TIME-RESOLVED PHOTOELECTRON STUDIES OF IBr^-: A CLASSICAL AND QUANTUM TUG-OF-WAR

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To understand the dynamics of molecular species, especially those involved in photochemistry, we often turn to classical mechanics, which, despite the assumed quantum nature of small, light particles, has been extremely helpful in describing the underlying photophysics and can often explain the big picture of the dynamics. One such example is the recent duel experimental and theoretical study on the photodissociation of IBr^- performed by Sanov and co-workers.[a] Of greater interest, though, is when does classical mechanics break down? More generally, when is a quantum approach needed to fully describe the system at the resolution of the experiment? In this work, we address these questions by investigating quantum interference effects on the time-resolved spectra of IBr^- where we look at how pulse width affects the overall signal. In the limit of an infinitely narrow pulse, we regain the Franck-Condon picture and the classical limit because all transitions are energetically allowed. In the limit of an infinitely wide pulse width, quantum interference effects become important and give rise to the bimodal character of the spectrum at short delay times ($\Delta t < 350$ fs). Results of the calculated IBr^- spectra are in good agreement with experiment and serve to illustrate how varying the pulse widths can shift the description of the dynamics from a classical picture to a quantum one.

[a] R. Mabbs, K. Pichugin, and A. Sanov, *J. Chem. Phys.*, **2005**, *122*, 174305.