Kinetics of the radiative relaxation of the highly excited C_{60}^{+*} ion

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The radiation of fullerene molecules from the intersection area of the C_{60} beam with an electron beam with an energy of $27 \leq E_e/\text{eV} \leq 100$ was studied experimentally under conditions of a single collision. It was found that ionized C_{60}^{+*} molecules make the main contribution to the radiation. The radiation intensity and the temperature of C_{60}^{+*} as functions of the energy E_e were measured. The kinetics of the radiation cooling of C_{60}^{+*} was studied and the rate of the radiation loss of the ion energy ($5.5 \cdot 10^5$ eV s^{-1}) was determined at a temperature of 3150 K. For the heat model of radiation at the wavelength $\lambda = 540$ nm, this corresponds to the emissivity $\varepsilon = 1.1 \cdot 10^{-2}$.

Key words: fullerene, molecular beam, electronic excitation, radiation, radiation cooling.

Deactivation of complex molecules by IR fluorescence is important for ion-molecular processes, because it determines, in particular, the rate of stabilization of an excited complex.[1] The vibrational temperature corresponding to the energy of excitation of the internal degrees of freedom of the molecules usually cannot be too high due to the fast enhancement of the competing dissociation processes. A different situation is observed in the relaxation of highly excited states of C_{60} molecules (see Refs. 2, 3). Fullerenes differ from the conventional polyatomic molecules by high activation energy of dissociation (>5 eV); in combination with high density of the vibronic states, this allows the molecule to reach high enthalpy. As a consequence, high radiation intensity can be expected. Study of fullerenes excited in a laser plasma[2] or by an electron impact[3] gave an unexpected result, namely, a structureless (up to a resolution of 0.1 nm) radiation spectrum resembling the spectrum of thermal radiation of condensed bodies was recorded. Note that the radiation spectrum observed previously[2,3] is formed by a single species because multiple transfer of absorption is ruled out due to the low density of the molecules ($<10^{11}$ cm^{-3}) and the small volume of the gas phase (~1 cm^3).

The authors of a theoretical study[4] believe that the radiation recorded[2,3] is due to optical transitions between nonequilibrium excited electronic states of fullerene molecules, whereas the continuous radiation spectrum is related to the high density of these states and to the broadening of transitions in the excited molecule. The fact that the pattern of the spectrum described previously[2,3] coincides with the thermal (Planck) spectrum presented in the study cited[4] has not been explained.

In order to elucidate the nature of this radiation and the features of the radiation channel for the deactivation of complex molecules, in this work we studied the radiation induced by the interaction of a C_{60} beam with a beam of low-energy electrons under conditions of a single collision. Radiation was recorded from the region of beam intersection in the $300 \leq \lambda \leq 850$ nm range of wavelengths. The beam of C_{60} molecules from an effusion source was formed at $T_0 = 800$ K using a collimating diaphragm. The electron beam (operating current ~60 μA) was obtained using an oxide cathode and collimated by diaphragms and a longitudinal magnetic field. The radiation was recorded by a photoelectron multiplier installed at the outlet of the monochromator or downstream of the filter. The optical system was calibrated against a standard source of thermal radiation, a SI-10-300 lamp. The experimental equipment, the procedure of the measurements, and the possible errors have been described in a previous publication[3] in which the electron-induced radiation from a beam of C_{60} molecules was observed for the first time. The emission spectrum obtained[3] is described by the modified Planck formula for the radiation of a spherical particle with a diameter $d \ll \lambda$.[5] The rate of emission of photons I_{ph} by such a particle in the $[\lambda, \lambda + \Delta\lambda]$ range of wavelengths is

$$I_{ph}(\lambda, T) = 2\pi c S \Delta\lambda \varepsilon(\lambda, T)/\{\lambda^4[\exp(hc/(\lambda kT)) - 1]\}, \quad (1)$$

where T is the particle temperature, S is the particle surface area.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 273—276, February, 2000.

The emissivity (the degree of "blackness") of the particle is equal to

$$\varepsilon = \varepsilon_0 d/\lambda. \qquad (2)$$

According to the Mie approximation, the maximum value $\varepsilon = 4\pi d/\lambda$. Although the C_{60} molecule is hollow, the dependence $\varepsilon(\lambda) \propto \lambda^{-1}$ apparently holds. The diameter of the electron shell of the molecule $d \approx 1$ nm.

In order to determine the contribution of the $C_{60}^{+\bullet}$ ions to the intensity of the observed radiation and to study the kinetics of cooling, an electric field with strength ξ was applied to the region of beam intersection. The deflectors were arranged along the axes of the molecular and electron beams. Under the action of the field, the "hot" $C_{60}^{+\bullet}$ ions, which are formed upon the thermal emission of an electron, escaped from the optical detection region over time $t_r(\xi)$. Note that due to the magnetic collimation of the electron beam, its parameters were not distorted by the field ξ. This fact was controlled by measuring the radiation intensity of the short-lived states of the N_2 molecule ($C^3\Pi_u$) and the N_2^+ ($B^2\Sigma_u^+$) ion. It can easily be demonstrated that for great ξ values, the time t_r and, hence, the radiation intensity of $C_{60}^{+\bullet}$ ($I^{+\bullet}$) are proportional to $\xi^{-1/2}$. By constructing plots for the radiation intensity $I(\xi)$ for various E_e and λ obtained in experiment in the $I(\xi)$—$\xi^{-1/2}$ coordinates and by extrapolating the plot to the origin of coordinates, we found the contribution of neutral C_{60} molecules to the radiation. At $E_e = 40$ and 65 eV, the contributions of the C_{60} molecules are 16 and 4%, respectively, *i.e.*, the charged species, $C_{60}^{+\bullet}$, serve as the main radiation source.

Figure 1 shows the variations of the radiation intensity I at 540 nm ($\Delta\lambda = 3.2$ nm) and the spectral temperature T (*i.e.*, the temperature obtained by approximation of the experimental radiation spectra using expressions (1) and (2) in the ($\ln(I \cdot \lambda^5) - 1/\lambda$) coordinates) as functions of E_e. It can be seen that as E_e increases from 32 to 48 eV, the temperature T increases from 2125 to 3094 K in proportion with E_e. According to the previous publication,[6] the maximum energy transferred by an electron to a C_{60} molecule at these E_e values varies from 22±2 to 38±2 eV. With allowance for the energy needed for ionization, equal to 7.6 eV, and for the initial internal thermal energy of a molecule in the effusion beam ($E_{v,0} = E_v(T_0) \approx 4.6$ eV), the maximum inner energy of the particles E_v ranges from 19±2 to 35±2 eV, and the vibrational temperature varies from 1892±175 to 3000±175 K. (The $E_v(T)$ curve was calculated for the neutral C_{60} molecule in the approximation of harmonic intramolecular vibrations based on a set of frequencies.[7] At $T > 1500$ K, the $E_v(T)$ function is adequately approximated by a linear function, E_v/eV ≈ 13.9 + 0.0143(T − 1500), proposed previously.[8]) Thus, the T values (see Fig. 1) proved to be close to the real vibrational temperature of the molecule. Note that, due to the appreciable dependence of I_{ph} on T in expression

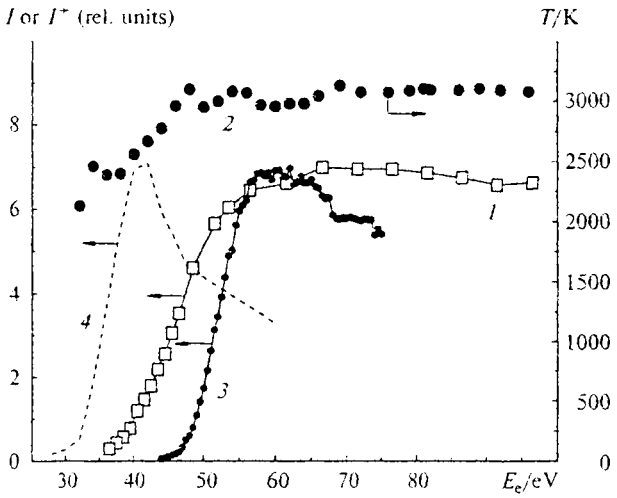

Fig. 1. Radiation intensity (*1*), spectral temperature of radiation (*2*), C_{58}^+ current at metastable fragmentation (*3*), and "delayed" ionization current (*4*) as functions of the energy of the electrons.

(1), the greatest contribution to the radiation is made by "hotter" particles.

The data presented in Fig. 1 indicate that at $E_e > 48$ eV, the T value varies only slightly. This can be accounted for by fragmentation of $C_{60}^{+\bullet}$ into C_{58}^+ and C_2. According to a previous publication,[9] the rate of this process is expected to increase substantially with in-

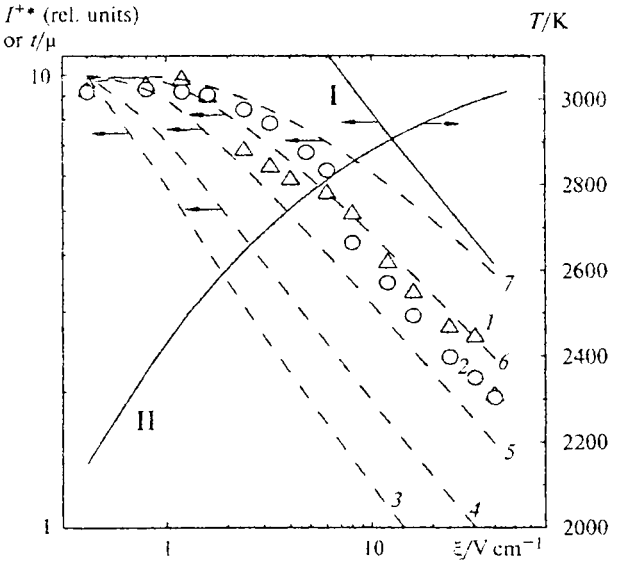

Fig. 2. Radiation of the $C_{60}^{+\bullet}$ ion: the points show the experimental results at E_e/eV = 40 (*1*) and 65 (*2*) dashed lines show the calculation points at $\varepsilon_0 = 0.01$ (*3*), 1 (*4*), 3 (*5*), 6 (*6*), and 12 (*7*). Calculated residence time of $C_{60}^{+\bullet}$ in the observation area (I) and the temperature of $C_{60}^{+\bullet}$ at the outlet of the observation area (II) depending on the strength of the extracting electric field.

crease in T. This is confirmed qualitatively by the known[10] dependence of the current I^- of the C_{58}^- ions formed upon thermal fragmentation on E_e for $7.7 < t < 31.2$ μs at $E_{v,0} = 4.6$ eV. This dependence is shown in Fig. 1 (curve *3*); the maximum in curve *3* appears due to the fact that t is restricted from below.

According to the data reported previously,[9] excitation of C_{60} results in thermionic emission ("delayed" ionization) to give "hot" $C_{60}^{+\bullet}$ ions. Figure 1 (curve *4*) shows the "delayed" ionization current found[6] for $45 < t < 213$ μs and $E_{v,0} = 8.2$ eV. It can be seen that the thermoemission current[6] and the radiation observed here appear at virtually the same E_e value. The decrease in the thermoionic current at $E_e > 40$ eV can be due to the fact that the characteristic thermoemission time becomes <7.7 μs. A qualitatively similar curve for the "delayed" ionization current after an electron impact has been found in our previous publication.[11]

Figure 2 shows the plots for the intensity of ion radiation $I^{+\bullet}(\xi)$ (the contribution of neutral molecules to the total radiation was subtracted) found for $E_e = 40$ eV (*1*) and 65 eV (*2*). Curve 1 shows the calculated $t_r(\xi)$ plot. The calculation was performed for an ion moving from the center of the beam intersection at an initial velocity vector equal to the velocity of C_{60} molecules in the beam. The space sensitivity of the detecting system (the size of the area from which the radiation was measured) was determined by scanning with a point radiator.

It can be seen in Fig. 2 that at low ξ values (*i.e.*, great t_r) the radiation intensity is not proportional to t_r. This type of behavior of $I^{+\bullet}(\xi)$ is associated with the radiation cooling of $C_{60}^{+\bullet}$ over the time of residence of the ion in the observation area. By using the $I^{+\bullet}(\xi)$ dependence, one can determine the rate of radiation cooling of $C_{60}^{+\bullet}$. For this purpose, we integrated the flow of radiation energy $q_\lambda = (hc/\lambda)I_{th}$ over λ using relations (1) and (2). This gave an analog of the Stephan—Boltzmann formula for a small particle

$$q = \varepsilon_0 \sigma_c T^5 S, \qquad (3)$$

where $\sigma_c = 24.8882\pi k^5 h^{-4} c^{-3} d$. Integration of the equation relating T to t gives

$$q\mathrm{d}t = -C\mathrm{d}T, \qquad (4)$$

where $C = 0.0143$ eV K^{-1} is the heat capacity of C_{60} at $T > 1500$ K[8]; hence, we can write

$$T(t, T_i) = T_i\{1 + t[4\varepsilon_0 \sigma_c T_i^4 S]/C\}^{-1/4}, \qquad (5)$$

where T_i is the initial temperature of the ion. Substitution of Eq. (5) into (1) affords an expression for the intensity of ion radiation $I_{ph}^{+\bullet}(t, T_i)$.

By integrating $I_{ph}^{+\bullet}(t)$ along the trajectory of movement of $C_{60}^{+\bullet}$ and taking into account the space sensitivity of the optical system used $\eta(r)$, we can obtain the number of photons recorded from one $C_{60}^{+\bullet}$ ion

$$N^{+\bullet} = \int_0^\infty I_{ph}^{+\bullet} \eta(r(t))\mathrm{d}t . \qquad (6)$$

Since the rate of formation of $C_{60}^{+\bullet}$ does not depend on ξ, the $N^{+\bullet}(\xi)$ curve should correspond to the experimental $I^{+\bullet}(\xi)$ curve to within some constant A.

The dashed lines in Fig. 2 show the results of calculations of $N^{+\bullet}(\xi)$ for $T_i = 3150$ K, $\lambda = 540$ nm, and several values of the constant ε_0. The calculated curves were superposed with one another at the minimum ξ value. To compare the experimental and calculated results, we minimized the deviation of $N^{+\bullet}$ from $I^{+\bullet}$ using the least-squares method by varying the constants A and ε_0 as free parameters. The best agreement was attained for $\varepsilon_0 = 5.7$ (see Fig. 2, point *1*) and $\varepsilon_0 = 6$ (point *2*); for $T = 3150$ K, this corresponds to a rate of energy loss of $5.5 \cdot 10^5$ eV s^{-1}. The results of calculation of the temperature of the $C_{60}^{+\bullet}$ ion leaving the observation area are also shown in Fig. 2 (curve *2*, $\varepsilon_0 = 6$, $T_i = 3150$ K).

The ε values obtained from direct optical measurements were found to be one or two orders of magnitude greater than those estimated based on indirect data.[8,12,13] This might be due to the difference between the initial temperatures of the particles. In the estimate, the temperature in previous studies[8,13] did not exceed 1800 K. The increase in the rate of cooling of $C_{60}^{+\bullet}$ at higher temperatures cannot be explained by the effect of fragmentation because the cooling rate observed at 65 eV was found to be equal to that for 40 eV, *i.e.*, in the absence of fragmentation (see Fig. 1, curve *3* and Refs. 8 and 10). Apparently, an increase in T brings about an increase in the ε value for the $C_{60}^{+\bullet}$ ion. We did not take into account the $\varepsilon(T)$ dependence because the range of temperature variation for the $C_{60}^{+\bullet}$ ion was rather narrow (see Fig. 2, curve 11).

Thus, the spectral temperature of radiation is close to the vibrational temperature of the emitting particle and increases from ~2100 to ~3150 K as the electron energy changes from ~27 eV to ~50 eV. The emissivity ε reaches $\sim 10^{-2}$ for $\lambda = 540$ nm at $d = 1$ nm. This value is half as great as the maximum ε value found in terms of the thermal model and is substantially higher than the value predicted by an alternative model.[4] The possibility of obtaining high-temperature fullerene and of maintaining high temperature makes this molecule an interesting object for the study of intermolecular energy exchange in the high-temperature region.

The authors are grateful to S. V. Drozdov and S. A. Psarov for assistance in the work.

This work was financially supported by the Russian Foundation for Basic Research (Projects No. 97-02-18510, 98-02-17845, and 98-02-17804) and by the Ministry of Education of the Russian Federation.

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Received May 14, 1999;
in revised form August 6, 1999