Dissipation enhanced vibrational sensing in an olfactory molecular switch

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Motivated by a proposed olfactory mechanism based on a vibrationally-activated molecular switch, we study electron transport between a donor-acceptor pair that is coupled to a vibrational mode and embedded in a surrounding environment. We derive a polaron master equation with which we study the dynamics of both the electronic and vibrational degrees of freedom beyond the usual semiclassical (Marcus-Jortner) rate analysis. We show: (i) that the semiclassical approach is generally unable to capture the dynamics predicted by our master equation due to both its assumption of one-way (exponential) electron transfer from donor to acceptor, which is typically invalid, and its neglect of the spectral details of the environment; (ii) that by additionally allowing strong dissipation to act on the odorant vibrational mode we can recover exponential electron transfer, though typically at a rate that differs from that given by the Marcus-Jortner expression; (iii) that the ability of the molecular switch to discriminate between the presence and absence of the odorant, and its sensitivity to the odorant vibrational frequency, are enhanced significantly in this strong dissipation regime, when compared to the case without mode dissipation; and (iv) that details of the environment absent from a Marcus-Jortner analysis can also dramatically alter the sensitivity of the molecular switch, in particular allowing its frequency resolution to be improved. Our results thus demonstrate the constructive role dissipation can play in facilitating sensitive and selective operation in molecular switch devices, as well as the inadequacy of Marcus-Jortner rate equations in analysing such behaviour over a wide range of parameters.

I. INTRODUCTION

Characterising the influence of the environment on the transfer of charge and energy in an open quantum system is a problem of significant current interest. In particular, resonant (or near resonant) interactions between environmental degrees of freedom and those inherent to the system are thought to play an important role in numerous physical processes. However, a comprehensive picture of such dynamics is only beginning to emerge due to the complexity of the systems in question. Here, by focusing on a proposed model for olfaction as a vibrationally-activated molecular switch, we explore the detailed effects of the environment on the dynamics of electron transfer (ET) in an open quantum system, aiming to gain physical insight into vibrationally-assisted transport processes more generally.

In fact, obtaining a deep understanding of olfaction, the mechanism for which is still being actively debated is an important problem in its own right for both fundamental science and industry. The prevailing theory, known as the lock-and-key model, explains how the odorant size and shape can provide discrimination in the receptor. However, this theory does not give a straightforward explanation of why it may be possible to distinguish the scents of some very similar odorants, for example between those that are deuterated and non-deuterated. It was suggested as early as 1938 that sensing the vibrational spectra of molecules via electron transfer, could play an important role in olfaction, supplementing (rather than replacing) the existing lock-and-key model. Recent work — constructing and exploring model systems that capture the important physical processes — has shown that this is indeed a viable proposition. The suggested mechanism, which harnesses vibrationally-assisted ET in a similar manner to inelastic electron tunneling spectroscopy can be viewed as an example of a molecular switch, wherein specific vibrations of an external molecule actuate the receptor and lead to a pronounced electron flow. Detection via the frequency of vibrations could help to discern two molecules that are otherwise very similar. However, the need for clear discrimination of the difference in ET dynamics in the presence and absence of the odorant imposes certain design principles on the molecular switch, which may or may not lead to the employment of quantum phenomena to optimise performance.

Previously, a receptor-odorant spin-boson model was introduced to describe the vibrationally-assisted ET process at the heart of the proposed mechanism. Using an analysis based on the semiclassical Marcus-Jortner (MJ) formula for the ET rate, it was shown that for certain parameter values the rates for ET in the presence and absence of the odorant can differ drastically. This explains how the ET process could help in molecular recognition via sensing of vibrational spectra; sensitivity of the switch to the presence or absence of the odorant can be understood as a significant difference in typical timescales, or more generally in the population dynam-
ics, for processes with or without the odorant coupled to the receptor. Additionally, in Refs. 27 and 29 further evidence supporting a vibrationally-assisted mechanism was obtained from sophisticated quantum chemistry calculations.

Inspired by the possibility of vibrational sensing in olfaction, we focus here on the physical model of a molecular switch tuned for frequency detection. We go beyond the MJ approach to look at both frequency selectivity and detailed dynamics in a variety of regimes in which a semiclassical analysis breaks down. Starting from a microscopic Hamiltonian describing the odorant (as an oscillator), receptor (as a donor-acceptor two-level system), and environment (as a collection of independent oscillators), we derive a polaron-representation master equation for the ET process. From this we may extract the relevant ET rates, extending previous analyses to a broader set of parameters and looking in more detail at the assumptions required for the MJ rates to be valid; in fact, these rates arise naturally from our master equation in the semiclassical limit where the temperature is high compared to the energy scales of the environment. In general, we find that the dynamics of donor-acceptor (DA) populations predicted by our master equation can differ considerably from that given by the simpler MJ rates. The main reason for this discrepancy is the assumption inherent to the MJ analysis of exponential ET from donor to acceptor, which we find to be invalid for a wide set of parameter values. Significantly, this includes regimes that have been suggested as being relevant for the olfactory process.

Our approach also has the crucial advantage of allowing us to additionally incorporate the effects of dissipation on the odorant mode, as it is treated explicitly in our formalism. We shall show that by introducing sufficiently strong mode dissipation, it is possible to bring the DA dynamics derived from our master equation into a simpler exponential form. However, even within this strongly dissipative regime, our master equation predictions can still differ markedly from the semiclassical MJ theory, depending upon the specific nature of the environment experienced by the DA pair. In particular, we show that while in the MJ case the receptor is very sensitive to the presence or absence of the odorant, it is far less so to the specific odorant vibrational frequency. We find, however, that the frequency resolution can be enhanced by considering environments which contain components of similar or larger energy to that set by the ambient temperature, i.e. by working outside the semiclassical limit. More generally, we show when considering odorant mode dissipation both the sensitivity of the switch to the presence or absence of the odorant, and to the resonance conditions between the odorant and the DA pair, can be significantly amplified in comparison to the dissipationless case. We thus find that odorant dissipation plays a constructive role in enhancing the vibrational sensing capabilities of our molecular switch.

II. MODEL OF OLFACTION

Unfortunately, few details are known about olfactory receptors and their properties. Some of the receptors are metalloproteins, which may help to explain how ET and donation could work in practice. Receptors most likely have rich electronic structures, but here, as is common, we assume that there exist specific electronic states that can be identified as a DA pair, with other levels well separated in energy. We model the vibrationally-assisted ET process using a spin-boson Hamiltonian. The DA pair is coupled to an environment represented by a bath of harmonic oscillators (which includes the vibrational degrees of freedom of the receptor) and to the odorant (when present in the receptor). The odorant is modelled as a single mode harmonic oscillator, though this could also be extended to a set of modes. Our Hamiltonian thus takes the form

\[ H = \epsilon_D |D\rangle\langle D| + \epsilon_A |A\rangle\langle A| + V(|A\rangle\langle D| + |D\rangle\langle A|) + \omega_0 a^\dagger a + (\gamma_D |D\rangle\langle D| + \gamma_A |A\rangle\langle A|)(a^\dagger + a) + \sum_k [\omega_k b_k^\dagger b_k + (\gamma_{kD} |D\rangle\langle D| + \gamma_{kA} |A\rangle\langle A|)(b_k^\dagger + b_k)]. \]

(1)

Here, \( X \), with \( X = D, A \), represents the donor (D) and acceptor (A) electronic state with on-site energy \( \epsilon_X \), and \( V \) refers to the tunnel coupling. The odorant molecular mode, with creation (annihilation) operator \( a^\dagger (a) \), has frequency \( \omega_0 \) and is coupled to the DA pair via \( \gamma_X \). The environmental oscillators, with creation (annihilation) operators \( b_k^\dagger (b_k) \) for modes of frequency \( \omega_k \), couple to the receptor electronic sites via \( \gamma_{kX} \). Transfer of an electron gives rise to changes in the local electric field and justifies the present form of interaction between the oscillators and the DA pair. Specific parameter values will be discussed below.

In Refs. 24 and 27 MJ formulas were employed to define two types of ET rate: elastic, in the absence of the odorant, and inelastic, in which the odorant is present. These rates were calculated using Fermi's golden rule, wherein the tunnelling term \( V \) is treated as a perturbation. This naturally gives rise to a representation of the receptor-odorant-environment basis in terms of displaced oscillator states — as can be seen from Eq. (1) by setting \( V = 0 \) — between which it is assumed that incoherent ET occurs. This is, in fact, a reflection of the polaron picture that we shall discuss in the next section. In Ref. 24 typical ET timescales were estimated to be \( \sim 100 \) ns (elastic) versus \( \sim 1 \) ns (inelastic), predicting the inelastic process to be much faster than the elastic one, as required for discriminating between the presence and the absence of the odorant. Ref. 27 also discusses a wider range of parameters in which a separation of timescales between the elastic and inelastic processes can be obtained.

Here, rather than following a Fermi golden rule calculation, we shall look instead at receptor ET dynamics and issues such as odorant vibrational frequency resolution.
from the perspective of the master equation formalism. This includes the MJ rate analysis as a limiting case, but can also go well beyond the restricted regime of validity of such an approach.

A. Estimated parameters

For consistency with the published literature, we follow the estimation of parameters presented in Refs. [23] and [27]. As mentioned, the relevant receptor electronic structure is not known, and neither are the typical energies $\epsilon_X$. In common with previous studies, we assume that the energy gap $\epsilon_D - \epsilon_A$ is relatively close to resonance with the odorant vibrational frequency $\omega_0$. We shall, however, explore an effective window of frequencies away from resonance to study the issue of molecular frequency recognition, i.e. we would like to explore whether the switch is sensitive merely to the presence or absence of the odorant, or to its particular vibrational frequency as well. Typical values for $\omega_0$ are in the range of 70 – 400 meV, and we choose $\epsilon_D - \epsilon_A = 200$ meV for the DA energy gap. The receptor binding pocket is thought to be around 5 – 15 Å in size, which leads to an estimate for the DA tunnel coupling of $V \sim 1$ meV [24]. Increasing $V$ acts to enhance the ET rate in the absence of the odorant in the receptor, which is disadvantageous as far as the switching mechanism is concerned. Keeping $V$ small in comparison to other system parameters is therefore well motivated physically. Estimates of the coupling between the DA pair and the odorant mode, and of the reorganization energy of the multi-mode environment, have been given as $(\gamma_D - \gamma_A)^2/\omega_0^2 \sim 0.01$ and $\lambda \sim 30$ meV, respectively. Here, we shall explore variations in the DA-environment coupling strength through the reorganisation energy, focussing on the range $\lambda \sim 10 – 60$ meV. Previously, the detailed properties of the environment, such as the spectral density,

$$J(\omega) = \sum_k (\gamma_{kD} - \gamma_{kA})^2 \delta(\omega - \omega_k),$$

(2)

were not discussed, as they do not enter the semiclassical MJ rates. They are, however, important for our more general analysis. We choose to work with an Ohmic environment, $J(\omega) \propto \omega$ as $\omega \to 0$, with a characteristic high frequency cut-off $\omega_c$, since in the absence of more detailed information, it straightforwardly reproduces the results of Refs. [23] and [27] in the semiclassical limit ($\beta \omega_c \ll 1$, where $\beta = 1/k_BT$ is the inverse temperature). We take the cut-off to be exponential, leading to the following spectral density defined also in terms of the reorganisation energy:

$$J(\omega) = \lambda \frac{\omega}{\omega_c} e^{-\omega/\omega_c}.$$ 

(3)

We shall vary the ratio $\omega_c/k_BT$ from low to high in order to explore the effect of widening the range of frequencies within the environment that can interact with the receptor DA pair. We assume that $T = 300$ K throughout, and summarise the model parameters in Table I.

| Parameter | Value | Parameter | Value |
|-----------|-------|-----------|-------|
| $\epsilon_D - \epsilon_A$ | 200 meV | $V$ | 1 meV |
| $\omega_0$ | 100 – 300 meV | $\lambda$ | 10 – 60 meV |
| $(\gamma_D - \gamma_A)^2/\omega_0^2$ | 0.01 | $\omega_c$ | $k_BT/k_BT$, $k_BT$, $2k_BT$ |
| $T$ | 300 K | $k_BT$ | 25.85 meV |

Table I. Table of parameter values used in this article.

III. POLARON MASTER EQUATION

As noted, for our system to act as an effective molecular switch, the Hamiltonian parameters should be such that unwanted transitions from donor to acceptor are avoided when the odorant is absent. This requires the tunnel coupling $V$ to be small compared to other energy scales in the problem. In this regime, it is convenient to move into a polaron transformed reference frame to remove the linear coupling terms in Eq. (1). Provided $V$ is indeed small, then perturbative expansions in the transformed basis are valid over a much wider range of system-environment coupling strengths than those in the untransformed case [19,59]. Let us consider the (unitary) polaron transformation $U = e^{-(S_A + S_B)}$ acting on our Hamiltonian, where

$$S_A = (u_D|D\rangle\langle D| + u_A|A\rangle\langle A|)(a^\dagger - a),$$ 

(4)

$$S_B = \sum_k (\alpha_{kD}|D\rangle\langle D| + \alpha_{kA}|A\rangle\langle A|)(b_k^\dagger - b_k),$$ 

(5)

with $u_X = \gamma_X/\omega_0$ and $\alpha_{kX} = \gamma_{kX}/\omega_k$. Note that we have transformed with respect to both the DA-environment and DA-odorant interaction terms here. By doing this, we shall end up with odorant degrees of freedom in the perturbative terms of our subsequent master equation. In the Appendices we briefly discuss an alternative approach in which the DA-odorant interaction is treated fully non-perturbatively. However, for the parameter regimes considered in this work the two approaches are always in agreement.

The polaron transformed Hamiltonian takes the form $H_{SP} = U^\dagger HU = H_{SP} + H_B + H_{IP}$, where

$$H_{SP} = \epsilon_D'|D\rangle\langle D| + \epsilon_A'|A\rangle\langle A| + \omega_0 a^\dagger a,$$

(6)

$$H_B = \sum_k \omega_k b_k^\dagger b_k,$$

(7)
and
\[ H_{IP} = V(|D⟩⟨A|A_+B_+ + |A⟩⟨D|A_-B_-). \] (8)

Here, \( \epsilon'_X = \epsilon_X - \omega_0u_X^2 - \sum_k \omega_k\alpha^2_k \) is the polaron-shifted on-site energy, and \( A_\pm = D(\pm(u_D - u_A)) \) and \( B_\pm = \Pi_k D_k(\pm(\alpha_{KD} - \alpha_{KA})) \) are the new oscillator interaction operators, written in terms of the displacement operators \( D(u) = e^{u_1A^\dagger - u^*_A} \) and \( D_k(\alpha_k) = e^{\alpha_k b^\dagger_k - \alpha_k b_k} \), respectively. Note that the polaron transformation leaves the operators \( |D⟩⟨D| \) and \( |A⟩⟨A| \), required for calculating DA populations, unchanged.

Tracing out the environment and treating the perturbative term \( H_{IP} \) up to second order in the standard Born-Markov approximations, we obtain a master equation in the polaron frame interaction picture (with respect to \( H_{SP} + H_B \)), given by
\[ \frac{d\tilde{\rho}_{SP}(t)}{dt} = -V^2 \int_0^\infty d\tau \left\{ \langle [A]|D⟩⟨A_-|t - \tau⟩\tilde{\rho}_{SP}(t)e^{-i\epsilon\tau} + \langle [D]|A⟩⟨A_+|t - \tau⟩\tilde{\rho}_{SP}(t)e^{i\epsilon\tau} \right\} C(\tau) + \text{H.c.}, \] (9)
see Appendix A for further details. Here, \( \tilde{\rho}_{SP}(t) \) is the reduced density operator describing the DA pair and odorant mode. The bath correlation function is
\[ C(\tau) = e^{-\int_0^\infty d\omega \frac{d\omega}{\beta}\coth(\beta\omega/2)\sin\omega\tau}, \] (10)
with \( \epsilon = \epsilon'_D - \epsilon'_A \) now the DA energy gap.

IV. ELECTRON TRANSFER DYNAMICS

Having derived our polaron master equation, we shall use it below to investigate the receptor ET dynamics beyond a MJ rate analysis. First, however, we show how the MJ rates arise from our master equation in the semiclassical limit, for both elastic and inelastic processes.

A. Odorant absent

Let us consider the population transfer from donor to acceptor for the case in which the odorant is absent, meaning that \( A_\pm(t) = \mathbb{1} \) in Eq. (9). We can then easily derive rate equations governing the donor \( (p_D(t)) \) and acceptor \( (p_A(t)) \) population dynamics. Our interest lies in the rates that appear in these equations
\[ \Gamma(\epsilon) = \int_{-\infty}^{\infty} d\epsilon e^{\pm i\epsilon\tau} C(\tau), \] (11)
where, by defining \( \Gamma_{DA} = V^2 \Gamma(\epsilon) \) and \( \Gamma_{AD} = V^2 \Gamma(-\epsilon) \), we obtain
\[ \dot{p}_D(t) = -\Gamma_{AD}p_D(t) + \Gamma_{DA}p_A(t), \]
\[ \dot{p}_A(t) = -\Gamma_{AD}p_A(t) + \Gamma_{DA}p_D(t). \]
In the limit that \( \Gamma_{DA} \gg \Gamma_{AD} \), these equations define exponential transfer of population from donor to acceptor at (approximately) the rate \( \Gamma_{DA} \), which we write as
\[ \Gamma_{DA} = V^2 \int_{-\infty}^{\infty} d\epsilon e^{i\epsilon\tau} e^{-\epsilon^2/\beta}, \] (12)
where
\[ \varphi(\tau) = \int_{0}^{\infty} d\omega J(\omega) \left[ (1 - \cos\omega\tau) \coth(\beta\omega/2) + i\sin\omega\tau \right]. \] (13)
For a low-frequency environment in which \( \beta\omega_c \ll 1 \), we may derive a simple form for \( \Gamma_{DA} \) which turns out to be the same as the MJ rate. Taking the spectral density defined in Eq. (9) and expanding \( \coth(\beta\omega/2) \approx 2/\beta \omega \) in Eq. (13), we find
\[ \varphi(\tau) \approx \frac{\lambda}{\beta\omega_c^2} [\omega_c(\epsilon^2 + 2\epsilon\tau) + \ln(1 + \omega_c^2\epsilon^2)]. \] (14)
In the regime in which we are presently interested, \( e^{-\varphi(\tau)} \) is strongly peaked around \( \tau = 0 \), such that we may expand \( \varphi(\tau) \) to second order in \( \tau \) to give
\[ \varphi(\tau) \approx i\lambda\tau + \frac{\lambda^2}{\beta}. \] (15)
With these assumptions we can write
\[ \Gamma_{DA} \approx V^2 \int_{-\infty}^{\infty} d\epsilon e^{i(\epsilon - \lambda)\tau} e^{-\epsilon^2/\beta}, \]
\[ = 2\pi V^2 \frac{1}{\sqrt{4\pi k_BT\lambda}} \exp \left[ -\frac{(\epsilon - \lambda)^2}{4k_BT\lambda} \right]. \] (16)
which agrees with the elastic rate (odorant absent) presented in Ref. [24] when \( \alpha_{KD} = -\alpha_{KA} \) is assumed, and as a consequence \( \epsilon \rightarrow \epsilon_D - \epsilon_A \). We apply this constraint on \( \alpha_{X} \) throughout the paper, although little modification would be required to account for the more general case. Choosing \( \lambda = 30 \text{ meV} \), and other parameters as outlined in Table I, we obtain \( \Gamma_{DA} = 5.67 \times 10^{-6} \text{ meV from Eq. (16)} \), which corresponds to \( \tau_{DA} = 1/\Gamma_{DA} = 116 \) ns as the DA transfer time in the absence of the odorant.

Of course, the limit \( \beta\omega_c \ll 1 \) used to derive Eq. (16) may not always be met, in which case we can use the more general form of Eq. (12) to define the DA elastic transfer rate. Importantly, this allows us to discuss lower temperatures and larger environmental cut-offs than those to which the MJ rates apply.

B. Odorant present

A similar rate can also be derived when the odorant is present in the receptor. In this situation, we must deal with a more complex system, as the reduced density
operator (after tracing out the environmental degrees of freedom) now encompasses both the two-level DA pair and the odorant harmonic oscillator. Obtaining general equations of motion for the DA populations becomes significantly more involved. However, this is unnecessary if we instead look at ET rates between specific states of the combined DA-odorant system. Let us assume that we initialize the system in the state \(|D,0\rangle\) (electron on the donor, odorant in its ground-state \(|0\rangle\)) and we are interested in the rate of ET to a state of the form \(|A,n\rangle\), where \(|n\rangle\) is an arbitrary Fock (number) state of the odorant. We are thus considering situations in which the receptor population transfer \(|D\rangle\to|A\rangle\) is accompanied by excitation of the odorant vibrational mode \(|0\rangle\to|n\rangle\), which may or may not act to enhance the rate associated with the process.

We return to the master equation [Eq. (9)] to derive an expression for the dynamics of the population of the acceptor and a given Fock state \(|n\rangle\) of the odorant, 
\[ \rho_{A,n} = \text{tr}_{S,O}(|A,n\rangle\langle n,A|\rho_{SP}(t)) = \langle n,A|\rho_{SP}(t)|A,n\rangle, \]
where the trace is taken over both the odorant (O) and the DA pair (S) degrees of freedom. Decomposing the DA-odorant density operator as 
\[ \hat{\rho}_{SP}(t) = \sum_{X,X',l,m} \hat{\rho}_{XIX'm}(t)|X,l(X',m)|, \]
where \(X, X' \in \{D,A\}\) and \(l, m\) are odorant Fock states, allows us to identify the different contributions to the change in population of the state \(|A,n\rangle\). In particular, if we assume that the only donor-odorant state of interest is one with no odorant excitations, \(|D,0\rangle\) — valid when we initialise the system in this state and energy splittings are large enough to suppress transitions to any other donor-odorant states — we may then define a rate of transfer \(|D,0\rangle \to |A,n\rangle\) as 
\[ \Gamma_{D0A_n} = \int_{-\infty}^{\infty} \langle e^{i\tau C} (\langle n|A_{-}(t-\tau)|0\rangle\langle 0|A_{+}(t-\tau)|n\rangle e^{-i\tau C^*} (\langle n|A_{-}(t-\tau)|0\rangle\langle 0|A_{+}(t-\tau)|n\rangle) \rangle V^2. \]

Using \(\langle n|D(\alpha)|0\rangle = (\alpha^n/\sqrt{n!})e^{-|\alpha|^2/2}\), it is straightforward to calculate the expectation values of \(A_{\pm}(t)\). We then arrive at 
\[ \Gamma_{D0A_n} = \frac{V^2(u_D - u_A)^n e^{-|u_D-u_A|^2}}{n!} \times \int_{-\infty}^{\infty} \exp (\frac{(e - n\omega_0 + \lambda)^2}{4k_BT\lambda}), \]
which generalises Eq. (12) in the presence of the odorant (\(\Gamma_{DA} = \Gamma_{D0A}\)). At this point we can again take the limit \(\beta \omega_c \ll 1\), and follow the same steps that led us from Eq. (12) to Eq. (16) to find 
\[ \Gamma_{D0A_n} \approx \frac{2\pi V^2}{n\sqrt{4\pi k_BT\lambda}} (\frac{u_D - u_A)^n e^{-|u_D-u_A|^2}}{4k_BT\lambda} \times \exp \left[ -\frac{(e - n\omega_0 + \lambda)^2}{4k_BT\lambda} \right]. \]

Once again, this result for the inelastic ET rates \((n > 0)\) agrees with the MJ form found in Ref. [23] when we assume \(u_D = -u_A\) and \(\alpha_{LD} = -\alpha_{LA}\), such that \(e \to \epsilon_D - \epsilon_A\). Using the values in Table I choosing \(A = 30\) meV and \(\omega_0 = \epsilon_D - \epsilon_A\), we obtain \(\Gamma_{D0A1} = 4.71 \times 10^{-4}\) meV, which corresponds to a transfer time of \(\tau_{D0A1} = 1/\Gamma_{D0A1} = 1.4\) ns. This is far shorter than the 116 ns transfer time found above in the absence of the odorant, as required for a viable molecular switch. Additionally, if we take the same parameter values and look at the rate for the two-phonon transition we then find \(\Gamma_{D0A2} = 1.24 \times 10^{-12}\) meV, and a corresponding time \(\tau_{D0A2} = 5.3\) s, confirming that the single-phonon process is dominant within this treatment. As before, in situations in which the limit \(\beta \omega_c \ll 1\) does not apply, we may instead use Eq. (18) to define the inelastic rates, again generalising the MJ rates to a wider range of parameters.

Of course, our master equation also allows us to calculate the reverse rates \(\Gamma_{A_nD}\) (as well as other rates such as \(\Gamma_{DnDm}\) and \(\Gamma_{AnAm}\), which do not play a major role). Following a derivation similar to that leading to Eq. (18), we find 
\[ \Gamma_{A_nD} = \frac{V^2(u_D - u_A)^2 n!}{n!} \times \int_{-\infty}^{\infty} \exp (\frac{(-e-n\omega_0)^2}{4k_BT\lambda}), \]
and, in the limit \(\beta \omega_c \ll 1\), 
\[ \Gamma_{A_nD} \approx \frac{2\pi V^2}{n\sqrt{4\pi k_BT\lambda}} (\frac{u_D - u_A)^n e^{-|u_D-u_A|^2}}{4k_BT\lambda} \times \exp \left[ -\frac{(e - n\omega_0 + \lambda)^2}{4k_BT\lambda} \right]. \]

Notably, the single-phonon reverse transfer rate, \(\Gamma_{A1D0}\), is equal to the donor-to-acceptor rate, \(\Gamma_{D0A1}\), when the odorant is resonant with the receptor (\(\omega_0 = \epsilon_D - \epsilon_A\)). We shall see below that this has important implications for the dynamics of the DA pair over a wide range of parameters, often invalidating the treatment of inelastic ET as being a one-way process.

C. Master equation dynamics versus ET rates

We are now in a position to compare our master equation with a model in which the donor population simply decays with the ET rates calculated in the previous section. Specifically, we would like to know how reliably we can apply a rate analysis, such as the MJ evaluation employed in previous studies [23,27], to parameter regimes estimated to be relevant to the olfactory process. We have already seen that with the odorant present, the possibility of transfer from acceptor to donor cannot be neglected when close to resonance. This is especially true when the inelastic process dominates, as the reverse rate in the elastic case is suppressed by a factor
Figure 1. **Donor and acceptor population dynamics.** Comparison of the donor, $p_D(t)$ (black, $p_D(0) = 1$), and acceptor, $p_A(t)$ (red, $p_A(0) = 0$), population dynamics as predicted by the polaron master equation (solid lines, calculated using 3 odorant states to ensure numerical convergence) and by the total donor-to-acceptor ET rate $\sum_{n=0}^{\infty} \Gamma_{DA,n}$ from Eq. (18) (dashed lines). The reorganisation energy $\lambda$ increases from left to right: $\lambda = 15$ meV in the left column, $\lambda = 30$ meV in the middle column and $\lambda = 60$ meV in the right column. The bath cut-off frequency $\omega_c$ increases from top to bottom, with $\omega_c = k_B T/10$ for panels (i - iii), $\omega_c = k_B T$ for panels (iv - vi) and $\omega_c = 2k_B T$ for panels (vii - ix). The odorant frequency is chosen to be resonant with the DA pair, i.e. $\omega_0 = \epsilon_D - \epsilon_A = 200$ meV, and other parameters are as listed in Table I.

~ $\exp \left[ - (\epsilon_D - \epsilon_A) \lambda / k_B T \right]$. We thus expect exponential decay from donor to acceptor to hold only when the ET is mediated primarily by the environment ($n = 0$), rather than by the odorant itself.

This intuition is borne out in Fig. 1, which shows a comparison between the DA population dynamics (in the presence of the odorant) calculated from our master equation (9), and predicted by the ET rates of Eq. (18). The receptor is taken to be initialised in the donor state, with the odorant mode and the environment in thermal states, of $H_O = \omega_0 a^\dagger a$ and of $H_B$, respectively. As can clearly be seen, the ET dynamics can differ considerably between the two methods. As expected, the best agreement is found for large reorganisation energies (right column), where elastic transfer due to the environment dominates over inelastic transfer via the odorant. On the other hand, when the odorant does play a significant role in mediating the ET, then the agreement is generally poor, with our master equation predicting DA dynamics that cannot be fitted by a single exponential form. This is particular true in the low-frequency environment limit ($\omega_c \ll k_B T$) shown in panels (i) and (ii), to which the MJ rates would usually be assumed to apply. These discrepancies suggest, in fact, that it is the combination of population accumulation within the odorant and the inherent competition between forward and backward processes that limits the timescale for complete transfer from donor to acceptor in the master equation.

We can thus gain further insight by looking at the population dynamics of the odorant mode. In Fig. 2 we plot the evolution of the lowest two odorant states as predicted by our master equation, for the same parameter sets as in Fig. 1. Note that other levels are never significantly populated, since the total initial energy is insufficient to further excite the mode. In the cases in which the odorant-assisted (inelastic) rate dominates, excitation is quickly transferred from the DA pair to the odorant. The electron is then equally likely to be found on the acceptor (having deposited energy to the odorant mode) as it is on the donor. Due to the equality of the forward and backward rates on resonance, the only way energy can now exit the system, to allow full ET to the acceptor, is into the environment, the timescale for which is dependent upon the reorganisation energy and cut-off frequency. Since the rate analysis that leads to the dashed curves in Fig. 1 ignores the possibility of reverse acceptor-to-donor transfer, it consequently overestimates the inelastic transfer rate.

Taking the Hamiltonian of Eq. 1 as a starting point, the receptor dynamics we find from our master equation suggests that the timescale for complete inelastic ET is not as rapid as that implied by the MJ rates. This clearly has the potential to compromise the sensitivity of the olfactory switch, though it could be argued that any inelastic population transfer occurring on a short enough timescale could still lead to detection of the odorant, al-
Odorant Ê0, Ê1 population

Figure 2. Odorant dynamics. Populations of the odorant ground state, \( p_{|0\rangle\langle 0|}(t) \) (black, \( p_{|0\rangle\langle 0|}(0) = 1 \)), and first excited state, \( p_{|1\rangle\langle 1|}(t) \) (red, \( p_{|1\rangle\langle 1|}(0) = 0 \)), calculated from Eq. (9). The reorganisation energy \( \lambda \) increases from left to right: \( \lambda = 15 \text{ meV} \) in the left column, \( \lambda = 30 \text{ meV} \) in the middle column and \( \lambda = 60 \text{ meV} \) in the right column. The bath cut-off frequency \( \omega_c \) increases from top to bottom, with \( \omega_c = k_B T/10 \) for panels (i - iii), \( \omega_c = k_B T \) for panels (iv - vi) and \( \omega_c = 2k_B T \) for panels (vii - ix). The odorant frequency is \( \omega_0 = \epsilon_D - \epsilon_A = 200 \text{ meV} \). Populations of higher Fock states are negligible at all times.

V. DISSIPATION ASSISTED ELECTRON TRANSFER

Given that, when present, the odorant is considered to be in the vicinity of the DA pair, it is reasonable to assume that it too interacts with the surrounding environment. Assuming a linear coupling form we can model the effects of the resulting mode dissipation in a straightforward manner, once Born-Markov and rotating wave approximations are made, by introducing an additional Lindblad term to the right-hand-side of our master equation (9)

\[
\mathcal{L}_{\text{diss}}[\hat{\rho}_{SP}] = -\frac{\gamma_0}{2}N_0(\alpha^d\alpha^b\rho_{SP} - 2\alpha^d\rho_{SP}\alpha^b + \rho_{SP}\alpha^b\alpha^d)
- \frac{\gamma_0}{2}(N_0 + 1)(\alpha^d\alpha^b\rho_{SP} - 2\alpha^d\rho_{SP}\alpha^b + \rho_{SP}\alpha^b\alpha^d).
\]

Here, \( \gamma_0 \) is the odorant dissipation rate and \( N_0 = (e^{\omega_0/k_B T} - 1)^{-1} \) is the phonon occupation number.

In Fig. 3 we investigate the effect of adding dissipation to the odorant. Specifically, we show a comparison of the dynamics in the absence of dissipation (\( \gamma_0 = 0 \), dotted curves), for moderate dissipation (\( \gamma_0 \sim \Gamma_{DA,1} \), dashed curves) and for strong dissipation (\( \gamma_0 \gg \Gamma_{DA,1} \), solid curves). In the limit of large dissipation, we see that the behaviour of the DA populations is consistent with that given by the transfer rates of Eq. (18), and the description of the dynamics as an exponential ET process from donor to acceptor once again becomes valid (note the agreement between the points and solid curves). Importantly, we can also see that adding mode dissipation actually assists the transfer of population from donor to acceptor. In fact, the timescale for complete ET is substantially reduced as the dissipation rate is increased, thus ensuring a greater variance between the transfer time in the presence and absence of the odorant. In this manner, mode dissipation is seen to be beneficial for the molecular switching process, allowing easier discrimination in the receptor between the cases with and without the odorant present.

A. Frequency resolution at strong dissipation

We can think of the olfactory model outlined herein in terms of a vibrational spectrometer, and one of the principle figures of merit for any spectroscopic device is its frequency resolution. The more sensitive the individual receptors are to resonance conditions between the DA pair and odorant, the better they will be able to distin-
Figure 3. Effect of odorant mode dissipation. Donor $p_D(t)$ (black, $p_D(0) = 1$) and acceptor $p_A(t)$ (red, $p_A(0) = 0$) populations as predicted by Eqs. (9) and (22) for different odorant dissipation rates: $\gamma_0 = 0$ (dotted curves), $\gamma_0 = 1$ ms$^{-1}$ (dashed curves), and $\gamma_0 = 1000$ ms$^{-1}$ (solid curves). Exponential ET dynamics governed by the rates given in Eq. (18), without mode dissipation, are also shown for comparison (points). The bath cut-off frequency $\omega_c$ increases from top to bottom, with $\omega_c = k_B T / 10$ in panel (i), $\omega_c = k_B T$ in panel (ii) and $\omega_c = 2k_B T$ in panel (iii). The reorganisation energy is $\lambda = 15$ meV in each case and the odorant frequency is taken to be on resonance with the DA splitting, $\omega_0 = \epsilon_D - \epsilon_A = 200$ meV.

Figure 4. Switch frequency resolution. Contour plots of $r = (\Gamma_{\text{tot}} - \Gamma_0) / (\Gamma_{\text{tot}} + \Gamma_0)$ as a function of odorant frequency $\omega_0$ and bath reorganisation energy $\lambda$. Top: $\omega_c = k_B T / 10$ (corresponding to the MJ limit). Middle: $\omega_c = k_B T$. Bottom: $\omega_c = 2k_B T$. Other parameters are given in Table I. Light regions correspond to $r \to 1$ (good odorant discrimination) and the darkest regions correspond to $r \to 0$ (poor discrimination). The red dashed lines shows the DA energy splitting.

To distinguish the vibrational spectra of different molecules. To explore this aspect in our model, in Fig. 4 we map out the ratio $r = (\Gamma_{\text{tot}} - \Gamma_0) / (\Gamma_{\text{tot}} + \Gamma_0)$ of tunneling rates as a function of odorant frequency $\omega_0$ and bath reorganisation energy $\lambda$. Here, the definition of $\Gamma_{\text{tot}}$ as the tunneling rate in the presence of the odorant and $\Gamma_0$ as the rate in its absence is made possible by the strong mode dissipation, $\gamma_0 = 1000$ ms$^{-1}$, which ensures exponential ET from donor to acceptor as just demonstrated. The top panel corresponds to the regime in which $\omega_c \ll k_B T$, therefore representing the behaviour predicted by the MJ rates of Eqs. (16) and (19), while the other panels encompass parameter ranges outside the MJ limit.

We see that in each plot there clearly exists a frequency window for which the tunneling rate is enhanced in the
It is worth noting also that the validity of the results depend between the presence and the absence of the odorant. This is illustrated in Fig. 5 which shows the ratio of the transfer time (90% population on the acceptor site) in the absence of the odorant to that in its presence for different levels of odorant dissipation. We use the transfer time to allow a meaningful comparison here, since there is no single rate that accurately describes the dynamics outside the strongly dissipative case. As the dissipation rate is decreased, the height of the peak also decreases, while its width remains similar (dotted curve) until the dissipation ceases to play a role (dashed curve). Thus, as the mode dissipation is weakened, the receptor frequency resolution is severely compromised, as well as its capability to distinguish between the cases with and without the odorant.

VI. SUMMARY

We have developed a dynamical theory of a molecular switch and applied it to investigate vibrationally-assisted ET in the context of a proposed olfactory process. We have shown that the dynamics of the olfactory receptor can differ dramatically from that predicted by semiclassical MJ theory, even for a low-frequency environment. The ET dynamics can, however, be brought back into agreement with a simpler rate analysis — though not generally the MJ rates unless the semiclassical limit is also taken — provided that strong dissipation is allowed to act on the odorant vibrational mode. This results in an enhanced switching with respect to the dissipationless case. Furthermore, we have found that low frequency environments, to which the MJ rates apply under strong odorant dissipation, do not provide good odorant frequency resolution in the ET rates. By modifying environmental parameters to move beyond the semiclassical limit it is, nevertheless, possible to substantially increase this resolution and thus select for odors of a particular frequency.

While our present model is motivated by the problem of describing olfaction in biological systems, it actually corresponds to a wide variety of physical settings in which vibrationally-assisted transport processes are important. Examples include nano-mechanical oscillators coupled to two-level systems, such as quantum dots and superconducting qubits, as well as other biological systems such as the photosynthetic reaction centre in certain organisms. Our results may also be especially relevant for the development of artificial molecular sensors, which could use the principles we have described in their design to aid in distinguishing chemical species based on their vibrational spectra.
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APPENDIX

A. Derivation of the master equation

In this Appendix we outline the general steps required to derive our polaron master equation. We start the analysis by writing the polaron-transformed Hamiltonian as (see Sec. III)

\[ H_P = U^\dagger H U = H_{SP} + H_B + H_{IP}, \]  

and moving into the interaction picture with respect to \( H_{SP} \) and \( H_B \). To derive the master equation we focus on the interaction part of the Hamiltonian which takes the form

\[
\tilde{H}_{IP}(t) = V \{ |D\rangle \langle A| \} A_+(t) B_+(t) + |A\rangle \langle D| A_-(t) B_-(t) \] 
\[ = \sum_j S_j(t) B_j(t), \]  

(24)

with \( j = \{+, -\} \) and

\[
S_+(t) = V |D\rangle \langle A| e^{i\epsilon t} A_+(t), \]
\[ S_-(t) = V |A\rangle \langle D| e^{-i\epsilon t} A_-(t). \]  

(25)

By considering the Liouville-von Neumann equation of motion for the density matrix of the whole system in the interaction picture, \( \tilde{\chi}_P(t) \), and tracing over the environment, we find:

\[
\frac{d}{dt} \tilde{\rho}_{SP}(t) = -i \int_0^t d\tau \text{tr}_B \left\{ \left[ \tilde{H}_{IP}(\tau), \tilde{H}_{IP}(s), \tilde{\chi}_P(s) \right] \right\}. 
\]  

(26)

Here, we have substituted in the solution to the full Liouville-von Neumann equation on the right-hand-side and have used \( \text{tr}\{[\tilde{H}_{IP}(\tau), \chi_P(0)]\} = 0 \). We then make the standard Born-Markov approximations. We assume that the evolution of the system is time local, such that it depends only on its current state, and that in the transformed frame the effective interaction ‘strength’ is small, so that we may write \( \tilde{\chi}_P(t) \simeq \tilde{\rho}_{SP}(t) \otimes \rho_{th} \) at all times, where \( \rho_{th} \) is a thermal state of the environment. The Markov approximation amounts to replacing the state at time \( s \) in the integrand of Eq. (26) with the state at time \( t \), changing variables such that\( s \to t - \tau \), and taking the integral to infinity:

\[
\frac{d}{dt} \tilde{\rho}_{SP}(t) = -i \int_0^\infty d\tau \times \text{tr}_B \left\{ \left[ \tilde{H}_{IP}(t), \tilde{H}_{IP}(t - \tau), \tilde{\rho}_{SP}(t) \rho_{th} \right] \right\}. 
\]  

(27)

In terms of the operators \( S_{\pm}(t) \) this now reads

\[
\frac{d}{dt} \tilde{\rho}_{SP}(t) = -\sum_{j,j'} \int_0^\infty d\tau \times \left\{ (|S_j(t), S_{j'}(t - \tau)\tilde{\rho}_{SP}(t)|) C_{jj'}(\tau) + |\tilde{\rho}_{SP}(t) S_{j'}(t - \tau), S_j(t)| C'_{jj'}(-\tau) \right\}, 
\]  

(28)

where

\[
C_{jj'}(\tau) = \text{tr}_B (B_j(\tau)B_{j'}(0)\rho_B), \]

(29)

and we have used \( [\rho_B, H_B] = 0 \). There are actually two types of correlation function, \( C_{\pm \pm}(\tau) \) and \( C_{\pm \mp}(\tau) \), but one of them vanishes \( (C_{\pm \pm}(\tau) \to 0) \) and the other satisfies \( C_{\pm \mp}(-\tau) = [C_{\pm \mp}(\tau)]^* \). We therefore arrive at our polaron master equation

\[
\frac{d}{dt} \tilde{\rho}_{SP}(t) = -\int_0^\infty d\tau \times \left\{ (|S_+(t), S_-(t - \tau)\tilde{\rho}_{SP}(t)|) + [S_-(t), S_+(t - \tau)\tilde{\rho}_{SP}(t)] C(\tau) + \text{H.c.} \right\}, 
\]

(30)

where we have written \( C(\tau) = C_{\pm \mp}(\tau) \). This is equivalent to Eq. (10) in the main text.

B. A more general master equation approach

Given the parameter regimes studied in this work, a polaron representation for the environmental degrees of freedom is the natural starting point for a perturbative treatment. However, one might worry about its validity when applied to the single mode odorant, as done in Sec. III. Here, we outline a more general approach to deriving a master equation for the ET process that includes the odorant mode directly into the system, rather than in any perturbative terms.

We treat the coupling between the odorant vibrational mode and the DA-pair non-perturbatively and track their combined dynamics explicitly. This is achieved by considering the Hamiltonian \( H'_b = e^{S_b} H e^{-S_b} = H_{SP} + H_B + H_{IP} \), where

\[
H_{SP} = \left( e^{\epsilon_D} |D\rangle \langle D| + e^{\epsilon_A} |A\rangle \langle A| + \omega_0 a^\dagger a \right) + (\gamma_D |D\rangle \langle D| + \gamma_A |A\rangle \langle A|)(a^\dagger + a). 
\]

(31)
We have now performed the polaron transformation only with respect to the bath degrees of freedom, giving an interaction Hamiltonian which is independent of the odorant:

\[ H'_{IP} = V \langle D | A | B_+ + | A | D | B_- \rangle , \]

(32)

cf. Eqs. [6] and [8].

In order to derive the subsequent master equation, we must move into the interaction picture with respect to \( H'_{SP} \). It is helpful, therefore, to find the basis in which \( H'_{SP} \) is diagonal:

\[ H'_{SP} = \sum_{n} E_n' | E_n' \rangle \langle E_n' | . \]

(33)

In practice, this can be done numerically, treating the odorant as a finite dimensional system, where the number of basis (Fock) states used is increased until the master equation dynamics has converged. We then write the interaction Hamiltonian in the interaction picture as

\[ \tilde{H}'_{IP}(t) = S'_+(t)B_+(t) + S'_-(t)B_-(t) , \]

(34)

where

\[ S'_+(t) = (S'_-(t))^\dagger = V \sum_{n,m} e^{-i(E_n - E_m)t} | E_n' \rangle \langle E_n' | \]

\[ \times \langle D | A | 1 \rangle \otimes 1 | E_m' \rangle \langle E_m' | , \]

(35)

and

\[ B_\pm(t) = e^{iH_B t} B_\pm e^{-iH_B t} . \]

We follow the procedure outlined in Appendix A and derive a Born-Markov master equation treating the polaron frame interaction Hamiltonian [Eq. (34)] to second order, but now keeping the odorant mode to all orders. In the polaron frame interaction picture (with respect to \( H'_{SP} + H_B \)), the new master equation reads

\[
\frac{d}{dt} \tilde{\rho}'_{SP}(t) = -\int_0^\infty d\tau \left\{ \left[ [S'_+(t), S'_-(t-\tau)] \tilde{\rho}'_{SP}(t) \right] \right. \\
+ \left. [S'_-(t), S'_+(t-\tau)] \tilde{\rho}'_{SP}(t) \right\} C(\tau) + \text{H.c.} \}
\]

(36)

where the bath correlation function \( C(\tau) \) is again given by Eq. (10), and \( \tilde{\rho}'_{SP}(t) \) is the reduced density matrix of the DA pair and odorant mode. Once the master equation is solved, the dynamics of the DA two-level system can be recovered by tracing out the odorant degrees of freedom. Similarly, one can trace out the electronic degrees of freedom to find the explicit dynamics of the odorant mode.

This more general approach can be applied over a wider range of parameters than the polaron master equation of Sec. [III] However, we have checked that in all cases considered in the main text the predictions of the polaron master equation are effectively identical to the more sophisticated treatment presented here. We thus expect the polaron master equation to be a valid description of the dynamics over the parameter regimes we consider.

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1. A. Nitzan, *Chemical Dynamics in Condensed Phases: Relaxation, Transfer and Reactions in Condensed Molecular Systems* (Oxford University Press, 2006).

2. V. May and O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems* (Wiley, 2011).

3. N. Lambert, Y.-N. Chen, Y.-C. Cheng, C.-M. Li, G.-Y. Chen, and F. Nori, *Nature Phys.* 9, 10 (2013).

4. Y.-C. Cheng and G. R. Fleming, *Annu. Rev. Phys. Chem.* 60, 241 (2009).

5. A. Olaya-Castro and G. D. Scholes, *Int. Rev. Phys. Chem.* 30, 49 (2011).

6. S. F. Huelga and M. B. Plenio, *Procedia Chem.* 3, 248 (2011).

7. H.-P. Breuer and F. Petruccione, *The Theory of open quantum systems* (Oxford University Press, 2002).

8. A. Ishizaki, T. R. Calhoun, G. S. Schlau-Cohen, and G. R. Fleming, *Phys. Chem. Chem. Phys.* 12, 7319 (2010).

9. A. Garg, J. N. Onuchic, and V. Ambegaokar, *J. Chem. Phys.* 83, 4491 (1985).

10. C. Olbrich, J. Strümpfer, K. Schulten, and U. Kleinekathöfer, *J. Phys. Chem. Lett.* 2, 1771 (2011).

11. S. Shin, P. Rebentrost, S. Valleeau, and A. Aspuru-Guzik, *Biophys. J.* 102, 649 (2012).

12. M. d. Rey, A. W. Chin, S. F. Huelga, and M. B. Plenio, *J. Phys. Chem. Lett.* 4, 903 (2013).

13. A. W. Chin, J. Prior, R. Rosenbach, F. Caycedo-Soler, S. F. Huelga, and M. B. Plenio, *Nature Phys.* 9, 113 (2013).

14. E. J. O’Reilly and A. Olaya-Castro, *Nature Commun.* 5 (2014).

15. E. K. Irish, R. Gómez-Bombarelli, and B. W. Lovett, *arXiv:1306.6650.*

16. G. Ritschel, J. Roden, W. T. Strunz, and A. Eisfeld, *New J. Phys.* 13, 113034 (2011).

17. J. Lim, M. Tame, K. H. Yee, J.-S. Lee, and J. Lee, *arXiv:1304.3967.*

18. A. Kolli, E. J. O’Reilly, G. D. Scholes, and A. Olaya-Castro, *J. Chem. Phys.* 137, 174109 (2012).

19. N. Christensson, H. F. Kauffmann, T. Pullerits, and T. Mančal, *Sci. Rep.* 3, 2029 (2013).

20. A. Chemu, N. Christensson, H. F. Kauffmann, and T. Mančal, *Sci. Rep.* 3, 2029 (2013).

21. L. Turin, *Chem. Senses* 21, 773 (1996).

22. L. Turin, *J. Theor. Biol.* 216, 307 (2002).

23. A. Keller and L. B. Vosshall, *Nat. Neurosci.* 7, 337 (2004).

24. J. C. Brookes, F. Hartoutsiou, A. F. Horsfield, and A. M. Stoneham, *Phys. Rev. Lett.* 98, 038101 (2007).

25. T. P. Hettinger, *PNAS* 108, 13449 (2011).

26. M. I. Franco, L. Turin, A. Mershin, and E. M. C. Skoulakis, *PNAS* 108, 3797 (2011).

27. I. A. Solov'ev, P.-Y. Chang, and K. Schulten, *Phys. Chem. Chem. Phys.* 14, 13861 (2012).

28. P. Kovacic, *J. Electrostat.* 70, 1 (2012).
E. R. Bittner, A. Madalan, A. Czader, and G. Roman, J. Chem. Phys. 137, 22A551 (2012).

S. Gane, D. Georganakis, K. Maniati, M. Vanvakias, N. Ragoussis, E. M. C. Skoulakis, and L. Turin, PLoS ONE 8, e55780 (2013).

D. J. Rowe, Chemistry and technology of flavors and fragrances (Blackwell, Oxford, 2005).

S. Gane, D. Georganakis, K. Maniati, M. Vamvakias, N. Ragoussis, E. M. C. Skoulakis, and L. Turin, PLoS ONE 8, e55780 (2013).

D. J. Rowe, Chemistry and technology of flavors and fragrances (Blackwell, Oxford, 2005).

R. Axel, Angew. Chem. Int. Ed. 44, 6110 (2005).

L. B. Buck, Angew. Chem. Int. Ed. 44, 6128 (2005).

S. H. Lee, O. S. Kwon, H. S. Song, S. J. Park, J. H. Sung, J. Jang, and T. H. Park, Biomaterials 33, 1722 (2012).

R. H. Farahi, A. Passian, L. Tetard, and T. Thundat, ACS Nano 6, 4548 (2012).

R. B. Silverman, The Organic Chemistry of Enzyme-catalyzed Reactions (Academic Press, London, 2002).

L. B. Buck, Angew. Chem. Int. Ed. 44, 6128 (2005).

D. J. Rowe, Chemistry and technology of flavors and fragrances (Blackwell, Oxford, 2005).

R. H. Wright, J. Theor. Biol. 64, 473 (1977).

R. H. Wright, The sense of smell (CRC Press, 1968).

C. J. Adkins and W. A. Phillips, J. Phys. C 18, 1313 (1985).

R. A. Marcus, J. Chem. Phys. 24, 966 (1956).

R. A. Marcus, Annu. Rev. Phys. Chem. 15, 155 (1964).

R. A. Marcus, J. Chem. Phys. 43, 679 (1965).

R. Marcus and N. Sutin, BBA - Rev. Bioenergetics 811, 265 (1985).

M. Bixon and J. Jortner, Adv. Chem. Phys. 106, 35 (1999).

T. Holstein, Ann. Phys. 8, 325 (1959).

T. Holstein, Ann. Phys. 8, 343 (1959).

B. Jackson and R. Silbey, J. Chem. Phys. 78, 4193 (1983).

A. Nazir, Phys. Rev. Lett. 103, 144004 (2009).

S. Jang, Y.-C. Cheng, D. R. Reichman, and J. D. Eaves, J. Chem. Phys. 129, 101104 (2008).

S. Jang, J. Chem. Phys. 131, 164101 (2009).

For $\omega_0 = 200$ meV and $T = 300$ K this corresponds to the odorant initial state being essentially the ground state, and is therefore consistent with the initial condition in the rate analysis.

The DA dynamics is generally well fitted by a biexponential form.

Note that the ET rates used to calculate the dashed curves in panels (i - iii) of Fig. 1 do agree with the MJ rates.

L. G. Remus and M. P. Blencowe, Phys. Rev. B 86, 205419 (2012).

N. Lambert and F. Nori, Phys. Rev. B 78, 214302 (2008).

A. D. Armour and M. P. Blencowe, New J. Phys. 10, 095004 (2008).

A. D. Armour and M. P. Blencowe, New J. Phys. 10, 095005 (2008).

D. Xu and K. Schulten, Chem. Phys. 182, 91 (1994).

R. E. Blankenship, Molecular mechanisms of photosynthesis (Blackwell, Oxford, 2002).

S. H. Lee, H. J. Jin, H. S. Song, S. Hong, and T. H. Park, J. Biotechnol. 157, 467 (2012).

L. Du, C. Wu, Q. Liu, L. Huang, and P. Wang, Biosens. Bioelectron. 42, 570 (2013).