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

G. BUNTINX*, G. GINESTET, I. GENER, G. COUSTILLIER and C. BRÉMARD

Laboratoire de Spectrochimie Infrarouge et Raman UPR-CNRS 2631, Centre d'Études et de Recherches Lasers et applications, Université de Lille I, Bât. C5, 59655 Villeneuve d'Ascq Cedex, France

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The laser photolysis (248 nm, 20 ns) of biphenyl (BP, S0) occluded in the void space of faujasitic zeolites (NaₙFAU), Naₙ(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 NaₙFAU (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 (NaₙFAU), Naₙ-(SiO₂)₁₉₂₋ₙ(AlO₂)ₙ (n = 0–96). The biphenyl (BP) can gain free access to the 13 Å diameter supereage through the 8 Å diameter 12-ring entrance port of the zeolites. The structure of Biphenyl (BP) is known

* Corresponding author.
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 $BP^+$ and the anion radical $BP^-$ have been well characterized previously in solution [1, 2]. We report here the photophysics of BP occluded in dehydrated faujasitic zeolites Na$_n$FAU ($n = 0, 56, 85$) using time-resolved resonance Raman spectroscopy and time-resolved UV-visible diffuse reflectance spectroscopy in the nano/microsecond time scale.

The freshly dehydrated Na$_n$FAU 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$_n$FAU 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 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 $S_n \leftrightarrow S_0$ BP transition which occurs around 250 nm for BP occluded into Na$_n$FAU ($n = 0, 56, 85$). The transient electronic absorption spectra are found to be characteristic of BP ($T_1$), $BP^+$, $BP^-$ and to the trapped electrons within the zeolites for all the delays between 1 and 100 µs [3]. The trapped electrons can be ascribed to Na$_4^{3+}$ as a counter part to $BP^+$.

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 ($BP^+$) as major species for zeolites Na$_n$FAU ($n = 56, 85$) 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 BP$^+$. 

It was recently found that both cation BP$^+$ and anion BP$^-$ 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