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RESEARCH ARTICLE

Natural Sciences

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(1 0 0) interface, the lightest isotopologues 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 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 modification of the potential energy surface moves states in and out of resonance, thereby changing which tunnelling gateways can be accessed in the isomerization reaction.

Key points

- The paper describes new systems that showcase resonance-enhanced condensed phase tunnelling.
- Condensed phase tunnelling as described in this work may have implications for astrochemistry.
- A previously hypothesized mechanism is subjected to subsequent experimental scrutiny – the hypothesis stands the test.

KEYWORDS
astrochemistry, gateway tunneling, isomerization, tunneling

INTRODUCTION

Particles with insufficient energy to overcome a potential barrier may nevertheless penetrate it by quantum mechanical tunnelling,[1] and for chemical reactions involving an activation barrier, this may lead to unexpectedly large reaction rates at low temperature.[2–4] Hence, tunnelling corrections to reaction rate theories have been developed.[5–7] These generally predict enhanced tunnelling for lighter isotopologues, as molecules with lighter masses exhibit longer de Broglie wavelengths that extend deeper into the classically forbidden region resulting in increased barrier penetration.

Recently, we reported experimentally observed tunnelling rates for the rotational isomerization of CO adsorbed to NaCl(1 0 0).[8] This reaction involves a metastable 'O-bound' CO – bound with its O-atom at a Na^+ surface-site – rotating to the lowest energy 'C-bound' structure, where the C-atom is bound to the Na^+.[9,10] The reaction proceeds at low temperature by thermally activated tunnelling through a barrier, and remarkably, the lightest isotopologue did not react the fastest. Indeed, this system showed a peculiarly non-monotonic kinetic isotope effect (KIE). Through comparison with quantum chemical calculations, we inferred a 'tunnelling gateway' mechanism involving transitions between a pair of bound (system) states – one localized predominantly on the reactant and one on the product side of the barrier – that come into resonance by the exchange of energy with a phonon of the environment (bath).[8] These resonances are not a simple function of mass, as they depend on the isotope-specific state energies; as the state energies do not change monotonically with mass, this leads to a non-monotonic KIE. However, the KIE is not a complete test of the gateway mechanism – isotopic substitution does not, for example, alter the underlying potential energy surface (PES), nor does it impact the phonon density of states (DoS) of the surrounding medium, both of which determine the resonances possible in the gateway mechanism.

When subjected to small changes to the underlying PES, the gateway-mechanism is expected to behave quite differently than traditional tunnelling models would under a similar perturbation. As the energies of the states involved in the gateways depend critically on the PES, even minor changes to the energy landscape can shift states in and out of resonance, resulting in entirely different gateways dominating the thermal tunnelling rates. Furthermore, these PES-induced changes to the reaction rates will be highly dependent on the isotopologue in question. In contrast, although conventional tunnelling models predict rates that are sensitive to changes in the PES, the impact on the rates are nearly identical for different isotopologues.

In this work, we experimentally investigate how small changes in the PES influence gateway tunnelling rates in the CO/NaCl(1 0 0) rotational isomerization reaction. Specifically, we compare measured tunnelling rates for CO adsorbates when buried under ∼100 monolayers of either N_2 or CO. Though these two systems have nearly identical DoS, the reaction is faster when buried under N_2; this is understood as a reduction in the classical isomerization barrier by about 50 cm^{-1} as compared to the CO overlayer system. As expected from the gateway tunnelling model, the increase in tunnelling rates is strongly isotopologue dependent. This strongly contrasts conventional tunnelling corrections used in chemistry, which predict nearly identical acceleration for all four isotopologues studied in this work. These observations provide further evidence that resonance-enhancement is fundamentally involved in condensed phase tunnelling.

EXPERIMENTAL METHODS

The details of the experimental procedure have been explained elsewhere[8,11,12]; only a brief description will be given here. A molecular beam setup is used to dose gas layers on an ultrahigh vacuum-cleaved NaCl (1 0 0) surface. First, a monolayer of one CO isotopologue ($^{12}C^{16}O$: Sigma-Aldrich; 99.99% ^{12}C and 99.95% ^{16}O, 99.9% chemical purity, $^{13}C^{18}O$: Sigma-Aldrich; 99.9% ^{13}C and 99.2% ^{18}O, 99.8% chemical purity and $^{13}C^{16}O$: Sigma-Aldrich; 99.07% ^{13}C and 97.2% ^{16}O, 99.99% and $^{12}C^{18}O$: Wuhan Newradar Trade; 96 at.% ^{18}O) is prepared on the surface at 25 K – a high enough temperature to avoid overlayer formation. In the next step, the sample temperature is lowered and dosed with CO (at 22 K) or N_2 (at 20 K) to allow for the adsorption of ∼100 additional layers. The sample is cooled by a dual-stage helium cryocooler (Sumitomo, RDK-408D2) and protected by a liquid N_2 cooled shield to approach temperatures <7 K. The sample temperature was adjusted by resistive heating using a Model 335 Lakeshore cryogenic control unit. Samples are characterised using a Fourier transformed infrared (FTIR) spectrometer (Bruker, Vertex 70 V).

For preparing metastable O-bound CO molecules, the sample held at <18 K is excited with ∼10,000 pulses of mid-IR light generated by difference frequency mixing in an $LiIO_3$ crystal of light from a tuneable dye (865–875 nm) laser (Sirah) and the 1064 nm fundamental of a 10 Hz seeded Nd:YAG laser (Continuum, Surelite III). The dye laser is pumped by the second harmonic output of the Nd:YAG laser. The mid-IR laser intensity at the sample (200 μJ in 5 ns focused to a diameter of 1 mm) is sufficient to saturate the CO $v = 0 \rightarrow 1$ vibrational transition in the monolayer leading to vibrational energy pooling and subsequent flipping of some molecules from the C-bound to the less stable O-bound configuration. As a result, the C-bound absorption in the FTIR spectrum is depleted and a new absorption appears, red shifted by ∼15 cm^{-1} and belonging to the O-down isomer. After raising the temperature to the desired value, the rotational isomerization reaction is monitored with the FTIR spectrometer in rapid scan mode. The thermal reaction was analysed by fitting the time-dependent band integrals in the absorbance FTIR spectra corresponding to the population of O- and

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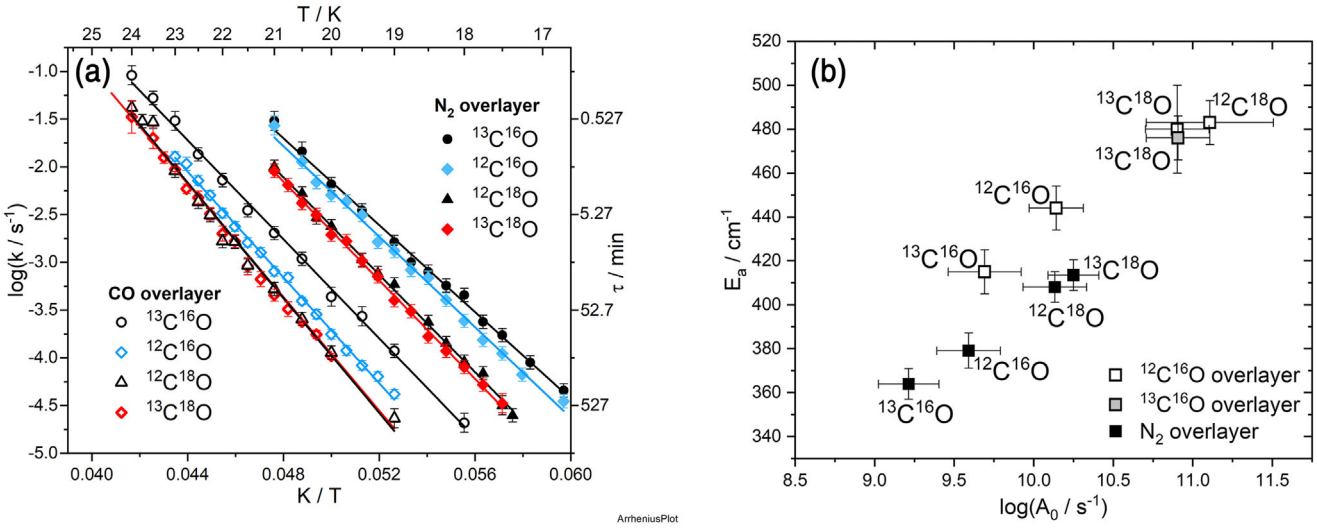

FIGURE 1 Arrhenius plots (a) and parameters (b) for the flipping of O-bound CO of four different isotopologues buried under CO and N_2. (a) Lifetimes of O-bound molecules buried under N_2 are an order of magnitude lower than those of molecules buried under CO. The isotope effects for both systems exhibit a non-monotonic mass-dependence. (b) Both systems show a correlation between activation energies and prefactors. Activation energies are reduced when N_2 replaces CO in the overlayer.

TABLE 1 Excitation frequencies used for the different samples.

Monolayer	Overlayer	Excitation (cm^{-1})
$^{12}C^{16}O$	$^{12}C^{16}O$	2152.5
$^{13}C^{16}O$	**$^{12}C^{16}O$**	2138.6
$^{12}C^{18}O$	**$^{12}C^{16}O$**	
$^{13}C^{18}O$	**$^{12}C^{16}O$**	
$^{13}C^{18}O$	**$^{13}C^{16}O$**	2091.7
$^{12}C^{16}O$	N_2	2152.5
$^{13}C^{16}O$	N_2	2104.9
$^{12}C^{18}O$	N_2	2101.0
$^{13}C^{18}O$	N_2	2052.5

Note: The species excited by the laser is indicated in bold.

C-bound molecules, respectively, by exponential decays as described in Ref. [8].

Samples consisting of the heavier isotopologues $^{13}C^{18}O$, $^{13}C^{16}O$ and $^{12}C^{18}O$ in the monolayer and buried under a lighter CO isotopologues (e.g. $^{12}C^{16}O$) are excited at the overlayer $v = 0 \rightarrow 1$ resonance frequency, which results in 10× more efficient excitation of vibrational quanta in the monolayer due to vibration-to-vibration (V–V) energy transfer from the lighter to the heavier isotopologue.[11] These samples were excited with about 2000 mid-IR laser shots before the thermal back reaction was initiated. Excitation frequencies used for the various samples are summarized in Table 1.

RESULTS

Figure 1a shows rotational isomerization rate constants for four isotopologues of CO buried under overlayers of CO (open symbols, k_{CO}) and N_2 (closed symbols, k_{N_2}), extracted from the time-dependent FTIR signals as discussed earlier. The observed rates obey an Arrhenius behaviour, that is the temperature-dependent rate constants are reasonably described by $k(T) = A_0 \ e^{-E_a/k_B T}$, where A_0 and E_a are the Arrhenius prefactor and activation energy, respectively, and k_B is the Boltzmann constant. As discussed previously,[8] this results from the fact that O-bound CO molecules with the thermal excitation of the hindered rotation, tunnel more efficiently than ground-state CO. Figure 1b shows the Arrhenius parameters derived from the rate constants of Figure 1a; indicative of a tunnelling reaction, the derived Arrhenius prefactors A_0 are much smaller than expected from transition state theory (TST) ($\sim 10^{12}$/s at 20 K). Furthermore, a strong correlation is seen between the prefactor and the activation energy, which has previously been shown to be a fingerprint of the gateway tunnelling mechanism.[8]

When the identity of the overlayer is changed from CO to N_2, we see that the tunnelling rates retain their Arrhenius-like behaviour, but the rates are increased by more than an order of magnitude. From Figure 1b, we see that each activation energy is lowered by the influence of the N_2 overlayer, with an average reduction of 55 cm^{-1}. We take this as an estimate of the reduction in the classical barrier height that occurs when CO is replaced with N_2 in the overlayer, as discussed in the following section.

Notably, the extent of acceleration is distinct for each isotopologue. This can be seen more clearly in Figure 2, where the ratios of experimental rates, k_{N_2}/k_{CO}, are shown versus temperature for all four isotopologues. This ratio may be taken as a quantification of the reaction rate acceleration induced by switching the overlayer from CO to N_2. The acceleration is not only highly isotope-specific but also is non-monotonically dependent on mass; for example, at $T = 20$ K, the acceleration is ordered as $^{12}C^{16}O$ (28 amu, $k_{N_2}/k_{CO} = 29$) > $^{12}C^{18}O$ (30 amu, $k_{N_2}/k_{CO} = 21$) > $^{13}C^{18}O$ (31 amu, $k_{N_2}/k_{CO} = 17$) > $^{13}C^{16}O$

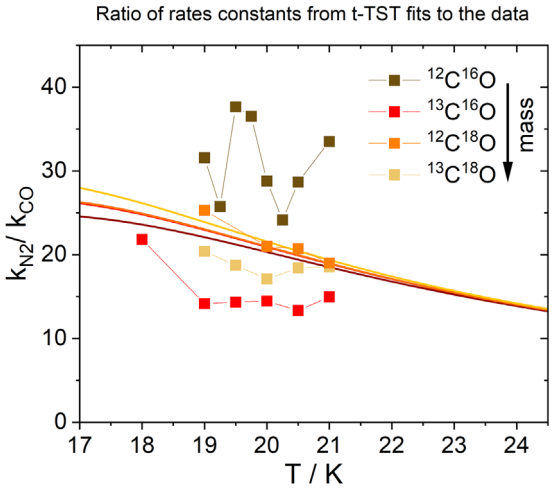

FIGURE 2 Isotopologue-specific acceleration of tunnelling for the CO orientational isomerization with N_2 and CO overlayer. The experimentally derived ratios (symbols) are compared to a tunnelling corrected transition state theory (TST-t) model employing an Eckart potential (solid lines). Notice the monotonic mass-dependence of the t-TST model compared to the mass-dependence seen in experiment. Details of the t-TST calculations are presented in the Supporting Information.

(29 amu, $k_{N_2}/k_{CO} = 14$). For comparison, we calculated isotopologue-specific rate constants from a tunnelling corrected TST (t-TST) model. The t-TST results were obtained employing an Eckart potential for the reaction coordinate as proposed originally by Miller[7] – for details see Section S1 with Tables S1 and S2 and Figures S1–S4. To simulate the influence of swapping overlayers from CO to N_2, the classical barrier height in the t-TST model is lowered by 46.5 cm^{-1}, while keeping the width of the barrier fixed. The corresponding results are also shown in Figure 2; the tunnelling is accelerated by about a factor of 20, and although the effect is small, one sees that the heavier the isotopologue, the higher the acceleration factor.

DISCUSSION

Gateway tunnelling can be described by a Fermi Golden Rule (FGR) tunnelling model, which involves the coupling of system states by a phonon bath.[7] Here, the system states are represented by two dimensional rotational/translational isomerization wavefunctions of CO on NaCl, which, for sub-barrier energies, are highly localized on either the reactant or the product side of the barrier. By coupling to the phonon bath of the surrounding medium, transitions between system states on opposite sides of the barrier may occur; this is especially likely when one of the states exhibits even a small degree of delocalization and when the emission or absorption of a single phonon brings the two states into resonance.[8] The combination of these accelerating factors leads to thermal rates dominated by population transfer between specific resonant state pairs, which provide a tunnelling gateway for isomerization. Altering the overlayer from CO to N_2 introduces changes to the PES and to the bath DoS, both of which can in principle alter the gateway tunnelling probabilities.

We surmise that the primary effect of swapping the overlayer from CO to N_2 is a change in the isomerization barrier height by about 50 cm^{-1}. We arrive at this value of the barrier height reduction in three different ways. First, we employed DFT methods – see Section S2 (Figures S6 and S7, Table S3) – to compute the minimum energy path for the two systems, which are shown in Figure S8. The classical barriers to the rotational isomerization of O-bound CO under a CO or an N_2 overlayer are found to be 630 and 540 cm^{-1}, respectively. The DFT-deduced barrier height reduction is therefore 90 cm^{-1}. Second, we noted that the isotopologue-averaged reduction in activation energies seen in Figure 1b is 55 cm^{-1}. Finally, we estimated the barrier height reduction using t-TST (refer to Section S1). Briefly, we fit the rate constants of Figure 1a for both CO and N_2 overlayer experiments by varying the classical barrier height in the t-TST model, assuming that the barrier width remains unchanged. This procedure yields a classical barrier height for all four isotopologues (Table S3). We took the isotopologue averaged change to the classical barrier height (46.5 cm^{-1}) as a measure of true change to the barrier height upon swapping of the overlayer. The fact that all three methods arrive at similar values of the barrier height reduction give us confidence in our previous assertion that the barrier height is reduced by on the order of 50 cm^{-1} by substituting the CO overlayer for N_2.

We further surmise that although the change to the N_2 overlayer reduces the classical barrier height, it only minimally changes the phonon DoS. When considering the phonon spectrum of the N_2 overlayer, the mass difference from a $^{12}C^{16}O$ overlayer is negligible, and the changes to the force constants derived from slightly different electrostatic interactions are also small. In Figure S9, we present first-principles DoS functions obtained from ab initio molecular dynamics simulations; the computed DoS functions for the two cases are quite similar. Thus, the experimentally observed acceleration arises primarily from the change in the PES induced by the change in overlayer identity.

We emphasize that the classical barrier heights obtained from t-TST fitting are isotopologue dependent. This confirms that the tunnelling physics based on continuum wavefunctions interacting with an Eckart potential are incapable of describing a condensed phase system influenced by resonant tunnelling. It is also worth noting that in the absence of sufficient isotopologue-specific rate data, one may be deceived into thinking that a t-TST approach is appropriate. Had we been content to apply t-TST to a single isotopologue in this system, the excellent fits seen in Figure S4 might have convinced us of the validity of t-TST.

To experimentally investigate the influence on gateway tunnelling induced by changes to the DoS associated with the overlayer, we compared $^{13}C^{18}O$ rotational isomerization rates under overlayers of $^{13}C^{16}O$ and $^{12}C^{16}O$. Figure 3 shows that no influence on the rates of the reaction can be detected. This is not surprising; in this system, CO interacts more strongly with NaCl than with molecules in the overlayer. The overlayer experiments discussed above represent an interesting experimental achievement, where key theoretical components – the underlying PES, and the phonon DoS – are, to some extent,

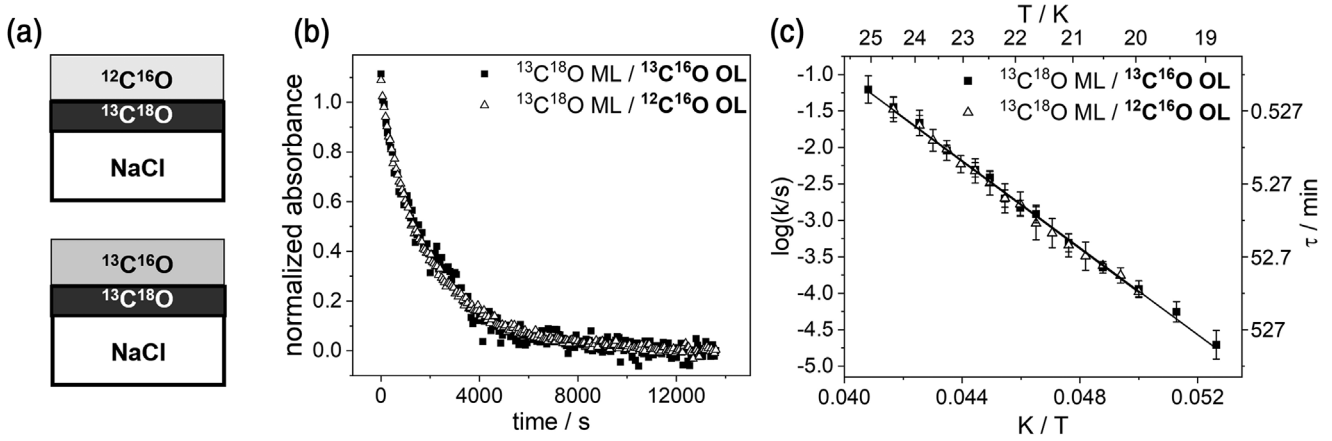

FIGURE 3 Effect of variation in the overlayer phonon spectrum on the decay of O-bound signal. (a) A schematic of the two samples; a monolayer of $^{13}C^{18}O$ is prepared under ~100 monolayers of either $^{12}C^{16}O$ or $^{13}C^{16}O$. (b) Comparison of the rotational isomerization kinetics for the two samples at 21 K. (c) Arrhenius plots for $^{13}C^{18}O$ buried under $^{12}C^{16}O$ and $^{13}C^{16}O$ overlap perfectly, showing that a change in isotope in the overlayer does not influence the reaction rate.

independently manipulated. In doing so, we show that for this system, gateway tunnelling is much more sensitive to the PES than to the phonon DoS.

CONCLUSIONS

In this work, we have shown now a second system where a heavier isotopologue ($^{13}C^{16}O$) tunnels faster than a lighter one ($^{12}C^{16}O$), indicative of the gateway tunnelling mechanism. As in the previous report, a large KIE is seen with an unusual mass-dependence that can be understood via resonance enhanced tunnelling. We compared these observations to a conventional tunnelling corrected TST, which predicts a much smaller KIE and an intuitive mass-dependence. In comparing the N_2 overlayer system to the CO overlayer system, the main difference is a reduction of the potential energy barrier for the rotational isomerization. This allows us to manipulate which tunnelling gateways are important to the reaction. This work gives further evidence that the gateway tunnelling mechanism is necessary to understand condensed phase tunnelling.

AUTHOR CONTRIBUTIONS

Data curation; formal analysis; investigation; software; validation; writing – original draft; writing – review and editing: Arnab Choudhury. *Formal analysis; software; visualization; writing – review and editing*: Shreya Sinha. *Data curation*: David Harlander. *Formal analysis; supervision; writing – review and editing*: Jessalyn DeVine. *Formal analysis; investigation; supervision; writing – review and editing*: Alexander Kandratsenka. *Formal analysis; methodology; supervision; writing – review and editing*: Peter Saalfrank. *Conceptualization; formal analysis; methodology*: Dirk Schwarzer. *Conceptualization-equal, writing – original draft-supporting, writing – review and editing-equal*: Alec M. Wodtke.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

Data will be provided by the authors upon any reasonable request.

ETHICS STATEMENT

The authors confirm that they have followed the ethical policies of the journal.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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