

Identifying the Marcus dimension of electron transfer from *ab initio* calculations

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Abstract

The Marcus model forms the foundation for all modern discussion of electron transfer (ET). In this model, ET results in a change in diabatic potential energy surfaces, separated along an ET nuclear coordinate. This coordinate accounts for all nuclear motion that promotes electron transfer. It is usually assumed to be dominated by a collective asymmetric vibrational motion of the redox sites involved in the ET. However, this coordinate is rarely quantitatively specified. Instead, it remains a nebulous concept, rather than a tool for gaining true insight into the ET pathway. Herein, we describe an *ab initio* approach for quantifying the ET coordinate and demonstrate it for a series of dinitroradical anions. These mixed valence systems span a range of behaviors in which the unpaired electron is either localized or delocalized. Using sampling methods at finite temperature combined with density functional theory calculations, we find that the electron transfer can be followed using the energy separation between potential energy surfaces (for localized systems) and the extent of electron localization (for delocalized systems). The precise nuclear motion that leads to electron transfer is then be obtained as a linear combination of normal modes. Once the coordinate is identified, we find that evolution along it results in a change in diabatic state and optical excitation energy, as predicted by the Marcus model. Thus, we conclude that a single dimension of the electron transfer described in Marcus–Hush theory can be found in the real systems as an intuitive nuclear motion.

1 Introduction

The transfer of electron density is implicated in nearly every chemical transformation and, for this reason, there has long been an intense interest in developing models for describing, predicting, and quantifying the pathways of electron transfer (ET). For the past 60 years, the dominant model has been the classical Marcus–Hush theory.^{1,2}

The theory originally described by Marcus treats ET between two separated redox sites (*i.e.*, intermolecular ET), giving rise to two electronic states, termed *a* and *b*. These states are represented on a reaction coordinate diagram by two harmonic potential energy surfaces (PES) as shown in Figure 1a. The electron transfer occurs when the nuclei (internal and solvent) are distorted such that the two surfaces have the same energy, at which point there is some probability of ET. This can be represented using Fermi’s golden rule yielding:^{3,4}

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |V_{\text{ab}}|^2 \frac{1}{\sqrt{4\lambda k_B T}} \exp\left(-\frac{\Delta G}{k_B T}\right), \quad (1)$$

where V_{ab} is the electronic coupling between the states (taken to be small in the original treatment), ΔG is the activation energy, and λ is the so-called reorganization energy, which is the vertical energy gap between the reactant minima and the product PES. The reorganization energy can be obtained by measuring this electronic transition, termed the intervalence charge transfer (IVCT) transition. Because the surfaces are treated as harmonic surfaces, measuring the IVCT energy provides the barrier to thermal ET: $\lambda/4$. Though this is a convenient way to parameterize the model, it disregards the specifics of the ET coordinate. A more chemically meaningful treatment would consider the nuclear motions involved in the ET and then derive a spring constant (f) for this motion as well as separate the minima (d) of the PES along the ET coordinate such that the reorganization energy is recaptured as $\lambda = d^2 f$.

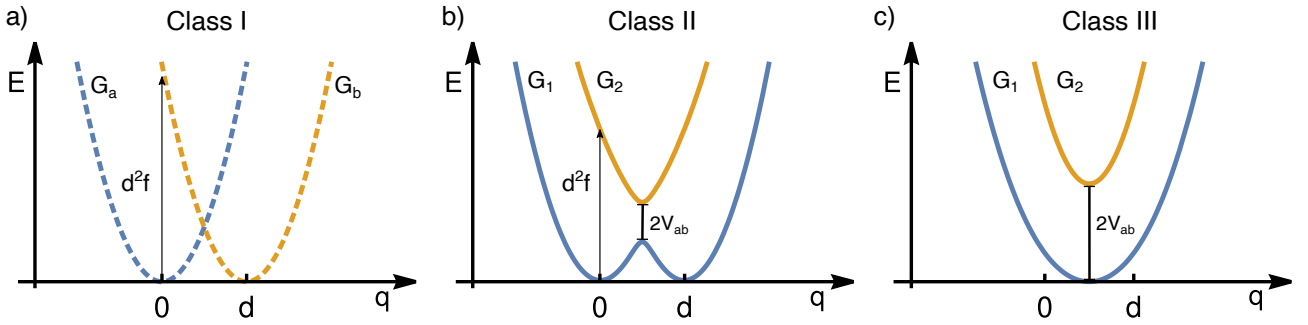


Figure 1: One dimensional potential curves of Robin–Day classes separated along the ET coordinate (q). The vertical arrow of length $d^2 f$ represents the reorganization energy. V_{ab} is the potential coupling between the initial diabatic states G_a and G_b that leads to the adiabatic states G_1 and G_2 .

The insight that would be gained by obtaining a precise description of the ET coordinate is made clear when considering systems with large degrees of electronic coupling. Hush expanded Marcus’ theory for such systems, retaining the connection between the electron transfer coordinate, the barrier to electron transfer, the curvature of the PES, and the displacement along the ET coordinate. Again, it was common to combine the effects of curvature and separation into a reorganization energy, though there have been treatments that explicitly consider the spring constant and separation.⁵ Large electronic coupling functions to mix the diabatic states G_a and G_b and produces two adiabatic states: a ground state G_1 and an excited state G_2 (Figure 1b and c). Thus, for significant coupling, ET will occur adiabatically, in which case the pre-exponential factor will reduce to a nuclear frequency along the ET coordinate ν_q . The resulting classical expression for the ET rate will be:⁶

$$k_{\text{ET}} = \nu_q \exp\left(-\frac{\Delta G}{k_B T}\right) \quad (2)$$

so that the importance of understanding the nuclear motions along the ET coordinate becomes obvious.

The ET coordinate is also implicated in other effects of electronic coupling, namely that increasing electronic coupling produces a movement of the ground state PES minima towards one another along the ET coordinate.

If coupling is strong enough, the minima merge, and the molecule has a single stable configuration with the unpaired electron delocalized over the redox sites. The shape of the ground state PES is so important that the dominant classification scheme for mixed valence systems, proposed by Robin and Day,⁷ is based upon it. In this classification, systems with minimal coupling (*i.e.*, diabatic) are termed Class I, systems with a single minimum are termed Class III, and the intermediate case is termed Class II. Movement along q away from the minimum in Class III therefore implies a greater extent of localisation, whereas movement along q between the minima in Class II leads to electron transfer. It is well established that solvation has a pronounced influence on the shape of the potential and can even lead to a switch in Class.^{8,9} While electronic coupling in these complexes is often discussed without reference to the PES spring constant and minima separation, it is also true that the final shape of the surface depends not only on the size of the electronic coupling, but also on the curvature and separation along the ET coordinate.¹⁰ Having a direct way of identifying the shape of the PES would therefore be of great value for disentangling these different contributors, comparing the properties of different chemical systems in more detail, and quantifying environmental effects.

The lack of attention paid to the spring constant and separation between PES minima comes from both experimental and theoretical limitations. On the experimental side, the primary probe of mixed valence molecules has been the IVCT band. The position, intensity, and shape of the IVCT band can be used to estimate the magnitude of electronic coupling.^{8,11} However, this band contains limited information about the spring constant of the surfaces and the separation of the PES minima. While vibronic progressions and resonance Raman experiments can shed some light onto these parameters, one cannot guarantee that all motion that contributes to ET will be captured. Nevertheless, determining these parameters remains of interest and other approaches have been devised, such as using the change in dipole moment upon excitation of the IVCT transition.^{12,13} In this approach, the idea is that electronic coupling, which reduces the separation between minima, will also reduce the degree of charge transfer and thereby the change in dipole moment upon ET. Thus, one can compare the magnitude of the observed dipole moment change to what would be expected without coupling and obtain an estimate of the shift in the minima due to coupling. However, this approach has several drawbacks. For one, estimating the change in dipole moment in the absence of coupling is difficult.^{14,15} Additionally, this approach cannot be used for Class I (often no IVCT band intensity) and Class III (no charge transfer) species. Finally, even if the approach were valid, what would be measured is not the ET coordinate directly, but a separation along it. Therefore, any specific chemical information about the nuclear motions involved is not obtained.

Efforts to determine the ET coordinate based in theory have also been made. As is common in light induced ET, one can attempt to perform a linear interpolation between the reactants and transition state, or the reactants and the products in order to understand what nuclear motions are implicated in ET. However, this approach is also restricted to Class II systems where two well defined minima and a transition state exist. For MV systems that are sensitive to the solvation environment, a linear interpolation approach would not be able to evaluate any solvent-induced change in nuclear motion or the decoupling of solvent and solute motion. Finally, as our results will show, a linear interpolation approach may furthermore contain motions that do not contribute to the ET process.

Taking into consideration the state of the art in ET research, there remains a need to describe the ET coordinate in a quantitative manner—including the nature of the nuclear motion, the separation along the ET

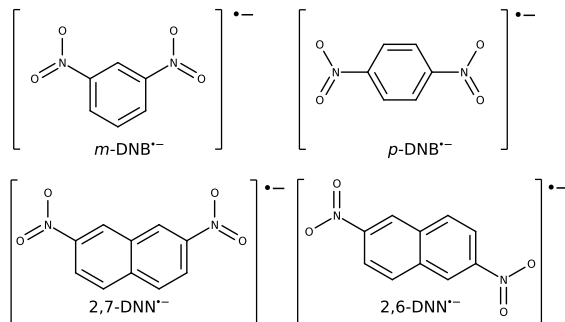


Figure 2: Structures and charge state of the studied mixed valence systems for which we demonstrate our approach.

coordinate, and the spring constant associated with the PES. Herein, we describe one such approach based upon quantum chemical calculations, demonstrating it for the mixed valence systems *meta*-dinitrobenzene ($m\text{-DNB}^{\bullet-}$), *para*-dinitrobenzene ($p\text{-DNB}^{\bullet-}$), 2,6-dinitronaphthalene ($2,6\text{-DNN}^{\bullet-}$), and 2,7-dinitronaphthalene ($2,7\text{-DNN}^{\bullet-}$), see Fig. 2.

These molecules have been well characterized experimentally and computationally so that the IVCT band and the rate of ET are known. They served as model compounds for exploring the adiabatic ET rate¹⁶ or for development of reliable electronic structure methods for MV systems.¹⁷ The Robin–Day classification of these compounds depends on the solvation environment¹⁸. In vacuum, all four compounds are expected to be Class III, while when placed in a dielectric continuum of acetonitrile, $m\text{-DNB}^{\bullet-}$ and $2,7\text{-DNN}^{\bullet-}$ transition to Class II.¹⁹ Alcohol solvents, which are capable of hydrogen bonding, show a very strong localization effect and high ET barriers.¹⁸.

We propose a method to identify the ET coordinate of a MV system regardless of its Robin–Day Class, which is achieved with a sampling procedure covering a representative set of thermally populated nuclear configurations and subsequent analysis of the electronic structures in this ensemble. The coordinate we identify appears to be an intrinsic property of the mixed valent molecule and can be used to predict the barrier height or reorganization energy of the system. We also show that, while this approach largely substantiates the Marcus–Hush model, it also raises some questions regarding interpretation of the model and reveals some of its limitations.

2 Methodology

For many years, computational predictions of spectroscopic properties of MV compounds were hampered by the fact that most theoretical methods tend to favour either a localized or a delocalized description. Solutions to this problem were found and discussed in seminal work by Martin Kaupp and coworkers.¹⁹ While one may think that wavefunction methods would be the best choice to adequately capture all important aspects of MV electronic structures, they can account for the Coulomb correlation only perturbatively and will thus favor a localized description of the system.¹⁹ In fact, the importance of Coulomb correlation in systems which tend to delocalize calls for a treatment of the electronic structure with Density Functional Theory (DFT).¹⁹ However, the approximated exchange correlation in most DFT functionals leads to the so-called self-interaction error (SIE) which stabilizes delocalized electronic states.²⁰ Hence, in many of the standard functionals, Class III

situations are favoured as a consequence of the SIE,¹⁹ which may lead to an incorrect assignment of a MV compound to Class III.

A practical approach towards correcting this behaviour has been found in adjusting the amount of exact exchange in global hybrid functionals.²¹ Furthermore, a proper treatment of the environment proved to have a significant impact on electronic localization or delocalization.^{22,23} Protocols like this were shown to perform well for MV systems ranging from small organic molecules^{17,22,24} to large dinuclear inorganic complexes.^{25,26,27} A novel and more rigorous approach towards a balance between correcting the SIE and an accurate description of exchange correlation was presented in the form of local hybrid density functionals.^{28,29} In these functionals, the amount of exact exchange depends on the position in real space: exact exchange dominates in regions of high or zero electron density, whereas regions of homogeneous electron density (*i.e.* bonding regions) are dominated by DFT exchange. Local hybrid functionals perform extraordinarily well in the prediction of spectroscopic properties of MV compounds, making them the state-of-the-art for theoretical studies of such systems.^{30,31,32}

To assess the interplay between the geometric and electronic structure of an MV system, it is clear that the picture derived from a single nuclear configuration will not represent reality. Therefore, a sampling procedure is needed that covers a set of thermally populated nuclear configurations with their associated electronic structures. The nuclear ensemble method³³ presents a simple and powerful method for simulating vibrationally resolved electronic spectra^{34,35}, for obtaining the initial conditions for non-adiabatic dynamics³⁶, or for exploring phase space properties.³⁷ The most common way to generate a nuclear ensemble is *ab initio* molecular dynamics which, however, comes with a great computational cost.³⁸

A significantly less demanding method for moderately sized molecules is the so-called Wigner sampling,³⁹ which is achieved by approximating the PES by a harmonic potential and evaluating the Wigner function⁴⁰ for thermally accessible vibrational states. The Wigner sampling method showed great performance when predicting absorption spectra⁴¹ and capturing temperature effects in the intersystem crossing of 2-nitronaphthalene.⁴² A strength of Wigner sampling is that it offers a more realistic sampling than *ab initio* molecular dynamics for high-frequency vibrational modes, because it accounts for the zero-point energy.⁴¹ However, it does not capture the decreasing spacing between levels and altered nature that is expected for an anharmonic oscillator and so undersamples anharmonic low-frequency modes. While we have chosen to use Wigner sampling here, it is conceivable that other sampling methods will perform equally well as long as a representative set of geometric and electronic structures is used.

Theoretical studies on mixed MV often assume a direct pathway between two well-defined structures, either adiabatic minima⁴³ or an adiabatic minimum and a totally symmetric structure¹⁷. Approaches to identify the ET dimension based on a statistical ensemble (like molecular dynamics) are either missing or do not focus on the interplay between electronic and geometric structure.⁴⁴ In state-of-the-art theoretical research of MV systems, a unified strategy towards a coordinate that describes electron transfer (Class II) or localisation (Class III) and that can be used to disentangle intra-molecular motion from solvent motion is missing.

Herein, we introduce a new approach for identifying the intramolecular ET coordinate. The starting point is an optimized geometry that represents an adiabatic minimum of the system and the Hessian matrix obtained from a frequency calculation. The phase space of the system under study is sampled using the Wigner sampling method as implemented in the SHARC package⁴⁵ at room temperature in vacuum or in implicit solvation. This

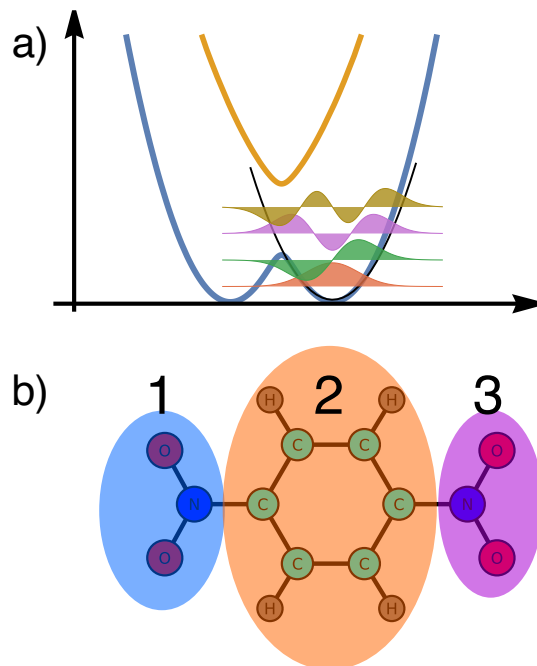


Figure 3: a) Schematic depiction of the approximated potential energy surface (black curve) employed in the Wigner sampling method. b) Definition of chemical fragments in a MV molecule to identify the electron position from a spin population analysis.

idea is illustrated in Fig. 3a) where the potential energy surface is approximated around the adiabatic minimum by a harmonic potential. A representative set of nuclear configurations is selected by evaluating the Wigner function for the relevant vibrational states whose thermal populations are estimated in Monte-Carlo fashion.⁴⁵ The next step is to run time-dependent DFT (TD-DFT) calculations with a small number of excited states for each selected geometry.

For each of the structures, it can be easily evaluated where the unpaired electron is localized: the position of this electron is defined as the weighted average of the spin populations s_i on specified molecular fragments, as illustrated in Fig. 3b) and given in Eq. 3,

$$e_{\text{pos.}}^- = 1 \cdot s_1 + 2 \cdot s_2 + 3 \cdot s_3. \quad (3)$$

The electronic properties, *i.e.*, the electron position or the excitation energy as discussed in more detail in the results section, are then correlated with the distortion in the direction of vibrational modes. To obtain these displacements, a transformation from Cartesian coordinates to normal coordinates is carried out according to Eq. 4, where $\mathbf{C}$ is a transformation matrix (obtained from the frequency calculation at the adiabatic minimum), $\mathbf{M}$ is a diagonal matrix of atomic masses, $\mathbf{r}$ is a vector of Cartesian coordinates, and $\mathbf{r}^0$ is the equilibrium configuration,

$$q_i = \sum_{j=1}^{3N} C_{ij}^T M_{ij}^{1/2} (r_j - r_j^0). \quad (4)$$

3 Computational methods

All calculations were carried out using the TURBOMOLE package⁴⁶. The local hybrid functional LH20t³⁰ was employed; in the SI we show additional tests using the BLYP35²¹ functional. Calculations used the def2-TZVP

basis set⁴⁷ for the carbon, nitrogen and oxygen atoms, and the def2-SVP basis set⁴⁷ for hydrogen atoms. The resolution of identity approximation for computation of the Coulomb integrals⁴⁸ was used. The convergence criterion for the self-consistent field method was set to $10^{-8} E_h$. As the integration grid, m3 in TURBOMOLE notation was used to obtain the energy. Solvation effects were modelled implicitly using a conductor-like screening model⁴⁹ (COSMO) with acetonitrile (ACN) as the modeled solvent. The five lowest excited states were determined using TD-DFT without the Tamm–Dancoff approximation and the same settings as described above. The phase space of all studied molecules was sampled using the Wigner sampling method as implemented in the SHARC package⁴⁵ at 300 K. 500 structures were generated as representative of the ensemble. Any scans performed along linear interpolation coordinates or the electron transfer coordinates identified with our approach used the LH20t/def2-TZVP electronic structure method described above and a step size of 0.002 or 0.005 Å. To evaluate the electronic structure progression along the Marcus dimension, CASSCF and NEVPT2 calculations were performed. The results and the respective computational details are given in the SI.

4 Results and discussion

4.1 Linear interpolation of Cartesian coordinates

Before demonstrating our approach for identifying the intramolecular ET coordinate, we show the results obtained from a linear interpolation of Cartesian coordinates (LICC) as has been used in the literature so far.⁴³ This method requires two well-defined structures in Cartesian coordinates, usually an adiabatic minimum and a totally symmetric structure representing the transition state. The reaction coordinate is obtained by linear interpolation between those structures.

We note that this approach cannot be applied to Class III systems where only one well-defined structure exists. Since MV systems can switch from localized to delocalized just by varying the solvation environment,^{18,50} LICC cannot identify the ET dimension in Class III systems and could not be used to decouple intramolecular and solvent motion. In addition, mapping the potential curves obtained by a LICC approach for a Class III system onto the diabatic (*i.e.* uncoupled) states of the underlying Marcus theory is thus precluded, and hence the progression of coupling strength, nuclear motion or force constants in a series of Class III systems or for borderline Class II/Class III cases¹⁰ could not be evaluated. Regardless of these conceptual limitations, we tested the LICC approach on *m*-DNB^{•−} in ACN. The LICC scans were performed between the adiabatic minimum and the totally symmetric molecule (Fig. 4a), and between the two adiabatic minima (Fig. 4d).

The ET dimensions obtained by LICC (Fig. 4a,d) are not anti-symmetric motions: a twisting motion of the oxygen atoms of one nitro group dominates the overall motion, and some hydrogen and carbon atoms of the aromatic ring have non-negligible contributions. In the adiabatic minimum, where the unpaired electron is localized on one side of the molecule (in this case, the nitro group on the left-hand side), the other nitro group is further away from the aromatic bridging unit and is slightly distorted, which will decrease the potential coupling with the bridging unit. A twisting motion is expected to be an important part of the ET only in cases of very large distortions.²⁶ For a nitro group perpendicular to the aromatic plane, the conjugation with the rest of the molecule breaks, and the potential coupling would thus tend to zero, making the ET adiabatically forbidden.

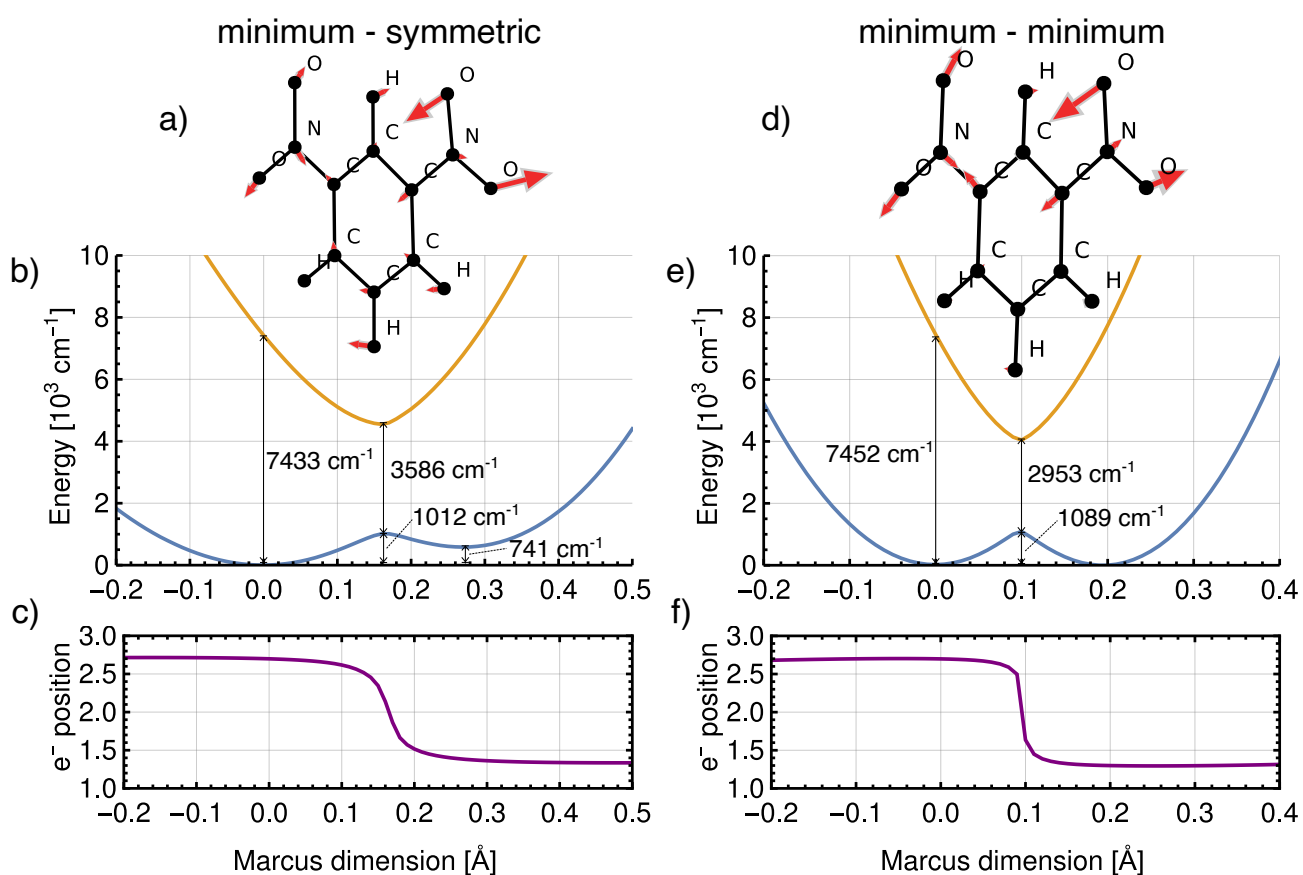


Figure 4: ET coordinates from the LICC approach and corresponding potential energy curves obtained from a scan along them. a) ET dimension obtained by LICC between the optimized geometry (adiabatic minimum) and the totally symmetrical one. b) Unrelaxed scan along the LICC dimension, with labels indicating the values of the reorganization energy, the electronic coupling, the height of the barrier, and the offset of the second minimum. c) Change of the electron position along the scanned coordinate according to the definition of fragments in Fig. 3 and Eq. 3. Panels d, e, f depict the same quantities for the ET coordinate obtained with LICC between the two adiabatic minima.

Unrelaxed scans along the two types of LICC coordinate (Fig. 4b,e) produce double-well potentials that change smoothly everywhere. For the LICC scan between the adiabatic minimum and the totally symmetric molecule, the minima do not have the same energy: the second minimum is destabilized by 741 cm^{-1} , which is more than half of the ET barrier. The potential obtained by scanning between the two adiabatic minima is symmetric and the barrier height agrees well with the value obtained by simulating experimentally measured EPR spectra (1000 cm^{-1}).⁵¹ The electron position as quantified by Eq. 3 changes upon overcoming the potential barrier in both cases (Fig 4c, f), with a sharper transition in the scan between the two adiabatic minima.

Clearly, the results of the LICC approach depend on the choice of the reference structures, and therefore it is unclear whether the ET coordinate obtained with a solvent model would lead to meaningful potentials when transferred into vacuum. Furthermore, a strong limitation of LICC is that it can only be applied to Class II systems, since for Class III systems no second geometric reference structure besides the adiabatic minimum exists. We will show in the following sections that by exploiting properties postulated in the Marcus model when interpreting the *ab initio* calculations, we arrive at a chemically intuitive dimension that drives electron transfer in Class II and leads to electron localization in Class III systems.

4.2 Electron transfer driven by vibrational modes

The ET coordinate represents nuclear movements associated with the transfer of the unpaired electron between the redox centres in the mixed-valent system. An intuitive concept of the ET coordinate is an anti-symmetric vibrational mode.^{52,53,54} In organic MV systems, the unpaired electron is often found on a multi-atom functional group, *i.e.* more delocalised than in inorganic complexes where the redox sites are mostly restricted to metal ions. Therefore, the ET coordinate cannot be conceived of as intuitively as in many inorganic complexes.⁵⁵ Herein, we present a method for obtaining the ET coordinate from *ab initio* calculations representing an ensemble.

Our task is to find an association between the distortions in the direction of each vibrational mode with a property that is most sensitive to progression along the ET coordinate. According to the Marcus model and the Robin–Day classification, this electronic property is the electron position in Class III cases, or the excitation energy in Class II cases. In Class III systems, even a small movement along the ET coordinate away from the adiabatic minimum can localize the electron on one of the redox centers to some extent. The electron position is thus an intuitive property to be correlated with vibrational motions.

This is, however, not the case in Class II systems, where in the vicinity of the adiabatic minimum the unpaired electron stays localized on the respective redox center. A dramatic change of electron position will occur only near the top of the barrier. The property that can uniquely define the ET coordinate in Class II system is the excitation energy to the first excited state. As the system progresses from the adiabatic minimum to the top of the barrier, the excitation energy will decrease. The nuclear configuration with the lowest excitation energy will thus correspond to the top of the barrier, as can be readily seen from the Marcus model (Fig. 1). We note that Class III systems cannot be treated this way because the excitation energy increases with the absolute value of nuclear displacements along the ET dimension. Consequently, the information whether a negative or positive displacement of any vibrational mode pushes the ET dimension forward or backward is lost.

Computing the correlation between a normal coordinate and the relevant ET property will reveal which vibrational modes contribute to the unique ET dimension. To this end, we plotted the relevant ET properties

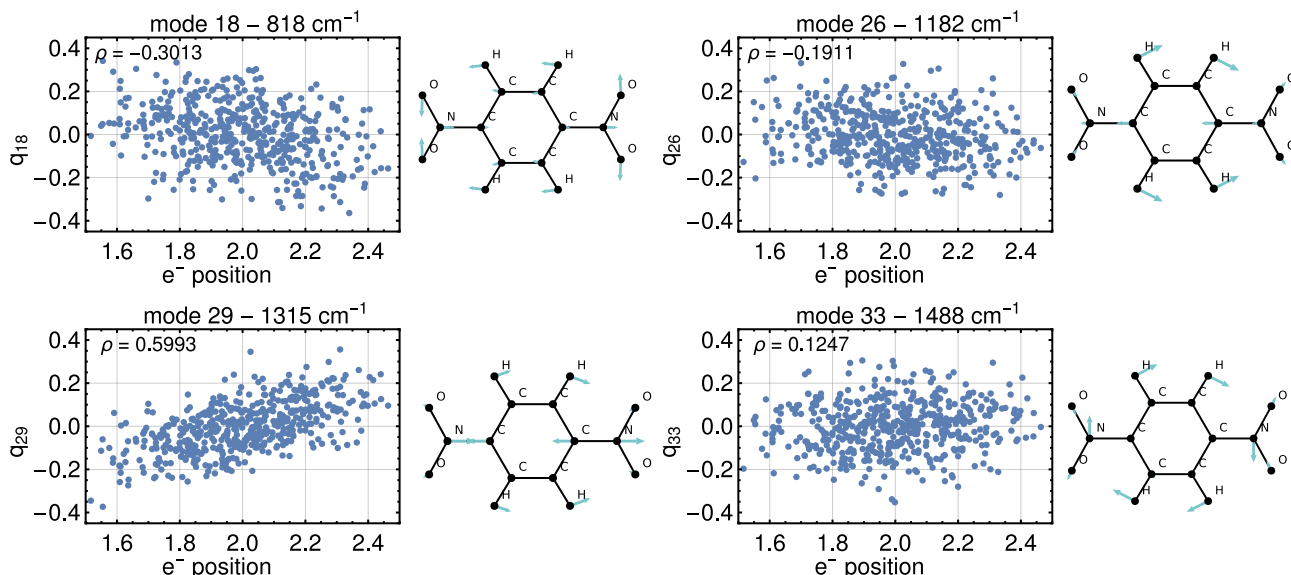


Figure 5: Normal coordinates plotted against the electron position with the corresponding vibrational mode for $p\text{-DNB}^{\bullet-}$ in ACN. Plot labels show the number of the vibrational mode and its harmonic frequency, ρ in the top-left corner indicates the respective correlation coefficient. All other normal modes exhibit a lower absolute value of ρ .

against the normal coordinates, see Fig. 5 for a Class III case and Fig. S2 for a Class II case. We focus here on the Class III case because there are no alternative methods to gain insight into the ET coordinate for Class III systems. In the Class III example shown in Fig. 5, a correlation with the electron position can be seen for some normal coordinates. The correlation with the antisymmetric stretching of C–N bonds (mode 29) is apparent at first glance, while the correlation with the ONO bending motion (mode 18) is less strongly pronounced. The importance of these modes for the ET dimension agrees with chemical expectations, *i.e.*, the ET is associated with changing the distance between redox center (NO_2 group) and bridging unit (benzene ring). All other vibrational modes correlate much less with the electron position. Very similar observations are made for a Class II system where, as explained above, the correlation is established using the excitation energy (see Fig. S2).

In both cases, there is no ultimate measure for deciding whether or how much these modes contribute to the ET dimension. In other words, it is not clear how much they contribute to the reorganization energy λ . Correlating the normal coordinate with the relevant ET property can only identify the relative importance of the vibrational modes. This finding underscores the need for a unified ET coordinate for which one would then know the spring constant f and the separation of the minima d , and therefore λ .

4.3 Marcus dimension of the electron transfer

As shown above, the ET dimension cannot be assigned to a single normal mode. A general approach towards composing the sought after ET dimension from the vibrational modes is to quantify how well aligned each mode is with the Marcus model. A linear combination of all vibrational modes should therefore result in the unique ET dimension, as proposed by Rudolph Marcus and refined in the Marcus–Hush model.¹

The correct combination of vibrational modes is obtained by a multi-component fit of all vibrational modes to the electron position for a Class III system, or to the excitation energy for a Class II system, see Eqs. 5a) and 5b), respectively. This procedure will account for all vibrational degrees of freedom. The independent

variables in the multi-component fit are the displacements in the direction of the vibrational modes (q_j) and the dependent variable is either the electron position ($e_{\text{pos.},i}^-$) or the excitation energy ($\Delta E^{D_0-D_1}$):

$$b_0 + b_1 \cdot q_{1,i} + \dots + b_{3N-6,i} \cdot q_{3N-6,i} = e_{\text{pos.},i}^- \quad (5a)$$

$$b_0 + b_1 \cdot q_{1,i} + \dots + b_{3N-6,i} \cdot q_{3N-6,i} = \Delta E_i^{D_0-D_1} \quad (5b)$$

The coefficients b_j are used to construct the Marcus dimension as a linear combination of vibrational modes, which are vectors of Cartesian displacements of individual atoms. The resulting Marcus dimension will therefore also take the form of a vector of Cartesian displacements.

Fig. 6 shows the result of the fit for $p\text{-DNB}^{\bullet-}$ (panel a) and $m\text{-DNB}^{\bullet-}$ (panel b) as examples. By comparison of Fig. 6a with Fig. 5 we can again identify mode 29 as the most prominent motion for the Marcus dimension in $p\text{-DNB}^{\bullet-}$. There are four other vibrational modes with significant contributions, some of them (*e.g.* mode 36) comprising only motions of hydrogen atoms. Motions like this are not expected to be a part of the Marcus dimension. Their large contributions are due to the fact that these vibrational modes will cancel out the more subtle motions of hydrogen atoms contained in the C–N stretching and O–N–O bending modes (*e.g.* modes 26 and 29), which drive the ET. The role of these modes is thus to cancel out the motion of atoms that are not important for the Marcus dimension. The remaining modes have small, but non-zero, contributions which would be overlooked if the Marcus dimension was determined only from the correlation plots.

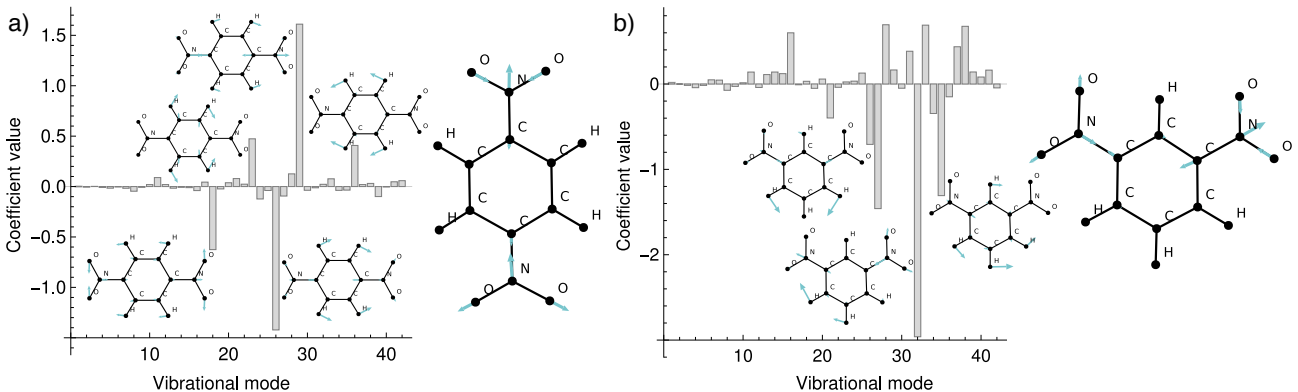


Figure 6: Coefficients obtained from the multi-component fit, including sketches of the normal modes with the largest coefficients. The resulting Marcus dimensions as linear combinations of the normal modes with expansion coefficients obtained from the multi-component fit are shown as sketches. a) Results for $p\text{-DNB}^{\bullet-}$, where the fit used the electron position according to Eq. 5a. b) Results for $m\text{-DNB}^{\bullet-}$, where the fit used the excitation energy according to Eq. 5b.

A similar situation is observed for $m\text{-DNB}^{\bullet-}$, see Fig. 6b. The vibrational modes with the largest coefficients contain C–N stretching motions. These modes are accompanied by motions of hydrogen atoms which are canceled out by other modes identified in the fitting procedure.

The fact that many modes contribute in non-negligible amounts shows that the Marcus dimension should not be thought of as a single anti-symmetric normal mode. Therefore, it is not possible to fully equate the absorption in a specific infra-red or Raman region with the ET coordinate: some important contributors to the Marcus dimension may be infra-red or Raman silent, or they may appear outside of the region of interest. In addition, there may be irrelevant absorption bands in the energetic region of interest.

The obtained Marcus dimensions for all dinitroradical anions are plotted in Fig. 7. The Marcus dimension is a motion localized on the nitro groups and the carbon atoms they are attached to. The most prominent

parts of the motions are C–N bond stretches and N–O bond stretches. The hydrogen atoms and all carbon atoms that are not part of the C–N bonds do not contribute significantly to the Marcus dimension. All motions are anti-symmetric which agrees with ET coordinate described by the Marcus model^{52,53,54}, and very similar amongst each other, which is expected for structurally and electronically similar compounds. We emphasize here that our procedure elucidates the participation of each atom in the reaction coordinate without making any prior assumptions, other than assuming the validity of the Marcus model.

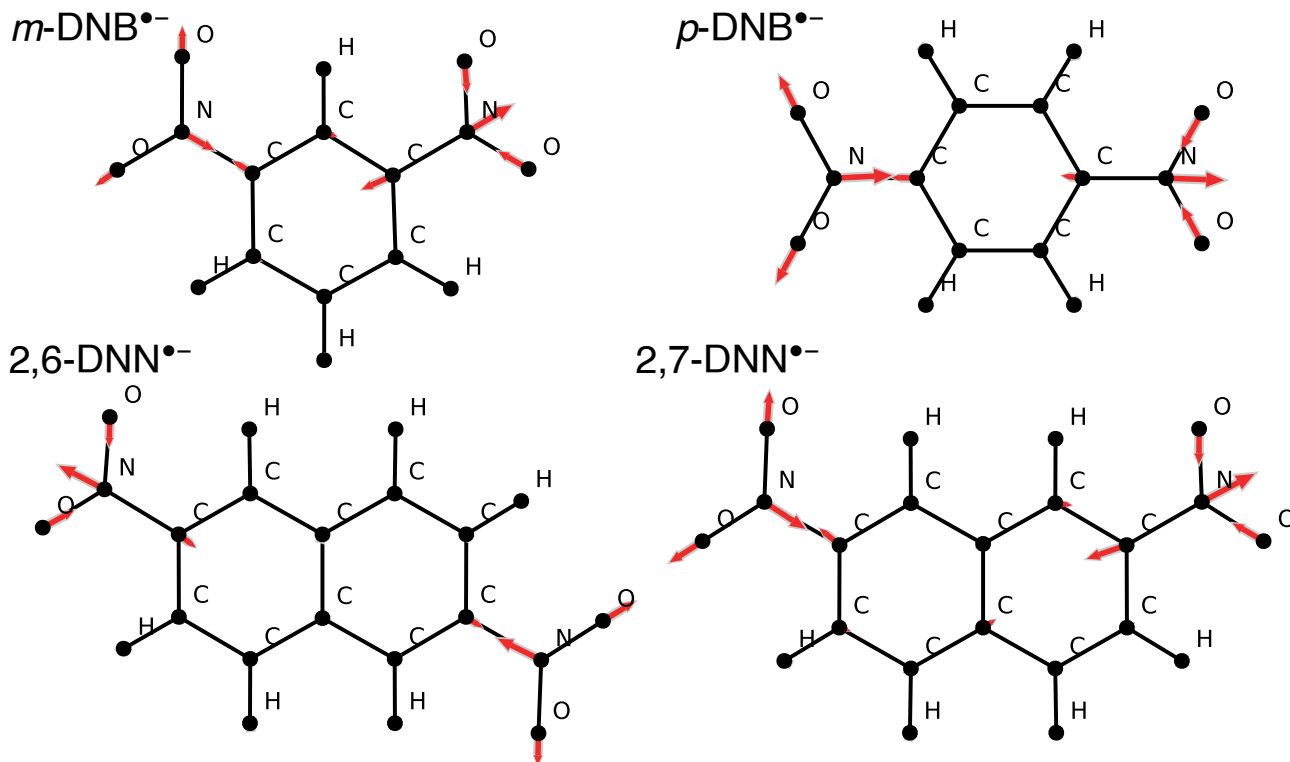


Figure 7: ET dimensions obtained from multi-component linear fits; shown here are the results for calculations in ACN. *m*-DNB^{•-} and 2,7-DNN^{•-} are Class II examples, and thus the fit was performed using the excitation energy to lowest doublet state as the ET property. *p*-DNB^{•-} and 2,6-DNN^{•-} are Class III examples, and thus the fit was performed using the electron position as the ET property.

Upon repeating the whole procedure in vacuum, where all studied systems belong to Class III, qualitatively the same motions are obtained (see SI). We note that even though *m*-DNB^{•-} and 2,7-DNN^{•-} switch from a localized to a delocalized system, the same Marcus dimension is observed. The results support our ansatz of using the electron position or the excitation energy as dependent variables in the multi-component fit, which clearly gives equivalent results. Moreover, these findings provide additional evidence that the motion identified in our procedure is the intrinsic ET coordinate in the respective molecule.

4.4 Scan along the Marcus dimension

As further evidence that the dimensions found above correspond to those originally proposed in the Marcus model and that the ET results from nuclear motion along this dimension, an unrelaxed scan was performed along the vibrational coordinate shown in Fig.7. In practice, the Marcus dimension is obtained as a vector of Cartesian displacements from the equilibrium configuration. This vector can be normalized and progress

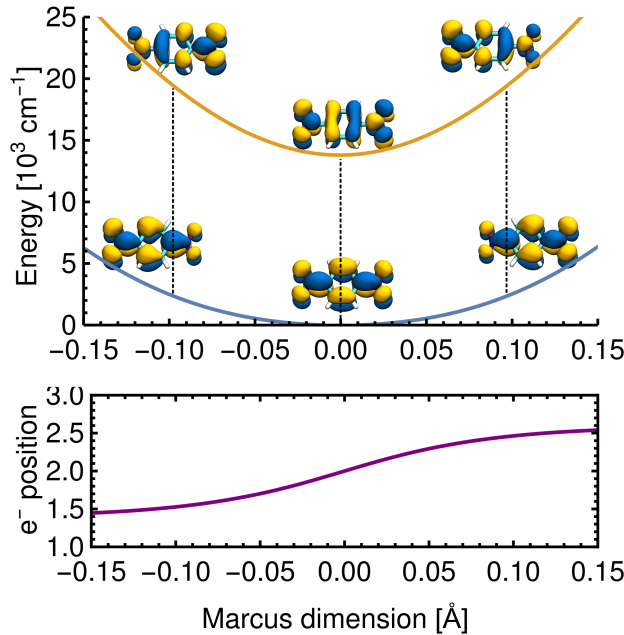


Figure 8: Reconstructed potential energy curves from geometries displaced in the direction of the Marcus dimension for p -DNB $\bullet^-$ in ACN. The scan was performed with a step size of 0.005 Å. The change of the electron position in the ground and excited states is illustrated in the upper panel using natural transition orbitals and quantified in the lower panel according to Eq. 3.

along the Marcus dimension can be measured in terms of the displacement of the nuclei from their equilibrium position.

First, we show the results for p -DNB $\bullet^-$, a Class III system. The potential energy surfaces of the ground and the first excited states are plotted in Fig. 8, where the localization or delocalization of the unpaired electron is illustrated by natural transition orbitals. The scan results in two nested parabolic-like surfaces with different curvatures. The adiabatic minimum is characterized by an electron delocalized over the entire molecule. Any motion along the Marcus coordinate will localize the electron to some extent on one of the nitro groups. This localization is reversed in the excited state. We therefore conclude that the system behaves according to Marcus' theory of ET and that the identified ET coordinate is correct.

Moving on to a Class II system, m -DNB $\bullet^-$ in ACN (see Fig. 9), the ground state energy profile is a double-well potential and the excited state is a harmonic-like potential with the minimum centered just above the top of the ground state barrier. The qualitative agreement of the *ab initio* energy profiles with the Marcus model is a necessary, but not sufficient, condition to demonstrate that this dimension is the ET coordinate. The motion along the Marcus dimension should result in a change of the diabatic state. In other words, by overcoming the ground state barrier the unpaired electron has to be transferred to the other center. At the equilibrium configuration (position 0 Å in Fig. 9), the unpaired electron is localized on the left-hand side nitro group in the ground state and on the right-hand side one in the excited state. At the top of the barrier, the unpaired electron is delocalized over the entire molecule. Once the barrier is overcome, the electron is localized on the right-hand side nitro group in the ground state and on the left-hand side one in excited state. This behaviour agrees exactly with the Marcus model, and hence the Marcus dimension we obtained from the multi-component fit is the dimension that facilitates electron transfer.

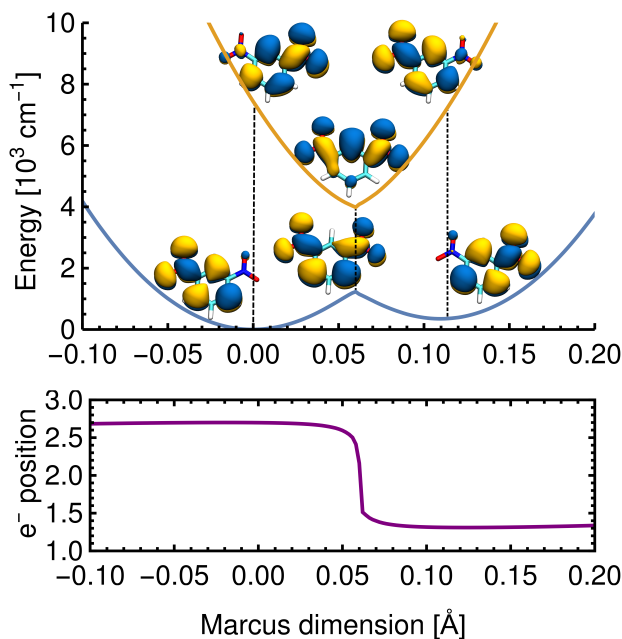


Figure 9: Reconstructed potential energy curves from geometries displaced in the direction of the Marcus dimension for $m\text{-DNB}^{\bullet-}$ in ACN. The scan was performed with a step size of $0.002 \text{ \AA}$. The change of the electron position in the ground and excited states is illustrated in the upper panel using natural transition orbitals and quantified in the lower panel according to Eq. 3.

There are, however, two regions with some deviations from the Marcus model: I) The double-well potential obtained from the *ab initio* scan is not symmetrical. Since the $m\text{-DNB}^{\bullet-}$ is a symmetrical system, both adiabatic minima in the double-well potential must have the same energy. The initial minimum (position $0 \text{ \AA}$ in Fig. 9) was found by geometry optimization and is therefore described properly. Displacing the molecular geometry along the Marcus dimension results in the second minimum which is higher by 350 cm^{-1} . Of course the obtained potential could be symmetrized easily, but we choose not to do this at this point because we do not expect to gain any additional insight from a symmetrized potential. We interpret the offset between the minima as the stabilisation that would be achieved by nitro group twisting, which implies that the electron transfer itself does not require twisting of the nitro group (see Fig. 7). In the LICC approach, this nitro group twisting is included, even though as suggested here it may not be inherently required for ET.

II) The ground state potential does not change smoothly at the top of the barrier; instead, it exhibits a cusp. The same is seen in the excited state where the energy minimum takes the shape of a cusp. This appears to be a direct result of our approach, considering that the size of the scan steps is $0.002 \text{ \AA}$ and it is therefore unlikely that the curvature was missed due to a too widely spaced grid. This observation does not agree with the Marcus model, where the potential curves are smooth everywhere. The top of the barrier is in the region of an avoided crossing so that a multideterminant method might be necessary. In the SI, we compare the scans of the potential energy curves obtained from DFT with wavefunction methods (CASSCF, CASSCF/NEVPT2). We show that the cusp might be an artifact of using a single reference method. However, a proper description of the potential curves requires a strongly correlated method due to the expected importance of dynamic correlation. This is relatively easily captured with an appropriately chosen density functional, but when using wavefunction methods it appears that very large active spaces in combination with a perturbative treatment will be needed.

Comparing the obtained potential with those resulting from the LICC approaches (Fig. 4), we notice that barrier from our approach is much thinner (LICC: 0.2 Å and ca. 0.3 Å vs. here: 0.12 Å). The barrier is ca. 200 cm⁻¹ higher than those obtained from LICC. This relatively small difference suggests that our approach does not reveal the minimum energy pathway, which is not a surprising result since the only constraint enforced in the fit is a correspondence to the Marcus model. We note that the potential curve resulting from the Marcus model applied to a many-dimensional system does not have to coincide with the minimum energy pathway for translating the coordinates of one adiabatic minimum to those of the other adiabatic minimum.

Our findings suggest that the adiabatic minima are actually spatially very close to each other in the many-dimensional space of atomic nuclei: they have to move by only 0.12 Å to reach the other adiabatic minimum. Considering that the barrier is rather thin and the height agrees with literature expectations,^{51,56} heavy-atom tunneling might be an important process for the ET. Even though this suggestion may be surprising at first sight, heavy-atom tunneling in organic compounds was found to be important for many reactions.^{57,58,59} It may therefore be worthwhile to reconsider the importance of heavy-atom tunneling for intramolecular electron transfer. For the two Class II systems studied here, we estimated the transmission coefficients through the barrier as 0.34 for *m*-DNB^{•-} and 0.13 for 2,7-DNN^{•-}, respectively (see SI for details). These perhaps unexpectedly high values suggest that ET might be observable even at very low temperatures. Having a tool at hand that facilitates the evaluation of whether heavy-atom tunneling is relevant for intramolecular ET is an additional demonstration of the utility of being able to specify the ET coordinate and to quantify the electronic structure evolution along it.

4.5 Parameterization of the Marcus model

With the procedure described above, the Marcus model can now be recovered in the potential obtained from a *ab initio* calculation. To this end, an analytical potential is parameterized to the Marcus–Hush theory so that it matches as closely as possible to the *ab initio* potential.

There are four quantities that ultimately characterize the *ab initio* potential energy surfaces: i) the excitation energy at the adiabatic minimum, ii) the height of the barrier, iii) the excitation energy at the top of the barrier, and iv) the distance between the adiabatic minimum and the top of the barrier. These are depicted in both panels of Fig. 10. The Marcus model has three parameters: the potential coupling V_{ab} , the separation of the minima of the diabatic states d , and their force constants f . Only the potential coupling $2V_{ab}$ can be read immediately from the scan; it is the excitation energy at the top of the barrier. With the knowledge of the potential coupling we can relate other quantities obtained from the scan to the Marcus model. A more detailed discussion on how to choose the input values for the parameterization and description of the entire procedure is given in the SI.

The resulting parameters of the Marcus model will depend on the choice of parameterization procedure (sketched in Fig. 10). If the parameterization uses the potential coupling, the height of the barrier, and separation of the adiabatic minimum from the top of the barrier (parameterization **A**, Fig. 10a), the obtained potential energy curves will agree better with the ground (D_0) than with the excited state (D_1), see Fig. 10a. This is due to the fact that the reorganization energy from the *ab initio* scan does not enter the parameterization. In contrast, if the parameterization uses the reorganization energy, the separation of the adiabatic minimum

and the top of the barrier, and the potential coupling (parameterization **B**, Fig. 10b), the shape of the potential curves for both ground and excited state will be better represented. However, the height of the barrier will not agree with the *ab initio* potential.

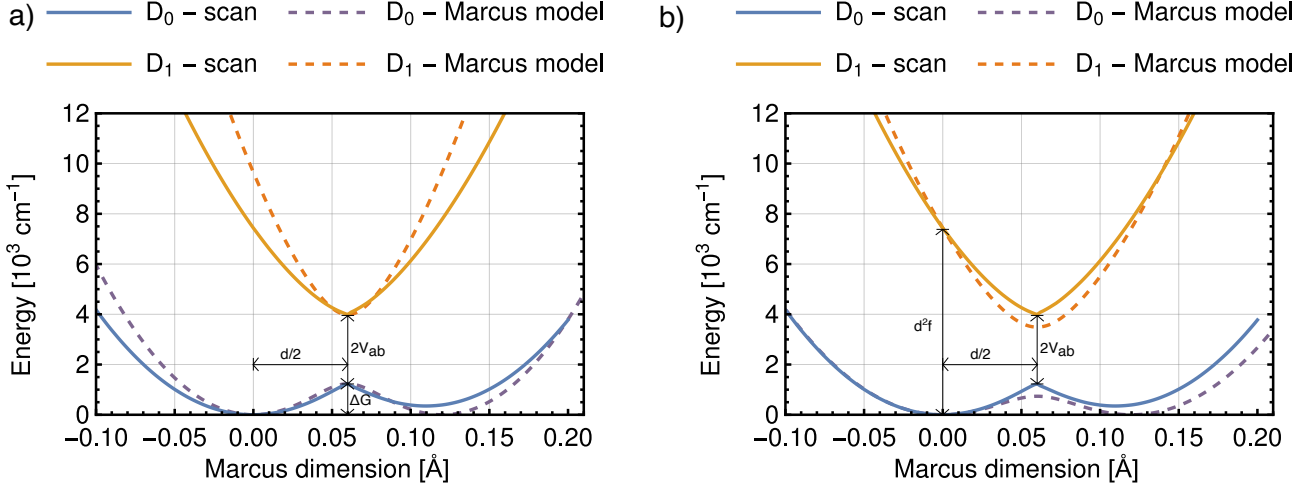


Figure 10: Potential energy curves obtained from the scan and from the parameterized Marcus model with two different parameterization procedures. As input parameters were used: a) the excitation energy at the top of the barrier, the height of the barrier and the distance from the left adiabatic minimum to the top of the barrier; b) the excitation energy at the top of the barrier, the excitation energy at the adiabatic minimum and the distance from the left adiabatic minimum to the top of the barrier. Results for *m*-DNB^{•-} in ACN.

The results illustrate that the Marcus model faithfully captures the general shape of the potential curves but does not result in quantitative agreement with the *ab initio* potential. This is reflected in the parameters obtained for the barrier height ΔG and the reorganization energy λ , see Table 1. A disagreement might be expected given that the Marcus model assumes harmonic diabatic states which might not be the case in a real system for which the anharmonicities of the diabatic states enter the *ab initio* potential. This is known in the literature and the model can be corrected by using “quartic augmented” diabatic surfaces.⁶⁰ In addition, the electronic structures at the top of the barrier are not described perfectly, but since the error introduced by the electronic structure method cannot be avoided or removed, the predicted shapes of the potential energy curves cannot be expected to agree exactly with the shapes in the Marcus model. We note that parameterizing the Marcus model for a specific system is not a straightforward procedure; in most cases it can be expected that a compromise between describing well either the barrier height or the reorganisation energy will need to be found to best represent the system.

Perhaps the most surprising result is the separation of the diabatic states d , which is unexpectedly low in all cases. Prior experimental studies of dinitroradical anions^{16,61} made use of the generalized Mulliken–Hush formula¹² to estimate the separation of diabatic states from the transition dipole moments, evaluated either experimentally⁶¹ or by using semi-empirical calculations.¹⁶ The d values ranged from 2 to 6 Å and were not clearly connected to the distance between the redox centers.

To elucidate in more detail which values for the separation of the diabatic states are realistic, we propose the following thought experiment. Starting from the Marcus model with a reorganization energy $\lambda = f \cdot d^2 \approx 8000 \text{ cm}^{-1}$ and a potential coupling $2V_{ab} \approx 2500 \text{ cm}^{-1}$ —values of this magnitude agree with this work as well as prior computational¹⁷ and experimental^{51,62} studies— the separation of the diabatic states is set to $d = 2 \text{ Å}$,

Table 1: Results from parameterization of the Marcus model. Rows labelled **A** and **B** correspond to the parameterization procedure illustrated in Fig. 10 a) and b), respectively.

		ΔG [cm^{-1}]	λ [cm^{-1}]	$2V_{\text{ab}}$ [cm^{-1}]	d [$\text{\AA}$]
A	$m\text{-DNB}^{\bullet-}$	1 233	9 652	2 752	0.125
	$2,7\text{-DNN}^{\bullet-}$	1 644	10 386	2 111	0.135
B	$m\text{-DNB}^{\bullet-}$	737	7 434	2 752	0.129
	$2,7\text{-DNN}^{\bullet-}$	970	7 510	2 111	0.138
<i>ab initio</i> scan	$m\text{-DNB}^{\bullet-}$	1 233	7 434	2 752	0.120
	$2,7\text{-DNN}^{\bullet-}$	1 644	7 510	2 111	0.132

the lowest value of the range mentioned above. The remaining degree of freedom in the Marcus model is the spring constant f . Assuming that one nitrogen atom is moving, the corresponding harmonic frequency $\omega^2 = \frac{f}{\mu}$ would be approximately 50 cm^{-1} .

Our results show that the Marcus dimension is mostly confined to C–N bond stretches, for which the expected harmonic frequencies are around 1000 cm^{-1} . The computed harmonic frequencies and phonon masses for all species studied herein agree with this estimate, see SI. Clearly, d has to be on the order of tenths of Ångström, as is demonstrated in our results, and it cannot be related to the real space distance between the redox moieties. Instead, since the Marcus dimension is a collective motion, d has to be thought of as a distance in the multi-dimensional space of atomic nuclei.

4.6 ET rate constant

In systems that conform to the Marcus model, the ET rate can in principle be assessed with the Marcus equation (Eq. 1).^{3,4} The expression is based on Fermi’s golden rule and is thus valid only for small values of the potential coupling V_{ab} . Another assumption employed in the Marcus equation is that all vibrational motions involved in the ET are small in frequency ($\hbar\omega \ll 2k_B T$); this is the so-called high temperature limit.³ The Marcus equation is widely used to predict the ET rate in proteins⁶³, the rate of the photoinduced ET⁶⁴, or the rate of the inter-system crossing.⁶⁵

For large potential couplings V_{ab} , the ET can be assumed to happen only adiabatically, *i.e.*, once the nuclei reach the top of the barrier the probability of the electron tunneling is close to one.⁴ In this case, the pre-exponential factor will reduce to a nuclear frequency along the ET coordinate ν_q and the ET rate can be calculated according to Eq. 2. The nuclear frequency ν_q is a well defined concept only in the harmonic potential. In the double-well potential this value has to be estimated, and we propose to use the harmonic approximation at the adiabatic minimum to obtain the force constant and subsequently the harmonic frequency (see SI for more details). Regardless of how ν_q is estimated, the value is approximately 10^{13} s^{-1} .

Table 2: ET rate constants in 10^{10} s^{-1} for Class II systems in ACN at 300 K. The classical rate is computed using Eq. 2. The Marcus equation refers to Eq. 1 with input values taken from parameterization scheme **A**.

	<i>m</i> -DNB	2,7-DNN
Classical	8.16	1.22
Marcus eq.	125.7	9.52
Experiment	4.63 ^{a,b}	0.31 ^c

^aValue from Ref. [56]; ^bRef. [51] reported value $1.54 \cdot 10^{10} \text{ s}^{-1}$; ^cValue from Ref. [16].

A comparison of ET rates according to the Marcus equation with the adiabatic rates is shown in Table 2. The adiabatic, *i.e.* classical, rate was computed using the barrier height from the scanned potential and the harmonic frequency at the adiabatic minimum. The parameters for the Marcus equation were taken from parameterization procedure **A**.

The ET rates listed in Table 2 favor the description with the more simplistic Eq. 2 over that with the Marcus equation (Eq. 1). We can identify two reasons for this finding: I) Both systems under study have large potential coupling values V_{ab} , which are outside the scope of the Marcus equation. II) The nuclear frequency in the Marcus dimension is larger than $2k_B T$. Note that the Marcus dimension is confined mainly to the stretching of C–N and N–O bonds which have frequencies of ca. 1000 cm^{-1} .

For systems with large potential coupling V_{ab} , the ET mechanism is adiabatic and the ET rate should be assessed classically (*i.e.*, with Eq. 2). Since the biggest error is introduced by the electronic structure method, choosing a different method of estimating the nuclear frequency ν_q would improve the value of the ET rate only through error cancellation. Classical treatment of ET is only possible for high temperatures; heavy-atom tunneling which might drive ET at low temperatures should in principle be possible due to the very narrow barrier. Another case where the classical theory will fail is a photoinduced ET which is, however, beyond the scope of this paper.

5 Conclusions

We propose a method for identifying the nuclear coordinate that promotes electron transfer in mixed valence systems by exploiting properties postulated by Marcus–Hush theory in the analysis of a thermally representative ensemble of *ab initio* calculations. As the characteristic electron transfer property, the electron position is chosen for Class III systems with complete delocalisation of the unpaired electron, and the excitation energy is chosen for Class II systems where a small barrier separates two adiabatic minima with localisation of the unpaired electron on one of the redox centers. The electron transfer coordinate, also termed Marcus dimension, is obtained as a linear combination of vibrational modes. A ramification is that the Marcus dimension is not simply equivalent to the absorption in a certain IR or Raman region; the *ab initio* analysis considers active and silent modes across all energies.

The method was demonstrated on a set of organic radical compounds with two nitro groups as the redox centers. The Marcus dimension was found to be a chemically intuitive antisymmetric motion mostly restricted

to the redox centres (nitro groups) and the atoms of the bridging unit (aromatic core) that they are attached to. The motion is qualitatively very similar for structurally similar compounds, and is retained even after an environmentally induced change from Class II ($m\text{-DNB}^{\bullet-}$ and $2,7\text{-DNN}^{\bullet-}$ in ACN) to Class III (both in vacuum). We have thus shown that our approach identifies the nuclear coordinate that is the electron transfer pathway in Class II compounds and leads to charge localization in Class III compounds. Scans along the Marcus dimension clearly demonstrate that the expected potential shapes are obtained, and furthermore provide the basis for recovering the Marcus model from *ab initio* calculations. To the best of our knowledge, this is the first approach for identifying the electron transfer coordinate that is applicable across all Robin–Day Classes.

The Marcus dimension we identify for Class II compounds appears to be an intrinsic property of the molecule, which implies a separation of the transition from one adiabatic minimum to the other into the electron transfer process and a distinct structural relaxation. This is underscored by comparison of our approach with the previously employed Linear Interpolation of Cartesian Coordinates, which is exclusively applicable to Class II compounds and renders a motion at odds with expectations that is furthermore clearly dependent on the choice of reference structure. It may be possible to devise an experimental test for our suggestion of separable electron transfer and structural relaxation events.

Our results point towards the electronic structure method continuing to be a limitation for theoretical studies of MV compounds. The Marcus dimension shows a cusp in a narrow region of the nuclear configuration space where an avoided crossing is expected; even though local hybrid density functionals perform exceptionally well in the adiabatic minima, it appears to fail here due to its single-reference nature. Treating this region with multiconfigurational methods (CASSCF/NEVPT2) provides qualitatively acceptable results but suggests that the extent of dynamical correlation requires larger active spaces or alternative strongly correlated methods.

The *ab initio* scans along the Marcus dimension show a small separation of the minima. The parameterization of the Marcus model results in a similar separation of the diabatic states of *ca.* 0.12-0.13 Å, *i.e.*, a much thinner barrier for electron transfer than had been previously suggested. This small distance in the multi-dimensional space of atomic nuclei suggests that heavy-atom tunneling may be a relevant contributor to intramolecular electron transfer. We estimated transmission coefficients of 0.34 for $m\text{-DNB}^{\bullet-}$ and 0.13 for $2,7\text{-DNN}^{\bullet-}$. Low temperature experiments may confirm this finding in future, which would be one way of obtaining experimental support for the concept of the Marcus dimension introduced here.

With a method for identifying the Marcus dimension of electron transfer in any mixed valence system for which TD-DFT calculations on a representative ensemble can be obtained, a more rigorous and quantitative discussion of electron transfer is now possible. It provides an opportunity to evaluate ET mechanisms involving molecular orbitals or electronic states proposed in the literature, *e.g.* incoherent hopping *vs.* coherent superexchange mechanisms, or two-state *vs.* multi-state models.^{6,55} Our approach is the first to provide the spring constant of the nuclear motion and the separation of the adiabatic minima. Individual access to all parameters of the Marcus model holds promise for disentangling electronic structure behaviour arising from the electronic coupling, the curvature of the PES and the separation of the minima, as well as quantifying the influence of environmental effects.

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