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# THE RADICAL CATION OF BITHIOPHENE: AN EXPERIMENTAL AND THEORETICAL STUDY

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The electronic absorption spectrum of the bithiophene radical cation prepared by $\gamma$-irradiation in a glassy Freon matrix is presented, together with the Raman spectra excited at 550 and 425 nm, in resonance with the two absorption bands. The 425 nm excited Raman spectrum was also recorded in a room temperature acetonitrile solution, in this case the radical cation was generated *via* a photoinduced electron transfer reaction. The resonance Raman spectra were interpreted with the help of density functional theory calculations. The results indicate the existence of at least two rotamers of the bithiophene radical cation. The time-domain method was applied to the simultaneous fitting of the absorption and resonance Raman spectra.

*Keywords:* Bithiophene; molecular orbital calculations; radical cation; resonance Raman spectroscopy

Apart from general scientific interest, the properties of radical ions in condensed media are also important in the context of materials science and technology. For the past few years we have been involved in the experimental and theoretical investigation of the radical cations of short linear conjugated polyenes [1–5], and of amine-based electron donors such as *N,N*-dimethylaniline [6] and *N,N*-dimethylpiperazine [7]. The interest in the properties of polyene radical cations is in part

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due to their proposed role in the conductivity of polyacetylene, and their possible involvement in biological redox reactions and in artificial photosynthetic systems. Recently we have extended these studies to the radical cation of bithiophene, the shortest oligomer of polythiophene, which in oxidized or reduced form is also a conducting polymer.

The radical cation of bithiophene was generated both by radiolysis and by laser flash photolysis. In the former experiments the radical cation was formed by $\gamma$-irradiation in a low temperature Freon glass, while in the latter case *via* a photoinduced electron transfer reaction between excited bithiophene and the electron acceptor fumaronitrile in a room temperature acetonitrile solution. The radical cation was investigated by electronic absorption and resonance Raman spectroscopy, and density functional theory calculations. Moreover, the time-domain formulation of optical absorption and resonance Raman scattering was used for the simultaneous fitting of the experiment absorption and Raman spectra.

The electronic absorption spectrum of the bithiophene radical cation in solution is known from the literature [8], and there is good agreement between this spectrum and the one we measured in the Freon glass (Fig. 1a). The spectrum consists of a relatively weak structureless band at 590 nm and a strong one at 425 nm. In the low temperature glass the latter exhibits a vibrational progression of $\sim 680\,\text{cm}^{-1}$.

We recorded Raman spectra in resonance with both absorption bands. The Raman spectra measured in resonance with the two electronic transitions are very different (Fig. 1b and c), whereas the spectra obtained at the same excitation wavelength in solution and in the glass are very similar. The assignment of the Raman spectrum was assisted by theoretical calculations of harmonic vibrational frequencies (DFT UB-LYP/6-31G*), which yield good agreement with the experimental values. Most of the bands observed could be assigned as fundamentals, overtones and combinations of totally symmetric ($a_g$) normal modes of the *s-trans* rotamer. One band is assigned as the first overtone of an out-of-plane ($b_g$) fundamental of the *s-trans* rotamer, while further two bands are assigned as combination tones involving this mode. This indicates that the radical cation does not remain planar in the resonant excited state. Finally, one band is identified as a totally symmetric ($a_1$) fundamental of the *s-cis* rotamer.

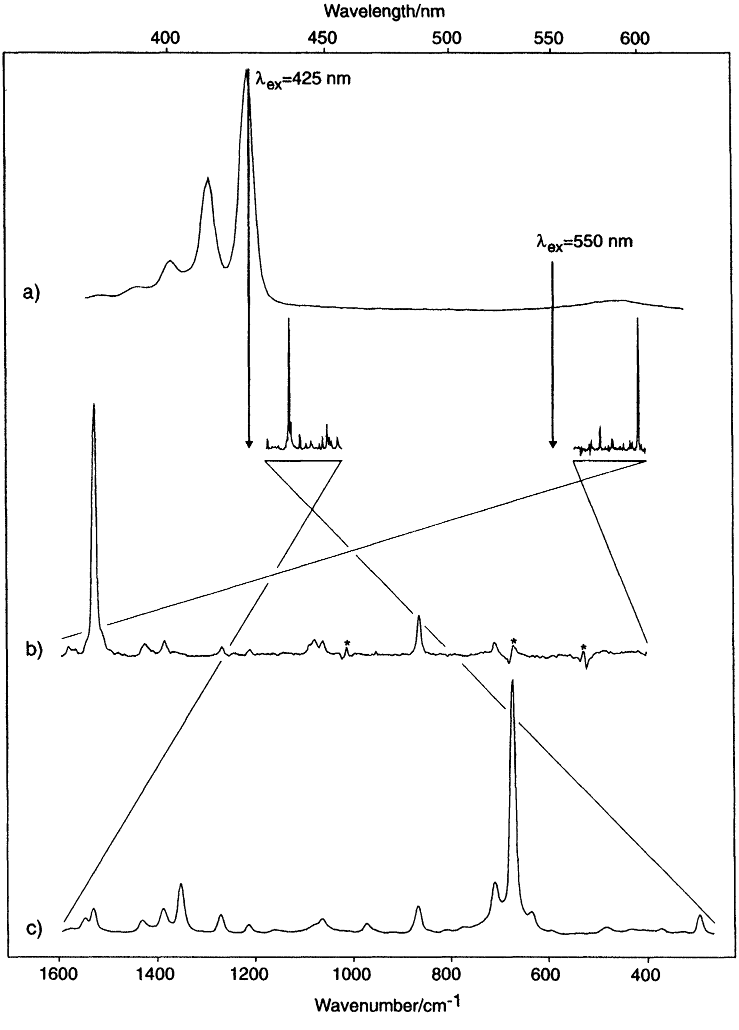

FIGURE 1 Electronic absorption spectrum (a) of the bithiophene radical cation in the Freon glass at 77 K, together with the resonance Raman spectra excited at 550 nm (b) and 425 nm (c).

The time-domain method employing a so-called standard assumptions case model, which ignores frequency shifts and Duschinsky rotation of the oscillators, has been applied to the simultaneous fitting of the 425 nm band in the absorption spectrum and of the Raman spectrum recorded in resonance with this electronic transition. The agreement between the measured and simulated spectra is excellent.

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