Manipulating tunnelling gateways in condensed phase isomerization

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Abstract

When a chemical reaction occurs via tunnelling, a simple mass-dependence is expected, where substitution of atoms by heavier isotopes leads to a reduced reaction rate. However, as shown in a recent study of CO orientational isomerization at the NaCl(100) interface [Choudhury et al., Nature **612**, 691 (2022)], the lightest isotopologue need not exhibit the fastest tunnelling; for the CO/NaCl system, the non-monotonic mass-dependence is understood through a new picture of condensed phase tunnelling where the overall rate is dominated by a few pairs of reactant/product states. These state-pairs – termed quantum gateways – gain dynamical importance through accidentally-enhanced tunnelling probabilities, facilitated by a confluence of the energetic landscape underlying the reaction as well as the phonon bath of the surrounding medium. Here, we explore gateway tunnelling through measurements of the kinetic isotope effect (KIE) for CO isomerization in a monolayer buried by many layers of either CO or N_2. With an N_2 overlayer, tunnelling rates are accelerated for all four isotopologues ($^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, and $^{13}C^{18}O$), but the degree of acceleration is isotopologue-specific and non-intuitively mass dependent. A one-dimensional tunnelling model involving an Eckart barrier cannot capture this behaviour. This reflects how a change to the potential energy surface moves states in and out of resonance, changing which tunnelling gateways can be accessed in the isomerization reaction.

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