Thermionic Emission and Fragmentation of C_{60}

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We analyze the rate of delayed (thermionic) ionization of photoexcited C_{60} molecules. The rate has a power-law dependence, indicating the presence of a continuum of rate constants. The value of the exponent provides information about the competition between delayed ionization and unimolecular fragmentation; it is equal to the ratio of the ionization energy and the activation energy for fragmentation. This result provides a novel method to measure the controversial bond dissociation energy of neutral C_{60}. We obtain a value of 11.9 ± 1.9 eV. [S0031-9007(97)02571-4]

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The phenomenon of delayed electron emission from fullerenes has attracted great interest during the past few years [1–13]. Ions C_{60}^+ are formed as late as 300 μs after multiphoton excitation with nanosecond laser pulses, for wavelengths ranging from 215 to 1064 nm. The vast body of observations suggests that this process represents the molecular analog of thermionic emission [12,13].

Several groups have analyzed the time dependence of this reaction in detail [1,6–9]. Information extracted from these spectra has often been expressed in terms of multiexponential decay curves. However, the physical significance of the respective rate constants, which may range from 10^4 to 10^7 s^{-1}, has remained obscure. Three or more constants are usually required to provide a reasonable fit to the data, unless the spectra are restricted to a very narrow time range. No clear correlation of these rate constants with photon energy, laser fluence, or internal energy of the neutral C_{60} precursor has emerged.

We solve this puzzle by showing that the delayed electron emission from hot, multiphoton-excited C_{60} follows a power law in time t,

$$I(t) = I_0 t^{-p}. \tag{1}$$

We are thus able to summarize the available quantitative knowledge of delayed electron emission in a single exponent. Its value does not depend on the details of the excitation process, as revealed by a comprehensive analysis of a large number of electron and ion spectra recorded by us, and of spectra published previously by Wurz and Lykke [6]. In particular, it is observed to be insensitive to the photon energy in the range from 2.3 to 4.7 eV.

The value of the exponent p, however, differs significantly from 1.0, indicating that thermionic emission competes with another decay channel, the emission of C_2 from the highly excited C_{60}. We apply statistical theory to this situation, based on the formalism developed by Klots [14]. Under certain conditions to be discussed below, one obtains the analytical result that p is, approximately, equal to the ratio of the ionization energy, Φ, and the activation energy for C_2 emission, D. This relation provides a novel method to determine the controversial dissociation energy D, because the ionization energy is accurately known. Our experimental result for the exponent, $p = 0.64 \pm 0.10$, translates to $D = 11.9 \pm 1.9$ eV. This value is significantly larger than most previously published experimental values, but close to theoretical results [11,15–19].

Our spectra are recorded as follows: An effusive source filled with 99.5% pure C_{60}, kept at 300 to 500 °C, produces a low-density molecular beam which, after multiple collimation and differential pumping, is intersected by an unfocused, collimated beam from a Q-switched, frequency-tripled Nd:YAG laser (355 nm, pulse duration 7 ns). Spectra of cations are recorded with a linear time-of-flight mass spectrometer: Prompt and delayed ions are extracted in a static field of 300 V/cm into a field-free drift tube towards a microchannel plate detector. Delayed formation of C_{60}^+ gives rise to a mass peak which is strongly tailed towards longer arrival times [1,6,7].

Great care has been taken to record spectra under conditions which avoid distortions arising from background, detector saturation, etc. Usually, we employ single-particle counting techniques and low count rates (order of one event per laser shot) to assure linearity of the detector response. Ion spectra exhibit relatively low time resolution, but they are mass selective. Contamination of the C_{60}^+ signal due to delayed formation of fragment ions is very small [7].

Electron spectra are recorded similarly, but we use another detector at a distance of only 5 cm to ensure 100% collection efficiency [8]. These spectra enjoy a much better time resolution, but the lack of mass selectivity makes it more challenging to avoid background. One has to suppress negative ions, secondary electrons from C_{60}^+ impact, photoelectrons originating from surfaces and background gas, etc. This has been accomplished by applying a static, homogenous magnetic field collinear with a very weak extraction field (10 V/cm), and using low laser intensity and low photon energy (3.49 eV). Details are given elsewhere [8].

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Representative electron spectra are shown in Fig. 1 on a semilogarithmic scale. The source temperature and laser fluence cover a wide range of 320 to 460 °C and 36 to 94 $\mathrm{mJ/cm^2}$, respectively. These spectra are clearly not single exponential. For a time range $t > 0.1\ \mu\mathrm{s}$, they may be fitted reasonably well by a sum of four exponentials [20].

However, as shown in the log-log plot in Fig. 2(a), these spectra follow a simple power law in time, at least over the time range 0.1 to 10 μs. Solid lines show the result of weighted nonlinear least-squares fits, the values of the exponents are around 0.60. The significant bending beyond 10 to 20 μs is likely due to the finite speed of the precursors, although a similar effect can be derived from the theory described below.

Figure 2(b) displays another electron spectrum (recorded with an enhanced digital resolution of 5 ns) and an ion spectrum (20 ns digital resolution), taken under nearly identical conditions as far as source temperature and laser intensity are concerned. Both curves feature very similar slopes of $p = 0.67$ and 0.65, respectively. Many more electron and ion spectra have been analyzed and were all found to follow a power law. The mean value of the exponent is $p = 0.64$. We conservatively estimate the error from the standard deviation of the distribution of exponents to find $\Delta p = 0.10$.

Analysis of data published by other researchers reveals a similar power-law behavior. In Fig. 2(c) we reconstruct electron spectra, recorded by Wurz and Lykke at photon wavelengths 266, 355, and 532 nm, respectively [6]. Dashed lines are calculated from the set of rate constants and amplitudes which the authors had fitted to their original spectra. Within the time range covered by the reported inverse rate constants, indicated as full dots in Fig. 2(c), the spectra closely follow a power law (solid lines) with exponents between 0.60 and 0.75.

Such a power-law dependence is characteristic of an ensemble of small, free particles which undergo thermally activated decay, provided their (vibrational) excitation energy varies essentially randomly from molecule to molecule. The properties of such an ensemble were originally discussed by Gspann and further developed by Klots [14,21]. The decay of this ensemble is described by a power law in time [Eq. (1)] with $p = 1.0$ if only one decay channel is active.

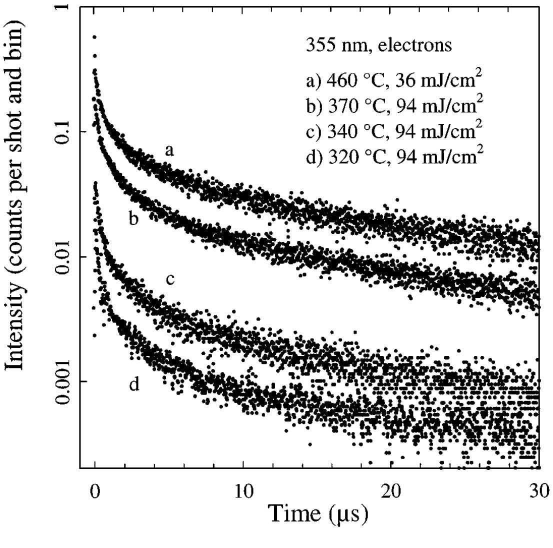

FIG. 1. Delayed electrons from C_{60}, recorded at 355 nm over a range of source temperatures (320 to 460 °C) and laser fluences (36 to 94 $\mathrm{mJ/cm^{2)}}$.

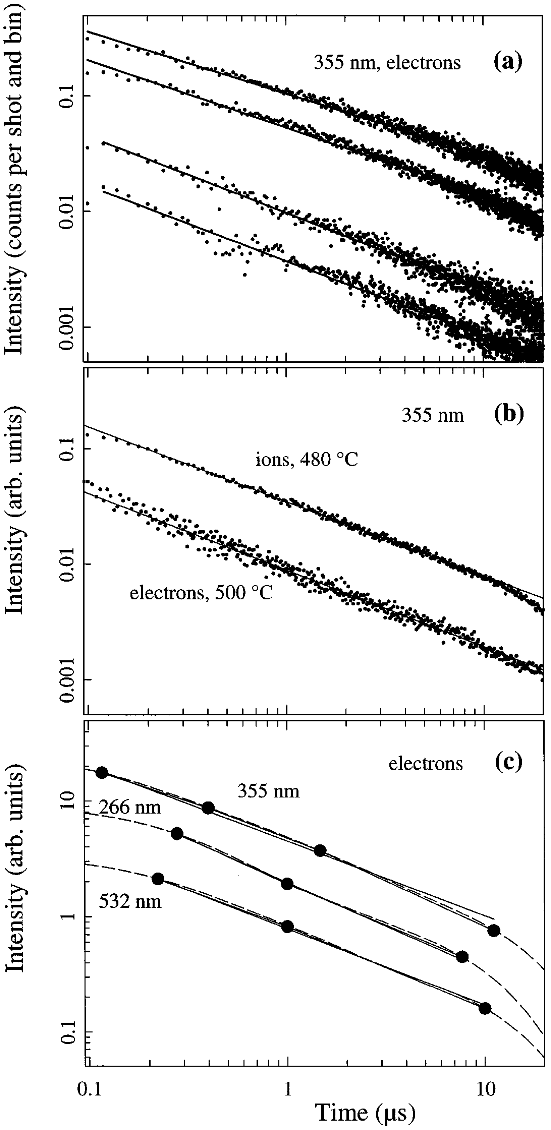

FIG. 2. (a) Electron spectra from Fig. 1, but on a double-logarithmic scale. (b) Comparison of delayed electrons and delayed ions, C_{60}^{+}. (c) Delayed electron spectra (dashed lines), reconstructed from effective time constants (full dots) as reported by Wurz and Lykke [6] for three different laser wavelengths. Solid lines represent least-squares fits of a power law, Eq. (1).

In the following we will show that an exponent smaller than 1.0 will be observed if another activated process competes with and dominates the one being measured. Neither the nature nor the efficiency of this other channel can be directly identified in our experiment, but only two other decay channels could possibly be significant: dissociation into $C_{58} + C_2$, and radiative cooling. The time scale of our experiment is such that dimer loss is, almost certainly, the dominant dissociation channel [3,22,23]. Loss of carbon atoms [24,25] or ion pair formation would be, for energetic reasons, insignificant. Radiative cooling will become relatively important only if much longer time scales are analyzed [16,26,27]. Hence, we will consider an ensemble of C_{60} which may emit either dimers (activation energy D, not well known) or electrons (activation energy $\Phi = 7.6 \pm 0.1$ eV [28]).

If the amount of energy absorbed by the molecules is sufficiently smooth, the ensemble-averaged thermionic emission rate k_e is given by

$$\langle k_e \rangle \propto \int_0^\infty dE\, k_e(E) \exp[-tk_e(E) - tk_a(E)], \tag{2}$$

where k_a is the C_2 loss rate, k_e the thermionic emission rate, and t the time elapsed since the laser pulse. If electron emission dominates ($k_a \ll k_e$), the right-hand side is proportional to t^{-1} [29] which is clearly seen experimentally *not* to be the case. In the opposite limit we can, by expressing the rates in a simple Arrhenius form, calculate the above average. Set

$$k_e = \omega_e \exp(-\Phi C_v/E), \qquad k_a = \omega_a \exp(-DC_v/E), \tag{3}$$

where the two ω's are simple frequency factors and we have absorbed a zero point in the definition of the energy. By expressing k_e in terms of k_a the ensemble electron emission rate is found to be

$$\langle k_e \rangle \propto \int_0^\infty dE [k_a(E)]^{\Phi/D} \times \exp\{-tk_a(E) - \omega_e t [k_a(E)/\omega_a]^{\Phi/D}\}. \tag{4}$$

This can be approximated by [29]

$$\langle k_e \rangle \propto \frac{t^{-\Phi/D}}{[ln(\omega_a t)]^2} \int_0^\infty dx\, x^{\Phi/D-1} \times \exp\left[-x - \frac{\omega_e t}{(\omega_a t)^{\Phi/D}}\, x^{\Phi/D}\right]. \tag{5}$$

When electron emission is small, the second term in the exponent is small. The exponential function can then be expanded and the integrals performed term by term. The first two terms give

$$\langle k_e \rangle \propto \frac{t^{-\Phi/D}}{[ln(\omega_a t)]^2} \left[\Gamma(\Phi/D) - \Gamma(2\Phi/D)\frac{\omega_e t}{(\omega_a t)^{\Phi/D}}\right], \tag{6}$$

where Γ is the gamma function. Because of the magnitude of $\omega_a t$ the logarithm can be considered constant. The second term is small, on the order of k_e/k_a. The expression is then essentially a power law in t with the power $-\Phi/D$. Hence $p \approx \Phi/D$. This result is fairly insensitive to the functional form of the rate constant. When the Arrhenius-like expressions are replaced by more accurate expressions, the correction is the order of only a few percent [30].

This result presumes a smooth distribution of excitation energy deposited into the molecules. This is not inconsistent with the nature of the excitation process, i.e., absorption of monoenergetic photons: The initial thermal energy of C_{60} emerging from the source already features a width (FWHM) of 1 to 2 eV [6].

Distinct rate constants in similar experiments have been observed only for much smaller clusters [31]. In our data distinct rate constants can be ruled out since the value of p is invariant to the source temperature. For example, in the temperature interval covered in Figs. 1 and 2(a) the thermal excitation energy changes by about half a photon energy while p is unchanged. Also, p is invariant to the wavelength of the excitation laser [Fig. 2(c)]. These observations prove that the energy distribution is indeed smooth.

The neutral fragments assumed by the theory have also been observed. Lykke [25] was able to prove the formation of neutral C_2 and other small fragments. Similarly, the neutral fragment C_{58} was identified by single photon ionization [6].

The result that $D > \Phi$ and at the same time $k_a > k_e$ implies that $\omega_a \gg \omega_e$. The ratio ω_e/ω_a can be estimated if the branching ratio k_e/k_a is known, by using the results of Ref. [21] to estimate the energy E. For example, the value $k_e/k_a = 0.1$ yields $\omega_e/\omega_a = 10^{-5}$. This differs from the value proposed in Ref. [5], but compares reasonably well with the ratio found when both rates are treated by detailed balance [30]. Conversely, the experimentally determined lower bound on the total delayed electron yield of 2.6% ± 1.1% [8] will allow a more precise estimate of the frequency factors. Furthermore, a calculation of the higher order corrections in Eq. (6) shows that even at such branching ratios the power law is only weakly modified, although a small negative curvature is introduced.

Our result of $D = 11.9 \pm 1.9$ eV for dissociation of C_{60} into $C_{58} + C_2$ exceeds several other recently published values, obtained by a variety of methods employing molecular beams of fullerenes, by 4 to 7 eV [11,15,16,19,22]. The disagreement is even more severe if one compares with values extracted from thermal decomposition of condensed C_{60} at relatively low temperatures [32]. On the other hand, our value is in excellent agreement with several calculations [17,18]. Furthermore, well-established heats of formation and the enhanced stability of C_{60} imply that D exceeds 7.8 eV [22]. Hence, our result is physically reasonable.

Summarizing, we have reproduced the available data on the time dependence of delayed electron emission with a single parameter which can be identified with the ratio of the ionization energy and the evaporative activation energy, D. The competition between the two different statistical decay channels provides a method to determine D for which we obtain 11.9 ± 1.9 eV.

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