Non-adiabatic effects in thermochemistry, spectroscopy and kinetics: the general importance of all three Born-Oppenheimer breakdown corrections

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S1. The use of a single-mode two-state model to describe complex molecular systems

An important feature is that the application of the linearly-coupled two-state model to any chemical problem always involves significant approximations such as the explicit treatment of only one molecular motion used typically to represent a complex problem, including the neglect of non-Condon effects associated with other modes.1 Nevertheless, such models are well known to be highly important to the development of chemical theory,2 but they fail at conical intersections and therefore for the broader understanding of general Jahn-Teller effects.3, 4 There are other ways in which multi-mode effects can become important for spectroscopy3 and ground-state chemical reactions, for example developing solvent control via fluctuations,5-7 timescale issues,8 or by friction forces that facilitate multiple re-crossings of transition-state surfaces,9 and these effects are also neglected in this explicit 1-mode treatment.

While many of the model systems considered in this work are intrinsically multi-mode in nature, none are Jahn-Teller active and none involve dynamics through conical intersections and so the single-mode approach remains qualitatively descriptive. For CT, non-Condon effects associated with the Ru-N symmetric-stretch mode modulating the electronic coupling would need to be included in any quantitative analysis.10 Indeed, for PRC quantitative high-resolution spectral analysis required full-quantum non-adiabatic dynamics involving 4 electronic states and 70 vibrational modes, 20 of which introduce non-Condon effects,11, 12 yet the one-mode two-state
model yields analytical expressions giving results accurate to 20% for the chemical properties of 34 mutant reaction centres.\textsuperscript{13,14} Also, for FcPC\textsubscript{60},\textsuperscript{15} 13 modes of widely varying frequency must be included in a full quantum analysis of charge-recombination rates, but none of these modes reduce the (weak) electronic coupling to the degree needed to access the conical intersection seam. The selection of an effective frequency for this molecule is problematic, however, as the actual mode frequencies span a very wide range. In such cases it is often advantageous describe low-frequency intermolecular motions differently to high-frequency molecular vibrations,\textsuperscript{16,17} this is a common scenario.

While symmetry breaking in molecules like benzene and ammonia are well described using single-mode models, these are closed-shell systems for which more than one electronic state is intricately involved. The issues are discussed in detail in our companion publication\textsuperscript{18} but briefly a renormalization of the parameters can be introduced that maps the problem onto an effective two-state system. However, different parameters are required in order to describe different physical effects, and the ones used in this work are those pertaining to the shape of the GS potential-energy surface. The FcPC\textsubscript{60} system is also closed shell but we choose the effective coupling parameters pertinent for charge-recombination kinetics rather than those pertinent to the ground-state structure.

S2. More accurate expressions for properties of the Born-Huang adiabatic surface

Section 4e reports approximate expressions for the properties of the Born-Huang adiabatic potential-energy ground-state surface for symmetric problems ($\Delta E = 0$) involving double-well potentials. Exact analytical solutions are difficult to obtain as the local minima in the Born-Huang potential $Q_{0}^{BH}$ are given by

$$\left( Q_{0}^{BH} \right)^2 = \frac{2}{\hbar \omega \lambda} \left( x^2 - J^2 \right)$$  \hspace{1cm} (S1)

where $x$ is the root $> |J|$ of the equation

$$0 = 2x^6 - \lambda x^5 - \frac{(\hbar \omega \lambda J)^2}{4}. \hspace{1cm} (S2)$$

In the limit of $2|J|/\lambda = 1$ and $\hbar \omega / \Delta E = 1$, the lowest-order approximate solution is

$$Q_{0}^{BH} \approx \pm Q_{m} \left[ 1 - \left( \frac{2J}{\lambda} \right)^2 \left( 1 - 4 \left( \frac{\hbar \omega}{\lambda} \right)^2 \right) \right]^{1/2}.$$  \hspace{1cm} (34)

More accurate solutions are:

$$Q_{0}^{BH} \approx \pm Q_{m} \left[ 1 + \frac{8h^2 \omega^2 J^2}{40h^2 \omega^2 J^2 + \lambda^4} \right] - \left( \frac{2J}{\lambda} \right)^2 \left( \frac{h \omega}{\lambda} \right)^2 \hspace{1cm} (S3)$$

and then

$$Q_{0}^{BH} \approx \pm Q_{m} \left[ \left( 1 + \frac{16h^2 \omega^2 J^2}{48h^2 \omega^2 J^2 + \lambda^4 + \left( \lambda^8 + 64h^2 \omega^2 J^2 \lambda^4 - 3072h^4 \omega^4 J^4 \right)^{1/2} \right)^2 - \left( \frac{2J}{\lambda} \right)^2 \left( \frac{h \omega}{\lambda} \right)^2 \right]^{1/2} \hspace{1cm} (S4)$$

Using Approx. (S3) for the geometry, the change in energy from that at the BO minimum is to lowest order:

$$\varepsilon_{-}^{BH} (Q_{0}^{BH}) - \varepsilon_{-} (Q_{0}^{BO}) \approx \frac{\hbar^2 \omega^2 J^2}{\lambda^3} = \frac{h \omega}{4} \left( \frac{2J}{\lambda} \right)^2 \left( \frac{h \omega}{\lambda} \right) \hspace{1cm} (34)$$

but more accurately is given by

$$\varepsilon_{-}^{BH} (Q_{0}^{BH}) - \varepsilon_{-} (Q_{0}^{BO}) \approx \frac{\lambda}{2} \left[ 1 - \left( \frac{1 + \frac{16h^2 \omega^2 J^2}{\lambda^4}}{\lambda^4} \right)^{1/2} + \frac{2h^2 \omega^2 J^2}{\lambda^4} \left( 4 + \frac{\lambda^8}{(\lambda^4 + 16h^2 \omega^2 J^2)^2} \right) \right]. \hspace{1cm} (S5)$$

Similarly, at this geometry the vibration frequency determined from the local force constant is to lowest order

$$\omega^{BH} \approx \omega \left[ 1 - \left( \frac{2J}{\lambda} \right)^2 \left( 1 - 10 \left( \frac{h \omega}{\lambda} \right)^2 \right) \right]^{1/2} \hspace{1cm} (34)$$

but more accurately is given by
\[ \omega^{BH} \approx \omega \left[ 1 - \frac{4J^2\lambda^4}{(\lambda^4 + 16\hbar^2\omega^2 J^2)^{3/2}} + \frac{8\hbar^2\omega^2 J^2 \lambda^8 [5\lambda^4 + J^2 (80\hbar^2\omega^2 - 24\lambda^2)]}{(\lambda^4 + 16\hbar^2\omega^2 J^2)^4} \right]^{1/2} \]  \hspace{1cm} (S6)

S3. Shortcomings of calculated energy-level spacings near the transition state evaluated using approximate BO-based methods.

Fig. S1 shows data for the energy of a spectroscopic transition between eigenstates near a transition state. First, two (GS or ES) BO eigenfunctions are selected whose energies are closest to that of the transition state and perturbation theory is then applied to derive corrections \( \Delta \epsilon^\pm_i \) for the individual state energies for non-adiabatic effects:

\[ \Delta \epsilon^\pm_i = \left\langle \Psi^\pm_i (r, Q) \right| \Delta H \left| \Psi^\pm_j (r, Q) \right\rangle + \sum_{s=r,-} \sum_{j \neq i} \left\langle \Psi^\pm_i (r, Q) \right| \Delta H \left| \Psi^s_j (r, Q) \right\rangle^2 \]  \hspace{1cm} (S7)

and hence improve the energy gap \( \nu_T \) between the two selected states, where \( \Delta H \) is one, two, or all three of the BO-breakdown corrections \( \Delta H^{DC} \), \( \Delta P^{FD} \partial / \partial Q \), and \( \Delta H^{SD} \) from Eq. (7). Shown in the figure are the relative errors in the calculated energy difference from the full operator (all 3 corrections) and using either just the DC, FD, and SD corrections only, as well as using just the FD and SD corrections combined. Once again, the results show that using any one or any combination of the three correction terms produces results in poor agreement with those obtained using the full BO breakdown terms.

While the evaluated energy difference does not in itself correspond to any physical kinetics property, chemical reactions occur because of the ensuing quantum dynamics after the reactants are prepared, and this quantum dynamics will be controlled by energy gaps such as the one examined. These results thus provide insight into the fundamental nature of chemical reactions across transition states. The results obtained directly parallel the results from the coherent-state wavepacket propagations described in the main text and indicate the fundamental nature of the cusp region.
The absolute values of the errors in the energy difference between the energies of the two BO eigenfunctions closest in energy to the TS, evaluated using first-order perturbation theory to include non-BO effects: BH- using only BH correction, FD- using only the first-derivative correction, SD- using only the second-derivative correction, FS- using both the FD and SD corrections. Light-gray regions require > 1024 vibrational basis functions for convergence whilst dark-gray regions have no transition state (Eq. (23)). Sample model compounds 1-9 are indicated, see Table 1.

S4. The fraction of the wavepacket depicting thermal reactions transmitted after one period of motion

The fraction of a wavepacket started on the GS surface at the energy of the transition state that is transmitted after one period of vibration is displayed in Fig. S2 for the whole parameter space used in this study. This fraction is pertinent to the understanding of BO-breakdown effects on thermal chemical reactions. Results obtained using the CA description and the BO description including all terms are in excellent agreement, indicating the calculations in the BO basis can indeed provide a good description of the dynamics. The absolute errors in the transmission evaluated using none, one, or two of the BO breakdown corrections only are also shown in the figure. Generally the raw BO approximation produces the worst results, with the application of any correction making some sort of improvement. At no point in the parameter space at which significant BO breakdown occurs does the application of any partial correction lead to quantitatively useful results, however, except by coincidence. This is particularly true for important charge-transfer systems such as 1 (DPP), 2 (Alq3), and 5 (CT), as well as for spectroscopically relevant systems such 4 (BNB) and 3 (3PYR). A key feature is that the fraction transmitted is highly independent of $E_0$. 
Fig. S2. Results from the propagation of a coherent-state wavefunction (if $J=0$) at the energy of the transition state (see Figs. 8 and 9), showing the fraction $\kappa_{LR}$ of the wavepacket located to the right of the TS after 1 period of motion evaluated using the full Hamiltonian in the CA electronic basis, else Hamiltonians in BO basis: full (using $FC=DC+FD+SD$ corrections, BO only, using DC correction only, FD correction only, SD correction only, or $FS=FD+SD$ corrections combined. The light-gray regions require > 1024 vibrational basis functions for convergence whilst no TS is found in the dark-gray regions (Eq. (23)). Sample model compounds 1-9 are indicated, see Table 1.
S5. Approximating the transmission coefficient

Fig. S3 shows the transmission coefficient $\kappa$ for a thermal chemical reaction (Eq. (38)) evaluated crudely from the coherent-state wavepacket trajectories or else evaluated using the Landau-Zener approximation at a temperature of $k_B T = \hbar \omega$. This data is then interpolated by the analytical form

$$\kappa \approx \frac{c \frac{2J}{\lambda} \left( \frac{\hbar \omega}{\Delta E} \right)^\alpha}{1 + c \frac{2J}{\lambda} \left( \frac{\hbar \omega}{\Delta E} \right)^\beta}$$

and the results shown in the figure. The two methods yield qualitatively similar responses but significant quantitative differences emerge.

S6. High-energy dynamics above the conical intersection as is pertinent to say photochemical processes

Figures S4 and S5 show the quantum dynamics of initial wavepackets for the situation intermediary between cases D and E ($2J/\lambda = 0.0316, \hbar \omega / \Delta E = 0.1, E_0 = 0$), and for case E with $2J/\lambda = 0.1, \hbar \omega / \Delta E = 0.1$, and $E_0 = 0$, respectively, with the initial wavepacket starting on the ES surface at an energy of 4 times the transition-state energy $\Delta E^\dagger$ (Eq. (20)) so as to mimic photochemical processes. As Fig. 1 shows, the impact of the 3 BO-breakdown corrections is quite different for a photochemical process than ground-state thermal processes. For thermal reactions, all 3 terms act individually to stop the reaction which would otherwise proceed as described by
(tunneling corrected) transition-state theory on the BO GS surface. However, for the photochemical scenario, direct reflection induced by DC acting on its own only momentarily delays the wavepacket without favoring either of the two final states, one of which is produced by surface hoping and the other by direct transmission on the BO ES surface. Also, whilst for thermal reactions the wavepacket propagations most readily reflect chemical reaction yields after one period of the GS motion, in Figs. S4 and S5 the best indication is given after one half of a period of the ES dynamics \( t \approx \pi / \omega \) instead.

In Fig. S4, the coupling is weak and the wavepacket in the CA basis stays primarily on the R diabatic state, with a small amount surface-hoping to L. These results are depicted in the BO basis (FC calculation) as near complete surface hoping occurring at the transition state to take the wavepacket to the GS. However, using the BO approximation (no correction terms) the wavepacket moves forward purely on the ES, as it also does using the Born-Huang adiabatic approximation (DC only) except that in this case the correction to the transition-state energy of \( \Delta \Delta e^\dagger = 25 \hbar \omega \) (Eq. \( ^\dagger \)) reflects a third of the wavepacket back. The FD-only and SD-only methods both seriously underestimate the surface hoping but when combined together give a qualitatively realistic description of the exact dynamics, with interferences between these terms and with the DC correction being essential to a quantitative description of the reaction process. In Fig. S5, the DC increase in the activation energy is only 2.5 \( \hbar \omega \), much less than the excess energy of the wavepacket above the transition state, and so this correction has much less effect. Now the FD-only approximation provides a good qualitative description of the dynamics, but inclusion of the SD correction is again required for quantitative analysis.

The FD-only method is the one generally used to consider photochemical non-adiabatic reactions but from these results we infer that this is only likely to be a good approximation if the non-adiabatic coupling is large, a common but perhaps not typical scenario. Indeed, the one-mode two state model that we apply would only be appropriate to describe this type of photochemistry if the conical intersection was energetically inaccessible, a situation not expected to be common. Hence the minimalist qualitatively descriptive description must involve a second vibrational mode, a mode whose primary effects are to reduce the coupling \( J \) to zero at the conical intersection whilst enhancing surface-hoping rates at the same time. This will thus act to enhance the effects of the SD contribution beyond those depicted herein.
**Fig. S4.** Quantum dynamics of a coherent-state (if $J=0$) wavepacket starting at the far left of the left-hand BO ES at the energy of four times the transition state for scenario half way between D and E ($2J/\lambda =0.0316$, $\hbar \omega / \Delta E = 0.1$, $E_0 = 0$). The wavepacket vibrational density is resolved onto the electronic basis states (either CA, with propagation based on Eq. (1), or else BO, with propagation based on Eq. (7)), superimposed as appropriate on either the CA potential-energy surfaces (red- L, blue-R) or else one or two of the BO or Born-Huang surfaces (green- GS, magenta- ES) for different Hamiltonians. BO dynamics is based on either: full corrections (FC=DC+FD+SD), BO only (no corrections), using DC correction only, FD correction only, SD correction only, or FS=FD+SD corrections.
Fig. S5. Quantum dynamics of a coherent-state (if $J=0$) wavepacket starting at the far left of the left-hand BO ES at the energy of four times the transition state for scenario E ($2J/\lambda = 0.1$, $\hbar \omega / \Delta E = 0.1$, $E_0 = 0$). The wavepacket vibrational density is resolved onto the electronic basis states (either CA, with propagation based on Eq. (1), or else BO, with propagation based on Eq. (7)), superimposed as appropriate on either the CA potential-energy surfaces (red- L, blue-R) or else one or two of the BO or Born-Huang surfaces (green- GS, magenta- ES) for different Hamiltonians. BO dynamics is based on either: full corrections (FC=DC+FD+SD), BO only (no corrections), using DC correction only, FD correction only, SD correction only, or FS=FD+SD corrections.