

Observation of fine structure in the optical spectrum of the fullerene C₇₀ in a crystalline matrix

B. S. Razbirin, A. N. Starukhin, A. V. Chugreev, Yu. S. Grushko,
and S. N. Kolesnik

A. F. Ioffe Physicotechnical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia; B. P. Konstantinov St. Petersburg Institute of Nuclear Physics, Russian Academy of Sciences, 188350, Gatchina, Leningrad Region, Russia

(Submitted 12 August 1994)

Pis'ma Zh. Eksp. Teor. Fiz. **60**, No. 6, 435–438 (25 September 1994)

A rich, narrow-line structure has been observed in emission and absorption spectra of molecules of the fullerene C₇₀ in a low-temperature crystalline matrix. This structure is due to electronic–vibrational ($T_1 \Rightarrow S_0$, $S_1 \Leftrightarrow S_0$) and purely electronic ($S_1 \Leftrightarrow S_0$) transitions between the ground state S_0 and the low-lying excited states T_1 and S_1 . © 1994 American Institute of Physics.

There have been several studies^{1–6} of the electronic–vibrational optical spectra of the most common fullerenes, C₆₀ and C₇₀. However, the significant spectral width of the observed absorption and emission bands of the fullerenes and of fullerene molecules in solutions^{3–6} hinder efforts to extract detailed information on the electronic and vibrational states of these entities. We have now shown that it is possible to obtain narrow-line spectra of fullerene molecules in solid solutions of organic crystals cooled to 2 K. The observed formation of narrow lines is shown to be due to the Shpol'skiĭ effect.⁷

The emission and absorption spectra of solutions of the fullerene C₇₀ in the visible and near-IR parts of the spectrum which have been reported in the literature consist of several broad bands. These bands are due to electronic–vibrational transitions involving various excited states of the molecule. A group of bands at 1.6–1.9 eV is linked with electronic–vibrational transitions from the first excited singlet state (S_1) of the molecule to the ground state (S_0), while the longer-wave emission at 1.2–1.6 eV is linked with transitions from the lowest-lying excited triplet state (T_1). Lowering the solution temperature from 300 to 77 K causes no substantial decrease in the width of the bands (Fig. 1).

We have now established that the changes which occur in the spectra of fullerenes upon a further lowering of the temperature depend strongly on the type of solvent. For example, cooling a C₇₀ solution in crystalline toluene to $T=2$ K leads to a clearly expressed effect: The broad emission and absorption bands break up into a system of narrow lines, with a width ≈ 1 meV. We have observed a similar effect in solutions of C₇₀ in ethylbenzene and *o*-xylene. In the case of other solvents, e.g., in the spectra of solutions of C₇₀ in benzene and carbon tetrachloride, there are no narrow lines.

Figure 1 shows a fragment of the spectrum of the fullerene C₇₀ in toluene (C₆H₅CH₃:C₇₀) in the region of singlet–singlet transitions ($S_0 \Leftrightarrow S_1$). We see that the spectra of crystalline C₇₀ (the fullerite) and of a glassy solution of C₇₀ in toluene consist, at $T=2$ K, of broad bands, while the spectrum of C₇₀ in a crystallized solution has a fine

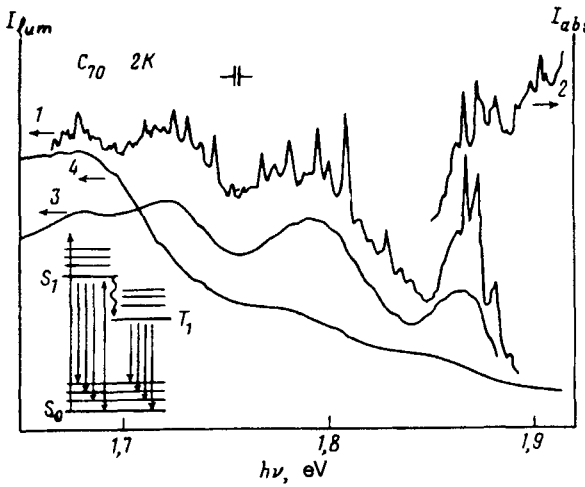


FIG. 1. Spectra of the photoluminescence (1) and absorption (2) in the region of transitions between the S_0 and S_1 singlet states of the C_{70} fullerene molecule in a crystalline toluene matrix (1, 2) and in a glassy matrix (3). Spectrum 4 is the photoluminescence of a crystalline C_{70} powder. The inset is the scheme of energy transitions.

structure. Figure 2 illustrates the onset of the narrow-line spectrum of C_{70} in crystalline toluene for radiative transitions from the triplet state ($T_1 \Rightarrow S_0$). In all the experiments, the luminescence was excited by an argon laser with $\lambda_{exc} = 4880 \text{ \AA}$.

Here are the basic features of the observed effect:

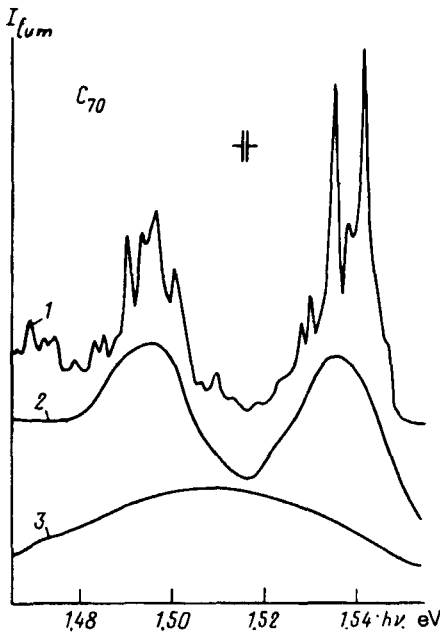


FIG. 2. Photoluminescenc spectra in the region of triplet-singlet transitions of the C_{70} fullerene molecule in crystalline (1) and glassy (2) toluene matrices. Spectrum (3) is the photoluminescence spectrum of a crystalline C_{70} powder.

- (1) In the region of the purely electronic transition (1.85–1.90 eV) there is a group of emission lines (a multiplet) which coincide in a resonant fashion with corresponding structure in the absorption spectrum.
- (2) The shape of this structure, by which we mean the number of lines in the multiplet, their spectral positions, and their relative intensities, depends strongly on the type of solvent.
- (3) The resonant group of lines, being the head group, is repeated as vibrational series in the emission and absorption spectra.
- (4) The observed vibrational frequencies of the fullerene C_{70} in the luminescence and absorption spectra do not depend on the type of solvent.

These features are basic characteristics of the Shpol'skiĭ effect. As in the studies by Shpol'skiĭ,⁸ a narrow-line spectrum arises in a fullerene–solvent system only for certain solvents. Since the intrinsic spectrum of the solvent (toluene) is in the UV region,⁹ the narrow-line emission and absorption spectra which we have observed in the visible and IR regions are due to electronic and electronic–vibrational transitions in C_{70} molecules, not in the solid matrix. This conclusion agrees with the rich statistical base from studies of Shpol'skiĭ systems, for which it has been shown that vibrational spectra in the narrow-line spectra that arise always belong to the vibrational spectrum of the impurity molecules. From an analysis of the emission spectrum of C_{70} toluene we found the following values for vibrational frequencies for $S_1 \Rightarrow S_0$ transitions (within 0.5 meV): $\hbar\omega_1=45.5$, $\hbar\omega_2=52.5$, $\hbar\omega_3=72.0$, $\hbar\omega_4=84.0$, $\hbar\omega_5=99.0$, $\hbar\omega_6=135.0$, $\hbar\omega_7=146.5$, $\hbar\omega_8=156.0$, and $\hbar\omega_9=202.5$ meV. For $T_1 \Rightarrow S_0$ transitions we found $\hbar\omega_{10}=45.0$ and $\hbar\omega_{11}=66.5$ meV. The spectra of the singlet and triplet states reveal different vibrational frequencies. This result is not surprising, since electronic–vibrational transitions occur between states of different symmetry.

Let us examine the narrow-line resonant part of the spectrum (the $S_0 \Leftrightarrow S_1$ transitions). It is natural to first link the onset of the multiplet structure in the region of the purely electronic transition (1.85–1.90 eV) with the presence of several nonequivalent positions of the molecules in the crystalline matrix. In addition, there may be a manifestation of an intrinsic fine structure of electronic levels of the C_{70} molecule. The center of gravity of the resonant multiplet structure in the solution is displaced slightly from the peak of the emission band of the purely electronic (resonant) transition in the spectrum of the fullerite. The magnitude of this shift, Δ , varies over an interval of a few meV, depending on the solvent. The characteristic parameter δ , i.e., the ratio of the shift to the energy ($E_{0,1}$) of the $S_0 \Leftrightarrow S_1$ electronic transition in the molecule, has a value $\delta = \Delta/E_{0,1} \leq 0.3\%$. Such a small difference between the energies of the electronic transitions in C_{70} in the molecular fullerite crystal and in the solution indicates that the interaction between the fullerene molecule and the matrix is quite tenuous (a van der Waals interaction). Following Shpol'skiĭ's model,⁸ we should call the narrow lines of purely electronic transitions observed in the spectra of the fullerene “quasilines,” under the assumption that they are broadened by nonuniform microscopic stress in the polycrystalline matrix. Some of the lines show hints of a fine structure, possibly associated with properties of intrinsic states of the fullerene molecule. Studying the lineshapes and the structure of the quasilines in the C_{70} spectrum is a problem of independent interest.

The width of the narrowest resonant lines is ≈ 0.5 meV. Their positions in the

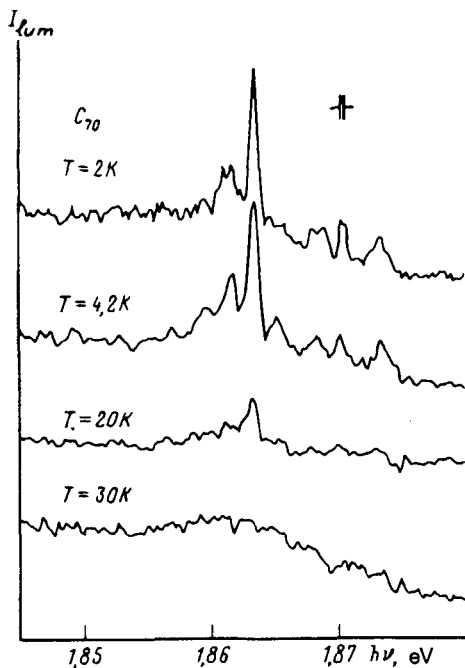


FIG. 3. Temperature dependence of the photoluminescence spectrum in the region of singlet-singlet transitions of the C_{70} fullerene molecule in a crystalline *o*-xylene matrix.

absorption and emission spectra agree within 0.5 meV. Some of the lines are accompanied by nearby wings, whose positions in the absorption and emission spectra are mirror-symmetric with respect to the resonance line. We observed this effect most clearly for the solution of C_{70} in *o*-xylene, whose spectrum (Fig. 3) is simpler than that of C_{70} in toluene. These wings appear to be acoustic bands which arise from a tenuous interaction of two subsystems: the C_{70} molecule and the crystalline matrix. The shape of the spectrum and its specific temperature dependence—the rapid disappearance of the narrow line ($h\nu = 1.8632 \pm 0.0001$ eV) with increasing temperature without any significant broadening, with a simultaneous intensification of the vibrational acoustic wing—indicate that we are dealing with an optical analog of the Mössbauer effect.^{8,10,11}

In summary, this study has demonstrated that the Shpol'skiĭ method is valid for producing fullerene-solids-matrix systems with narrow-lying electronic-vibrational spectra. This result opens up extensive opportunities for utilizing the broad variety of spectroscopic methods to study the new allotropic forms of carbon known as fullerenes.

This study was carried out as part of the "Fullerenes and atomic clusters" Program of the Intellectual Collaboration Foundation.

¹V. M. Loktev, *Fiz. Nizk. Temp.* **18**, 217 (1992) [*Sov. J. Low Temp. Phys.* **18**, 149 (1992)].

²A. V. Eletskiĭ and B. M. Smirnov, *Usp. Fiz. Nauk* **163**, 33 (1993) [*Phys.-Usp.* **36**(3), 202 (1993)].

³D. Kim *et al.*, *Am. Chem. Soc.* **114**, 4429 (1992).

⁴S. P. Sibley *et al.*, *Chem. Phys. Lett.* **188**, 187 (1992).

⁵C. Reber *et al.*, *J. Phys. Chem.* **95**, 2127 (1991).

⁶Y. P. Sun and C. E. Bunker, *J. Phys. Chem.* **97**, 6770 (1993).

⁷*Encyclopedic Dictionary of Physics* (Sovetskaya Entsiklopediya, Moscow, 1983).

⁸É. V. Shpol'skiĭ, *Usp. Fiz. Nauk* **80**, 255 (1963) [*Sov. Phys. Usp.* **6**, 411 (1963)].

⁹*Absorption Spectra of Molecular Crystals* [in Russian], ed. by V. L. Broyde and A. F. Prikhot'ko (Naukova Dumka, Ki ev, 1965).

¹⁰E. D. Trifonov, *Dokl. Akad. Nauk SSSR* **147**, 826 (1962) [*Sov. Phys. Dokl.* **7**, 1105 (1963)].

¹¹E. F. Gross *et al.*, *Dokl. Akad. Nauk SSSR* **147**, 338 (1962); **154**, 1306 (1964) [*Sov. Phys. Dokl.* **7**, 1011 (1963); **9**, 164 (1964)].

Translated by D. Parsons