

Isolation and Spectral Properties of Kr@C₆₀, a Stable van der Waals Molecule

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Abstract: The stable van der Waals molecule krypton inside C₆₀ was isolated by HPLC from a mixture containing 99.9% empty C₆₀. Four passes through a semipreparative PYE [2-(1-pyrenyl)ethylsilyl] column provided 140 μg of 90% pure Kr@C₆₀, as confirmed by mass spectrometric analysis. The ¹³C NMR spectrum of Kr@C₆₀ contains a single line shifted 0.39 ppm downfield from the C₆₀ resonance. UV–visible spectroscopy shows that krypton incorporation causes a red shift of ca. 45 cm⁻¹ in the lowest singlet transition of C₆₀. Three of the four allowed vibrational fundamentals are observed by infrared spectroscopy; each shows a small frequency increase in Kr@C₆₀. A 12% acceleration in triplet state decay is measured at 77 K and attributed to an “endohedral heavy atom effect” induced by the krypton atom. It is concluded that coupling between the krypton atom and the π-electron system of the fullerene is small but significant.

Introduction

Nonbonded or van der Waals interactions are important in determining the properties of solids and liquids and in the binding of enzymes to substrates and inhibitors. They have been studied experimentally by using colliding molecular beams and by obtaining spectra of weakly bound van der Waals complexes. These studies are limited by the very short lifetimes of the species involved. Fullerenes containing noble gas atoms or molecules inside can be regarded as extremely stable van der Waals complexes with well-defined geometries. Studies of their properties can supplement studies with other methods.

If one could assume that a noble gas atom inside a fullerene did not interact with the fullerene electrons, only the mass would be changed by the inclusion. This addition could be considered analogous to the addition of neutrons to a nucleus to make an isotope leaving the charge unchanged. It was initially thought that the chemical properties of isotopes would be the same; however, the many small differences that were found, called isotope effects, have been interesting and very useful. Fullerenes containing noble gas atoms may be considered analogues of isotopes of the fullerenes.

Noble gas atoms have been introduced into fullerene molecules by treating the fullerene with the gas under high temperature and pressure.^{1,2} Even though there is no formal bond between the noble gas atom and the carbons of the fullerene

cage, the molecules formed have high barriers for escape of the atom and are stable. Treatment at 650 °C and 3400 atm yields product where only 1 in 1000 fullerene molecules is labeled with a noble gas atom (with xenon incorporation about 3 or 4 times less). The incorporation fraction is determined by pyrolyzing the material at ~1000 °C to release the gas, which is analyzed with a mass spectrometer,³ or by generating the fullerene ions and measuring the mass spectrum due to the labeled fullerenes.⁴

We found that repeating the high-temperature, high-pressure treatments on material recovered from one run increases the proportion of labeled fullerenes significantly to at least 0.4% incorporation. Even with this increased incorporation, measurement of spectroscopic properties is not possible because of interference from the large amount of empty fullerene. The sole exception is ³He@C₆₀, because ³He is an excellent NMR nucleus and can be detected with high sensitivity. Only molecules labeled with ³He produce peaks in the NMR spectrum and empty C₆₀ does not interfere. ³He NMR has therefore proven to be an invaluable tool not only for evaluating the magnetic properties of fullerenes⁶ but also for monitoring the products of their chemical transformations.⁷ To study other noble gas-containing fullerenes, one needs to isolate them with relative high purity.

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It was shown previously that chromatography can partially enrich krypton- and argon-containing fullerenes. On various open alumina columns, the incorporation factor of Kr@C₆₀ was enhanced modestly in the latest eluting portion of the C₆₀ peak.⁸ HPLC was also reported to produce an appreciable separation of Ar@C₆₀ from C₆₀. However, determination of the exact purity was hampered by a lack of material after three successive fractionations.⁹

We report here an extension of the HPLC procedure enabling us to obtain 90% pure Kr@C₆₀ in reasonable yield from a crude mixture consisting mostly of empty C₆₀. Additionally, the properties of Kr@C₆₀ have been investigated through ¹³C NMR spectroscopy, IR and UV–visible absorption spectroscopy, and triplet state kinetics. Results from all of these measurements point to a small but detectable interaction between the endohedral krypton atom and the π -electron system of the C₆₀ cage.

Experimental Section

HPLC Procedure. Multi-stage HPLC was employed with use of a semipreparative PYE [2-(1-pyrenyl)ethylsilyl] column (10 × 250 mm) and toluene as eluent.¹⁰ The mixture containing C₆₀ and Kr@C₆₀ was first dissolved in *o*-dichlorobenzene. Each injection consisted of 0.1 mL of the solution and was eluted at a flow rate of 2 mL/min through the column. The amount of fullerene per injection ranged from 0.2 to 0.8 mg. Starting with 131 mg of the crude mixture, over 100 injections were made. Material emerging from the latter part of the C₆₀ peak between 12.8 and 17.0 min was collected. This also included the epoxide, C₆₀O, which eluted at 15.1 min. All 19.5 mg of the material obtained after the first pass was treated with triphenylphosphine¹¹ at 45 °C for 2 h to reduce the epoxide to fullerene before a second cycle of fractionation was carried out. The fraction from 12.8 to 17.0 min was again accumulated and re-injected for a third pass and, subsequently, a fourth pass to yield 0.14 mg of highly enriched Kr@C₆₀.

Mass Spectrometry. The analysis was done by electron ionization mass spectrometry (Micromass ZAB-SE) using the water-cooled solids probe for sample introduction. Special modifications were made to optimize heat flow from the probe heater to the sample cup. In particular, the boron nitride probe tip was replaced with a copper tip that was bored to provide an especially snug fit for the sample cup. Sample cups made from thin-walled 1.5 mm Mettler melting point capillaries were used.

The solids probe was heated at 60 °C/min from 200 to 550 °C with a 10-min isothermal hold at the highest temperature. Mass spectral data were acquired continuously over the range from 1000 to 200 Da at 10 s/decade of mass. The ion source temperature was maintained in excess of 400 °C during these analyses. Care was taken to ensure that the end of the sample cup did not physically touch the ion source and cause high voltage breakdown. At these extreme temperatures, leakage currents can develop from ion source to ground along the sample cup if the source and sample make contact. These sample-handling precautions were required because fullerene has such a high sublimation point and is only evaporated at the highest temperature of the solids

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probe. Only with these precautions and modifications were we able to obtain mass spectra with consistent quantitative results.

¹³C NMR Spectroscopy. The NMR spectrum was taken on a Bruker AM-500 instrument running at a ¹³C frequency of 125 MHz. The fullerene was dissolved in a 50:50 mixture of benzene and benzene-*d*₆ introduced for locking. No relaxation agent was added, as the protons in the benzene relaxed the ¹³C nuclei. The benzene-*d*₆ triplet was used as a reference at 128 ppm. A line broadening of 2 Hz was applied when the FID was processed.

Infrared Spectroscopy. FT-IR was performed with a Midac M-1200 spectrometer at a resolution of 1 cm⁻¹ in absorbance mode. The 90% Kr@C₆₀ material was dissolved in approximately 25 μ L of carbon disulfide (Fischer, spectroanalyzed) and deposited onto a CsI window. The solvent was removed by air evaporation to leave a coat of solid material on the surface. The CsI plate was mounted in the sample compartment, which was flushed with N₂ for 10 min before acquisitions were taken of the background and, subsequently, the sample. The background was subtracted, giving the absorption spectrum of Kr@C₆₀.

Optical Spectroscopy. A solution was prepared by dissolving a small quantity of enriched solid Kr@C₆₀ in approximately 2.5 mL of a 1:1 mixture of methylcyclohexane and isopentane. The resulting solution had an estimated concentration of 16 μ M based on its absorbance at 330 nm and the assumption of a molar absorptivity unchanged from C₆₀. The sample was cooled to form a 77 K glass in an Oxford Instruments Optistat-DN cryostat equipped with fused silica windows. We measured the ultraviolet–visible spectrum of this glassy solution using a GBC model 918 spectrophotometer with a spectral slit width of 0.2 nm. Spectra of C₆₀ were obtained for comparison by using the same procedure.

Triplet Kinetics. Triplet-state kinetics measurements were made on a specialized time-resolved absorption instrument described in detail elsewhere.¹² Briefly, the same sample described above was optically excited at 77 K by 532 nm pulses from a Q-switched Nd:YAG laser. The triplet states formed by subsequent intersystem crossing were probed by the absorption of a collinear, continuous beam from a 676 nm diode laser. With signal averaging, this system provided systematic and random error levels below 6 × 10⁻⁶ absorbance units. Transient separation spectra were measured from 550 to 950 nm with use of a separate apparatus based on a monochromated incandescent probe source.

Results and Discussion

Chromatography. After three passes through the column, a distinct shoulder appeared on the C₆₀ peak at 13.2 min. A pass consists of multiple injections with the enriched fractions combined. The area under this shoulder was approximately 10% of the main C₆₀ peak, in good agreement with mass spectrometric analysis of the material, which gave a Kr@C₆₀ content of 11 ± 2%. A fourth fractionation yielded 0.14 mg of 90% pure Kr@C₆₀. The composition was estimated from the 9:1 ratio of the peak areas on the detector trace from the HPLC. Figure 1 shows the chromatogram of a mixture consisting of roughly 40% C₆₀ and 60% Kr@C₆₀, obtained in a separate experiment. Figure 2 shows a mass spectrum of a sample of Kr@C₆₀, showing the multiplet due to the distributions of krypton and carbon isotopes. The agreement between the theoretical and experimental distributions demonstrates that the material is Kr@C₆₀ and not something else with the same nominal mass.

Based on our current findings on Kr@C₆₀, we offer an interpretation of DiCamillo's results⁹ obtained from the separation of C₆₀ and Ar@C₆₀ on a smaller PYE column (4.6 × 250 mm). The first peak is clearly C₆₀. The second peak, actually a shoulder on the C₆₀ peak, is Ar@C₆₀. From their chromatogram,⁹ the separation factor between C₆₀ and Ar@C₆₀ is estimated to be about 1.04–1.05. We believe that the third peak in their spectrum is the epoxide, C₆₀O, which results from air oxidation of C₆₀.

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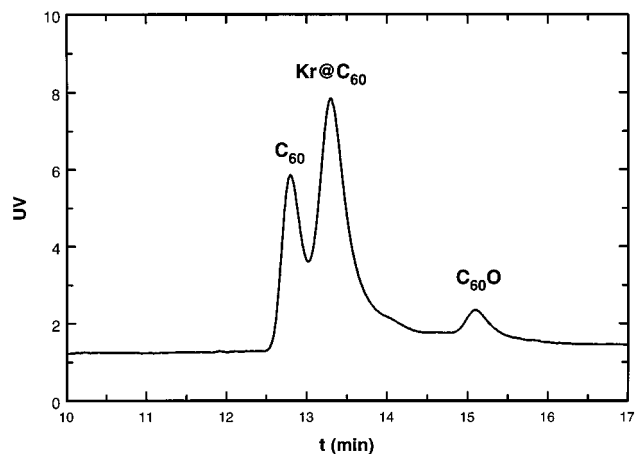


Figure 1. Chromatogram of a mixture of C₆₀ and Kr@C₆₀ on the PYE column. There is also a small peak due to the epoxide, C₆₀O.

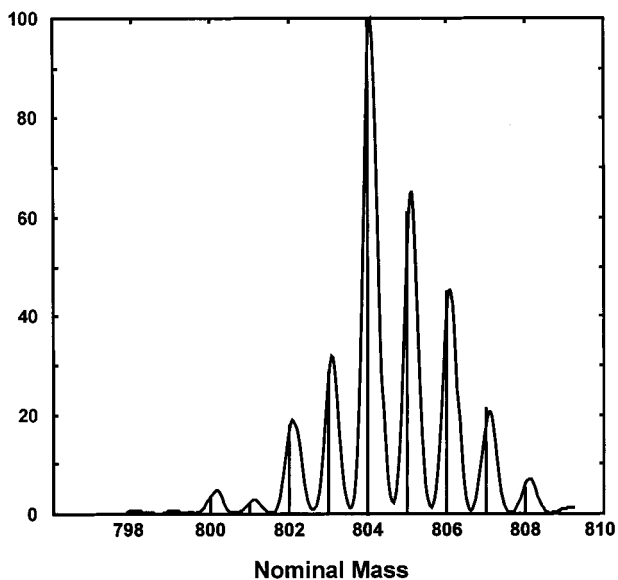


Figure 2. A comparison of the measured isotopic distribution (continuous plot) with the theoretical isotopic distribution (stick plot) for Kr@C₆₀. The measured data were taken from a sample that contained slightly less than 1% of the krypton labeled fullerene. The offset in mass between the measured and theoretical spectra is due to the use of nominal mass assignment algorithms for the measured spectrum. The results clearly indicate the presence of the krypton labeled fullerene in the chromatographic fraction.

Although using a solvent like toluene as the mobile phase produces better separation of the fullerenes than one in which the fullerenes have a higher solubility, it is not very efficient for preparative purposes. We used a small quantity of dissolved fullerenes in *o*-dichlorobenzene per injection. Larger amounts of fullerene clog the guard column (PYE 4.6 × 250 mm), because the fullerene precipitates in the toluene, where it is less soluble.

In the first stage of separation, two peaks were observed: C₆₀ and, presumably, the dimer C₁₂₀, which eluted at 12.8 and 22.6 min, respectively. HPLC of a C₁₂₀ sample provided by Komatsu *et al.*¹³ gave a peak with retention time similar to the latter. The dimer must have formed during the high-temperature and pressure treatment of C₆₀, as it was not present in the starting material. Even though the retention times of C₆₀ and Kr@C₆₀ at 25 and 45 °C appear unchanged, the higher temperature

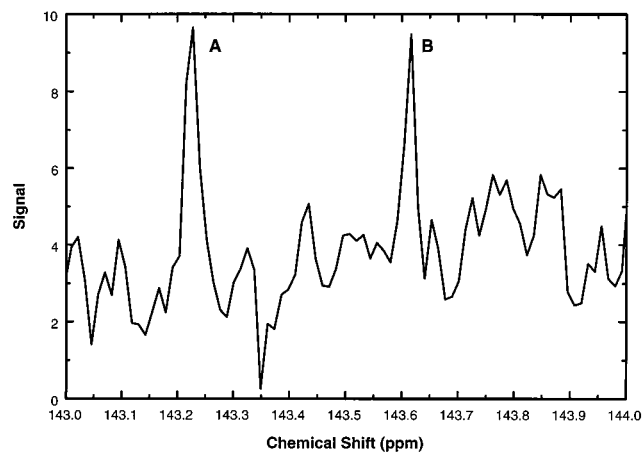


Figure 3. The ¹³C NMR Spectrum of a mixture of 40% C₆₀ and 60% Kr@C₆₀. Peak A is due to C₆₀ and peak B to Kr@C₆₀.

condition was used in the separations. In general, a higher temperature reduces the tendency for peaks to tail in the HPLC. Peak tailing would be problematic given the small separation of Kr@C₆₀ and C₆₀.

We found by mass spectrometry that the first half of the C₆₀ peak is depleted in krypton-containing C₆₀ while the latter part is enriched in the “kryptonite”. Our fractionation has, therefore, focused on the latter half of the C₆₀ peak. Some of the material, especially after the first stage of separation, also contained the epoxide, C₆₀O, which gave an interfering peak at 15.1 min. This peak, identified by comparison with the oxide formed by the photooxygenation of C₆₀ in benzene, is easily removed by reducing it with triphenylphosphine at 45 °C for several hours.¹¹ Not only is the Kr@C₆₀ that was lost to the formation of C₆₀O recovered, but also uncertainties in the collection of the Kr@C₆₀ peak are eradicated.

We investigated the separation of C₆₀ and Kr@C₆₀ on two other columns: a Buckyclutcher column (4.6 × 250 mm) and a 3-[(pentabromobenzyl)oxy]propylsilyl (PBB) silica column (4.6 × 250 mm). In both cases, a sample of unlabeled C₆₀ was first injected into the column followed by a sample containing 40% C₆₀ and 60% Kr@C₆₀. The mixture appeared on the Buckyclutcher column as a single peak with the same width as that for pure C₆₀, indicating no separation of C₆₀ and Kr@C₆₀. On the PBB column, the mixture gave a single peak with a slightly broader width than for the pure C₆₀ peak, suggesting only slight separation. In contrast, the PYE column gave two distinct peaks for this mixture, see Figure 1. The separation factor between C₆₀ and Kr@C₆₀ is a constant 1.09, from 25 to 60 °C with toluene as a solvent. This is larger than the separation factor for Ar@C₆₀.⁹

¹³C NMR Spectroscopy. Figure 3 shows the ¹³C NMR spectrum of the mixture of 40% C₆₀ and 60% Kr@C₆₀. Peak A at 143.23 ppm is due to C₆₀, while peak B at 143.62 ppm is due to Kr@C₆₀. The sample with 90% Kr@C₆₀ gives only peak B. Peak A has been observed for pure C₆₀. Thus, putting a Kr atom inside C₆₀ causes a downfield shift of 0.39 ppm (49 Hz). Bühl¹⁴ calculated the shift for Xe@C₆₀ to be 1 ppm downfield from C₆₀, and speculated that the shift for Kr@C₆₀ would be about half as large.¹⁵

Infrared Spectroscopy. Figure 4 shows the IR spectra of C₆₀ in the top panel and of the 90% Kr@C₆₀ sample in the bottom panel. The four bands A–D in the top panel were

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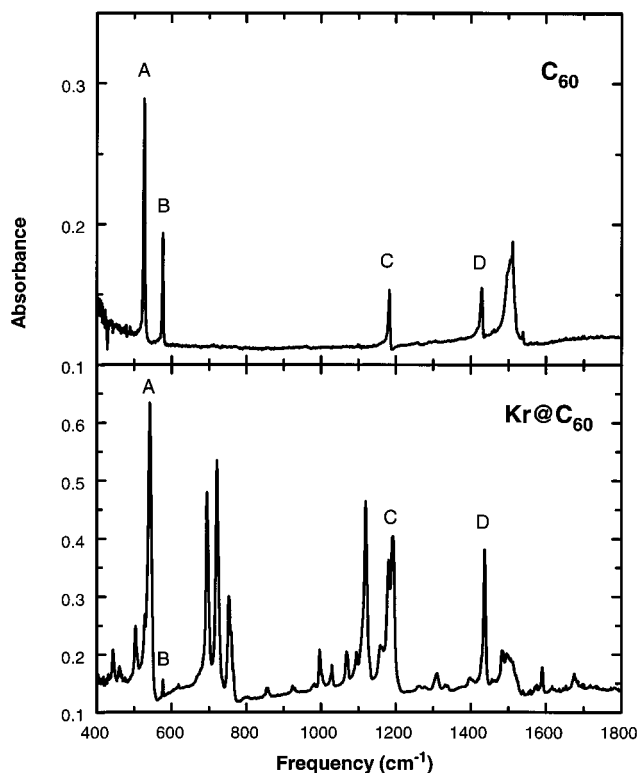


Figure 4. The infrared spectra of C_{60} (top panel) and $Kr@C_{60}$ (bottom panel).

Table 1. IR Bands (All Values Are in cm^{-1})

peak	C_{60}		$Kr@C_{60}$		shift
	freq	width ¹	freq	width ¹	
A	526.5	3.9	541.9	11.1	+15.4
B	576.1	2.9	576.1		
C	1182.2	5.8	1192.8	22.2	+10.6
D	1428.5	7.7	1436.7	6.3	+8.2

previously reported in the literature.¹⁶ The one at 1500 cm^{-1} is due to residual CS_2 left in the thin film. The most obvious feature of the spectrum for $Kr@C_{60}$ is the presence of many additional absorption bands. These are most likely due to one or more impurities and are discussed below. Three of the four bands (A, C, and D) are seen in the spectrum for $Kr@C_{60}$. However, each is shifted to higher frequency and, except for D, broadened. In each case, there is a small shoulder corresponding to the 10% empty C_{60} in the sample. For band B, only the residual peak due to the empty C_{60} is seen. The $Kr@C_{60}$ band for this mode is either missing or, more likely, broadened so much as to be lost in the background. Table 1 lists the band positions and widths.

C_{60} has 174 vibrational degrees of freedom. Simple group theory shows that these fall into 46 normal modes and that only the four modes with T_{1u} symmetry are IR allowed. $Kr@C_{60}$ has three additional degrees of freedom corresponding to the vibration of the Kr atom inside the cage. These are degenerate with T_{1u} symmetry and are, therefore, IR allowed. Calculations with the molecular mechanics program MM3¹⁷ predict this frequency to be around 100 cm^{-1} , far below the limit of our

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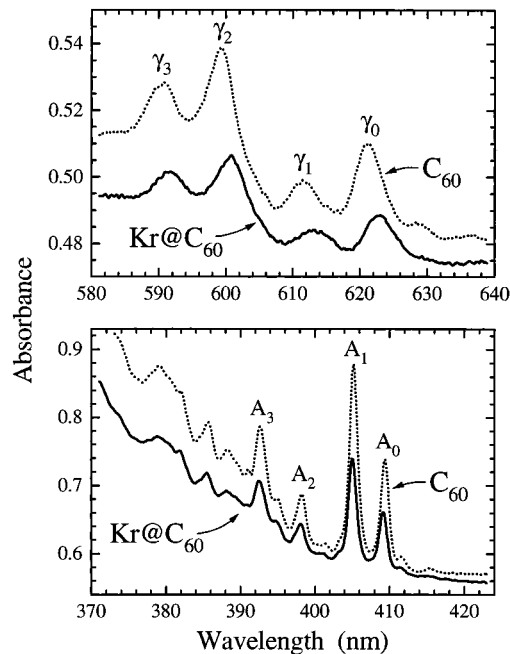


Figure 5. Ground-state absorbance spectra of $Kr@C_{60}$ and C_{60} dissolved in methylcyclohexane/isopentane glasses at 77 K.

spectrometer. However, this mode will be coupled to the other four T_{1u} modes, and the coupling will be slightly different depending on how many quanta are in the low-frequency mode. At 300 K, 95% of the molecules have one or more quanta of vibrational excitation in this mode. Anharmonic coupling to the other modes produces a broadening of the other four bands, as seen in the spectrum.

The extra features in the spectrum seem to indicate that the icosahedral symmetry in $Kr@C_{60}$ is broken. However, they do not correlate with any of the forbidden modes in C_{60} .¹⁸ They are probably due to small amounts of impurity. C_{60} and $Kr@C_{60}$ are large molecules with high symmetry and no polar groups. They are, therefore, poor IR absorbers, and only a few micrograms of an IR active molecule could easily account for these lines. This impurity could be a minor component of the original reaction mixture that happens to elute along with $Kr@C_{60}$ and is, therefore, enriched with it. It could be some background impurity eluted more or less continuously from the column, or it could be an impurity in the solvents used to process the $Kr@C_{60}$. We cannot readily identify it from the spectrum. Unfortunately, its presence greatly complicates further experiments. It would be instructive to retake the spectrum at low temperature on an instrument with better resolution, range, and sensitivity. This would enable us to sharpen the lines and perhaps see additional ones, the low-frequency IR allowed modes and many of the forbidden lines.

Optical Spectroscopy. The top frame in Figure 5 shows the ground-state absorption spectra measured for C_{60} and $Kr@C_{60}$ in the 600 nm region. The absorption patterns are similar for the two species except for a noticeable red shift of the $Kr@C_{60}$ features. We attribute the proportionally greater intensity of the C_{60} bands to a higher sample concentration. The bottom frame shows the 400 nm region, in which the two spectra show similar absorption patterns and smaller shifts. We have labeled the prominent absorption bands using the notation of Leach, *et al.*¹⁹

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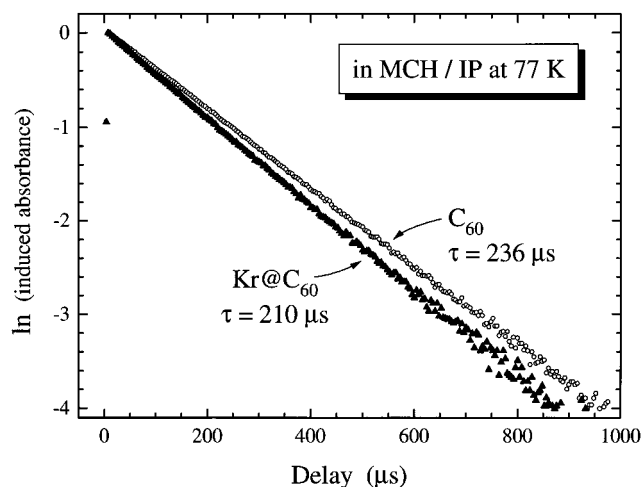


Figure 6. Triplet decay kinetics of Kr@C₆₀ and C₆₀ in methylcyclohexane/isopentane glasses at 77 K measured by time-resolved induced absorption at 676 nm following 532 nm excitation. The two traces have been normalized to permit easier comparison; absolute peak induced absorbances were approximately 2.6×10^{-3} .

Gasyňa *et al.*²⁰ assigned the 600 nm bands to a symmetry-forbidden ${}^1T_{1g} \leftarrow {}^1A_{1g}$ system in which γ_0 and γ_2 are false origins separated from γ_1 and γ_3 , respectively, by one quantum of the lowest-frequency h_g vibration. From the spectral peak positions, we deduce that the $\nu_8(h_g)$ mode has a frequency in the ${}^1T_{1g}$ state of 255 or 246 cm^{-1} for C₆₀ and 254 or 257 cm^{-1} for Kr@C₆₀. It seems that krypton incorporation leaves this vibrational frequency unchanged or slightly increased. By contrast, comparison with the ground-state vibrational data compiled by Schettino *et al.*¹⁸ shows that this mode's frequency decreases by ca. 12 cm^{-1} on electronic excitation to ${}^1T_{1g}$. We interpret the red shift of the Kr@C₆₀ bands as a krypton-induced decrease of approximately 45 cm^{-1} in the ${}^1T_{1g}$ electronic origin energy.

The 400 nm bands have been assigned to ${}^1T_{1u} \leftarrow {}^1A_{1g}$, the lowest allowed electronic transition in C₆₀.^{19,21} Band A₀ was identified as the origin of this system.¹⁹ Our spectra show that krypton incorporation slightly increases this origin frequency, by 10 to 15 cm^{-1} out of 24 000 cm^{-1} . This change is smaller and of opposite sign compared to that found for the 600 nm ${}^1T_{1g} \leftarrow {}^1A_{1g}$ system. The separations of bands A₁, A₂, and A₃ from the origin were previously assigned to single quanta of the lowest frequency h_g mode, an a_g mode, and an h_g mode, respectively.¹⁹ We, therefore, deduce vibrational frequencies in the C₆₀ ${}^1T_{1u}$ state of 254 cm^{-1} for $\nu_8(h_g)$, 431 cm^{-1} for $\nu_2(a_g)$, and 1045 cm^{-1} for $\nu_4(h_g)$. For Kr@C₆₀, the corresponding frequencies are 249, 429, and 1040 cm^{-1} . Although our values have uncertainties of a few cm^{-1} , it appears that krypton incorporation reduces these vibrational frequencies by ca. 1% in the ${}^1T_{1u}$ electronic state. Such krypton-induced changes are clearly much smaller than the 5 to 10% frequency reductions caused by electronic excitation.¹⁸ Judging by the unchanged intensity of the forbidden 600 nm system compared to the allowed 400 nm system, these spectra provide no evidence that krypton incorporation lowers the symmetry of C₆₀.

Triplet Kinetics. It is known that unimolecular triplet decay in C₆₀ is dominated not by phosphorescence but by nonradiative relaxation to the ground electronic state.²² In Figure 6 we plot

the triplet population kinetics as the logarithm of the normalized induced absorbance vs delay after excitation. It is clear that the Kr@C₆₀ triplet state decays more rapidly than that of C₆₀, although we observe virtually identical triplet-triplet absorption spectra. Detailed kinetic analysis of the Kr@C₆₀ data shows that it may be accurately represented as a superposition of two independent first-order decays, a minor (10% amplitude) component with the lifetime of C₆₀ and a major (90% amplitude) component with an exponential lifetime of 210 μs . We assign the major component to Kr@C₆₀ and conclude that endohedral incorporation of Kr into C₆₀ increases its intrinsic triplet decay constant at 77 K by approximately 12%, from 4240 to 4760 s^{-1} .

The accelerated triplet decay may be attributed to the "heavy-atom" effect, in which the substantial spin-orbit coupling of a high-Z atom is electronically shared with the chromophore under study, thereby relaxing the spin-forbidden character of both radiative and nonradiative transitions connecting singlet and triplet states.^{23,24} Such heavy-atom effects have, to date, been classified as "internal" or "external," depending on whether the heavy atom is covalently bound to the chromophore or is contained in the solvent. Our results for Kr@C₆₀ represent the first case in a new category: the "endohedral heavy-atom effect". Theoretical predictions of the magnitude of this effect would be of great interest but will likely be even more challenging than heavy-atom effect calculations on simple systems.²⁴ For empirical comparison, we note that Morgan and Pimentel²⁶ deduced a significant increase in the triplet non-radiative decay constant of matrix-isolated dimethylamino-benzonitrile in the presence of an adjacent krypton atom. The milder endohedral effect seen here suggests that the krypton atom interacts rather weakly with the surrounding C₆₀ π -electron system.

Conclusions

Measurable quantities of Kr@C₆₀ have been successfully isolated with HPLC. This separation was feasible because of a small difference in retention times for Kr@C₆₀ vs C₆₀. The endohedral krypton atom might slightly perturb the π -orbitals of the carbon shell and thereby alter the interactions with the column packing; however, Dunitz²⁷ suggests that dispersion forces between the krypton and atoms in the binding site might explain the result. ¹³C NMR spectra show a single resonance in Kr@C₆₀ that is shifted downfield by 0.39 ppm relative to that of C₆₀. This small shift also suggests a weak electronic interaction between krypton and C₆₀, while the single resonance indicates retention of I_h symmetry, at least on the slow NMR time scale. Similar conclusions are drawn from low-temperature UV-visible absorption spectra. Here the lowest singlet excited state of Kr@C₆₀ is found to be shifted down in energy by ca. 45 cm^{-1} but absorption intensities suggest no relaxation of I_h symmetry. Infrared absorption spectra reveal vibrational transitions increased in frequency by approximately 10 cm^{-1} and broadened in Kr@C₆₀ compared to C₆₀. Finally, krypton incorporation is found to accelerate the nonradiative decay of triplet-state Kr@C₆₀ by 12% relative to C₆₀ in the first example of the endohedral heavy atom effect.

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All of our results point to a small but significant coupling between the krypton atom and the π -electron system of the surrounding fullerene shell. Because of the larger size of xenon atoms, we expect that Xe@C₆₀ will show stronger perturbations and correspondingly greater changes in the properties of the surrounding fullerene. Experiments are underway to explore this possibility.

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