Detection of spectroscopically-silent reaction intermediate by ultrafast X-ray scattering

Understanding reaction mechanism requires to establish all intermediates and rate constants. Whereas time-resolved spectroscopy has served as the major tool in this regard, it generally cannot provide quantitative relative populations of all intermediates especially when the complexity of the investigated system increases. This is due to the practical difficulty of accurately calculating the optical cross-section from the molecular structure. In extreme cases, major intermediates may escape spectroscopic detection simply because they are optically silent. Here we show that time-resolved X-ray scattering can solve this fundamental problem and illustrate that time-resolved scattering and time-resolved spectroscopy are indispensable complements in revealing detailed reaction mechanisms. The triangular metal carbonyl cluster $\text{Ru}_3(\text{CO})_{12}$ provides an excellent model system for such a purpose since it has served as the paradigm for the photochemistry of transition metal carbonyls and its photolysis has been extensively studied by spectroscopy in solid matrices and in solution. Previous studies using time-resolved infrared spectroscopy have identified two transient photochemical intermediates, $\text{Ru}_3(\text{CO})_{11}(\mu - \text{CO})$ and $\text{Ru}_3(\text{CO})_{10}(\mu - \text{CO})_{12}$. By using ultrafast solution X-ray scattering, we identify a new intermediate as well as the two known intermediates. Modelling of the time-dependent scattering curves using the scattering from potential intermediate structures in solution calculated by density functional theory and molecular dynamics simulations clearly indicates that the major and hitherto undetected intermediate is one of the $\text{Ru}_3(\text{CO})_{10}$ complex isomers which has only terminal carbonyls. This explains that it has escaped detection in previous ultrafast infrared studies based on the characteristic absorption bands of the bridging carbonyls.