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Ultrafast Dynamics in Dimeric Hemoglobin Probed by Time-Resolved Resonance Raman Spectroscopy

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Abstract

Time-resolved anti-Stokes Raman spectroscopy is selective for vibrationally excited modes, and it is therefore a powerful method for measuring vibrational energy relaxation.¹⁻² The intensity ratio of anti-Stokes and Stokes scattering is expected to provide the most direct information about relative vibrational populations. Here, we applied this technique to explore the vibrational energy relaxation of heme in the globin matrix upon ligand photodissociation of *Scapharca inaequivalvis* dimeric hemoglobin (HbI).

Anti-Stokes time-resolved resonance Raman spectra upon the photodissociation of carbon monoxide (CO) between -5 and 20 ps are shown in Figure 1 (A). A CO-ligated heme group was photodissociated by pump pulse of 571 nm, the subsequent relaxation process was monitored by probe pulse of 442 nm. Anti-Stokes intensities are highest at a 1 -ps delay, when the ν_3 , ν_4 , ν_5 , and ν_7 bands were observed at 1458 , 1351 , 1130 , and 683 cm^{-1} , respectively. These bands lost intensity as the delay time increases and reached their equilibrium intensities at a 20 -ps delay as depicted in Figure 1 (B). An analysis of the temporal changes of anti-Stokes band intensities showed that the anti-Stokes intensity develops within the instrument response time. This is consistent with the photodissociation of CO from the heme taking place within 50 fs. The instrument response was deconvoluted from the decay of the anti-Stokes intensity using a Gaussian fit to the cross correlation signal. This analysis obtained the decay constants of 1.2 ± 0.1 ps for the ν_4 band and 3.3 ± 0.5 ps for the ν_7 band. Because there was no intensity change in the Stokes ν_4 and ν_7 bands in the 3 to 20 -ps time range, the observed intensity decay in the anti-Stokes ν_4 and ν_7 bands can be ascribed to vibrational energy relaxation. The temporal changes of the band intensities for HbI are very similar to those for horse myoglobin.³ The observed dynamics will be discussed in terms of alternative quaternary structures of HbI.

Keywords: vibrational energy relaxation; time-resolved resonance Raman spectroscopy; homodimeric hemoglobin

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Fig. 1: Time-resolved anti-Stokes resonance Raman spectra (A) and temporal changes of band intensities (B).