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Short Communication

Unusual Raman spectra of para-nitroaniline by sequential Fermi resonances

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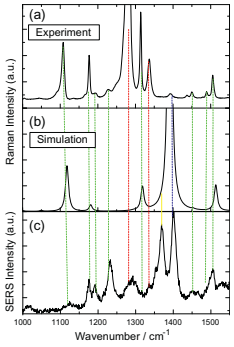
HIGHLIGHTS

- The unusual Raman spectra of para-nitroaniline by sequential Fermi resonances were experimentally observed.
- Theoretical simulation successfully interpreted experimental findings.
- Experimental SERS spectrum of para-nitroaniline further confirms above conclusion.

GRAPHICAL ABSTRACT

Unusual Raman spectra of para-nitroaniline by sequential Fermi resonances were successfully observed and interpreted theoretically.



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ABSTRACT

In this communication, we report the unusual Raman spectra of para-nitroaniline (PNA) by sequential Fermi resonances. The combinational mode 1292 cm^{-1} in the experimental Raman spectrum indirectly gains the initial spectral weight at 1392 cm^{-1} by three sequential Fermi resonances. These Fermi resonances result in the strong interaction between the donor group of NH_2 and the acceptor group of NO_2. Our theoretical calculations provide reasonable interpretation for the abnormal Raman spectra of PNA. Experimental surface enhanced Raman scattering (SERS) spectrum of PNA further confirmed our conclusion, where the strongest Raman peak at 1292 cm^{-1} is very weak, while the Raman peak at 1392 cm^{-1} becoming the strongest Raman peak, which is consistent with the theoretical simulations.

Introduction

With an NH_2 donor and an NO_2 acceptor substituted on a phenyl ring, para-nitroaniline (PNA, see Fig. 1(a)) plays an essential role as the prototype model of push-pull chromophores, which

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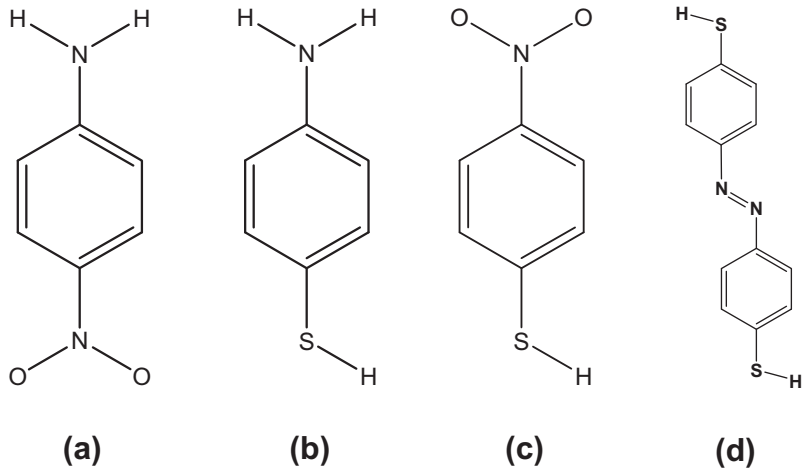

Fig. 1. The chemical structures of (a) PNA, (b) PATP, (c) 4NBT and (d) DMAB.

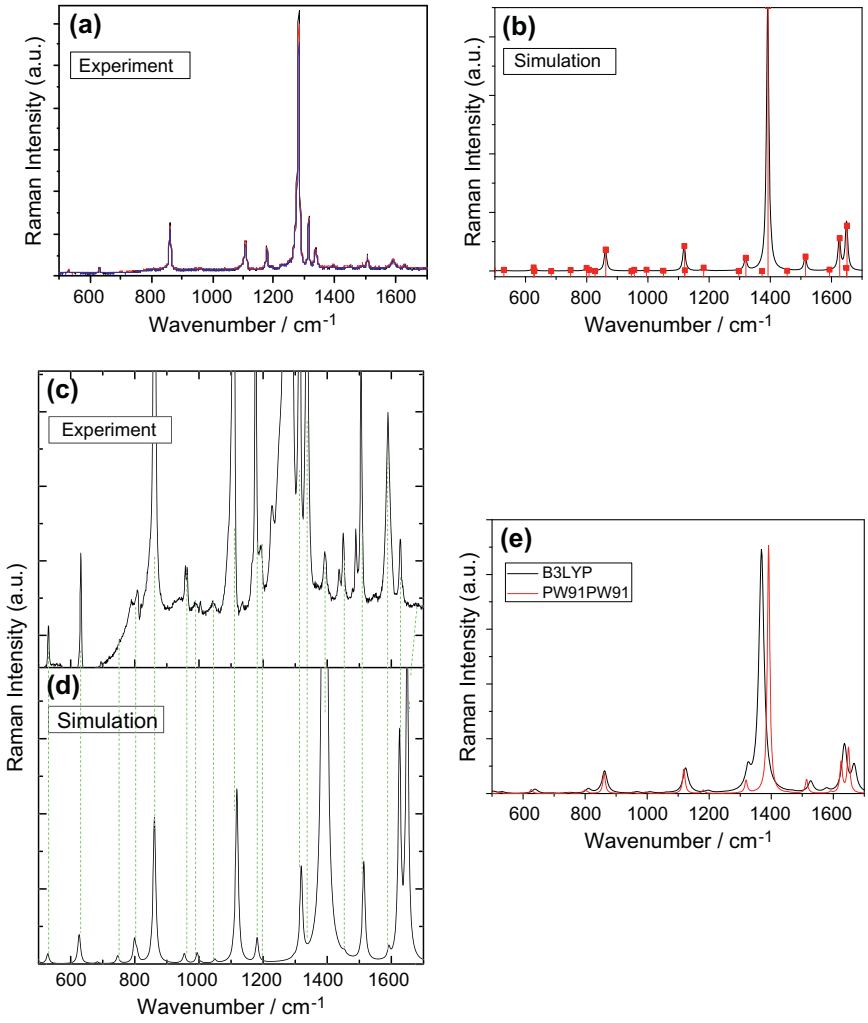

Fig. 2. (a) The experimental and (b) simulated Raman spectra, (c) and (d) the comparisons between experimental and simulated Raman spectra, and (e) the comparison of simulated spectra with different functions, and not the scale of the frequencies was done using the experimental peak at 859 cm^{-1}.

shows an exceptionally strong charge transfer character accompanied by a large polarizability and hyperpolarizability [1]. Recently, experimental and theoretical works have revealed that PATP (with NH_2 group, see Fig. 1(b)) and 4NBT (with NO_2 group, see Fig. 1(c)) can be oxidized and reduced to DMAB assisted by surface plasmon resonance [2–12]. What kinds of chemical reaction will be occurred for PNA assisted by surface plasmon resonance? Can oxidization and/or reduction reactions will happen by surface plasmon? It is great interesting issue for the field of chemical reaction on surface. Before answer this question, we must firstly study the optical