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Vibrational Raman scattering from excited triplet state chrysene by time-resolved resonance Raman spectroscopy[a]

G. H. Atkinson[b] and L. R. Dosser

Department of Chemistry, Syracuse University, Syracuse, New York 13210

It has been recently demonstrated that the vibrational spectroscopy[1-9] and kinetic behavior[10] of short-lived, reactive species in solution can be measured by time-resolved resonance Raman (TR^3) scattering. In these real time experiments, the reactive species is formed by laser photolysis and its vibrational Raman spectrum is obtained using pulsed laser excitation and multiwavelength detectors.[7] The reaction kinetics are derived from the time-dependent intensities of resonance Raman bands arising from both stable reactants and products as well as the reactive intermediates. Results to date have been for photochemically formed intermediates. Photophysically formed excited electronic states, however, also have distinct vibrational degrees of freedom and thereby fulfill the criteria for detection by TR^3 spectroscopy. We report in this communication the observation of spontaneous vibrational Raman scattering from the excited $^3B_u^+$ state of chrysene dissolved in oxygen-free n-hexane.

Experimentally, the frequency-tripled output of a Nd : YAG laser at 354.7 nm (50 ns pulsewidth FWHM) was used to populate the first excited singlet $^1B_{3u}^-$ state of chrysene (Fig. 1). Subsequent intersystem crossing leads to the population of the excited $^3B_u^+$ state within the 50 ns excitation pulsewidth.[11] Resonance Raman scattering is then generated by tuning the output (0.01 nm bandwidth, 1 μs pulsewidth FWHM) of a pulsed dye laser into resonance with the transient triplet–triplet ($^3A_g^-$–$^3B_u^+$) absorption transition between 470 and 640 nm (Fig. 1).[12-17] The resultant resonance Raman spectrum monitors the vibrational degrees of freedom of chrysene in the excited $^3B_u^+$ state. By controlling the time delay (Δ) between the excitation (Nd : YAG) and the probe (dye) lasers, the intensity of resonance Raman scattering directly measures the time-dependent population of the excited $^3B_u^+$ state.

The 900–1100 cm^{-1} region of the Raman spectrum for chrysene-h_{12} is presented in Fig. 2(a). This spectrum was obtained using only the probe (dye) laser operating at 570 nm. Only vibrational Raman bands from the solvent, n-hexane, are observed since the concentration of chrysene is low (10^{-4} M) and no resonance enhancement from the $^1B_{3u}^-$–$^1A_g^-$ absorption transition (361 nm) involving ground-state chrysene is induced by 570 nm excitation.

When a TR^3 experiment ($\Delta = 1$ μs) is performed on the same sample, however, a new Raman band is observed at 982 cm^{-2} [Fig. 2(b)]. The intensity of the 982 cm^{-1} band decreases as the delay increases to 3 μs [Fig. 2(c)]. Similar time-dependent Raman bands are found at 1095 and 1342 cm^{-1}. When the same experiment is performed on a 10^{-4} M solution of chrysene-d_{12} in n-

hexane ($\Delta = 1$ μs), a new TR^3 spectrum is obtained containing Raman bands at 952 and 1012 cm^{-1} [Fig. 2(d)]. The frequencies for all of these observed time-dependent Raman bands are not affected by the use of either different solvents (e.g., THF) or chrysene concentrations (10^{-4}–10^{-2} M).

The identification of these time-dependent Raman bands with an intermediate of chrysene derives from several observations: (1) the vibrational Raman bands measured in the TR^3 spectra are not found in the Raman spectrum of ground-state chrysene[18,19] and appear under excitation conditions (wavelength and concentration) which preclude any Raman scattering other than that induced by resonance enhancements, (2) the band frequencies are not affected by significant changes in the solvent or concentration of chrysene, and (3) the frequencies of the time-dependent bands exhibit a pronounced deuterium shift.
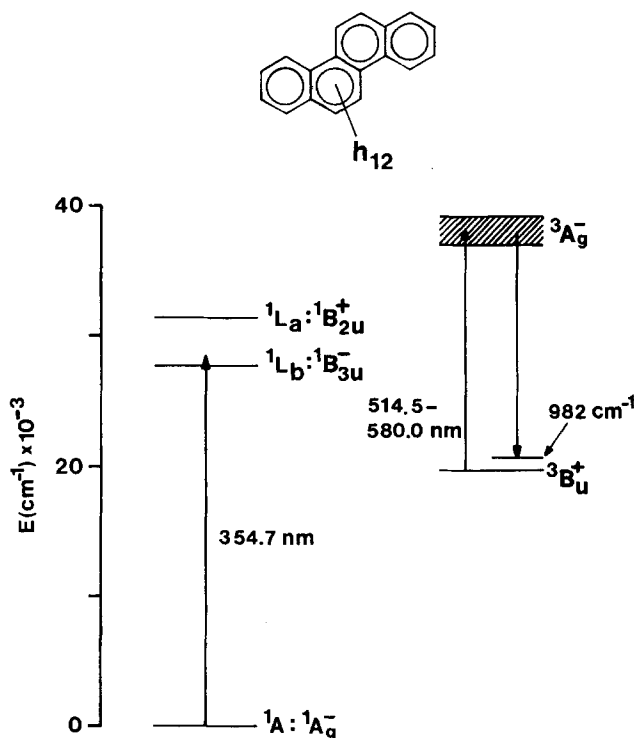

FIG. 1. Electronic energy levels in chrysene-h_{12}. The lowest energy singlet state (^1L_b: $^1B_{3u}^-$) is populated by laser excitation at 354.7 nm. Subsequent intersystem crossing leads to the population of the lowest energy triplet state (^3L_a: $^3B_u^+$). TR^3 scattering is generated by laser excitation in the 514.5 to 480.0 nm region which is resonant with the $^3A_g^-$–$^3B_u^+$ transition. The assignments of term symbols to chrysene levels are taken from Refs. 13, 16, and 17.
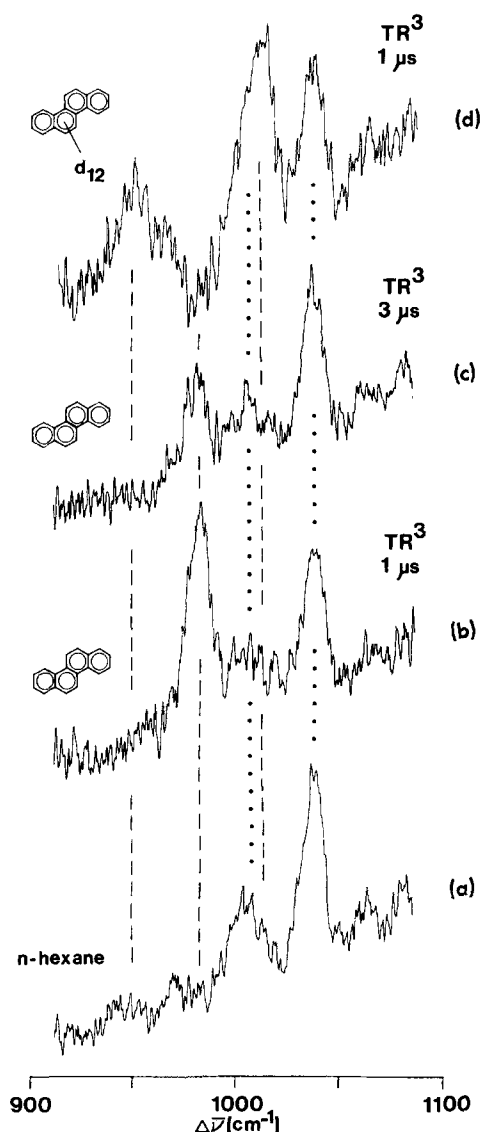
FIG. 2. TR^3 spectra of 10^{-4} M samples of chrysene-h_{12} and -d_{12} (a) Raman spectrum of chrysene-h_{12} in oxygen-free n-hexane obtained with 570 nm excitation from the probe laser only. (b) and (c) TR^3 spectra of chrysene-h_{12} for $\Delta = 1$ and 3 μs, respectively. (d) TR^3 spectrum of chrysene-d_{12} for $\Delta = 1$ μs. Excitation and probe lasers operate at 354.7 nm and 570.0 nm respectively for all TR^3 spectra shown. The frequency positions are marked by filled circles (●) for solvent bands and by dashes (−) for chrysene-h_{12} and -d_{12} bands.

These new bands have three additional characteristics which associate them with the excited $^3B_u^*$ state of chrysene. First, the same time-dependence is measured for all of the TR^3 bands observed in a given isotopic species yielding exponential lifetimes for chrysene-h_{12} of 3.8 μs and for chrysene-d_{12} of 5.5 μs. The first value corresponds closely to the 3.4 μs lifetime calculated for $^3B_u^*$ chrysene-h_{12} in oxygen-free n-hexane.[20-22] Furthermore, the increased lifetime of the TR^3 bands (~45%) caused by deuteration agrees well with the 40% longer $^3B_u^*$ lifetime observed for chrysene-d_{12} relative to chrysene-h_{12}.[23]

Second, the intensities of these TR^3 bands are strongly dependent on the wavelength of the probe laser. The intensity of the 982 cm^{-1} band from chrysene-h_{12}, for example, increases sharply as the probe laser is tuned from 580 nm to shorter wavelengths, reaching a maximum near 570 nm. The intensity then slowly decreases as the probe laser wavelength decreases. This observed dependence for the intensity of the 982 cm^{-1} band on the probe laser frequency in the 514–580 nm region closely reproduces the transient $^3A_g^- - ^3B_u^*$ absorption band in chrysene.[11-14] These data, therefore, suggest that this time-dependent Raman band arises from the enhancement effects of the $^3A_g^- - ^3B_u^*$ transition.

Third, no time-dependent bands are observed when the sample is brought into equilibrium with molecular oxygen. Oxygen does not perturb the normal Raman spectrum of chrysene[18,19] and its influence on time-dependent bands is thought to derive from its well known role as a triplet state quencher. In an air-saturated solution of n-hexane, the lifetime of the $^3B_u^*$ has been reduced to 360 ns[20-22] which is below the time-resolution of our instrumentation (i.e., 1 μs).

[a] This research is supported by a grant from the National Science Foundation.

[b] Author to whom correspondence should be addressed.

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