

Flashing Carbon on Cold Surfaces

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Received: December 1, 2003; In Final Form: January 15, 2004

The formation of carbon particles on cold surfaces takes place when rare-gas solids containing trapped carbon vapor molecules are sublimed. This formation process is accompanied by violent effects such as flashes of light emission and splashing of luminous fragments, both observable with the naked eye. The recorded optical emission spectrum shows a continuum attributable to a blackbody radiation of ~ 2500 K. We believe the violent effects are associated with exothermic reactions following the rearrangement of bonds, which leads from the metastable sp-carbon chains to the more stable sp² form of carbon particles.

Introduction

Graphite and diamond are known as stable allotropes of carbon. The former consists of sp²-hybridized carbon atoms in a planar triangular configuration, while the latter consists of carbon sp³ bonds with a three-dimensional tetrahedral configuration. Recently, hollow closed systems of fullerenes and nanotubes consisting of graphitic layers with curvature have been found as a third allotrope.^{1–3} A further allotrope would be a system of sp carbon atoms with a linear configuration.⁴ So far, such a structure has been established only for molecular species as, for example, in linear C_n molecules.^{5,6} Because of the nature of the bonding, the thermodynamic stability of these allotropic systems differs. The transformation of one form to another more stable form is thus expected to be exothermic.

Carbon materials often exhibit explosive reactions. In air, He, Ar, at atmospheric pressure or in a vacuum Ajayan et al. reported reformation of single-walled nanotubes (SWNTs) into open graphitic sheets upon exposure to light of a photoflash.⁷ Boese et al. reported that highly unsaturated dehydroannulene derivatives with sp-carbon skeletons exhibited explosive reactions when heated in a furnace under vacuum to form carbon particles of onion- and tube-like structures.⁸ Suzuki et al. observed blackbody emission from laser-ablated carbon vapor in a buffer gas of argon under conditions where the yield of fullerenes in the obtained soot is high. Interestingly, these authors noticed an increase of the emission intensity long after the laser excitation occurred, and attributed this to an exothermic reaction in which fullerene molecules are formed.⁹ In the quoted experiments, however, the reaction was initiated with aid of an external energy input, i.e. a photoflash,⁷ ambient heat,⁸ or a laser pulse.⁹

In this letter, we present evidence for the spontaneous, highly exothermic reaction of carbon molecules that transform into particles on a cold surface well below 50 K. Among other effects, this process is accompanied by flashes of light clearly visible to the naked eye.

Experimental Section

Carbon vapor molecules were produced either by evaporation of resistively heated graphite rods or by laser ablation of graphite

targets in a vacuum. The vapor, consisting of carbon atoms and molecules (predominantly C₃), was co-condensed with an excess of argon or neon gas on a reflecting substrate (a rhodium-coated sapphire slab) held at 3–6 K, forming a solid matrix in which the carbon species were trapped (see, for example, refs 10 and 11). During the deposition, the pressure of the vacuum system was increased by the noble-gas flow to 5×10^{-6} Torr, while the base pressure without the gas flow was on the order of 10^{-9} Torr. After preparation, the matrix was warmed slowly at a rate of about 1–2 K/min. During this warm phase, pictures of the matrix were taken by a video camera (PAL or NTSC). In addition, the relative abundance of carbon molecules was monitored in absorption using a Fourier transform infrared (FTIR) spectrometer (Bruker 113V, resolution of 0.1 cm⁻¹). The emission spectra were recorded by an optical multichannel analyzer (OMA) spectrometer at 1 nm resolution (Princeton Applied Research Model 1236, $f = 0.5$ m, 147 G/mm¹⁰ or Acton SP308, $f = 0.3$ m, 150 G/mm¹¹). The time profile of the optical emission was measured using a photomultiplier detector (Hamamatsu R928, 185–900 nm) and a digitizing oscilloscope (LeCroy 9350L, 500 MHz).

Results and Discussion

Figure 1(a) shows the picture of a typical argon matrix sample before annealing at 6 K. In the center of the argon-coated sample holder, a brownish spot of ~ 8 mm in diameter indicates the area which contains most of the trapped carbon vapor molecules. The dark color is mainly due to the rather strong electronic absorption of larger linear C_n molecules with $n = 15–21$ ¹² which form during matrix deposition. Laser-induced emission experiments (using the 590 nm C₃ phosphorescence¹³) have shown that outside the brownish spot there is a halo of trapped carbon vapor molecules with rapidly decreasing concentration. Figure 2 shows the infrared (IR) absorption spectra during annealing from 7 K (bottom) to 44 K (top). In the assignment of absorptions we followed the literature.^{6,14} Linear C_n molecules ($3 \leq n \leq 9$) dominated at 7 K. As the temperature increased, small molecules such as C₃ (the line at 2040 cm⁻¹) diminished and became negligible at 41 K, while larger molecules such as C₆ (1952 cm⁻¹) and C₉ (1998 cm⁻¹) increased to 18 K and retained their intensity up to 41 K.

In the spectra shown in Figure 2, wiggles of the baseline became conspicuous in particular at frequencies below 1600 cm⁻¹.

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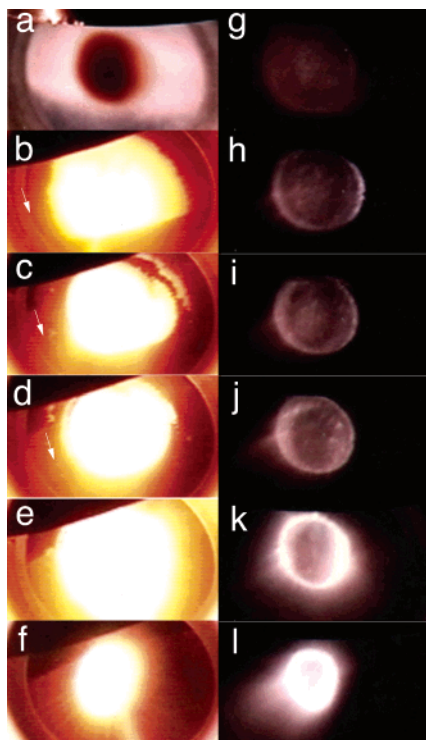


Figure 1. Selected pictures in a record of the video camera, in (a), a typical Ar-matrix sample containing trapped carbon vapor molecules at 6 K before annealing (illuminated by external light). In (b)–(f), a series of flashes for an Ar-matrix sample at ~ 43 K (taken in the dark), and in (g)–(l), a series of flashes for another matrix sample recorded at reduced sensitivity. Each flash was seen only in one frame of the video camera (1/30 s/frame).

These wiggles originate from interference between IR beams reflected from top and bottom surfaces of the matrix layer and are associated with the layer thickness. The inset in Figure 2 shows the calculated thickness of the matrix as a function of the temperature. The change of the fringe pattern above 34 K indicates that the thickness of the matrix decreases due to sublimation. On further annealing from 41 to 43 K, the molecular absorption lines in the IR spectrum suddenly disappear. In the final stages of sublimation, we usually observe several flashes (between 2 and 15, depending on the sample) within a few minutes.

Figure 1(b)–(f) shows pictures of a series of flashes obtained on an argon matrix sample. The light appeared orange or even white. There was no obvious regularity in the time of occurrence of a flash. Arrows in Figure 1(b)–(d) indicate the position of the edge of the matrix, which with the sublimation moved inward from one flash to the next. To show the intensity distribution more clearly, Figure 1(g)–(l) shows flashes of another matrix sample recorded with reduced sensitivity. Initially, the halo and the outer edge of the carbon deposit produces a ring-like emission, which intensifies and shrinks in diameter. The final and most intense flash covers the entire remaining surface. In some pictures, for example in Figure 1(j), we see bright spots and shooting star-like features, i.e. particles splashing into vacuum. The flashing material must be carbon, because we did not observe any flash without carbon molecules in a matrix.

We propose a mechanism by which the multiple flashes and the shrinking areas are explained (see Figure 3). First, as the matrix sublimates (Figure 3(a),(b)), carbon molecules being trapped in the subliming layer, e.g. long carbon chains, large mono- or polycyclic rings, or other structures predominantly

consisting of sp bonds (see, for example, refs 15 and 16), accumulate on the surface to form nested aggregates in macroscopic scales (Figure 3(b)). Second, ignition of an exothermic reaction takes place at a relatively dense position of the aggregates (Figure 3(c)). This reaction is a spontaneous conversion in which sp bonds of nested carbon chains convert into sp² bonds, i.e., a cyclization into hexagonal graphitic structures takes place. Third, the reaction propagates within the aggregates in contact (Figure 3(c),(d)). These steps (Figure 3(a)–(d)), which produce a single flash, repeat several times as the rare-gas matrix becomes thinner and shrinks in extension (Figure 3(d)–(f)), since the sublimation proceeds from the edge to the center of the sample holder. The observation of multiple flashes means that the matrix beneath the reacting surface is thermally well isolated from the flashing particles.

Figure 4(a) shows the time profile of three independent flashes. The flash started with a relatively short, intense pulse of light within a few microseconds, which was followed by moderate emission for a few hundreds of microseconds. After reaching a maximum at around ~ 250 μ s, the emission decayed nearly exponentially for 1000 μ s. For many flashes, similar profiles, namely, ignition (< 3 μ s), propagation (~ 250 μ s), and extinction (~ 1 ms), were commonly observed. Optical emission spectra integrated over the whole period of time of a single flash (> 1 ms) are shown in Figure 4(b). The spectrum in Figure 4(b) is a superposition of three spectra (red lines) of independent flashes measured in three different wavelength ranges of 360–500, 400–650, and 600–900 nm. The intensity calibration was performed by measuring the spectrum of a furnace at 1100 °C and by assuming it to be a perfect blackbody. The intensity of blackbody radiation is represented by the Planck formula,

$$I_{\lambda} \propto \lambda^{-5} [\exp(hc/\lambda kT) - 1]^{-1}$$

where I_{λ} , c , h , k , and T denote the emission intensity at wavelength λ , the speed of light, Planck's constant, Boltzmann's constant, and the temperature of the emitter, respectively. Using this equation, we calculated Planck curves I_{λ} for selected temperatures that are represented as solid and dashed lines in Figure 4(b). After correcting our data by the wavelength-dependent intensity calibration factor, the only remaining parameter for merging the three spectral segments is a scaling factor, i.e., the vertical position in the log scale in Figure 4(b). The composite spectrum of the three different spectral ranges (red lines) fits well with a Planck curve for 2500 K.

We also observed flashes upon sublimation of carbon-containing solid Ne, N₂, O₂, and H₂ matrixes. For Ne, we noticed flashes at around 16 K, i.e. at a lower temperature than for the case of Ar. The optical spectra of the flashes in Ne matrixes are shown in the inset in Figure 4(b). Fitting Planck curves yields blackbody temperatures ranging from 2210 to 2530 K.¹¹ In the case of N₂ (not shown), the flashes occurred at 40 K and again a Planck temperature of ~ 2500 K can be derived. The coincidence of the spectral temperatures for different matrixes suggests that this blackbody temperature is somehow characteristic for elemental carbon.

Here, a few questions arise from the observations. (1) Is the phase transition which we already addressed really the energy source for the flash? (2) What is the significance of the characteristic temperature ~ 2500 K?

Concerning the second question, it is noticeable that the competition between fragmentation and radiative cooling determines the temperature of a flashing particle. Mitzner and Campbell observed blackbody emission from laser-ablated C₆₀

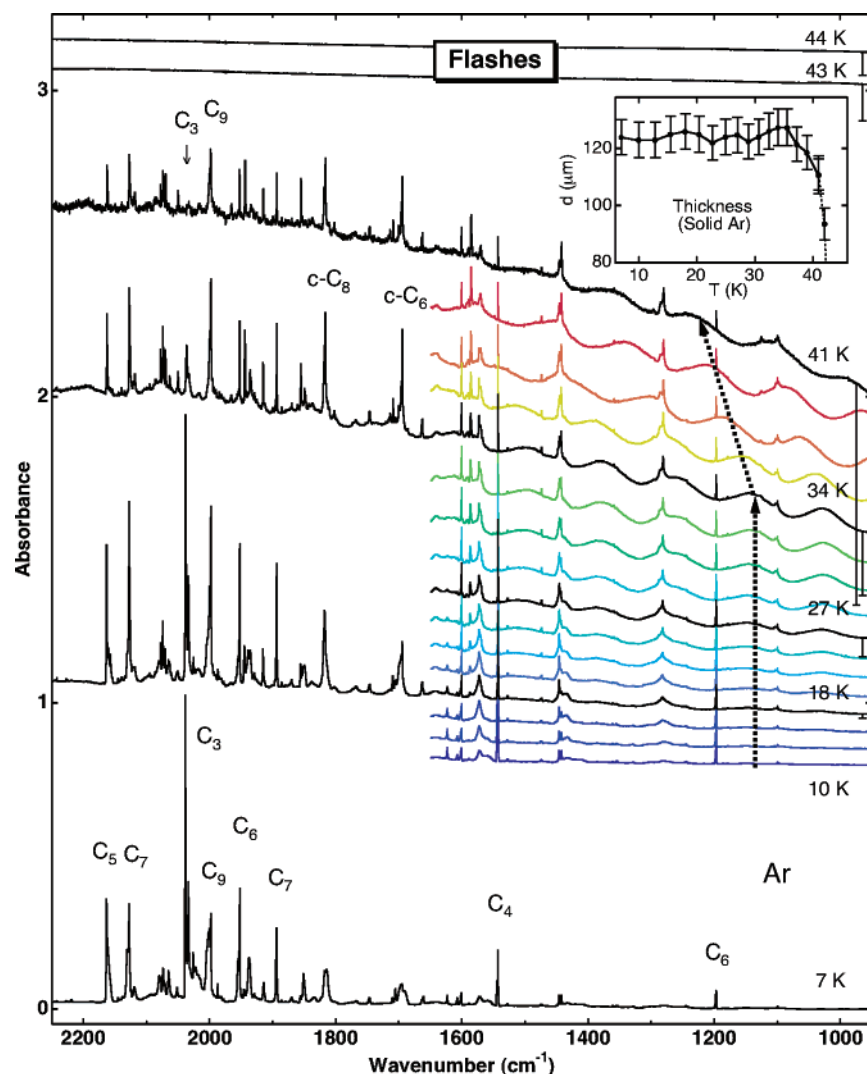


Figure 2. Infrared (IR) absorption spectra during annealing from 7 to 44 K of an Ar matrix containing trapped carbon vapor molecules. The assignment of peaks to linear species is given as C_n , while presumably cyclic species as $c-C_n$ (refs 27, 28). The dashed arrows indicate the positions of a maximum of the interference fringe system. The inset shows the thickness of the matrix calculated from the fringes as a function of substrate temperature. The vertical sticks at the right-hand side indicate the offset for the selected spectra from the bottom spectrum.

in a vacuum and compared energy-loss rates between different cooling mechanisms. According to them, the cooling rate by fragmentation becomes faster than that by blackbody emission above a temperature range between 2250 and 2850 K.¹⁷ The blackbody temperature of ~ 2500 K observed in the present work fits well with this range. Therefore, we conclude that carbon particles reaching such temperatures start fragmenting into smaller molecules.

To answer the first question, we estimate the energy of the flash. For simplicity, we assume that the flash lasts for 100–200 μs at a blackbody temperature of 2500 K. Using the Stephan-Boltzmann law $\epsilon = \sigma_{\text{SB}} T^4 S \Delta t$ (σ_{SB} : Stephan-Boltzmann constant, T : temperature, S : area, and Δt : duration of a flash), the radiative energy ϵ is calculated as 11–22 mJ/flash. The amount of carbon within a matrix is estimated from the weight loss of carbon rods and the reduction factor due to skimming for a molecular beam, which gives 40 μg or $n = 2 \times 10^{18}$ atoms/matrix. Finally, multiple flashes should be taken into account; taking the typical number of flashes to be $N \sim 6$, the total energy released is estimated as $\epsilon N/n \sim 0.2\text{--}0.4$ eV/atom.

Assuming that the blackbody radiation carries most of the released energy, we compare the above figure with the latent heat liberated when transitions between different thermodynamically stable forms of carbon occur. The stability can be estimated

from the typical bond energies for carbon single (3.60 eV), double (6.32 eV), and triple bonds (8.67 eV).¹⁸ The acetylenic chain with alternating single and triple bonds would have ~ 6.13 eV/atom for the bond formation, while the cumulenenic chain without bond alternation would have ~ 6.32 eV/atom. For graphite, a simple estimate amounts to ~ 7.44 eV/atom (the bond order is ~ 1.5). Thus, sp-carbon chains are higher in energy by $\sim 1.12\text{--}1.31$ eV/atom compared to graphite, a figure significantly larger than our estimated energy release of $\sim 0.2\text{--}0.4$ eV/atom. However, one has to realize that the final product of our experiments is not graphite but an amorphous carbon network with strained and bent sp^2 bonds.¹¹ Molecular dynamics simulations indicate that such networks are ~ 0.8 eV/atom higher in energy than graphite.¹⁹

As already mentioned, the metastable material before the flash is probably an aggregate consisting mostly of sp-carbon moieties, because linear-chain molecules are precursors of this material (see Figure 2). Such an sp-carbon system has been suggested to exist as carbyne in which one-dimensional carbon chains stack to form a bulk structure.⁴ However, most previous researchers had problems in stabilizing such a phase.⁴ Nevertheless, a Raman signal around ~ 2100 cm^{-1} should provide evidence for the presence of sp-carbon or a carbyne structure.^{20,21} Recently, Milani and co-workers produced a carbon film by

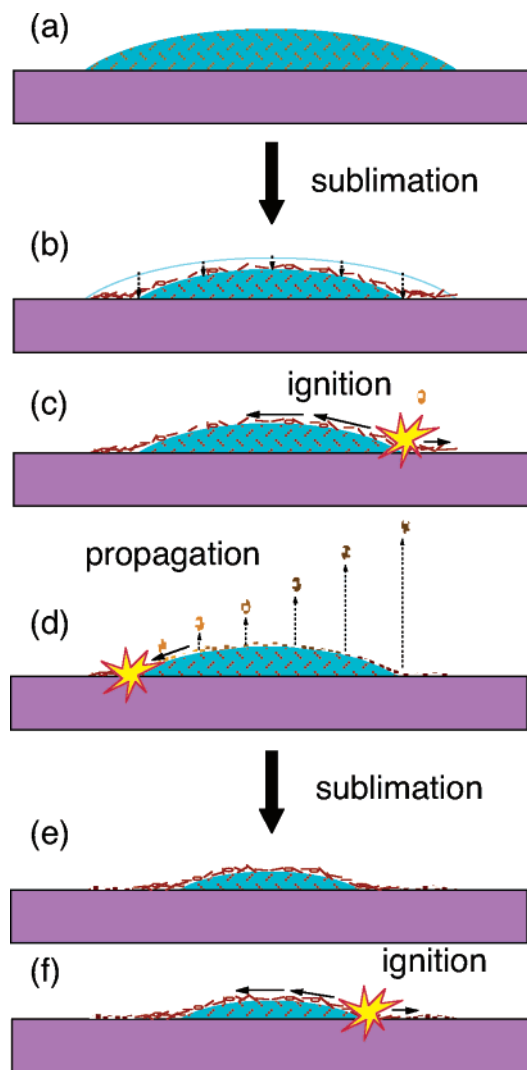


Figure 3. A schematic drawing for the mechanism of flashes. Upon sublimation of the matrix (a–b), trapped linear and cyclic carbon molecules accumulate to form nested aggregates on the surface (b). Then an explosive reaction takes place spontaneously (c) and propagates within the aggregates by blowing up reaction products into vacuum (d). These steps (a–d), consisting of a single flash, repeat several times to shrink in extension (e–f) until complete evaporation of the matrix sample.

the method of cluster beam deposition under ultrahigh vacuum. This film clearly showed Raman peaks at 2100 and 1980 cm^{-1} , which the authors attributed to polyynes with alternating single and triple bonds and to cumulenes without bond alternation, respectively.²² Our preliminary in-situ Raman spectroscopy of the carbon material that is quenched on the cold surface by rapid cooling during the sublimation stage seems to yield similar results.¹¹

Violent energy release upon sublimation of cold matrixes containing reactive carbonaceous chain molecules may also occur in space, for example, on the surface of cometary nuclei. Even though such cometary carbon molecules may have saturated ends and thus may not be as reactive as the pure carbon chains we studied here, the cross linking of bonds should still release substantial amounts of energy. Thus, graphitic surface layers may form and/or particles may be ejected (for comet Halley^{23,24}). In dense interstellar clouds where, despite the low temperatures, molecules and dust grains seem to coexist,^{24–26} the release of chemical energy from carbon sp to sp² conversion may help to volatilize icy mantle layers on cold dust grains

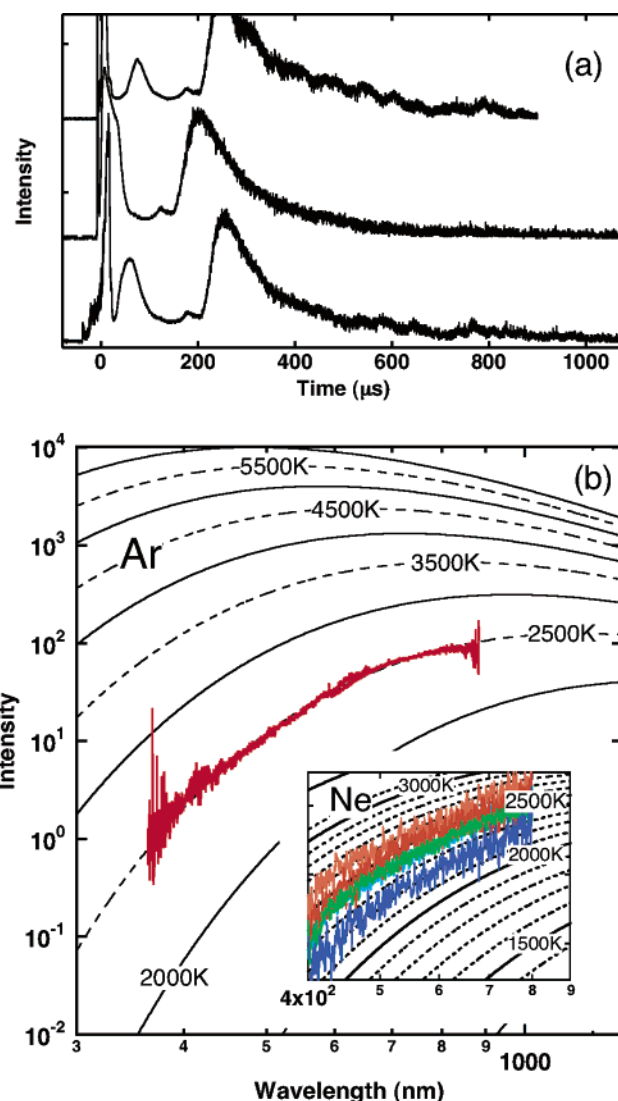


Figure 4. Time profiles (a) and optical emission spectra (b) of flashes observed during sublimation of Ar matrixes. For (a), total emission intensity is measured for three independent flashes as a function of time. For (b), spectra are measured in three different optical ranges (red lines). The solid and dashed curves (black lines) represent theoretical Planck curves of the blackbody radiation for selected temperatures. The inset in (b) shows the emission and the fitting Planck function in a Ne matrix.

and to emanate part of the carbonaceous chains and particles into the gas phase.

Acknowledgment. We thank Professor Donald R. Huffman (The University of Arizona) for his helpful comments and Professor Paolo Milani (University of Milano) for valuable discussions. This work was supported by MPI für Kernphysik collaboration program 2000–2001, the Grants in Aid from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), and a Project in CREST of Japan Science and Technology Agency (JST).

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