also function as sites for further chemical modification of fullerenes, e.g., by esterification. Exxon has taken out four patents on these fullerol materials. Fred Wudl and colleagues have functionalized fullerenes with amines. Amos Smith and colleagues at Penn have made $C_{60}O$ and, more recently, $C_{60}(CH_2)$, in which the methylene bridges the bond between two six-membered rings. In other words, the substitutional chemistry of fullerenes is steadily becoming understood.

It is certainly in CRDEC's interest to retain an active research program in fullerene chemistry so that the surface of fullerenes can be functionally modified to enhance absorbent properties. As CRDEC assesses the importance of fullerenes as novel adsorbents, it will be important to provide highly pure and well characterized samples for further experimental studies. If any fullerenes are ever incorporated into air purification devices, it will be useful to know that polynuclear aromatic hydrocarbons, which are potential carcinogens, have been eliminated from the absorbent materials.

VIII. Note on personnel

In experimental work of the type that we are doing, continuity of personnel is very important. One of the key members of my experimental group has been Professor Li Dayin, a Visiting Scholar at Drexel University who has a faculty appointment in physical chemistry at Beijing Normal College. Professor Li has done the outstanding solubility measurements discussed above while being supported under the auspices of the Chinese government during the period of this contract.

---

[65] Chiang, L. ; Swirczewski, J. W.; Hsu, C. S.; Chowdhury, S. K.; Cameron, S.; Creegan, K., J. Chem. Soc. Chem. Comm. , , 1993, in press

Table 1. Correlation of FTIR and percent hydrogen content of C60 samples.
% H determined by Rutherford backscattering and neutron activation analysis.
intensity ratio determined from FT-IR

C60 sample identification	date of FTIR spectrum	composition information	atom fraction H *	FT-IR intensity ratio**
NIST (1991)	9/3/92	".0057H/C"	0.0057	3.2
bad C60, Kniaz	8/13/92	"C60, H6"	0.1	19.4
C60, H 0.3 Kniaz	9/17/92	"C60, H 0.3"	0.005	2.7
Penn 200	10/13/92		0 #	1.7
Penn 220 residue	11/23/92		0 #	1.7
C60, H1.0 Kniaz	9/17/92	"C60, H1.0"	0.017	2.2
Penn 220 sublimate	11/23/92		0.001 @	1.8
Penn 202	10/13/92		0.012 @	4
Extriumf/MC-1-66A	9/3/92		0.065 @	13.2

* atom fraction = (atoms of H)/(atoms of H + atoms of C)

**ratio = [int.(2760 - 3100 cm-1]/[int(2620-2760 cm-1]

\# atom fraction H defined to be zero in these samples

@ computed atom fraction H from linear regression fit to first five points

Table 2. Summary of Experimental Calorimetry Results: Heat of Combustion of C_{60}

Calibration Results	Experimental Results
2518.803 J·K^{-1}	-35806.22 J·g^{-1}
2518.095	-35810.67
2517.727	-35798.46
2518.218	
2517.562	
2517.881	
$\overline{2518}$. 05 ± 0.18 J·K^{-1}	$\overline{-3}$5805.1 ± 3.5 J·g^{-1}

Table 3. Summary of the Thermochemical Results for C_{60}

$\Delta_c U^0_m$ (C_{60}, cr, 298.15 K) = -(25803.9 ± 5.6) kJ·mol^{-1}
$\Delta_c H^0_m$ (C_{60}, cr, 298.15 K) = -(25803.9 ± 5.6) kJ·mol^{-1}
$\Delta_f H^0_m$ (C_{60}, cr, 298.15 K) = (2193.3 ± 9.6) kJ·mol^{-1}

Table 4. Experimental Determinations of the Enthalpy of Formation of Solid C_{60}

Beckhaus et al	Steele et al	Our results
2280 ±12 kJ/mole	2422 ± 12 kJ/mole	2193 ± 10 kJ/mole

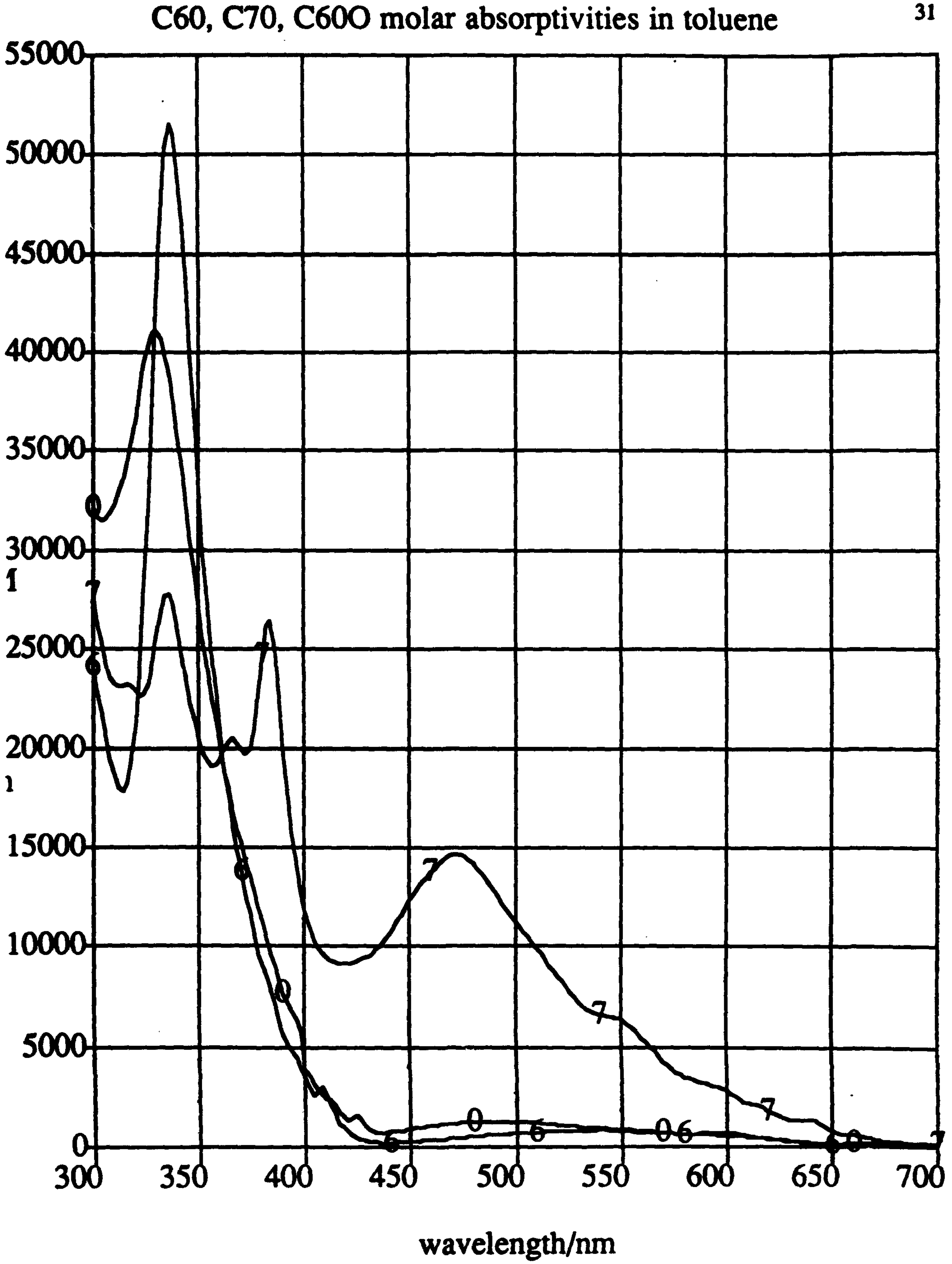

Figure 1A. Molar Absorptivity of C_{60}, C_{70}, and $C_{60}O$ in Toluene; 300 - 700 nm

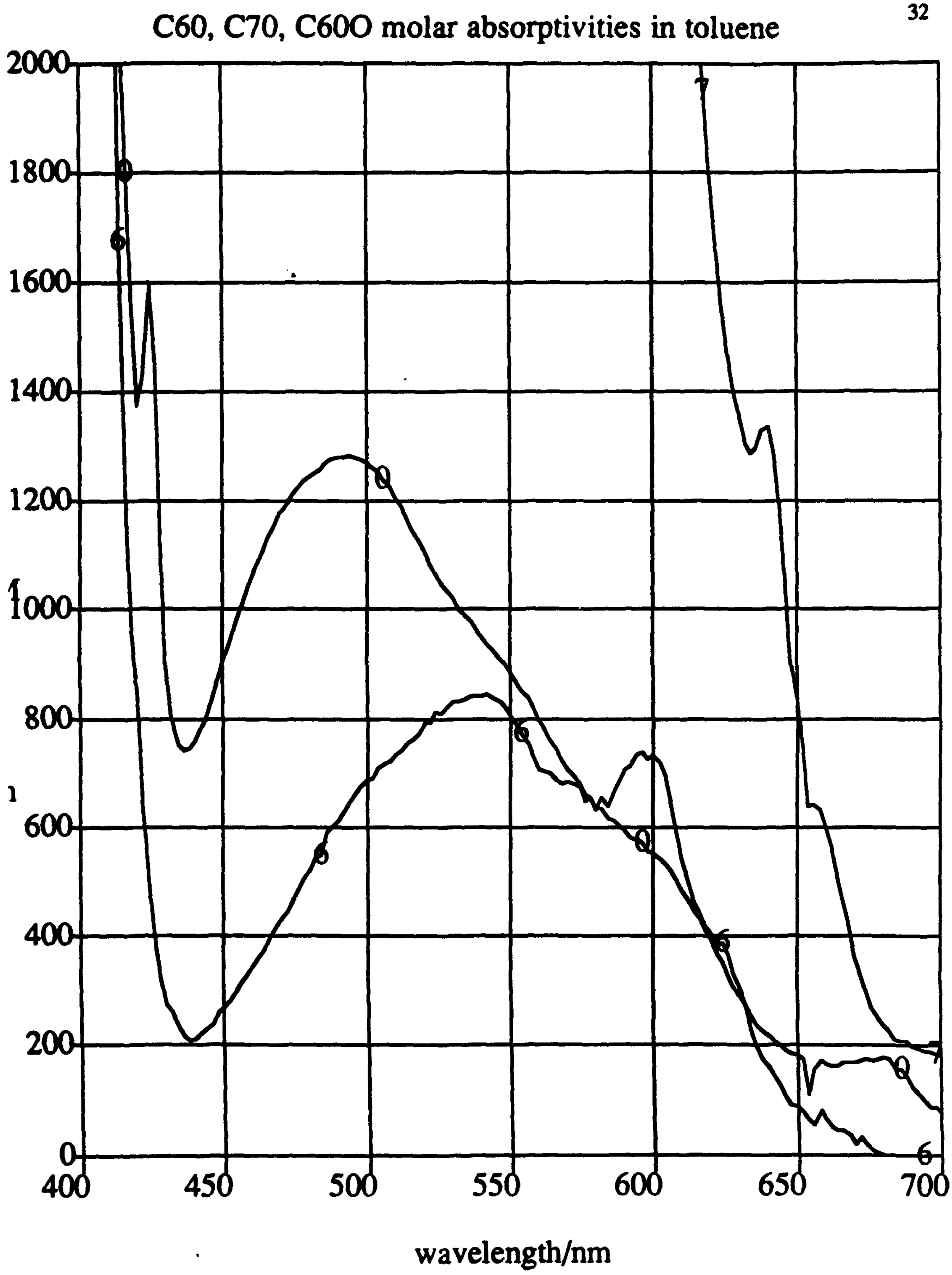

Figure 1B. Molar Absorptivity of C_{60}, C_{70}, and $C_{60}O$ in Toluene; 400 - 700 nm

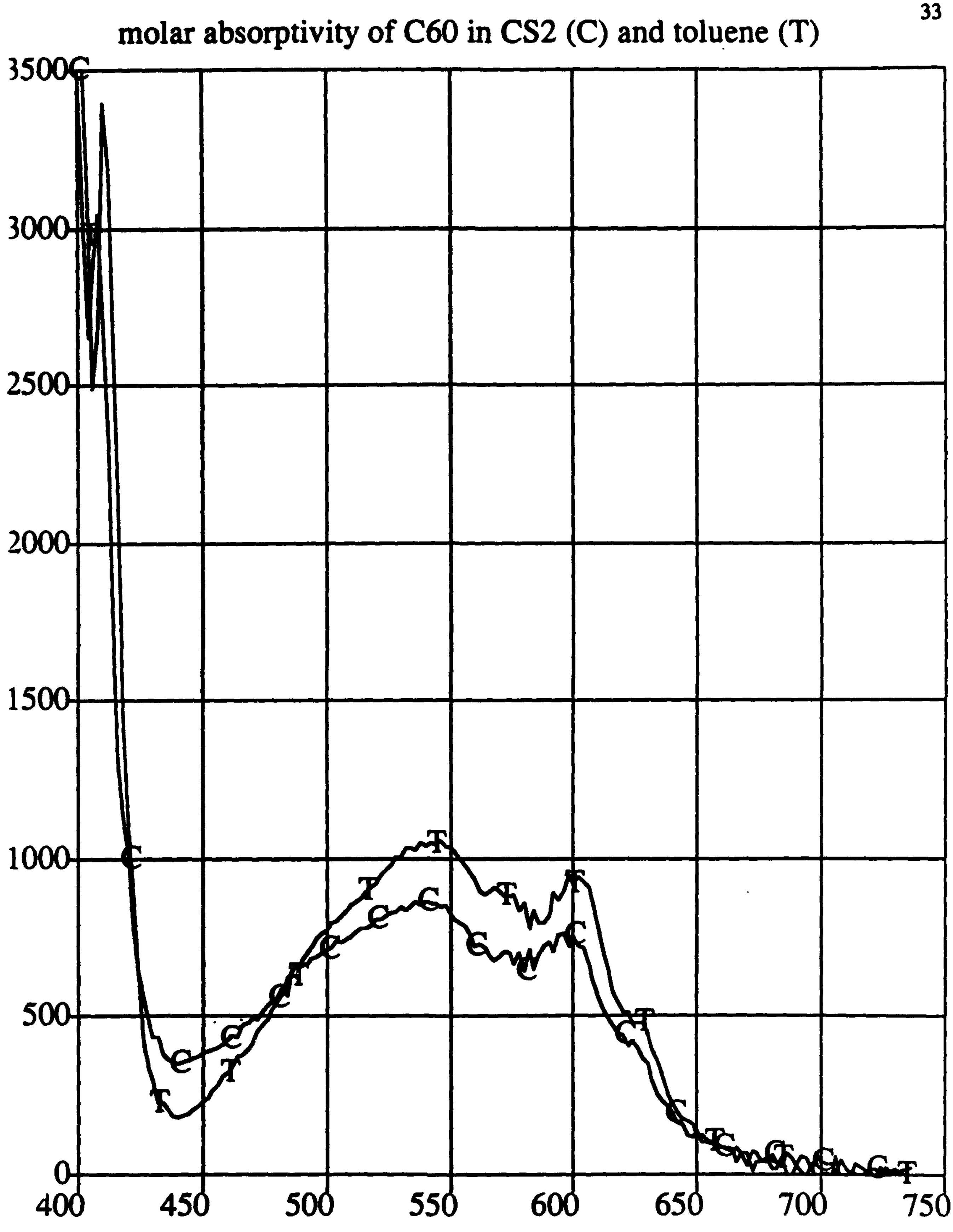

Figure 2. Molar Absorptivity of C_{60} in CS_2 and in Toluene: A Comparison

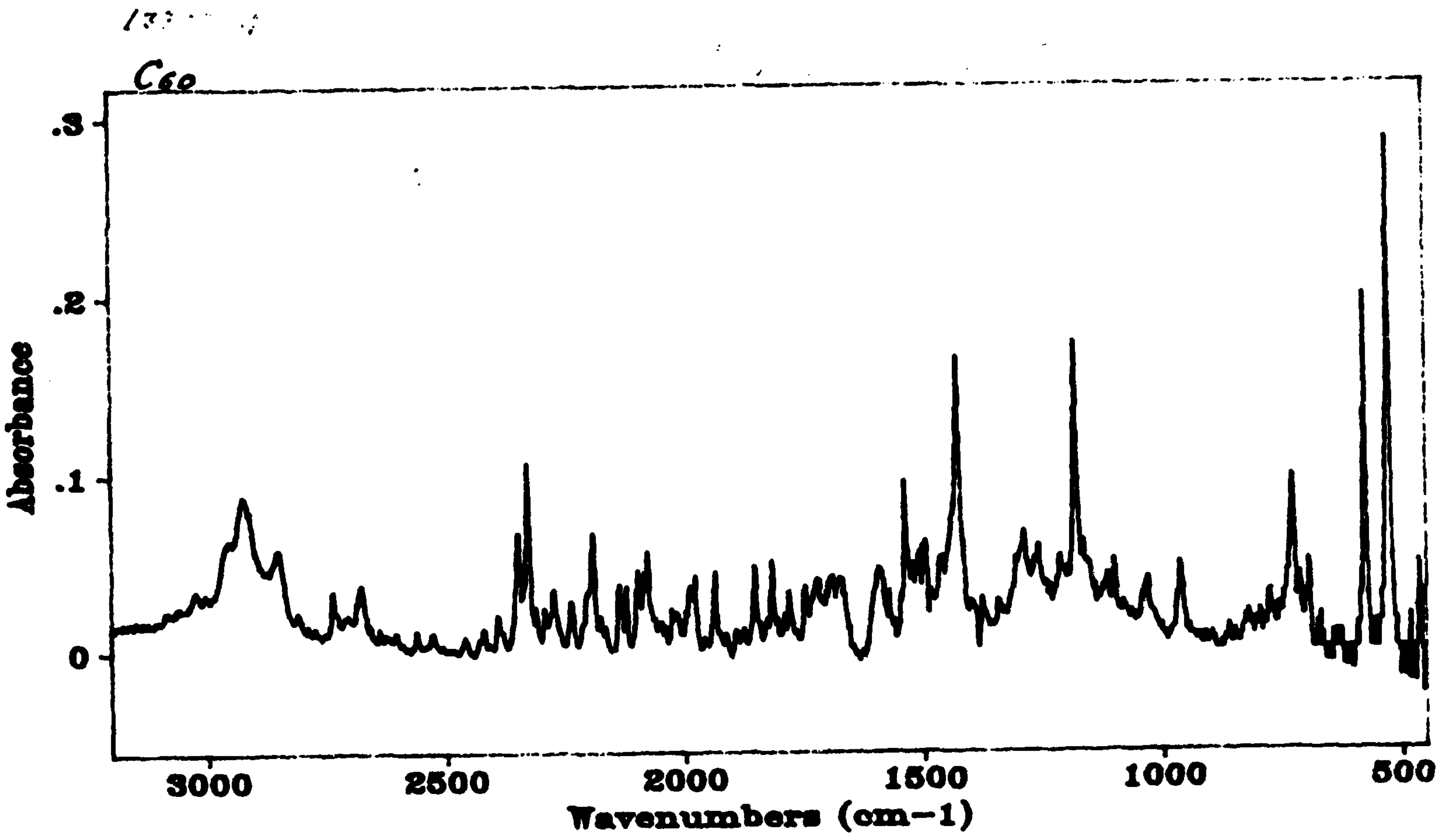

Figure 3A. Diffuse Reflectance FTIR Spectrum of C_{60} Sample with Residual Hydrocarbon; (Note C-H Stretch Band Region, 2800 - 3050 cm^{-1})

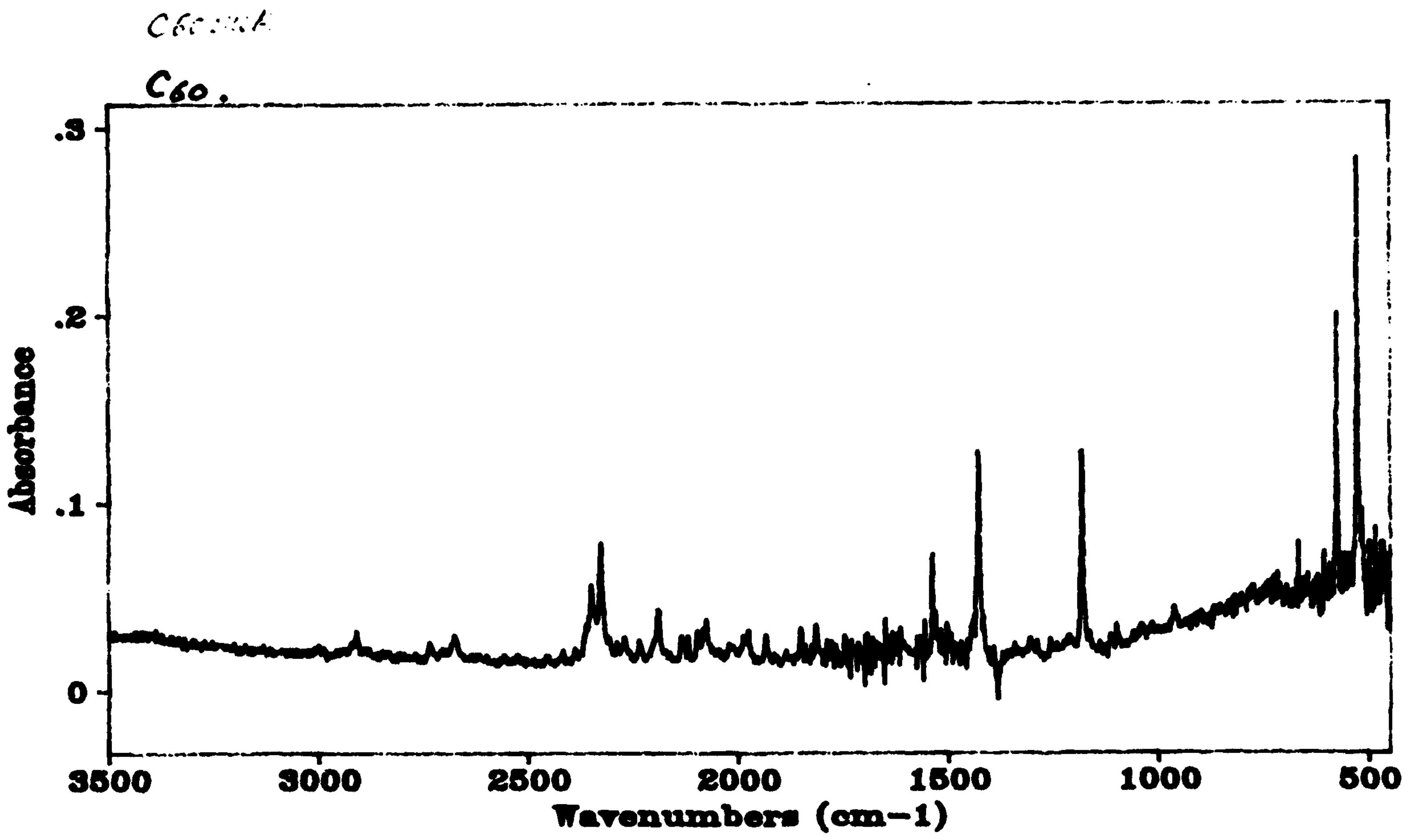

Figure 3B. Diffuse Reflectance FTIR Spectrum of Sublimed C_{60} Sample; (Note the Absence of C-H Stretch Bands)

Lee #2

C_{70}

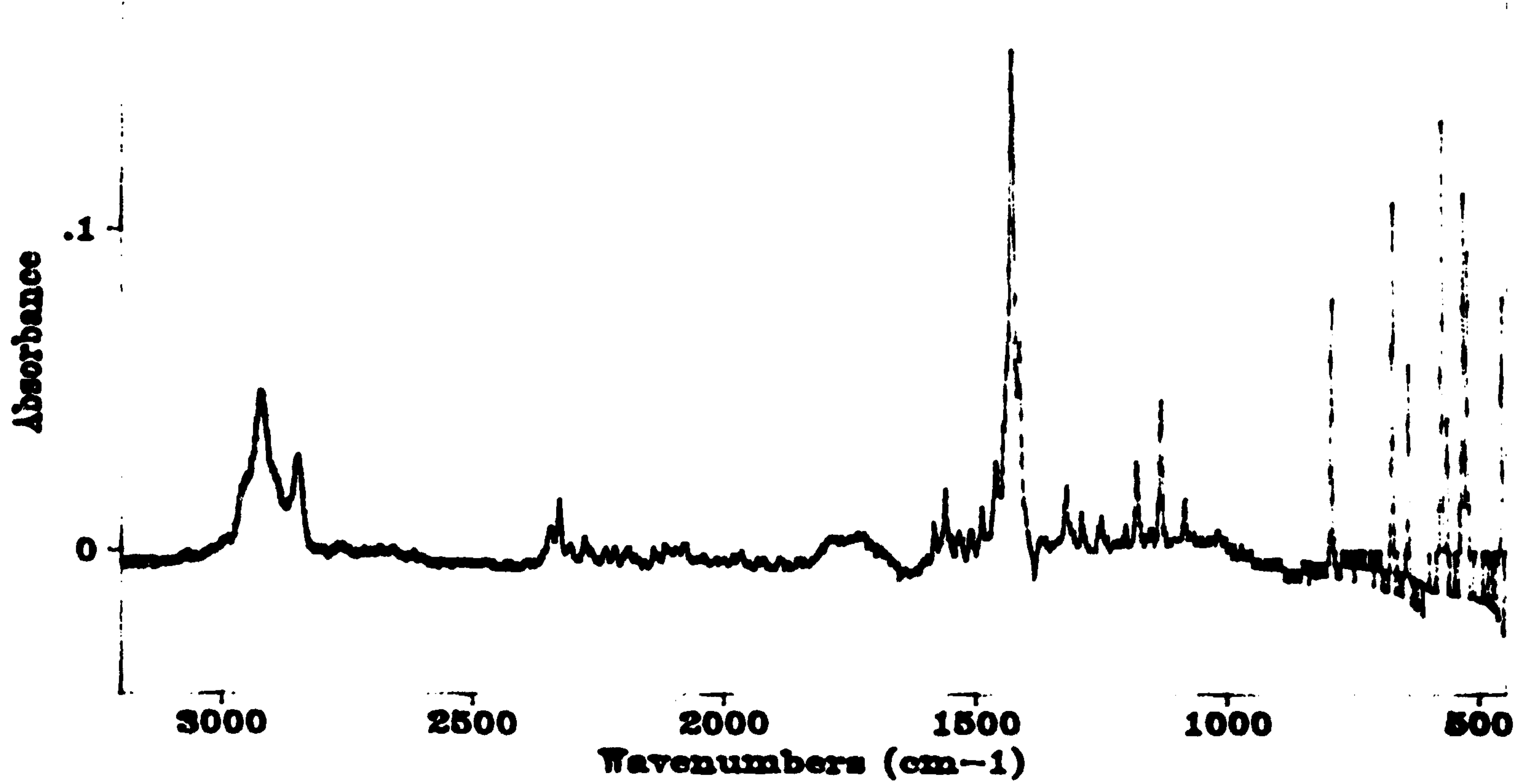

Figure 4A. Diffuse Reflectance FTIR Spectrum of C_{70} Sample with Residual Hydrocarbons

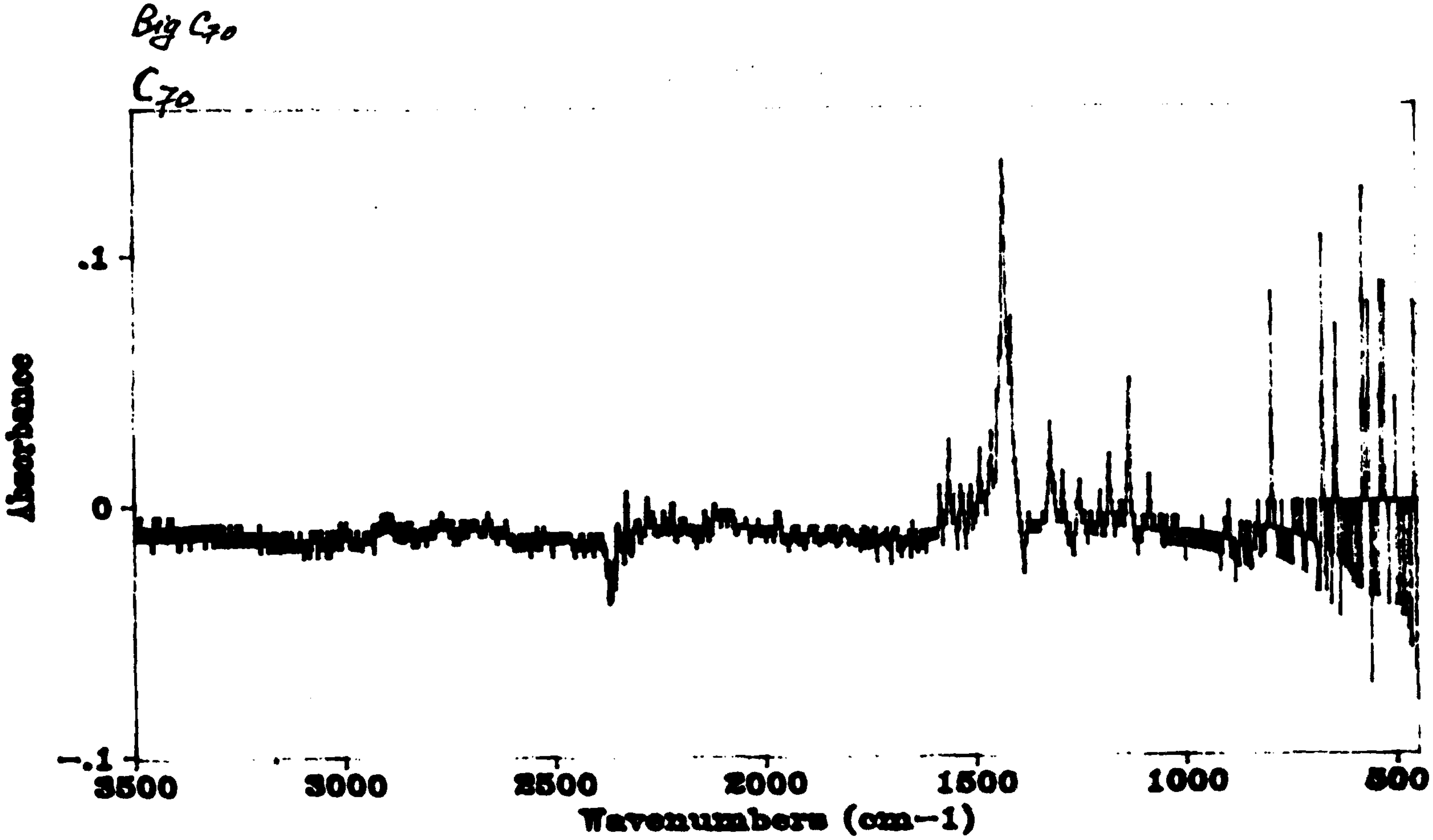

Figure 4B. Diffuse Reflectance FTIR Spectrum of Sublimed C_{70}

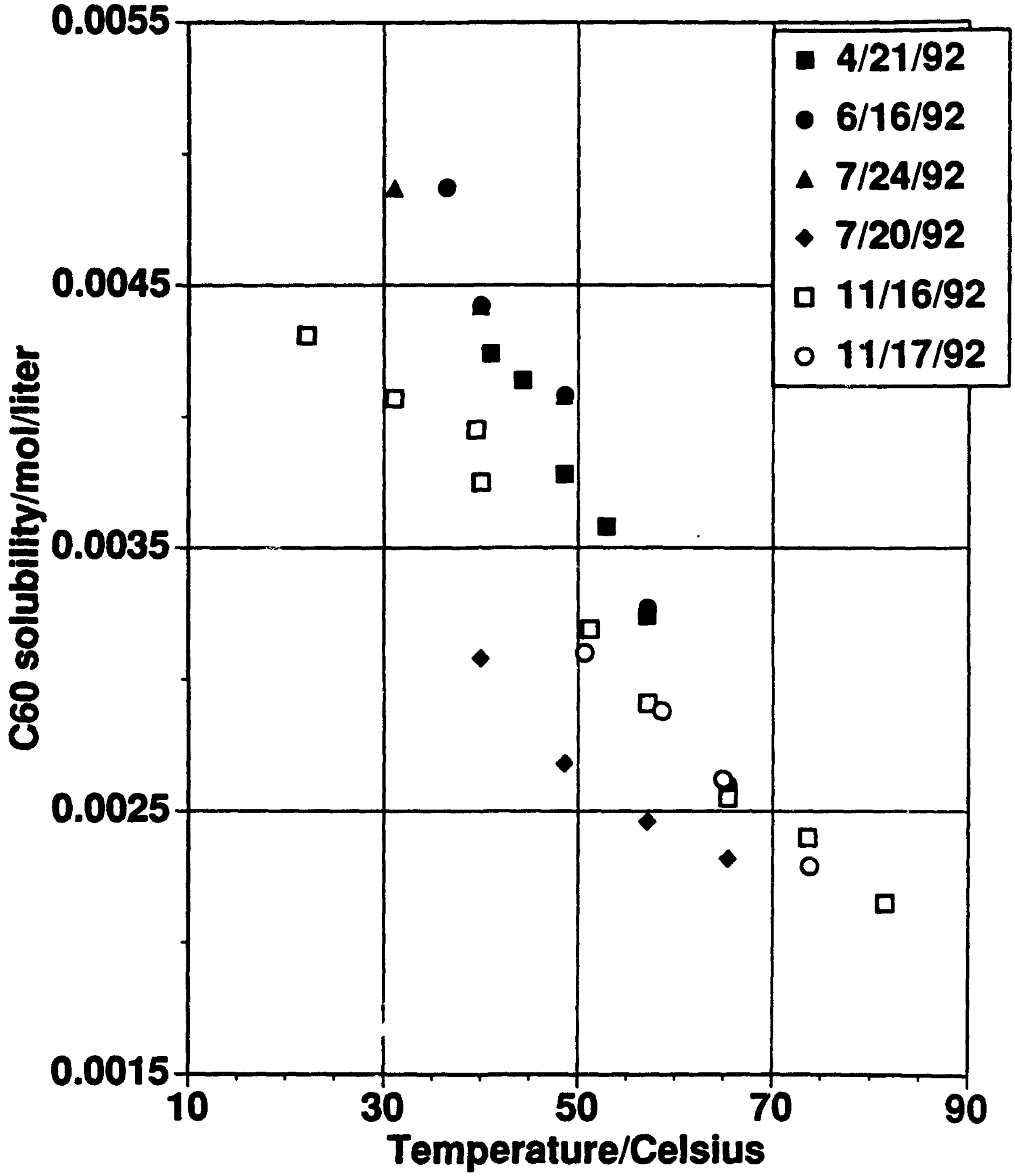

Figure 5. The Solubility of C_{60} in Toluene as a Function of Temperature

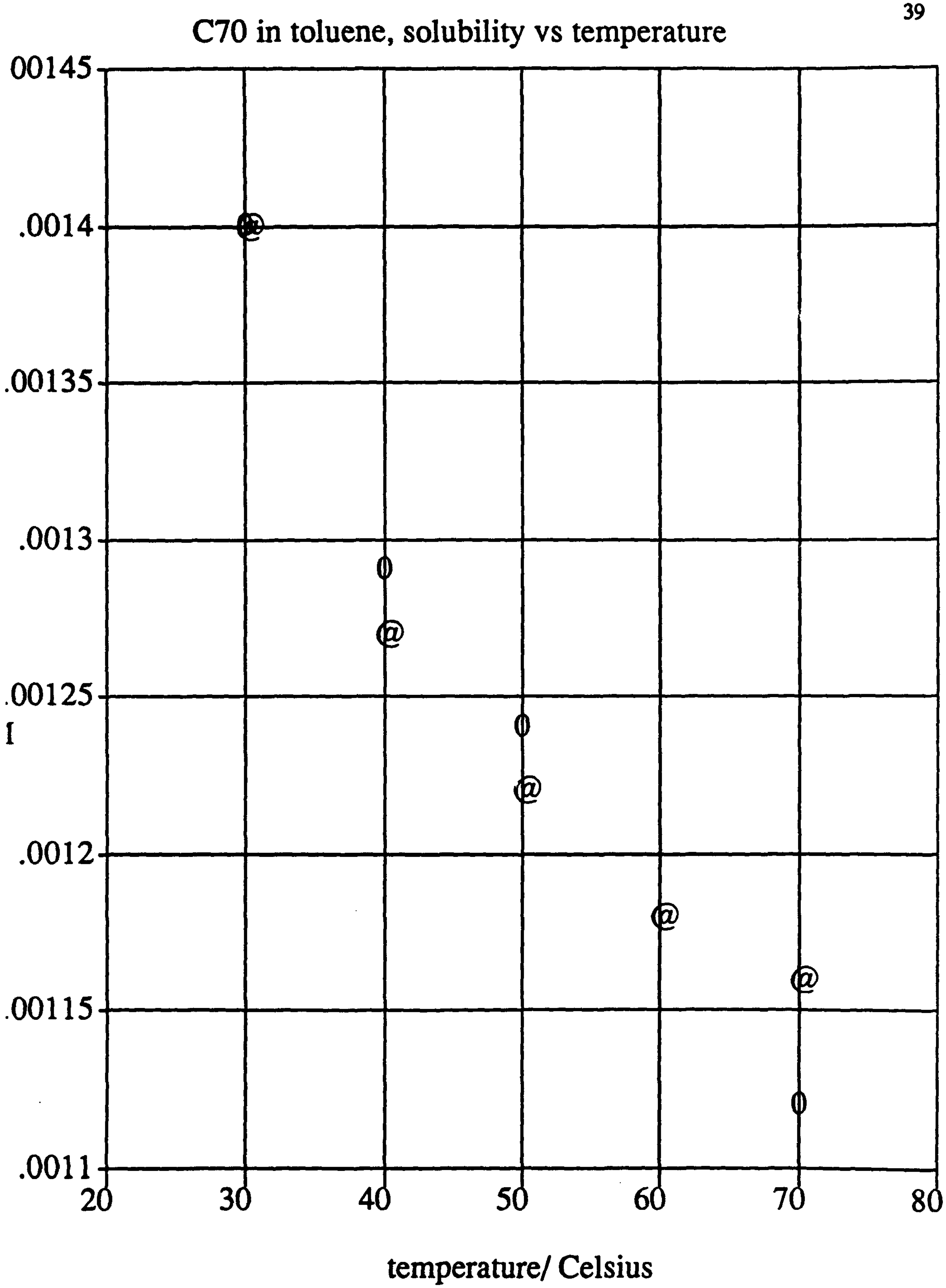

Figure 6. The Solubility of C_{70} in Toluene as a Function of Temperature

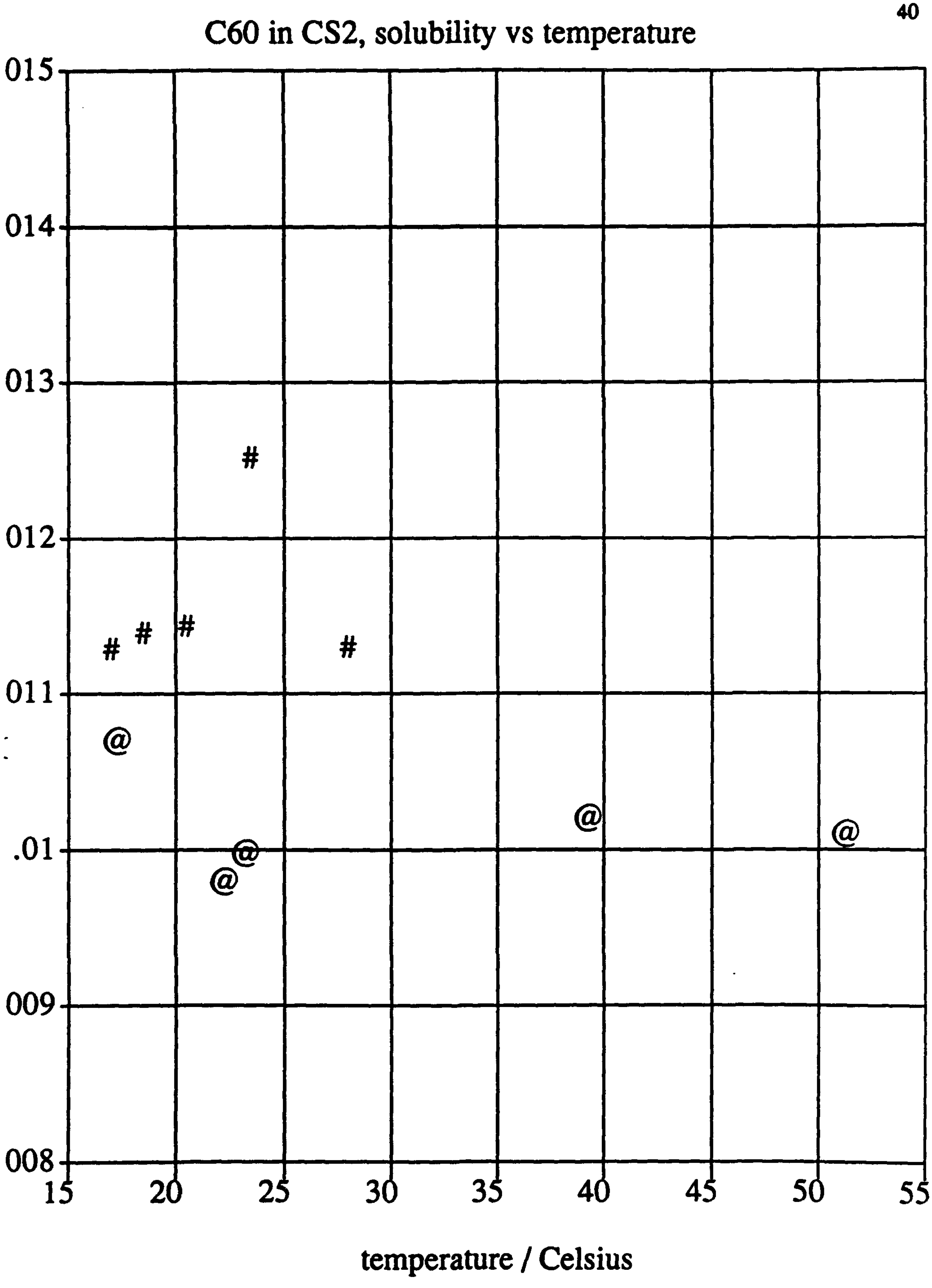

Figure 7. The Solubility of C_{60} in Carbon Disulfide as a Function of Temperature

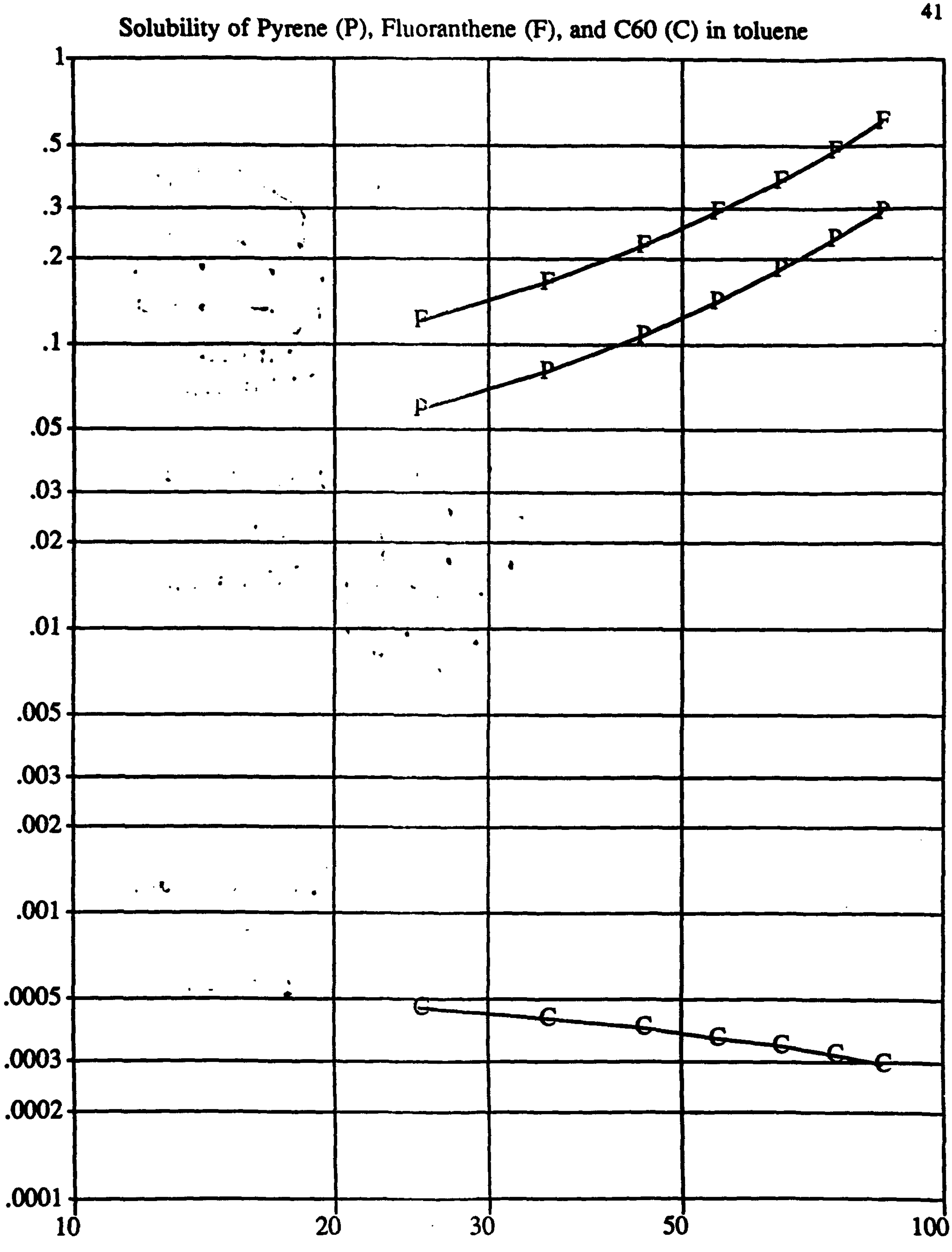

Figure 8. Temperature Dependence of the Solubility of Fluoranthene, Pyrene, and C_{60}

Enthalpy of Formation of Different Allotropic Forms of Carbon (kJ per mole of C)

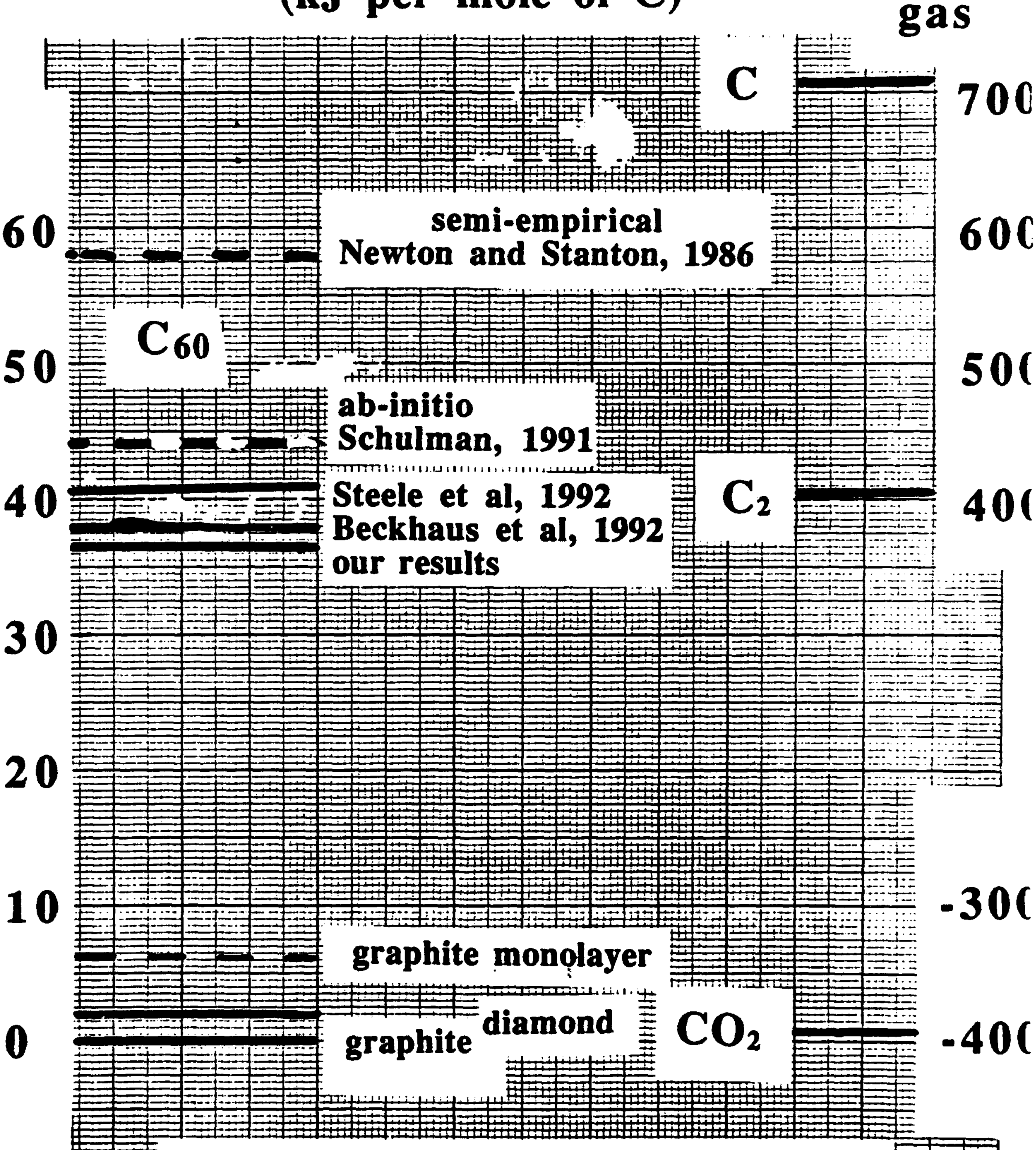

Figure 9. Enthalpy of Formation of Different Allotropic Forms of Carbon

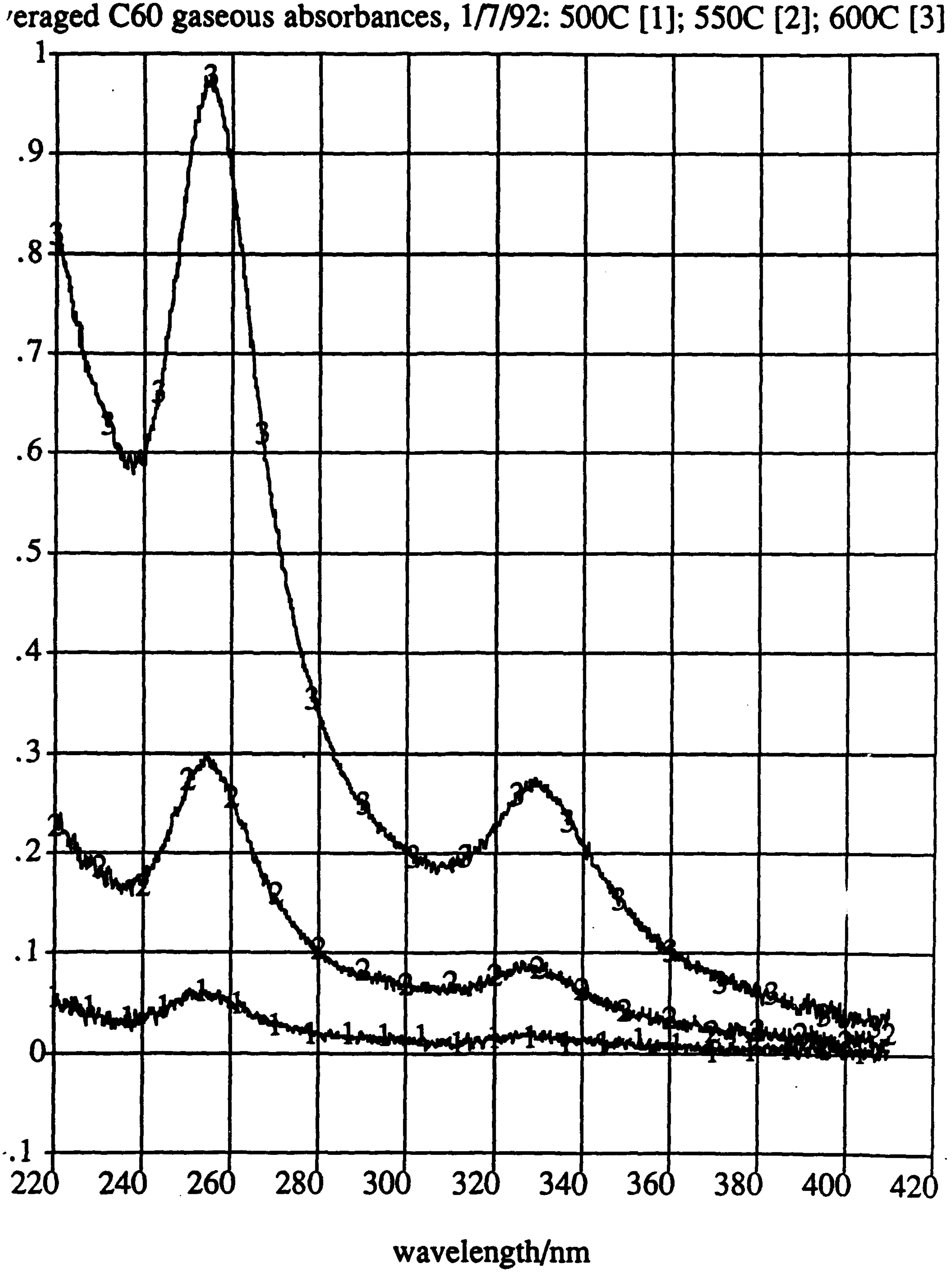

Figure 10. Ultraviolet Absorbance of C_{60} Gas at 500 °C, 550 °C, and 600 °C, $220 < \lambda < 400$ nm, Cell Pathlength = 10 cm

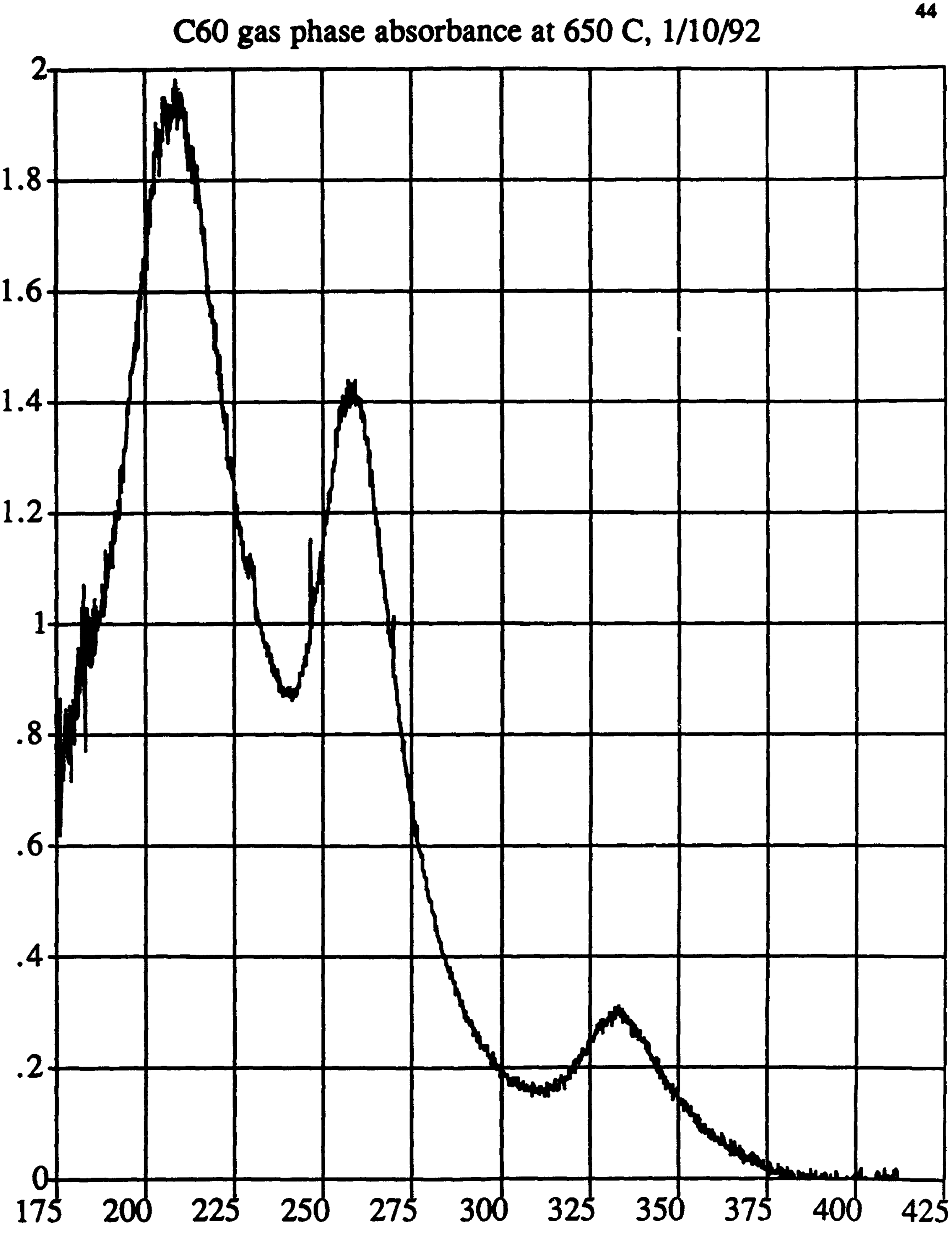

Figure 11. Ultraviolet Absorbance of C_{60} Gas at 650 °C, $180 < \lambda < 400$ nm

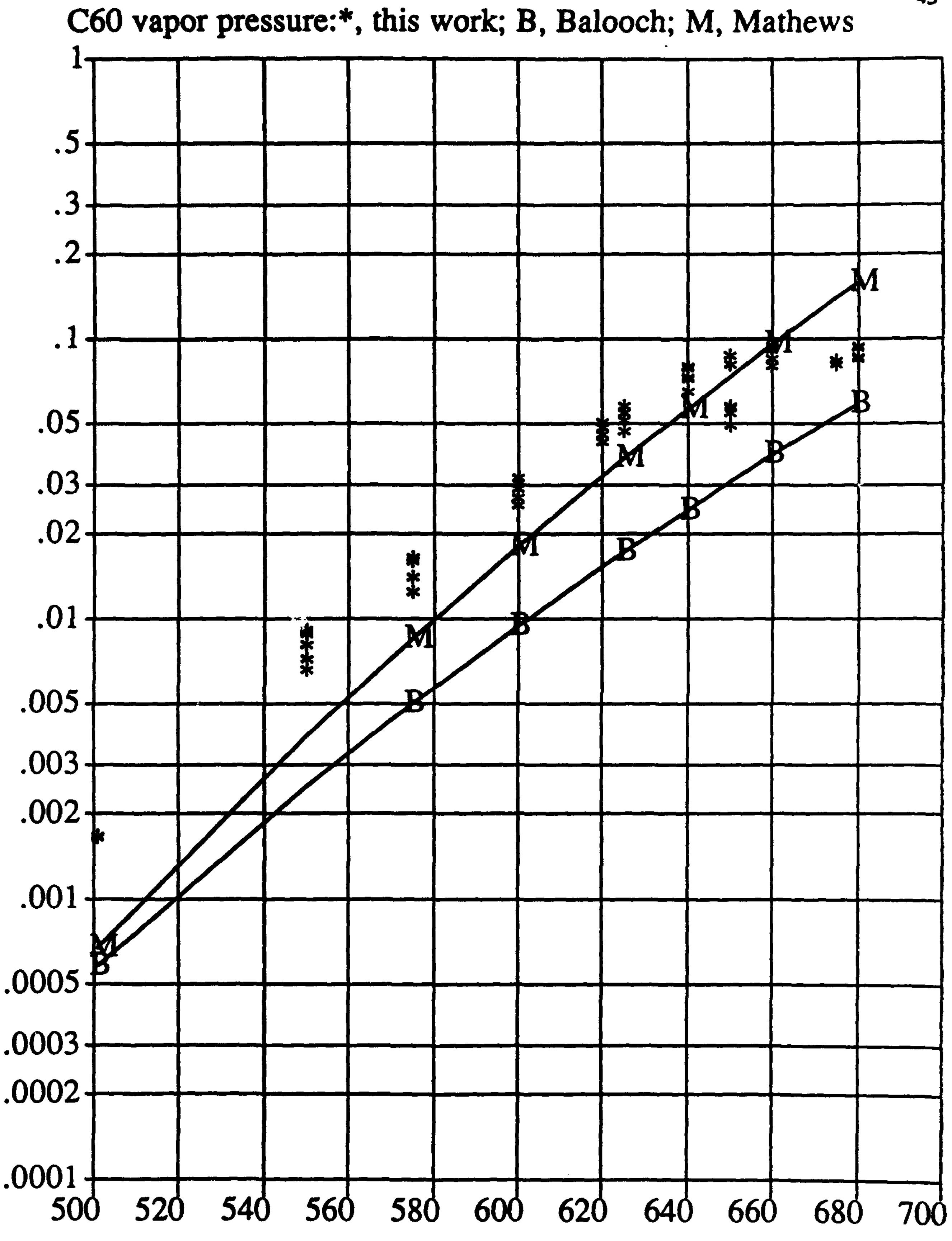

Figure 12. Vapor Pressure of C_{60} as a Function of Temperature