

Resonance Raman scattering (RS) spectra of triplet molecules

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The RS spectra of *p*-terphenyl, 1,2-benzanthracene, and phenanthrene, which were transferred by direct photoexcitation to triplet states, were obtained for the first time. It is shown that the spectra contain new important information about the molecular structure and other properties.

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As is known,^{1,2} molecules can be transferred to the metastable, triplet state by photoexcitation or as a result of electron impact (radiolysis). The purpose of our work was to investigate the vibrational transitions in triplet molecules by means of resonance RS spectra. In view of the accessibility, simplicity, and unambiguity of the experiment, the photoexcitation method served as the basis of investigation. We investigated solutions of *p*-terphenyl, 1,2-benzanthracene, and phenanthrene that were vitrified at $T = 77$ K in ethyl alcohol or a mixture of it with methyl alcohol. The initial concentration of the materials was about 10^{-4} M. A steady-state concentration of triplet molecules (estimated at a value of 10^{-5} M) was achieved by pumping with the radiation of a dc mercury lamp or the radiation of a nitrogen laser with a pulse repetition rate of about 90 Hz at the 337.1-nm line. The pump radiation was focused by means of quartz optics on the surface of the samples, which were placed in a quartz Dewar with liquid nitrogen. The 488.0 and 457.9-nm radiation of an argon laser, which was sharply focused at the same point of the sample, served as a probe. The scattered light, which was collected at the slits of a DFS-24 double monochromator, was detected with an FEU-79 photomultiplier.

The conventional synchronous-detection method was used to eliminate interference from the fluorescence and phosphorescence background. In this method the argon-laser radiations were chopped with the optimum frequency, which was determined beforehand from the condition of the minimum fluctuational noise. Since the pump-pulse repetition rate of the nitrogen laser is significantly greater than the reciprocal lifetimes of the triplet states (0.1-4 sec in our case), this did not prevent obtaining an adequate steady-state population of these states. This problem did not arise when a dc mercury lamp was used for pumping. As a result of synchronous detection, the electrical signals from the fluorescence and phosphorescence backgrounds were attenuated by about three orders of magnitude, and only the fluctuational noise associated with them was recorded on the potentiometer; this allowed us to obtain in high-quality RS spectra of the triplet molecules.

The unambiguity of identification of these spectra is demonstrated by the following set of facts. The initial concentrations of the substances were chosen so small that

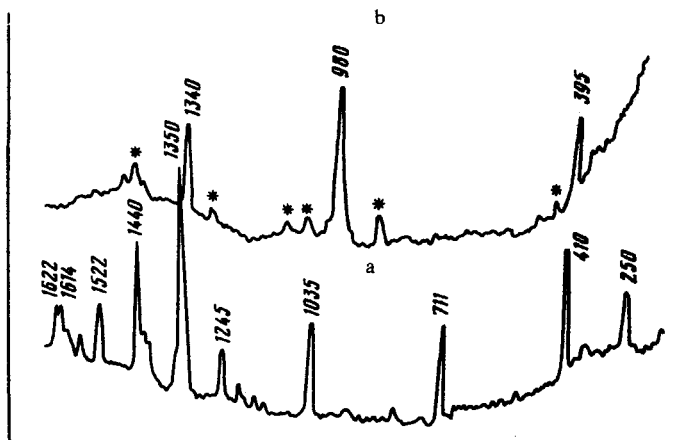


FIG. 1. (a) RS spectrum of phenanthrene molecules in the ground state; (b) resonance RS spectrum of molecules of the same material in the lower triplet state. Excitation is accomplished by Ar^{+2} laser ($\lambda = 488.0$ nm and $P = 100$ mW); the slit width is 6 cm^{-1} . The numbers denote the line frequencies in reciprocal centimeters and the asterisks denote the solvent lines.

the intensity of the RS spectra of their molecules in the ground, singlet state was beyond the observation threshold under nonresonance excitation conditions. Therefore, only the solvent lines were observed in the RS spectra before pumping was begun. The intensity of these lines greatly decreased after the pumping was turned on. This indicated the appearance of induced absorption. In addition, new lines appeared in the spectra. Turning off the pumping resulted in a complete reestablishment of the original spectral pattern with characteristic times approximately equal to phosphorescence decay times.

The first obtained resonance RS spectra of the triplet molecules of phenanthrene and 1,2-benzanthracene, together with the normal spectra of the same substances whose molecules are in the ground, singlet state, are shown in Figs. 1 and 2. We can see that the transition of molecules to the triplet state corresponds to a significant change in their vibrational spectrum. The changes affect the number, position, and relative intensity of the spectral lines. The last factor may be due to the resonance excitation of the RS spectra involved in the selective amplification of certain oscillation modes.³ Assuming that this is the most probable reason for the apparent depletion of the spectrum lines (especially striking in the phenanthrene case), we do not exclude in the other cases the possible influence of the increased symmetry of the excited molecules on the spectra. Thus, the excitation of π electrons for *p*-terphenyl results in a lowering of the barriers to the delayed rotation of the benzene rings, so that the initially nonplanar molecule becomes planar, i.e., its symmetry increases.^{4,5} As regards the general tendency of decreasing the vibrational frequencies (which amounts to several tens of reciprocal centimeters, on the average), this definitely indicates that the electrons of the triplet molecules are excited to the antibonding states. In fact, the unambiguous correlation of the line-analogs in the RS spectra of the triplet and unex-

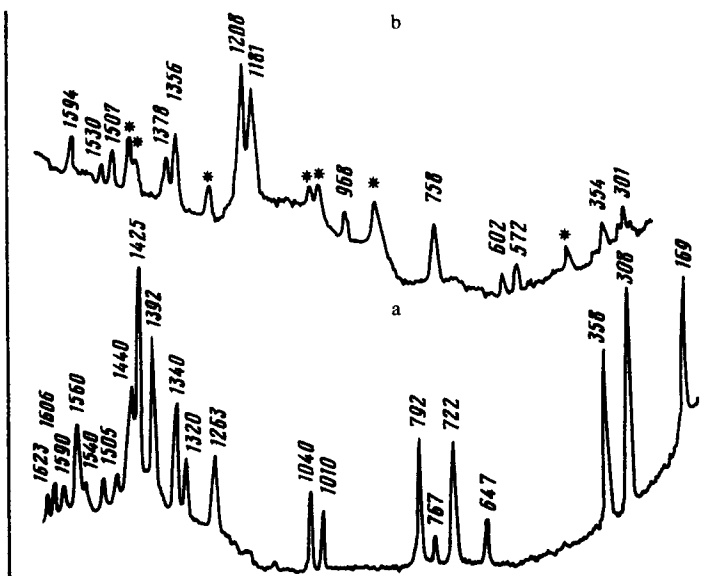


FIG. 2. (a) RS spectrum of 1,2-benzanthracene molecules in the ground state; (b) resonance RS spectrum of molecules of the same substance in the lower triplet state. Excitation is accomplished by Ar^{+2} laser ($\lambda = 488.0 \text{ nm}$ and $P = 100 \text{ mW}$); the slit width is 6 cm^{-1} . The numbers denote the line frequencies in reciprocal centimeters and the asterisks denote the solvent lines.

cited-singlet molecules is not always obvious. Therefore, the correct interpretation of the results will require model calculations. We also note that the RS spectra of the triplet molecules correlate better with the spectra of the same molecules in the first, excited, singlet state. However, producing the latter is a major problem in itself. In the same sense, a parallel investigation of cation radicals is also of interest.

Thus, the resonance RS spectra of triplet molecules obtained by us by simple technical means are very typical and contain diverse and unique information about this interesting state.

¹A. N. Terenin, *Fotonika molekul krasitelei* (Photonics of Dye Molecules), Nauka Leningrad, 1967.

²S. MacGlynn, T. Adzumi, and M. Kinoshita, *Molecular Spectroscopy of the Triplet State* (Russ. Transl., Mir, Moscow, 1972).

³J. Tang and A. C. Albrecht, In: *Raman Spectroscopy*, Vol 2, Ed. H. A. Szymanski, Plenum Press, New York-London, 1970, p. 33.

⁴P. J. Wagner, *J. Am. Chem. Soc.* **89**, 2820 (1967).

⁵M. I. Wakayama, *Chem. Phys. Lett.* **70**, 397 (1980).

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