

Nanosecond-Gated Detection of Room-Temperature Fluorescence of C₆₀ in Solution

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Fluorescence spectra of C₆₀ in *n*-hexane at room temperature, obtained under excitation at 514.5 and 337.1 nm, are presented. The spectra were measured with subnanosecond laser excitation in a 5-ns gate synchronous with the excitation. The emission, in the range 1.5 to 2.2 eV for excitation at 514.5 nm (2.41 eV), is characterized by a narrow peak at 2.05 eV (i.e., 606 nm, 7.2 nm FWHM) which is predominant in the spectrum, while many resolved vibronic structures emerge, down to energies as low as 0.4 eV, in the spectrum obtained with excitation at 337.1 nm (3.68 eV).

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Because of the very efficient intersystem crossing to the excited triplet states of C₆₀, the lowest of which is 1.6 ± 0.1 eV above ground state [1], the emission spectra of this molecule in solution at room temperature have never been measured, while a number of investigations were carried out on the lowest triplet state(s) [1–6]. The first excited singlet state lifetime could only be determined by excite-and-probe transient absorption measurements and values in the range 650 to 1300 ps were found [2,6–8], while a single report exists in which a lifetime value of 1.17 ns was determined from the direct observation of the fluorescence decay in toluene at room temperature [8]. On the other hand, knowledge of the optical properties would allow the most straightforward correlation with theoretical calculations of C₆₀ electronic and vibrational structures. Such a correlation has been stated only with results of optical absorption measurements [9,10] and Raman spectroscopy [11]. In contrast, all photophysical and excited-state kinetic properties of C₆₀ [12–14], including fluorescence [9,13–20], have been extensively studied at low temperatures, where they are affected by the interactions among the molecules themselves (in films or crystals) or between C₆₀ and the neighboring solvent molecules. It may be difficult to interpret such experimental data because only theoretical models concerning the isolated molecule have been developed, due to the high number of degrees of freedom of C₆₀ [21–25], while C₆₀ at low concentration in liquid solution could represent a good approximation of the free molecule. Laser cooling [26] of C₆₀ in a molecular beam would produce high-density samples of noninteracting molecules, ideal for incontrovertible assignments of the optical transitions. Of course, laser cooling requires the existence of a fluorescent transition with sizable quantum yield.

In this paper we present high-resolution fluorescence

spectra in the range 0.22 to 3.5 eV that were obtained at room temperature from an *n*-hexane solution using subnanosecond laser excitation and nanosecond-gated detection with an optical multichannel analyzer (OMA). The C₆₀ powder, kindly donated by Dr. P. Milani (Dipartimento di Fisica, Milano), was prepared and purified as described in [27]. A sample of 0.6 mg was put in 4 ml *n*-hexane for UV spectroscopy (Fluka Chemie AG, Buchs, CH) and stirred for 1 h with ultrasound. Floating particulates were allowed to deposit for at least 1 day. The spectra were thus taken on the top part of the (saturated) solution [28]. The fluorescence, emitted at 90° to the excitation beam by the solution contained in a quartz fluorometer cuvette, was passed through suitable cutoff filters and imaged onto the entrance slit (500 μm width) of a Chromex 500IS 0.5 m spectrograph (300 grooves/mm, blaze wavelength 2 μm). It was detected with an EG&G OMA. The instrument has a 1455R-700-G detector with S25-ERMA photocathode and 1024 diode array, equipped with a microchannel plate for gated amplification (700 intensified elements), and a 1471A detector interface. The detector was operated at -5°C . A gate of 5 ns duration, which opened, unless otherwise specified, at the time of the excitation pulse, was used to obtain all spectra reported here. To cover the whole spectral range in which C₆₀ fluorescent emission could be observed, the monochromator had to be tuned to a number of wavelengths, in 50 nm steps. In each step, which covered a 104.3 nm interval, the signal was averaged over 1000 repetitions, for excitation at 514.5 nm, and 100, for excitation at 337.1 nm. The data taken in a step were then matched in wavelength with those of the next one. A detailed description of the experimental setup and the data manipulation will be given elsewhere.

Figure 1 shows the recorded emission spectrum, plotted as a function of energy (eV), for excitation with a

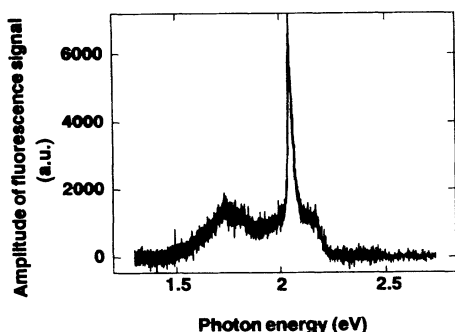


FIG. 1. Fluorescence detected under excitation at 514.5 nm (2.41 eV) from a C_{60} *n*-hexane solution (optical density 0.03 at λ_{exc}) as a function of the emitted photon energy.

nitrogen-pumped dye-laser pulse (514.5 nm, PTI PL 201 laser) of less than 0.5 ns duration. The most noticeable feature is the narrow peak at 2.05 eV (606 nm) that falls on the top of a broad band vanishing only above 2.2 eV, where the emission is cut by the filter used to reject the scattered excitation (cutoff wavelength 590 nm). The peak is not observed in pure *n*-hexane and is as short-lived as is the emission at all other wavelengths. In fact, we repeated the measurements for increasing values of the delay between the opening of the amplifier gate and the excitation pulse and found that the fluorescence signal decays, at all wavelengths, as fast as the detected laser pulse. To better evaluate the bandwidth of this sharp emission, we measured it with a high-resolution grating (1200 grooves/mm, blaze wavelength 500 nm), mounted in the same spectrograph, and found a value of about 7.2 nm (FWHM, full width at half maximum). The secondary (broad) peak in Fig. 1 occurs at 1.73 eV and seems to exhibit a vibrational structure emerging from noise (see, for instance, the bump at 1.81 eV). Fluorescence at 1.71 eV, which is very near to the wavelength at which we find the secondary peak for C_{60} in *n*-hexane solution, has been previously reported to contribute, with a shoulder, to the emission spectrum of a C_{60} film mea-

sured with 514.5 nm excitation at room temperature [15]. Other measurements, carried out with the same excitation wavelength on both films and powders, revealed the presence of a shoulder at 1.77 eV, but only for temperatures below 90 K [19], while Reber *et al.* [13] reported that the highest emission peak, for C_{60} film at 20 K, occurs at 14150 cm^{-1} , i.e., 1.75 eV. For C_{60} in solution, we do not find any evidence of emission at 1.68 eV, where both Pichler *et al.* [15] and Sauvajol *et al.* [19] observed maximum fluorescent emission.

The spectrum in Fig. 1 shows that an intense emission occurs at energies well above 1.9 eV, where no fluorescence has been previously reported for C_{60} in any situation, though none of the reported measurements was performed on solutions at room temperature. To further investigate such a high-energy emission, we moved the excitation wavelength to 337.1 nm and used, in front of the monochromator, a filter with shorter cutoff wavelength (380 nm). The excitation was provided by a high-pressure nitrogen laser (PTI PL 2300, London, Ontario) generating pulses of 0.5 ns duration. Figure 2 shows the emission spectrum we obtained on the same solution as in Fig. 1. While with excitation at 514.5 nm, the fluorescence in the region 1.9 to 2.2 eV predominates over that around 1.7 eV, it appears to be almost negligible in Fig. 2. On the contrary, a band is observed peaking at 2.87 eV and a number of peaks arise at low energies, while both the peak at 1.73 and the bump at 1.81 eV are preserved. Three peaks arise at 1.61, 1.30, and 1.02 eV and minor peaks are detected at 1.68, 1.44, 1.35 (shoulder), and 0.98 eV. Substructures underlay the further peaks at 0.83 and 0.58 eV, the latter being the most intense we detect with our apparatus. The higher energy of the exciting photons is responsible for the vibronic structure clearly observable at energies below 1.9 eV, while the reason why it is hardly visible in Fig. 1 must be related to the fact that the 514.5 nm wavelength corresponds to the very long wavelength edge of the C_{60} absorption spectrum [13,29,30]. In the latter case, the excitation energy, 2.41 eV, is above that reported for the symmetry-forbidden highest occupied molecular orbital

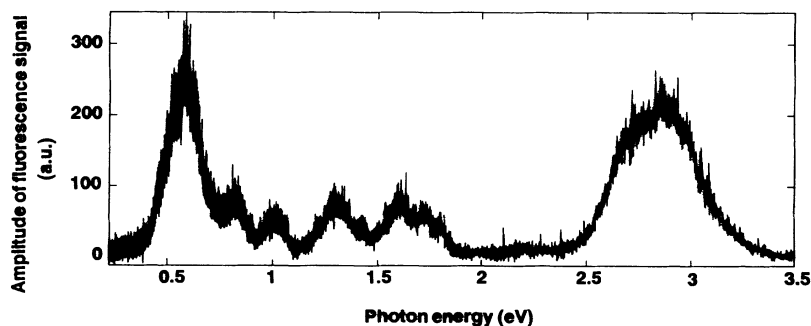


FIG. 2. Fluorescence detected under excitation at 337.1 nm (3.68 eV) from a C_{60} *n*-hexane solution (optical density 1.21 at λ_{exc}) as a function of the emitted photon energy.

to lowest unoccupied molecular orbital (HOMO-LUMO) transition, ${}^1T_{1g}^{-1}A_g$, as evaluated either from the onset of the absorption [2.02 eV [25], $15\,478\text{ cm}^{-1}$ (1.91 eV) or $15\,678\text{ cm}^{-1}$ (1.94 eV) [10]] or from the difference of first oxidation to first reduction energies (2.21 eV [25], 2.32 eV [31]), or from photoemission spectra (1.9 eV [32]) or from theoretical calculations [$16\,500\text{ cm}^{-1}$ (2.04 eV) [25], 1.9 eV [21], 2.2 eV [22]], but definitely below that of the first allowed optical transition, ${}^1T_{1u}^{-1}A_g$ [2.87 eV [21], 2.8 eV [22], 3.04 eV [23], or $24\,900\text{ cm}^{-1}$ (3.09 eV) [25]]. Thus the only structures one should expect in the spectrum excited at 514.5 nm are those originating from the vibrational mode(s) promoting the HOMO-LUMO transition [33]. A careful analysis of the data in Fig. 1 is being carried out to establish which vibronic transition is responsible for the sharp resonance at 2.05 eV, which falls in the region of the HOMO-LUMO gap. We think that, upon excitation at 337.1 nm (3.68 eV), both allowed and forbidden dipole transitions are excited. The emission peaking at 2.87 eV could correspond to the ${}^1T_{1u}^{-1}A_g$ transition, while the structured low-energy spectrum may come from further forbidden transitions not excited at 514.5 nm, as well as from the allowed ${}^1T_{1u}^{-1}T_g$ transition. Note that the values reported for the energies of the ${}^1T_{1u}$ and 1A_g states [21,22,25] differ by values in the range 0.6 to 1.05 eV.

Works are in progress to determine the excitation spectrum of the emission peak at 2.05 eV by tuning the dye laser that provides the excitation pulse, in order to attribute this emission line. If it is confirmed to be a relatively intense fluorescence transition of C_{60} , it will be of interest for implementing experiments of laser cooling of C_{60} in beams. We cannot assess if the strength of this transition and the kinetics of its excited state will allow C_{60} beams to be efficiently cooled, because numerical simulations presently feasible can only be based on models developed for cooling of atomic beams. Our feeling is that it is worthwhile to set up an experiment once the optimal energy of the incident (exciting) photons is established.

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