SPECTROSCOPY AND DYNAMICS OF NEAR-INFRARED METASTABLE SPECIES IN SOLUTION PHASE

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Through the development of ultrasensitive near-infrared (NIR) detecting systems we have opened up a new territory both on NIR spectroscopy and dynamics in solution phase. We have explored the O_2 $^1\Sigma_g^+ \rightarrow {}^1\Delta_g$ (0,0) 1930 nm, $^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$ (0,0) 765 nm and O_2 dimol $(^1\Delta_g)_2$ $\rightarrow (^3\Sigma_g^-)_2$ (0,0) and (0,1) at 634 and 703 nm emission, respectively in CCl_4. Consequently, the photophysics of $^1O_2$ dimol ($(^1\Delta_g)_2$) and O_2 ($^1\Sigma_g^+$) states in solution has been studied in details. The quantum yield of O_2 $^1\Sigma_g^+ \rightarrow$ $^3\Sigma_g^-$ 765 nm emission was measured to be 1.94×10^{-7}, and consequently, the radiative decay rate of $^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$ transition was deduced to be 1.55 ± 0.04 s^{-1}. By comparing the dimol $(^1\Delta_g)_2 \rightarrow (^3\Sigma_g^-)_2$ emission intensity with the tetra-tert-butylphthalocyanine delayed fluorescence induced by a two-step energy transfer from the O_2 ($^1\Delta_g$) state, a lower limit of the dissociation rate constant of the dimol was estimated to be $(5.2 \pm 0.3) \times 10^{10}$ s^{-1} in CCl_4. On the other hand, through the study of Nile Blue A delayed fluorescence induced by energy transfer from the $^1O_2$ dimol, a radiative lifetime of $(1.2 \pm 0.3) \times 10^3$ s^{-1} for $^1O_2$ dimol was deduced in $CDCl_3$.

In another approach, spectroscopy and dynamics of $I(^2P_{1/2})$ in solution have been investigated via the iodine atom $^2P_{1/2} \rightarrow {}^2P_{3/2}$ emission in solution. The resulting emission spectra in the region of 1200-1600 nm reveal cooperative electronic-vibrational iodine-solvent transitions, furnishing insight into the atom-solvent interactions. The dynamics of energy-transfer between $I(^2P_{1/2})$ and $^1O_2$ in solution were first studied with detailed kinetics presented.