

TIME-RESOLVED RESONANCE RAMAN STUDY OF BIPHENYL OCCLUDED IN THE SUPERCAGES OF FAUJASITIC ZEOLITES

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The laser photolysis (248 nm, 20 ns) of biphenyl (BP, S₀) occluded in the void space of faujasitic zeolites (Na_nFAU), Na_n(SiO₂)_{192-n}(AlO₂)_n with $n = 0, 56, 85$ has been studied by time-resolved resonance Raman spectroscopy combined with time-resolved diffuse reflectance UV-visible absorption spectroscopy in the ns–μs time scale. The excitation (370 nm, 8 ns) of the RR scattering in the wavelength region of the UV electronic absorption of the transient species provides clear evidence of the radical cation (BP^{•+}) as major species for zeolites Na_nFAU ($n = 56, 85$). The amount of triplet state (BP, T₁) depends on the aluminum content and in a less extent on the fluence of the pump laser at the sample.

Keywords: Biphenyl; zeolite; time-resolved Raman spectroscopy; diffuse reflectance UV-visible transient absorption; nanosecond

The ever-increasing interest in photophysics and photochemistry in organized and constrained media has recently encouraged the use of the time-resolved resonance Raman spectroscopy to characterize short-lived species generated in the void space of crystalline porous aluminosilicate solids such as faujasitic zeolites (Na_nFAU), Na_n(SiO₂)_{192-n}(AlO₂)_n ($n = 0–96$). The biphenyl (BP) can gain free access to the 13 Å diameter supercage through the 8 Å diameter 12-ring entrance port of the zeolites. The structure of Biphenyl (BP) is known

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to change with its physical state. It exists as a planar (D_{2h}) structure in the crystalline state above 40 K, but takes twisted (D_2) structure in the gaseous state. The ground electronic state (S_0), the lowest excited singlet state (S_1), the lowest excited triplet state (T_1) as well as the cation radical $BP^{\cdot+}$ and the anion radical $BP^{\cdot-}$ have been well characterized previously in solution [1, 2]. We report here the photophysics of BP occluded in dehydrated faujasitic zeolites Na_nFAU ($n = 0, 56, 85$) using time-resolved resonance Raman spectroscopy and time-resolved UV-visible diffuse reflectance spectroscopy in the nano/microsecond time scale.

The freshly dehydrated Na_nFAU are loaded by the BP molecules through adsorption from the gas phase at different coverages namely 1, 2, 4, 8 and 16 BP per unit cell (8 supercages). The (S_0) siting location and conformation of BP sorbed in Na_nFAU at different loading were deduced from FT-Raman spectroscopy as well as molecular dynamics (MD) and Monte Carlo (MC) simulations. These supercages are large enough to accommodate up to two BP molecules. BP takes twisted structures in the void space and the average occupation time in one supercage is found to be less than 25 ps from MD data at low coverage. At higher coverage the main trends are retained until the saturation of the void space.

The laser pump excitation (248 nm, 20 ns, 0.05–3 mJ, 10 Hz) is in resonance with the $S_n \leftarrow S_0$ BP transition which occurs around 250 nm for BP occluded into Na_nFAU ($n = 0, 56, 85$). The transient electronic absorption spectra are found to be characteristic of BP (T_1), $BP^{\cdot+}$, $BP^{\cdot-}$ and to the trapped electrons within the zeolites for all the delays between 1 and 100 μ s [3]. The trapped electrons can be ascribed to Na_4^{3+} as a counter part to $BP^{\cdot+}$.

The probe excitation (370 nm, 8 ns) of the RR scattering in the wavelength region of the UV electronic absorption of the transient species provides clear evidence of the radical cation ($BP^{\cdot+}$) as major species for zeolites Na_nFAU ($n = 56, 85$) at different delays after the pump pulse for all the experimental coverages. This photoionization is considered to take place by a biphotonic process. The amount of triplet state (BP, T_1) depends on the aluminum content of the host and in a less extent on the fluence of the pump laser at the sample. The time-resolved resonance Raman spectra of BP occluded in $Na_{56}FAU$ (Fig. 1) have a good resemblance with that reported previously in

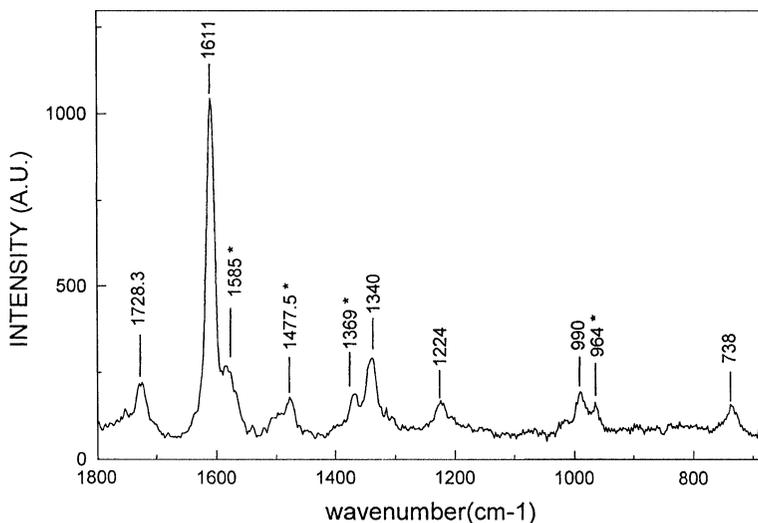


FIGURE 1 Transient Resonance Raman spectrum of BP occluded in Na_{56}FAU zeolite excited at 370 nm and recorded 150 ns after the pump excitation at 248 nm. The asterisks indicate the T_1 bands, the remaining bands are characteristic of the radical cation $\text{BP}^{\cdot+}$.

acetonitrile solution [2]. It was recently found that both cation $\text{BP}^{\cdot+}$ and anion $\text{BP}^{\cdot-}$ radical are generated simultaneously when BP occluded in Na_{56}FAU at high coverage is photoexcited at 266 nm [3]. Unfortunately, the present time-resolved resonance Raman spectra (370 nm) do not provide clear evidence of the anion radical.

References

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