Radiative Cooling of C_{60}

J. U. Andersen, C. Brink, P. Hvelplund, M. O. Larsson, B. Bech Nielsen, and H. Shen
Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark

(Received 1 May 1996)

We have studied the radiative cooling of negatively charged fullerene ions by following the thermionic emission as a function of time after injection into the heavy-ion storage ring ASTRID. It is argued that electron emission can be used as a calibrated thermometer to measure the cooling rate. For $C_{60}{}^-$ at ~1500 K the cooling corresponds to a radiation intensity of ~190 eV/s, which is 2 orders of magnitude more than expected from infrared active vibrations. [S0031-9007(96)01602-X]

PACS numbers: 36.40.−c

The formation of fullerene molecules is a surprisingly commonplace phenomenon, accompanying, for example, soot formation when you burn a candle [1]. And yet, the physics and chemistry of the process are far from simple and are still incompletely understood. We address here the radiative cooling of hot C_{60} molecules. In Ref. [1], Smalley argues that electronic transitions can hardly be important because of the large HOMO-LUMO gap (highest occupied to lowest unoccupied molecular orbital, about 1.7 eV). Instead, he suggests that the radiation is emitted by the infrared active vibrations [2].

An estimate of the cooling rate at $T \sim 1800$ K was obtained by Kolodney, Budrevich, and Tsipinyuk from observation of the depletion of thermal C_{60} beams by fragmentation, and they conclude that the measured cooling is much faster than expected from emission by infrared active vibrations [3]. It is difficult to judge the accuracy of this result because it is derived from observation in a rather short time interval of the competition between cooling and fragmentation, $C_{60} \rightarrow C_{58} + C_2$, and the activation energy for this process is not known. We have studied the cooling of negatively charged fullerenes by observation over two decades in time of the competition between cooling and electron emission. The electron affinity is well known [1,4], and, with the additional information available on attachment cross sections for low-energy electrons [5–7], a reliable statistical formula can be established for thermionic electron emission. The formula can be tested against lifetimes measured for $C_{60}{}^-$ molecules with definite temperature [6], and hence thermionic emission can be used as a calibrated thermometer.

The experiments were performed at the heavy-ion storage ring ASTRID [8]. A pulse of negatively charged fullerene ions from an electron-impact ion source was injected into the ring at 50 keV, and the decay of the stored current was followed by the observation of neutral decay products with a channel-plate detector in one of the four 90° magnets of the ring. As shown in Fig. 1, there is initially a high rate which is attributed to thermionic emission from the hot molecules. The rate decreases by 3–4 orders of magnitude until at $t \sim 100$ ms it becomes so low that the yield of neutrals is dominated by collisions with rest-gas molecules, mainly H_2. This contribution to the yield decays exponentially with a lifetime of order 10 s, corresponding roughly to a geometrical cross section for destruction.

To interpret the data, we use a statistical model. The electron bombardment in the source produces fullerene molecules with a broad distribution in internal energy. For a C_{60} molecule with energy E we define a microcanonical temperature by the relation between the average internal energy and the temperature in a thermal equilibrium, $E = 7.4 + 0.0138(T - 1000)$ eV for $T > 1000$ K, as derived from the vibration frequencies calculated by Stanton and Newton [2] with a reduction by 10% [9]. The heat capacity, $C = 0.0138$ eV/K, is consistent with the value given in Ref. [3].

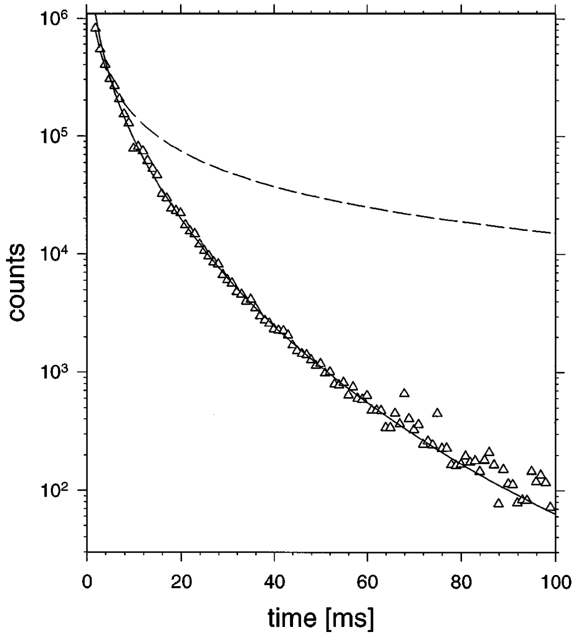

FIG. 1. Rate of decay by thermionic emission of a stored $C_{60}{}^-$ beam. A contribution from collisions with the rest gas has been subtracted. The curve through the data points corresponds to Eqs. (10) and (11) with $\tau_c = 4.3$ ms and $n = 7.6$, and the other curve to a t^{-1} dependence.

The distribution in temperature changes with time both due to cooling and due to depletion by electron emission. It is convenient to introduce the initial temperature T_i as a variable in the distribution function $g(T_i,t)$, which then changes only by depletion,

$$\frac{d}{dt}\,g(T_i,t) = -\nu \exp\!\left(-\frac{E_b}{kT(t)}\right) g(T_i,t)\,. \qquad (1)$$

We have introduced a simple Arrhenius expression for the rate of emission and approximated the cooling by a continuous decrease of the temperature $T(t)$, with $T(0) = T_i$. With the solution of Eq. (1) for $g(T_i,t)$, the emission yield may be expressed as

$$\begin{aligned} I_e(t) = & \int dT_i\, \nu \exp\!\left(-\frac{E_b}{kT(t)}\right) \\ & \times \exp\!\left[-\int_0^t dt'\,\nu \exp\!\left(-\frac{E_b}{kT(t')}\right)\right] g(T_i,0)\,. \qquad (2) \end{aligned}$$

If we disregard cooling, we have $T(t') = T_i$, and the integration in the exponent gives just a factor t. The integral over T_i is then dominated by a narrow region in temperature around a value $T_m(t) = E_b/[k\ln(\nu t)]$, where $\ln(\nu t) \sim 25$ for $t \sim 10$ ms, and we may therefore approximate slowly varying functions by constants,

$$\begin{aligned} I_e(t) = & \int dT_i\, \frac{kT_i^2}{E_b t}\, g(T_i,0) \\ & \times \frac{-d}{dT_i}[\exp(-\nu t e^{-E_b/kT_i})] \cong \frac{T_m g(T_m,0)}{t\ln(\nu t)}\,. \qquad (3) \end{aligned}$$

Hence, in the absence of cooling, the intensity should vary as t^{-1}, and the nearly exponential decrease observed in Fig. 1 is strong evidence for cooling.

The depletion from the high-temperature end of the distribution $g(T_i,t)$ stops when the emission becomes so slow that it is quenched by cooling. This happens at a time τ_c, when the rate of relative change of the emission rate becomes equal to the emission rate itself,

$$\begin{aligned} \frac{1}{\tau_c} &= -\frac{d}{dt}\ln\!\left[\nu \exp\!\left(-\frac{E_b}{kT}\right)\right] \\ &= \ln(\nu\tau_c)\frac{-d}{dt}\ln T, \qquad T = T_m(\tau_c) \equiv T_c\,. \qquad (4) \end{aligned}$$

For temperatures near T_c the decrease with time of the exponent in Eq. (1) is then to first order given by $-t/\tau_c$. If we introduce this in Eq. (2), the integration can be carried out as before but the time dependence is modified to $t_c^{-1}[\exp(t/\tau_c) - 1]^{-1}$, expressing a transition at $t \sim \tau_c$ from proportionality to t^{-1} to exponential decrease with time constant τ_c. For $t > \tau_c$ the distribution is frozen, $g(T_i,t) \sim g(T_i,\tau_c)$, and the emission decreases due to cooling alone.

To make the analysis quantitative, we need values for the parameters ν and E_b in Eq. (1). We can use the same statistical argument that leads to the Richardson formula for electron emission from a surface area S of a metal with work function ϕ,

$$I_e = AT^2 S(1 - r)\exp\!\left(-\frac{\phi}{kT}\right), \qquad (5)$$

where $A = mk^2/2\pi^2\hbar^3$ and r is the average reflection coefficient for thermal electrons. This formula is derived from a detailed balance between attachment and emission when the chemical potential is the same inside and outside the surface, $\mu = -\phi$ [10].

For $C_{60}{}^-$ the electron affinity is $E_a = 2.67$ eV [4]. Since the energy level of the additional electron is 6 times degenerate (t_{1u}), the $C_{60}{}^-$ state corresponds to a Fermi distribution with chemical potential $\mu = -E_a - kT\ln 5$, but, instead of this modification of μ, we divide the pre-exponential factor by 5.

The effective surface area S and the reflection coefficient r may be obtained from experiments [5–7]. We shall use an "electronic" radius of 4.3 Å for C_{60}, which corresponds to a cross section of 58 Å^2. The experiments indicate that above a threshold the attachment cross section for low-energy electrons is roughly geometrical, $r = 0$. At very low energies the cross section decreases exponentially, corresponding to the penetration of a barrier of ~0.25 eV, which has been explained by the absence of s-wave attachment [11]. We include this barrier in the effective work function, which becomes $E_b = 2.92$ eV, while the pre-exponential factor is $\mathrm{AST}^2/5 = 3.5 \times 10^6 T^2\ \mathrm{s}^{-1}$.

The first systematic measurement of thermionic emission from fullerenes agreed poorly with such a description [12], but, as discussed in Ref. [7], there was probably a large error in the estimated temperatures in those experiments, where the excitation of the molecules derived from slow surface collisions. In contrast, the excitation energy is well defined when negative fullerene ions are formed by absorption of a low-energy electron [6], and we may compare with lifetimes measured for bombarding energies of 8–12 eV, corresponding to internal temperatures of the order of 1800 K. For 10 eV the lifetime was measured to be 82 ± 15 μs (Ref. [6], Fig. 4).

To calculate the expected lifetime we first evaluate the effective temperature for the decay of the molecule. Exiting an oven at 850 K [7], the ions have an average internal energy of 5.7 eV and to this should be added an electron affinity of 2.67 eV and the kinetic electron energy of 10 eV, leading to $E = 18.37$ eV. From the basic description of a statistical equilibrium between a small and a large system [10] it is clear that to first order in E_b/E the temperature in the Boltzmann factor should correspond to the energy $E - E_b/2$, as discussed also by Klots [13]. This average energy is 16.9 eV, corresponding to an emission temperature $T_e = 1690$ K. The lifetime then becomes $\tau \sim 50\ \mu$s, in fair agreement with the measurements as is also the calculated energy dependence. Thus, the formula in Eq. (5), with the parameter values discussed above and with the finite-heat-bath correction to the temperature, is supported both by strong theoretical arguments and by the best available experimental data.

Let us now turn to the cooling, which may be expressed as

$$-\frac{dT}{dt} = S\sigma\varepsilon_e C^{-1}T^4, \tag{6}$$

where S is the surface area, $\sigma = 3.54 \times 10^9$ eV Å^{-2} K^{-4} s^{-1} the Stefan-Boltzmann constant, and ε_e the emissivity coefficient. With a dielectric description of the interaction between the radiation field and the molecule [14], one obtains an absorption cross section given by

$$\sigma_{\mathrm{abs}} = \frac{\pi d^2}{4} 4\pi \frac{d}{\lambda} \operatorname{Im}\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right), \tag{7}$$

where d is the diameter, λ the wavelength of the radiation, and $\varepsilon(\omega)$ the dielectric function which includes resonances corresponding to both vibrational and electronic excitations. From detailed balance, the ratio of this cross section to the geometrical one is the emissivity coefficient at wavelength λ.

As argued below, the radiation is dominated by the electronic contribution and not all the radiation is emitted by the additional electron in the anion. The interaction of C_{60} with visible light is dominated by broad collective dipole resonances at about 6 and 10 eV which can be reproduced by a model with a local dielectric function inside a spherical shell, corresponding to a total of 20 electrons and a plasmon energy $h\omega_0 \sim 11$ eV [15],

$$\varepsilon = 1 - \frac{\omega_0^2}{\omega(\omega + i/\tau)}, \tag{8}$$

where τ is a damping time. The formula (7) is modified for this geometry [16], but the result is quite well represented by Eq. (7) with a reduced plasma frequency, $\omega_0/1.3$. From the formulas (7) and (8) we obtain for the emissivity coefficient in the limit of long wavelengths

$$\varepsilon_e(\omega) \cong 12\pi \frac{d}{\lambda}\left(\frac{1.3\omega}{\omega_0}\right)^2 \frac{1}{\omega\tau}, \tag{9}$$

where both ω and $1/\tau$ have been assumed small compared to ω_0. In this expression, $1/\tau$ can be used as an adjustable parameter. For small metal particles [17], a typical estimate is $1/\tau \sim 2v_f/d$, where v_f is the Fermi velocity of the electron gas, and, for our case, this would correspond to $\hbar/\tau \sim 1$ eV.

If τ is independent of frequency (and temperature), the emissivity coefficient averaged over the Planck distribution of blackbody radiation will be proportional to T^2, and according to Eq. (6) the cooling rate will then be proportional to T^6. We shall use a power law in a fit to the measured decay curve but leave the power n as a free parameter. Thus, we associate the emission rate $I_e(t)$ with a narrow distribution in T, which for $t > \tau_c$ moves down in temperature due to the cooling, $-dT/dt \propto T^n$. It is most convenient to use the electron-emission temperature $T_e = (E - E_b/2)/C$ as the variable T and then correct by $+E_b/2C$ in the interpretation of the cooling as the emission of heat radiation (Fig. 2). In addition to the power n, the fitting parameters are the characteristic cooling time τ_c and a normalization factor. The value of T_c is given by Eq. (4) with $\nu = \mathrm{AST}_c^2/5$, and we introduce the notation $G = \ln(\nu\tau_c)$. The cooling rate at T_c is also fixed by Eq. (4), $-d/dt \ln T = (G\tau_c)^{-1}$, and we can write down an explicit solution for the time dependence of T for initial temperature $T_i = T_c$,

$$T = T_c\left(1 + \frac{t}{\tau_c}\frac{(n-1)}{G}\right)^{-1/n-1}. \tag{10}$$

For the emission rate we may use the expression

$$I_e(t) = \frac{I_0(T/T_c)^2}{\exp(GT_c/T) - \exp(G)}, \tag{11}$$

with T given by Eq. (10). This approximation contains the reduction of the electron emission for $t > \tau_c$ due to cooling, and by subtracting the term $\exp(G)$ in the denominator we have also included the transition to a t^{-1}

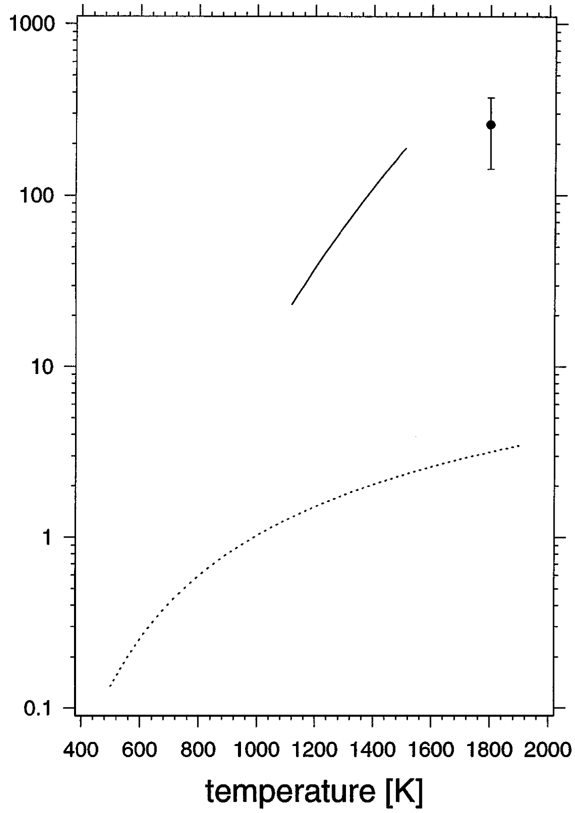

FIG. 2. Radiation from a C_{60}^- molecule as a function of temperature. The solid curve corresponds to Eq. (9) with $\hbar/\tau = 0.38(T/1500)$ eV. The dotted curve gives the radiation from infrared active vibrations [Eq. (12)] and the point at 1800 K is the estimate in Ref. [3] of radiation from C_{60}.

dependence for $t \le \tau_c$, as discussed above. Comparison with a numerical integration of Eqs. (1), (2), and (6) shows excellent agreement for $I_e(t)$ if a value of n larger by ~0.6 is used in Eqs. (10) and (11).

As seen in Fig. 1, the fit to the measurements is very good with the parameters $\tau_c = 4.3$ ms and $n = 7.6$, which should then be corrected to $n \sim 7$. The value of G becomes $G = 24.1$, and the characteristic temperature is then $T_c \sim 1400$ K, while the corresponding temperature for the emission of heat radiation is higher by $E_b/2C$, i.e., $T \sim 1500$ K at $t = \tau_c$. The radiation intensity at this temperature is $-C dT/dt \sim 190$ eV/s, and, if we interpret this value in terms of the formulas in Eqs. (6) and (9), the damping term becomes $\hbar/\tau = 0.38(T/1500)$ eV.

The radiation intensity from the infrared-active vibrations may be estimated from the dipole derivatives $\partial D/\partial s$ calculated in Ref. [2]. For a single mode with displacement coordinate s and frequency ω, the intensity is given by

$$I_r = \frac{2\hbar\omega^3}{3M_c c^3}\left(\frac{\partial D}{\partial s}\right)^2 \frac{1}{\exp(\hbar\omega/kT) - 1}, \tag{12}$$

where M_c is the mass of a carbon atom. The calculated total radiation intensity from the 3×4 infrared-active vibrations in C_{60} is given in Fig. 2. Symmetry breaking by the additional electron in $C_{60}{}^-$ and the combination of modes will increase the intensity but not by the two orders of magnitude required to reproduce our measurements. Even if all the vibrations were assumed to contribute, with dipole derivatives similar to those calculated for the infrared-active modes, an order of magnitude would still be missing in the estimated intensity at 1500 K.

We have shown then that thermal electron emission can be used to study quantitatively the radiative cooling of $C_{60}{}^-$. The observed very high cooling rates can only be explained by an electronic mechanism, and $C_{60}{}^-$ radiates at ~1500 K nearly as strong as a small metal particle.

A dielectric model can account for the observations, but the large HOMO-LUMO gap in C_{60} would seem to block the scattering of electrons, and the mechanism for decay of plasma oscillations into vibrational heat, characterized by the lifetime τ in Eq. (8), remains to be explained. The coupling of electrons and vibrations in C_{60} is strong and is probably responsible for the observed superconductivity at quite high temperatures in fullerides [4,11,18]. Maybe it causes the bands of electronic states to be strongly broadened at high temperatures.

We have obtained supporting evidence [19] for our interpretation of the experiment from observation of the increase in delayed electron emission due to heating by a Nd:YAG laser. The cross section for absorption of the 1.17 eV photons is larger by an order of magnitude than that given by the free-electron model [Eq. (7)], and this may be explained by the presence of a transition in the $C_{60}{}^-$ anion near the laser wavelength [20]. Based on Ref. [20], we estimate that the two transitions in the anion near 1000 nm may account for more than half of the observed radiation intensity at 1500 K. However, the comparison in Fig. 2 with the radiation from neutral C_{60} at 1800 K, estimated by Kolodney, Budrevich, and Tsipinyuk [3], indicates that the additional electron in $C_{60}{}^-$ is not alone responsible for the radiative cooling.

This project was supported by the Danish National Research Foundation through the Research Center ACAP. It is a pleasure to acknowledge stimulating discussions with Klavs Hansen during a visit to the Center [21].

[1] R. E. Smalley, in *Atomic and Molecular Clusters*, edited by E. R. Bernstein (Elsevier, Amsterdam, 1990), Chap. 1.
[2] R. E. Stanton and M. D. Newton, J. Phys. Chem. **92**, 2141 (1988).
[3] E. Kolodney, A. Budrevich, and B. Tsipinyuk, Phys. Rev. Lett. **74**, 510 (1995).
[4] C. Brink, L. H. Andersen, P. Hvelplund, D. Mathur, and J. D. Voldstad, Chem. Phys. Lett. **233**, 52 (1995).
[5] D. Smith, P. Spanel, and T. D. Märk, Chem. Phys. Lett. **213**, 202 (1993).
[6] T. Jaffke, E. Illenberger, M. Lezius, S. Matejcik, D. Smith, and T. D. Märk, Chem. Phys. Lett. **226**, 213 (1994).
[7] S. Matejcik, T. D. Märk, P. Spanel, D. Smith, T. Jaffke, and E. Illenberger, J. Chem. Phys. **102**, 2516 (1995).
[8] P. Hvelplund, Phys. Scr. **T59**, 244 (1995).
[9] R. K. Yoo, B. Ruscic, and J. Berkowitz, J. Chem. Phys. **96**, 911 (1992).
[10] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965). Electron emission is discussed in problems 9.23 and 9.24.
[11] E. Tosatti and N. Manini, Chem. Phys. Lett. **223**, 61 (1994).
[12] C. Yeretzian, K. Hansen, and R. L. Whetten, Science **260**, 652 (1993).
[13] C. E. Klots, Z. Phys. D **21**, 335 (1991).
[14] C. E. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (John Wiley, New York, 1983).
[15] D. Östling, P. Apell, and A. Rosén, Z. Phys. D Suppl. **26**, 282 (1993).
[16] A. Ding, in *Electron Collisions with Molecules, Clusters, and Surfaces*, edited by H. Ehrhardt and L. A. Morgan (Plenum Press, New York, 1994), p. 195.
[17] W. P. Halperin, Rev. Mod. Phys. **58**, 533 (1986).
[18] O. Gunnarsson, H. Handschuh, P. S. Bechthold, B. Kessler, G. Ganteför, and W. Eberhardt, Phys. Rev. Lett. **74**, 1875 (1995).
[19] J. U. Andersen, C. Brink, P. Hvelplund, M. O. Larsson, and H. Shen (to be published).
[20] D. R. Lawson, D. L. Feldheim, C. A. Foss, P. K. Dorhout, C. M. Elliott, C. R. Martin, and B. Parkinson, J. Electrochem. Soc. **139**, L68 (1992).
[21] K. Hansen and E. E. B. Campbell, J. Chem. Phys. **104**, 5012 (1996).