

TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY OF SHORTLIVED RADICALS AND TRIPLET STATES

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During the past few years infrared and Raman spectroscopy has shown to be applicable to the study of chemical reactions, wherein free radicals are observed as shortlived transients(1,2). Resonance Raman spectra have been obtained from radicals generated electrochemically, by fast flow methods, and by pulse radiolytic methods(2). In the present paper we want to present to our knowledge the first application of Resonance Raman spectroscopy(RRS) to molecules excited into the lowest triplet state.

In a previous paper(1) we reported the resonance Raman spectrum of the shortlived radical anion of p-terphenyl in solution. It was shown that vibrational data of radicals with a lifetime of the order of a few microseconds can be obtained. The present paper deals with the same molecule, but excited into the triplet state. We are thus in the position to compare vibrational frequencies of the parent molecule, its shortlived anion and its triplet state.

The experimental setup used is shown in Fig.1. A 30 ns pulse of 2 MeV electrons from an electron accelerator irradiates the sample and initiates a series of reactions. These are first investigated by conventional absorption spectroscopy to establish lifetimes, absorption spectra and concentrations of the transients. Thereafter a flashlamp-pumped dye laser is used as an excitation source for Raman scattering. The laser pulse can be delayed in time with respect to the electron pulse and its wavelength can be tuned into an allowed electronic absorption band of the transient. The Raman spectrum is analyzed by means of an image intensifier coupled to a TV-camera and gated synchronously with the dye laser pulse. Gating is essential to avoid interference from Cerenkov light from the high energy electrons. A single TV-image is stored on a videodisk and the intensity is integrated over the height of the spectral lines in a line integrator. Spectra are stored on magnetic tape for further data handling.

A 0.01 molar solution of p-terphenyl in liquid benzene was investigated. It is well known(3) that triplet states form upon pulse radiolysis of solutions of organic molecules in benzene.

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Fellows of the Danish National Science Research Council.

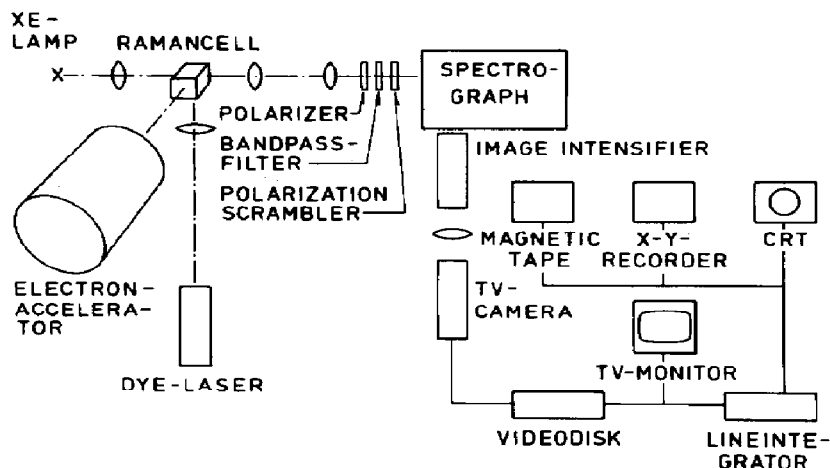


Fig.1 experimental setup

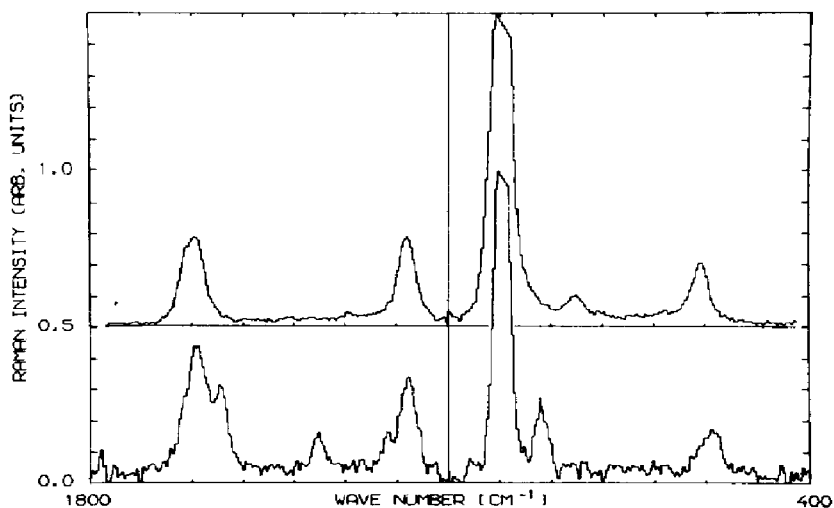


Fig.2 Upper trace: Raman spectrum of a 0.01 molar solution of p-terphenyl in benzene, lower trace: resonance Raman spectrum of the same solution 600 ns after irradiation with a 30 ns pulse of 2MeV electrons. Each spectrum recorded with 2 laserpulses (as indicated by the vertical line), excitation wavelength 459.0 nm.

The mechanism proposed in the literature is formation of a radical cation-electron pair of a solvent molecule followed by fast recombination into a low energy excited state and subsequent energy transfer to solute molecules leaving these in the lowest excited triplet state. In the case of p-terphenyl we observed a transient absorption with a maximum at 460 nm and a lifetime of few microseconds depending on irradiation dose. The wavelength of the laser was then tuned to the absorption maximum of the transient and the resonance Raman spectrum recorded with only two laser pulses. This is shown in Fig.2, where the spectra of the solution without and with pulsing the electron accelerator can be seen. A comparison of the recorded vibrational frequencies of the parent molecule p-terphenyl, its radical anion and its lowest triplet state are in progress.

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2. R.E. Hester in "Advances in Infrared and Raman Spectroscopy", R.J.H. Clark and R.E. Hester, Eds., Heyden 1978, vol. 4, chapter 1
3. R. Cooper and J.K. Thomas, J. Chem. Phys. 48, 5097 (1968)