Photo-induced metal–ligand bond weakening, potential surfaces, and spectra

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Abstract

This review will focus on three aspects of spectroscopic research. The first is the theoretical explanation of Adamson’s rules in terms of ligand-field theory. The explanation made the

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connections between electronic spectroscopy and photochemical activity. The second is the development of new methods of relating bonding changes deduced from spectroscopy with the excited-state distortions of a molecule (i.e. the actual bond lengths and bond angles of the molecule in the excited state). The time-dependent theory of electronic and resonance Raman spectroscopy focuses on the dynamics that occur after absorption of a photon, and provides a new point of view of the time evolution of the molecule. The final aspect is the dynamics of molecules when multiple coupled excited electronic states and multiple normal coordinates are involved. Amplitude transfer between states leads to intensity borrowing, intersystem crossing, and interference dips that can be measured spectroscopically. This review emphasizes the interplay between theory and experiment and between the static and dynamic views of the properties of excited electronic states of metal-containing molecules. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Of the many important contributions to the area of inorganic photochemistry made by Adamson, two provide the impetus for this review. The first was a set of summary statements about the photochemical reactivities of chromium(III) ammine complexes that are known as ‘Adamson’s Rules’ [1]. These rules stated the relationships between the photochemical reaction products and the spectrochemical properties of the ligands. They stimulated both theoretical and experimental work, the result of which is a detailed understanding of the photochemistry of ionic metal systems.

The second contribution that motivates this review is Adamson’s highlighting of the difference between the molecule as it exists immediately after absorption of a photon and the molecule after relaxation processes have occurred. He provided the appellation ‘thermally equilibrated excited state’ or ‘THEXI’ state to the latter [2]. This clever name drew attention to the fact that the absorption of a photon initiates a series of dynamic processes and that the molecule may have changed significantly even though it is in the same electronic state.

At the time that the above two contributions were published, the primary focus of attention in inorganic photochemistry was on the rates of various processes; from this point of view photochemistry was a branch of the study of inorganic reaction mechanisms. Adamson’s rules shifted attention to the ‘strength’ of metal–ligand interactions as measured by electronic absorption spectroscopy and interpreted by crystal-field theory. The spectrochemical series was needed to define the ‘weak’ and ‘strong’ field axes of the molecule. Photochemical reactions are dynamic processes, but crystal-field theory treats excited states like rungs on a ladder where each rung is the energy of a given electronic excited state. The THEXI state idea suggested that the rungs are somehow not stationary and that a different set of rungs should be used to represent the thermally equilibrated states.
This review will focus on the chain of research that received its impetus from the publication of Adamson’s Rules and THEXI states. The first link in the chain was the theoretical explanation of Adamson’s rules in terms of ligand-field theory [3–13]. This work made the connection between electronic spectroscopy and photochemical activity. The second link in the chain was the development of new methods of relating bonding changes deduced from spectroscopy with the excited-state distortions of a molecule (i.e. the actual bond lengths and bond angles of the molecule in the excited state) [14–16]. The distorted molecule is closely related to Adamson’s THEXI state. The time-dependent theory of spectroscopy focused on the dynamics that occur after absorption of a photon, and provided a convenient method for calculations as well as a new point of view of the time evolution of the molecule. Resonance Raman spectroscopic methods and intensities in resonance Raman spectra were developed as methods of measuring excited-state distortions one normal mode at a time. The final link in the chain of concepts reviewed here was the development of theoretical methods for following the dynamics of molecules when multiple coupled excited electronic states are involved [17–20]. Amplitude transfer between states leads to intensity borrowing and interesting interference effects that can be measured spectroscopically. An alternative title of this review, following the links in the chain, is the evolution from a static to a dynamic view of properties of excited electronic states of metal-containing molecules.

This review is organized into three parts. In the first section, the connection between Adamson’s rules and crystal-field theory is discussed. In the second part, dynamics is introduced and bond-length and -angle changes that result from populating excited states is reviewed with an emphasis on the time-dependent theoretical interpretation of electronic and resonance Raman spectra. In the final part, dynamics in metal systems with coupled electronic states is discussed and illustrated with intensity borrowing, intersystem crossing, and interference dips. The focus of this review is decidedly spectroscopic; the interplay between theory and experiment and between the static and the dynamic is emphasized.


In this section we provide a brief overview of the connections between Adamson’s rules and ligand-field theory. At the heart of the theory is metal–ligand bond weakening, which occurs in excited ligand field electronic states. The specific directionality of weakening in the metal complex is associated with specific states; the directionality predicts and explains specific ligand labilization in photochemistry experiments.

The fundamental idea behind the theory is that excited electronic states of transition metal complexes have bonding properties that are different from those of the ground state. These properties can be predicted in a straightforward manner from ligand-field theory. This idea can be applied to any metal complex with any coordination number, but the greatest experimental detail and the most advanced
theoretical development involved the ligand field or d–d excited states of six-coordinate complexes of metals with d^3- and d^6-electron configurations. The development of the theory was spurred by the publication of Adamson’s rules [1]. The first rule states that the axis having the weakest average crystal field will be the one labilized. The second rule states that if the labilized axis contains two different ligands, then the ligand of greater field strength preferentially aquates. The theoretical basis for these rules consists of two steps. Step one predicts which axis will be photolabilized. Step two predicts which ligand on the labilized axis will be preferentially labilized if the two ligands are different.

2.1. State energies and wavefunctions

The first step is to determine the relative energies of the excited electronic states and to find the d-orbital wavefunctions for these states [3,8,10]. The changes in bonding that occur when a given excited state is populated may be deduced from the wavefunctions of that state. For example, if the transition involves promotion of an electron from a bonding d_{xz} orbital to an antibonding d_{z^2} orbital (corresponding to wavefunctions |d_i d_j...d_{xz}| and |d_i d_j...d_{z^2}| for the ground and excited state, respectively), the π bonding in the xz plane of the complex will be weakened and the σ bonding along the z-axis will be weakened. These bond weakenings will lead to ligand substitution photochemistry along the z-axis.

A partial correlation diagram for a six-coordinate d^3 complex is shown in Fig. 1. The right side of the diagram represents the splittings for positive values of D_{t}, the tetragonal splitting parameter. The ‘g’ subscripts that appear with the states on the right side of Fig. 1 are valid under D_{4h} symmetry. Under C_{4v} symmetry the g subscript is dropped. The actual order in any particular complex must either be determined experimentally (for example by using single crystal-polarized spectra) or by fitting a spectrum calculated from theory to that observed. Both methods have been applied to chromium(III) complexes, and the actual orderings of the quartet states and of the corresponding one-electron d-orbital energies are known for many different complexes.

In order to discuss the chemical consequences of excitation to the upper quartet energy states, we also need to know the quartet state wavefunctions. They are given in Table 1. The two states of E symmetry can mix. This mixing (‘configuration interaction’) results in new wavefunctions that are linear combinations of the original ones. The mixing coefficient λ is a function of the tetragonal crystal-field parameters and reduces to zero for octahedral complexes. The wavefunction of most importance in the following discussion is that of the lowest spin-allowed excited state, \(^{4}E_g\)('T_{2g}). The wavefunctions \(\phi'_3\) and \(\phi'_4\) for this state, including the mixing, are given in Table 1.

2.2. Bonding changes and prediction of the labilized axis [3,8,10]

In the electronic transition from the ground to the excited electronic state, electron density is lost from the ground state and acquired by the excited state.
Thus, the two important changes in the bonding that must be considered are: (1) the change arising from loss of an electron from the molecular orbital of the ground state; and (2) the change arising from adding an electron to the molecular orbital of the excited state. The following discussion will be based on the orbitals given in Table 1.

The ground state of all of the mixed ligand tetragonal complexes considered here (\(4^1\)) consists of one electron in each of the \(d_{xy}, d_{xz}\) and \(d_{yz}\) metal orbitals (see Table 1). These three metal orbitals are all of \(p\) symmetry. When the ligand is a \(\pi\) donor (i.e., its orbitals of \(\pi\) symmetry that interact most significantly with the metal

![Correlation diagram for a six-coordinate d⁢³ complex.](image)
are full), then the three metal orbitals are part of \( \pi \) antibonding molecular orbitals. When the ligand is a \( \pi \) acceptor (i.e., its orbitals of \( \pi \) symmetry that interact most significantly with the metal are empty) then these three metal orbitals are part of \( \pi \) bonding molecular orbitals. If no ligand \( \pi \) orbitals are available (amine ligands, for example) then these \( d \) orbitals are nonbonding. In the examples discussed here, the only \( \pi \) interacting ligands are those with filled \( \pi \) orbitals. Thus, loss of electron density from the \( d_{xy} \), \( d_{xz} \) and \( d_{yz} \) metal orbitals results in a strengthening of the \( \pi \) bonding in the complex. The spin-allowed transitions results in stronger \( \pi \) bonds. The direction or axis along which the bond is strengthened will be determined by the nature of the excited state. Transitions to some excited states deplete the \( d_{xy} \) orbital, resulting in stronger \( \pi \) bonds in the \( xy \) plane, while others deplete the \( d_{xz} \) and \( d_{yz} \) orbitals, resulting in stronger \( \pi \) bonding in the \( z \) direction.

The excited state to which an electron is promoted in the spin-allowed transitions involves the unoccupied \( d_{x^2-y^2} \) and \( d_{z^2} \) orbitals. They are part of \( \sigma \) antibonding molecular orbitals. If the excited state wave function is primarily \( d_{z^2} \) in character, \( \sigma \) bonding along the \( z \)-axis will be weakened. (\( d_{x^2-y^2} \) character weakens \( \sigma \) bonds in the \( xy \) plane.) All spin-allowed transitions will thus result in a weakening of the \( \sigma \) bond between the metal and a ligand in addition to the \( \pi \) strengthening discussed above.

As an illustration of the analysis of the bonding changes, consider first the simple case of \( ^4B_{1g} \rightarrow ^4B_{2g}(^4T_{2g}) \). Here the transition clearly involves a promotion of an electron from the \( d_{xy} \) to the \( d_{z^2} \) orbital as may be verified from the wavefunctions \( \phi_1 \) and \( \phi_2 \). The loss of electron density from the \( d_{xy} \) orbital increases the \( \pi \) bonding in the \( xy \) plane at the same time that the increase in electron density in the \( d_{z^2} \) orbital weakens the \( \sigma \) bonding in the \( xy \) plane. The net overall effect on the bonding will depend on the relative \( \sigma \) and \( \pi \) bonding abilities of the in-plane ligand since the \( \sigma \) and \( \pi \) effects oppose each other. If the in-plane ligands are ammonia,
for example, the $\pi$ bonding in the $xy$ plane is negligible and cannot be strengthened. (The $d_{xy}$ orbital is formally nonbonding.) The net result is a weakened metal in-plane ligand bond.

As a second illustration of the analysis of the bonding changes caused by a particular transition, consider $^4B_{1g} \rightarrow ^4E_g (^4T_{2g})$. Here the transition involves a promotion of an electron to a degenerate pair of wavefunctions. For the transition from $\phi_1$ to $\phi_2$ the major orbital change is promotion of a $d_{xz}$ electron to $d_{z^2}$. For the transition from $\phi_1$ to $\phi_3$ the major orbital change is promotion of a $d_{yz}$ electron to $d_{z^2}$. The state is degenerate because $d_{xz}$ and $d_{yz}$ orbitals are degenerate. In both cases, the loss of the electron from the $d_{xz}$ or $d_{yz}$ orbital strengthens the $\pi$ bonding in the $z$ direction. However, populating the $d_{z^2}$ orbital weakens the $\sigma$ bonding in the $z$ direction. Because the $\sigma$ antibonding orbitals are higher in energy than the $\pi$ antibonding orbitals, populating the former will have the greatest labilizing effect. $\sigma$ bonds are generally stronger than $\pi$ bonds; turning on $\sigma$ antibonding has a greater weakening effect than turning on $\pi$ antibonding. The analysis for the other spin-allowed transitions is carried out in a similar manner.

As a specific example of the prediction of the labilized axis, consider $\text{Cr(NH}_3)_4\text{Cl}_2^+$ in aqueous solution. The chloride ligand is weaker in the spectrochemical series than ammonia and it is a weaker $\sigma$ donor and better $\pi$ donor than ammonia. The lowest excited quartet state is $^4E$. From the wavefunctions in Table 1 and the summary of the bonding changes discussed above, the $z$-axis will be the labilized axis because $\sigma$ bonding is weakened predominantly along that axis. The photochemical experiment shows that a chloride ligand is lost.

If there are two different ligands on the labilized axis found in step one, which of them is labilized to the greatest extent? The answer is that the ligand that experiences the greatest antibonding also experiences the greatest labilization [6,10]. This answer is dissatisfying because it does not provide predictive power unless the bonding properties are known. Two methods of estimating the bonding properties have been used for photochemical predictions: a molecular orbital parameterization and a crystal field parameterization. The weakness inherent in both is that the parameters for both of the ligands interacting with the specific metal must be known. Modern molecular orbital methods make it easy to calculate the bonding properties of any type of ligand. For ionic ‘Werner’ complexes where crystal-field theory parameters have been calculated, useful estimations can be made based on those parameters without having to carry out a full MO calculation.

How big of a change of the metal–ligand bond is actually caused by populating antibonding orbitals and depopulating bonding orbitals? In the theoretical interpretation of ligand-field excited-state photochemistry discussed above, the ligand that is lost in the photoreaction is identified in terms of its labilization. Labilization is associated with the metal–ligand bond that experiences the most antibonding. It is important to know more about the amount of labilization. If the antibonding were large enough, the metal–ligand interaction could become repulsive and the photoreaction could be dissociative. On the other hand, the labilized bond, although weakened, could still be attractive and therefore additional factors would be required in order for the reaction to occur. The latter situation is the most common
for ionic ‘Werner’ complexes because the most important bonding interactions responsible for the stability involve bonding molecular orbitals that are not involved in the electronic transition. The transition from a weakly π interacting d orbital to a weakly antibonding σ orbital certainly weakens the bond but does not result in a bond order of zero in the excited state. The excellent agreement between the theoretical determination of the labilization and the experimental identification of the leaving ligand shows that the bonding changes are of fundamental importance. In Section 4 a quantitative theoretical calculation of the change in the bond length accompanying d–d excitation is presented.

3. Bond-length changes in excited electronic states

Absorption of a photon occurs without any change in the structure of the molecule; the excited molecule initially has the same structure as the unexcited, ground state molecule. However, it generally will be vibrationally excited; after it relaxes to its lowest vibrational level, the structure will be different. This relaxed structure is Adamson’s THEXI state [2]. We now need to include the dynamics of the excited molecule because the structure will change as a function of time. The distortions that the molecule undergoes can be categorized as symmetry preserving or symmetry destroying. Symmetry preserving distortions involve totally symmetric normal modes of vibration, and the point groups of the molecule in its ground and excited states are the same. Symmetry destroying distortions involve asymmetric normal modes of vibration and the point group changes. The former are responsible for long vibronic progressions in electronic spectra; the latter are important in making symmetry ‘forbidden’ transitions become allowed.

In this section the use of theory to calculate the changes in structure, (i.e. metal–ligand bond-length changes (Δ)) from absorption spectra, emission spectra and/or resonance Raman spectra will be presented. The close connections between the theoretical interpretation of ligand-field excited-state photoreactions and spectroscopy were shown in Section 2. The magnitude of bond-length changes caused by populating antibonding orbitals can also be measured by using spectroscopic techniques, and the results can be correlated with the photochemistry. The analysis in this section uses the time-dependent theoretical point of view because the unity between electronic and resonance Raman spectroscopy and the interpretation of the spectroscopic effects of multiple mode distortions can readily be seen [14–16,21,22]. The time-dependent theory emphasizes the dynamics of the processes that lead to specific features in the spectra.

Cross-sections of the multidimensional surface along one normal mode that will be used to discuss the theory for both electronic absorption and Raman spectroscopy are shown in Fig. 2(a and b), respectively. In both types of spectroscopies, the initial vibrational wave packet (φ) makes a vertical transition and propagates on the potential surface of the excited state, which, in general, is displaced relative to that of the ground state. The displacement (Δ) is the difference in geometry between the ground and the excited states. The displaced wave packet is not a
Fig. 2. Potential surfaces used to illustrate the time-dependent theory of (a) electronic absorption and (b) resonance Raman spectroscopy. The time-dependent overlaps are shown in (c) and (d), and the spectra are shown in (e) and (f).
stationary state and evolves according to the time-dependent Schrödinger equation. In electronic absorption spectroscopy, the quantity of interest is the overlap of the initial wave packet with the time-dependent wave packet, \( \langle \phi | \phi(t) \rangle \). In Raman spectroscopy, the quantity of interest is the overlap of the moving wave packet \( \phi(t) \) with the final state of interest, \( \phi_f \). \( \phi_f \) is characterized by the normal mode \( k \) with vibrational quantum number \( n_k \). It is important to note that the potential surface where the wave packet propagates is the same in both types of spectroscopy. Therefore, resonance Raman spectroscopy gives the same type of information about the excited state as electronic absorption spectroscopy. When emission or absorption spectra are smooth, it is not possible to obtain the distortions from the intensities of vibronic bands because the bands from individual vibrational modes overlap to produce a smooth profile and all of the information is hidden. However, smooth and unstructured resonance Raman excitation profiles can be used to determine the distortions because the excited-state information is ‘filtered’ into each excitation profile of a particular mode being examined.

3.1. Electronic absorption spectroscopy

The propagating wavefunction, \( \phi_i(t) \), is given by the time-dependent Schrödinger equation. In dimensionless form, it is

\[
i \frac{\partial \phi_i}{\partial t} = -\frac{1}{2M} \nabla^2 \phi_i + V_i(Q)\phi_i = H_i \phi_i \tag{1}
\]

where \( H_i \) denotes the Hamiltonian, \( V_i(Q) \) is the potential energy as a function of the configurational coordinate \( Q \) and \(-1/2M\nabla^2\) is the nuclear kinetic energy. The split-operator method developed by Feit and Fleck is used to calculate \( \phi_i(t) \) [23,24]. Both the configurational coordinate \( Q \) and the time are represented by a grid with points separated by \( \Delta Q \) and \( \Delta t \), respectively. The time-dependent wavefunction \( \phi(Q, t + \Delta t) \) is obtained from \( \phi(Q, t) \) with

\[
\phi(t + \Delta t) = \exp \left( \frac{i\Delta t}{4M} \nabla^2 \right) \exp \left( \frac{i\Delta t}{4m} \nabla^2 \right) \phi(Q, t) + O(\Delta t)^3
\]

\[
= \hat{P}V\hat{P}\phi(Q, t) + O(\Delta t)^3 \tag{2}
\]

The magnitude of damped overlap, \( |\langle \phi_k | \phi(t) \rangle \exp(-\Gamma^2 t^2)| \) is plotted versus time in Fig. 2(c). The overlap is a maximum at \( t = t_o \) and decreases as the wave packet moves away from its initial position \( (t_o) \). It reaches a minimum when it is far away from the F–C region \( (t_k) \). At some time later \( t_c \), the wave packet may return to its initial position giving rise to a recurrence of the overlap. This time \( t_c \) corresponds to one vibrational period of the mode.

The electronic absorption spectrum in the frequency domain is the Fourier transform of the overlap in the time domain. The absorption spectrum is then given by

\[
I(w) = C \omega \int_{-\infty}^{+\infty} \exp(i\omega t) \left\{ \langle \phi | \phi(t) \rangle \exp \left( -\Gamma^2 t^2 + \frac{iE_0}{\hbar} t \right) \right\} dt \tag{3}
\]
with $I(\omega)$ the absorption intensity at frequency $\omega$, $E_0$ the energy of the electronic origin transition, $\Gamma$ is a phenomenological Gaussian damping factor, and $C$ is a constant. Fig. 2(e) shows the Fourier transform of the overlap, which is shown in Fig. 2(c). In the frequency domain (absorption spectrum), the vibronic spacing $\omega$ is equal to $2\pi/\tau_c$.

The physical picture of the dynamics of the wave packet in the time domain described above provides insight into the absorption spectrum in the frequency domain. The width of the spectrum is determined by the initial decrease of the overlap, which in turn is governed by the slope of steepest descent. The larger the distortion, the steeper the slope, the faster the movement of the wave packet and the broader the spectrum. Any other features in the spectrum are governed by the overlap at longer times. For example, the vibronic spacing $\omega$ in the frequency domain is caused by the recurrence at time $t_c$ corresponding to one vibrational period. The magnitude of the damping factor to be discussed later causes the magnitude of recurrences to decrease and gives the width of the individual vibronic bands.

In most transition metal and organometallic compounds, many modes are displaced. In the case of many displaced normal modes, the total autocorrelation in a system with $k$ coordinates is given by

$$\langle \phi | \phi(t) \rangle = \prod_k \langle \phi_k | \phi_k(t) \rangle$$

(4)

### 3.2. Raman spectroscopy

The Raman scattering cross section is given by [22]

$$\chi_R = \frac{i}{\hbar} \int_0^\infty \left( \sum_{\nu=1}^n \mu_{\nu}^* \langle \phi_\nu | \phi(t) \rangle, \exp(-iE_0^\nu t - \Gamma^\nu t) \exp\{i(\omega_\nu + \omega_I)t\} \right) \, dt$$

(5)

where $| \phi_f \rangle = \mu | \chi_f \rangle$ is the final vibrational state, $\chi_0$ of the ground electronic surface multiplied by the transition electric dipole moment, $\mu$, $| \phi(t) \rangle = \exp(-iH_{ex}(t)\hbar)|\phi \rangle$ is a moving wave packet propagated by the excited state Hamiltonian, $| \phi \rangle = \mu | \chi \rangle$ is the initial vibrational state of the ground electronic surface multiplied by the electronic transition moment, $\Gamma$ is the damping factor, $\hbar\omega_0$ is the zero point energy of the ground electronic surface and $\hbar\omega_I$ is the energy of the incident radiation.

The example of a one normal mode problem illustrates many of the important features of the calculation. The magnitude of the damped overlap $\langle \phi_f | \phi(t) \rangle \exp(-\Gamma t)$ for $f = 1$ is plotted versus time in Fig. 2(d). At time zero ($t_0$), $\phi$ makes a vertical transition to the upper surface. In contrast to the overlap of the absorption, the overlaps $\langle \phi_f | \phi(t) \rangle$ at $t = 0$ are identically zero because $\phi$ and $\phi_f$ are orthogonal eigenfunctions. However, $\phi$ is not an eigenfunction of the upper surface and begins to evolve on the upper surface according to the time-dependent Schrödinger equation. There is a peak in $\langle \phi_f | \phi(t) \rangle$ after $\phi(t)$ has moved away from the F–C region ($t_a$). The maximum is followed by a decrease as $\phi(t)$ moves further away. It reaches a minimum when it is far away from the F–C region ($t_b$). On the other hand, $\phi(t)$ will return to its initial position at time $\tau$ after one vibrational period.
Each return is responsible for an additional peak. There are two maxima in $|\langle \phi_f | \phi(t) \rangle|$ as the wave packet goes from and comes back to its initial position. The classical turning point falls between these maxima. At the end of each vibrational period, $\phi(t)$ and $\phi_f$ are once again orthogonal and $|\langle \phi_f | \phi(t) \rangle|$ drops to zero. The overlap for the Raman and the absorption are different because the former has two maxima in one vibrational period and the magnitude of the overlap at time zero is 0 instead of 1.

The Raman scattering amplitude in the frequency domain is the half Fourier transform of the overlap in the time domain as shown in Eq. (5). The Raman intensity $I_{i\rightarrow f}$ into a particular mode $f$ is

$$I_{i\rightarrow f} \sim \omega_c \omega_v^2 [\alpha_F]^*[\beta_F]$$

where $\omega_v$ is the frequency of the scattered radiation. In the frequency domain (the excitation profile in Fig. 2(f)), the vibronic spacing $\omega$ is equal to $2\pi/\tau$.

The resonance Raman excitation profiles are a collection of all the resonance Raman intensities of a given mode at various excitation wavelengths. The more familiar Raman spectrum is a plot of the intensities of the modes versus their vibrational frequencies at a specific excitation wavelength. The width of an excitation profile is determined by the total displacements of all the vibrational modes displaced in the excited state the same way as that of the absorption and emission spectra. It thus contains information about the distortions of all of the normal modes. However, each individual vibrational mode has its own excitation profile. Therefore each normal mode’s profile contains the information about that specific mode and the distortions can be obtained from the relative intensities of the excitation profiles. This mode specificity is an advantage of using the excitation profiles when envelopes are smooth.

### 3.3. Electronic emission spectroscopy

The time-dependent theoretical treatment of the electronic emission spectrum is very similar to that of the absorption spectrum because the two potential surfaces involved are the same. The principal difference is that the initial wave packet starts on the upper (excited state) electronic surface and propagates on the ground electronic state surface. The emission spectrum is given by [15]

$$I(\omega) = C \omega^3 \int_{-\infty}^{+\infty} \exp(i\omega t) \left( \langle \phi | \phi(t) \rangle \exp\left(-\frac{iE_0}{\hbar}t\right) \right) dt$$

where all of the symbols are the same as those in Eq. (4). $I(\omega)$ is the intensity in photons per unit volume per unit time at frequency of emitted radiation $\omega$. Note that for emission, the intensity is proportional to the cube of the frequency times the Fourier transform of the time-dependent overlap. Note also that the relationship between spectral features and the distortions are the same as those discussed for absorption.
3.4. Applications to metal-containing molecules

The focus of the previous discussion has been on the dynamics of wave packets on potential surfaces. The major factor affecting the dynamics is the displacement along a normal coordinate of the minimum of the excited state potential surface relative to that of the ground state. The displacements for a molecule of interest are calculated by varying the displacements until the calculated spectrum fits the experimental spectrum. Because the electronic and resonance Raman spectra are calculated from the same potential surfaces, the fit to one type of spectrum can be checked by comparison to a different type of spectrum, e.g. potential surfaces that were used to fit a Raman spectrum can also be used to calculate the emission or absorption spectrum. A good fit serves as a check on how well the surfaces represent the excited states of the molecule.

Many examples of the determination of excited state distortions have been published, and several reviews have appeared [15,17,25]. In some cases, detailed comparisons between resonance Raman and electronic spectra calculated from the same potential surfaces have been made, and distortions along multiple normal coordinates have been calculated. The spectra and distortions of molecules in which the excited state involves intervalence electron transfer [26–28], vibrational mode coupling [29], and resonance de-enhancement have been treated [28,30].

An important application of the calculations of excited state distortions is to assist in assigning excited states [31–36]. This application takes advantage of the fact that different transitions involve specific differences in the orbitals that are populated and depopulated. For example, in a metal complex containing ligands A and B, a metal to ligand A charge transfer will involve orbitals on ligand A, a metal to ligand B charge transfer will involve orbitals on ligand B, and a d–d transition would not strongly involve ligand orbitals that are remote from the metal. Thus a metal to A charge transfer would cause significant distortions on ligand A. In multi-ligand complexes, the location of the biggest distortions in the complex can assist in assigning an observed band in the spectrum.

4. Coupled electronic states

The electronic spectra of transition metal compounds form a rich area for investigating the effects of potential surface coupling because one of the important sources of state coupling, spin–orbit coupling, is large and because frequently many excited electronic states with different displacements and force constants lie relatively close together in energy [15,37,38]. One of the most important spectroscopic consequences of spin–orbit coupling is ‘intensity borrowing’ in which a formally spin-forbidden transition ‘borrows’ or ‘steals’ intensity from a spin-allowed transition. The appearance of spin-forbidden transitions in the spectra of metal complexes is frequently explained in this way [37–39]. A second important consequence of spin–orbit coupling is unexpected vibronic structure. Progressions in a vibrational normal mode may be induced in forbidden transitions, or the relative
intensities of the members of a progression may take on unusual patterns. These effects may reveal themselves in the band envelopes in unresolved spectra or most interestingly in the vibronic bands themselves in resolved spectra. A third consequence of the coupling is the appearance of interference dips, i.e. sharp losses in intensity in broad, unresolved bands.

Discussions of intensity borrowing, for example by spin–orbit coupling of two states of different spin multiplicity, usually involves a static picture that focuses on the electronic wavefunctions. The emphases are on how much of one electronic wavefunction is mixed into the second and the resultant effect of the mixing on the oscillator strength of the formerly forbidden transition [36–38]. The amount of the allowed ($\psi_a$) character in the forbidden ($\psi_f$) state is equal to

$$|c| = \frac{\langle \psi_a | H_{\text{spin–orbit}} | \psi_f \rangle}{(E_f - E_a)} \quad (8)$$

If the oscillator strength for a transition from the ground state to the allowed state is $f_a$, the oscillator strength for the forbidden transition will be

$$f_f = f_a \frac{E_f}{E_a} \frac{\langle \psi_a | H_{\text{spin–orbit}} | \psi_f \rangle^2}{(E_f - E_a)^2} \quad (9)$$

where $E_f$ and $E_a$ are the energies of the forbidden and allowed electronic transitions, respectively. The spin–orbit perturbation scrambles the allowed and forbidden excited states and enables the spin-forbidden transition to borrow intensity from the spin-allowed transition. Superficially it might appear that the vibronic structure would not be affected, an expectation far from the actual result. The quantum mechanical calculation is not trivial because the coupling of potential surfaces along normal coordinates results in a situation where the Born–Oppenheimer separability of nuclear and electronic wavefunctions cannot be made.

In this section we calculate how an electronic transition to a state with a spin different from that of the initial state acquires intensity by spin–orbit coupling with a third state. We also show how the vibronic structure in the ‘forbidden’ transition is affected by the coupling. The physical picture of the wave packet dynamics and the quantitative details are discussed. The theory is applied to the resolved vibronic structure in the emission spectra of Mn(V) in ionic lattices.

4.1. Theory

For absorption transitions to two coupled excited states, two wave packets, $\phi_1$ and $\phi_2$ moving on the two coupled potential surfaces are needed [17–20,40]. The total overlap $\langle \phi | \phi(t) \rangle$ is

$$\langle \phi | \phi(t) \rangle = \langle \phi_1 | \phi_1(t) \rangle + \langle \phi_2 | \phi_2(t) \rangle \quad (10)$$

The propagating wavefunction, $\phi_i(t)$, is given by the time-dependent Schrödinger equation. For two coupled states it is given by
\[
\frac{i}{\hbar} \hat{\phi}_i = \begin{pmatrix} H_1 & V_{12} \\ V_{21} & H_2 \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}
\]  
(11)

with the diagonal elements \( H_i \) of the total Hamiltonian as given in Eq. (1).

The generalization of Eq. (2) to the case of two coupled potentials requires that the exponential operators \( \hat{P} \) and \( \hat{V} \) be replaced by \( 2 \times 2 \) matrices operating simultaneously on \( \phi_1(Q, t) \) and \( \phi_2(Q, t) \)

\[
\begin{pmatrix} \phi_1(Q, t+\Delta t) \\ \phi_2(Q, t+\Delta t) \end{pmatrix} = \begin{pmatrix} \hat{P}_1 & 0 \\ 0 & \hat{P}_2 \end{pmatrix} \begin{pmatrix} \hat{V}_{12} \\ 0 \\ 0 \\ \hat{V}_{21} \end{pmatrix} \begin{pmatrix} \phi_1(Q, t) \\ \phi_2(Q, t) \end{pmatrix} + O[(\Delta t)^3]
\]  
(12)

The kinetic energy operator \( \hat{P} \) is independent for \( \phi_1 \) and \( \phi_2 \) in the diabatic basis, i.e. its matrix is diagonal. The potential energy operator \( \hat{V} \) is more intricate. The exponential operators must be given in terms of potentials that diagonalize the potential matrix in the total Hamiltonian, Eq. (11), i.e. in terms of the adiabatic potentials \( V_a \) and \( V_b \). These potentials are calculated from the diabatic potentials \( V_1 \) and \( V_2 \) and the coupling \( V_{12} \):

\[
V_a = c_1 V_1 + c_2 V_2 = \frac{1}{2} (V_1 + V_2) - \sqrt{(V_1 - V_2)^2 + 4V_{12}}
\]

\[
V_b = c_2 V_1 + c_1 V_2 = \frac{1}{2} (V_1 + V_2) + \sqrt{(V_1 - V_2)^2 + 4V_{12}}
\]  
(13)

From Eq. (12) it is obvious that \( \phi_1(t) \) and \( \phi_2(t) \) are mixed (formally via the off-diagonal matrix elements \( \hat{V}_{12} \)) at each time step. Details of the computer implementation of Eq. (12) are given in the literature [17–20,40].

It is interesting to note the different roles of \( \hat{P} \) and \( \hat{V} \). \( \hat{P} \), the momentum operator, transfers wavefunction amplitude \( \phi_i \) among grid points along \( Q \) at each time step, but does not transfer amplitude between the diabatic parent states 1 and 2. These changes are easily monitored by looking at the wave packet \( \phi_i(t) \) after every time step. On the other hand, \( \hat{V} \), the potential energy operator, transfers amplitude between the electronic states at each time step, but does not couple grid points along \( Q \). The amplitude transfer between the diabatic potentials can be followed by calculating the norms \( \langle \phi_i(t) | \phi_i(t) \rangle \) for \( \phi_i(t) \) and \( \phi_j(t) \) after every time step. The norms are a quantitative measurement for the amount of population change between the two states.

Both operators affect the total overlap \( \langle \phi | \phi(t) \rangle \) and therefore the spectra. Only the calculation which simultaneously involves both coupled states according to Eq. (12) gives the correct total overlap. All calculations involving only one surface lack the contribution of the population change between the states to the total dynamics due to nonadiabatic transitions or ‘surface hopping’. In the time-dependent picture it is straightforward to see how these population changes, direct manifestations of the breakdown of the Born–Oppenheimer approximation, occur and what their influences are on the absorption spectrum.
4.2. Induced oscillator strength in absorption spectra [19,41]

In the time-domain picture, amplitude transfer between surfaces due to coupling can cause a spin-forbidden transition to gain intensity in the electronic spectrum. A forbidden transition means that the initial wave packet is multiplied by zero (the transition dipole moment) and thus does not have any amplitude on the potential surface of the state (called ‘state 1’) with spin multiplicity different from that of the ground state. However, for the spin-allowed transition the wave packet is multiplied by the non-zero transition dipole moment and the wave packet is transferred vertically from the ground state onto the potential surface (called ‘state 2’). When spin–orbit coupling between the two states is non-zero, amplitude is transferred from state 2 to state 1.

The quantitative relationship between amplitude transfer in the time domain and observed intensity in the spectrum in the frequency domain depends upon how fast the amplitude transfer occurs and how much amplitude is transferred. These two aspects are interrelated and depend in part on the coupling strength and the shapes and positions of the potential surfaces.

Amplitude transfer between the surfaces is calculated from the populations of the two surfaces as a function of time. The population $P_i (i = 1, 2)$ is defined as the norm of the time-dependent wavefunction $\phi_i(t)$:

$$ P_i = \langle \phi_i(t) | \phi_i(t) \rangle \quad (14) $$

At zero time, the population of state 1 is zero and that of state 2 is one.

A pair of coupled potential energy surfaces that will be used to illustrate intensity borrowing are shown in Fig. 3(a). Excited state diabatic potential surfaces 1 and 2 have an identical vibrational frequency of 600 cm$^{-1}$, their minima are displaced by 0.07 and 0.19 Å, respectively, along the configurational coordinate $Q$ and the energy separation of the excited state minima is 4800 cm$^{-1}$. The ground state potential surface has a vibrational frequency of 700 cm$^{-1}$. The energy of the electronic origin transition is 11 200 cm$^{-1}$.

The norm of the wavefunctions as a function of time is shown in Fig. 4(a) for three different couplings $V_{12}$. The transfer of wave packet amplitude starts at the first time step of the calculation. Two trends are observed in Fig. 4(a). First, the ‘average population’ of state 1 increases with increasing coupling. The higher population leads to higher intensity for the transition to state 1 in the absorption spectrum. Second, the initial transfer of wave packet amplitude to state 1 during the first few time steps increases as the coupling increases. This trend is apparent from the magnitude of the first peak of the population at 6 fs. Therefore the intensity borrowing increases as a function of coupling even in completely unresolved, broadband spectra, which are determined by the short-time wave packet dynamics.

The calculated absorption spectra for the potential surfaces in Fig. 3(a) are shown in Fig. 5. All of the calculations are done with dipole moments of zero and one for the transitions to states 1 and 2, respectively. In the uncoupled case ($V_{12} = 0$ cm$^{-1}$) only the allowed transition is seen in the spectrum. At moderate coupling strength ($V_{12} = 400$ cm$^{-1}$) the forbidden transition appears as a series of lines on
the high-energy side of the allowed transition with enough intensity to be experimentally observable. The lines become more intense at a coupling strength $V_{12}$ of 700 cm$^{-1}$.

The ratios of the intensities of the forbidden and allowed absorption bands are plotted in Fig. 4(b) as a function of $V_{12}$. They show a nonlinear intensity increase that can be well described by a second order polynomial. A dependence of the intensity ratio on the square of the spin–orbit coupling parameter is predicted from simple perturbation theory [36,39], in agreement with our time-dependent calcula-

![Potential energy surfaces](image)

Fig. 3. Potential energy surfaces for the calculations of intensity borrowing. The adiabatic and diabatic surfaces are shown as bold and dotted lines, respectively. The labels 1 and 2 denote diabatic surfaces with small (or zero) and large displacements, respectively. (a) The highest energy diabatic potential surface represents the state to or from which the electronic transition is forbidden. (b) The lowest energy diabatic potential surface represents the state to or from which the electronic transition is forbidden. This state is undisplaced along the normal coordinate from the ground state.
Fig. 4. Top: time dependent populations of the diabatic potential surfaces in Fig. 3(a). Three coupling strengths are shown: $V_{12} = 0 \text{ cm}^{-1}$ (dashed lines), $V_{12} = 400 \text{ cm}^{-1}$ (dotted lines) and $V_{12} = 700 \text{ cm}^{-1}$ (solid lines). Bottom: ratio of the intensities of forbidden to allowed absorption bands (Fig. 3) as a function of the coupling strength. The points denote ratios determined from calculated spectra with $J = 15 \text{ cm}^{-1}$. The dashed curve is a least squares fit to a parabola. The ratio of the average populations of states 1 and 2 at three coupling strengths is given by the open squares.

The ratios $P_1/P_2$ of the ‘average populations’ of states 1 and 2 for the three couplings shown in Fig. 4(a) are included in Fig. 4(b) for comparison. The average populations are calculated as the mean values of the populations in the time range shown in Fig. 4(a). They almost perfectly reproduce the dependence of the spectroscopic intensity ratios on coupling strength, indicating that wave packet amplitude transfer between states 1 and 2 is indeed the determining factor for intensity borrowing.

4.3. Vibronic structure in absorption spectra induced by coupling

In this section we will focus on the intensity distributions in vibronic progressions in electronic absorption spectra arising from coupled electronic excited states. Our goal is to show how the time-dependent point of view provides both a physical picture and an exact quantum mechanical calculation of the full vibronic part of the problem.
The transfer of amplitude between the two diabatic surfaces means that the wave packet exhibits dynamics on both coupled surfaces. Thus the spectra will show vibronic features from both surfaces. Because amplitude is transferred between surfaces and the wave packet is constantly changing, the vibronic structure in the spectrum will be different from that caused by placing the initial wave packet onto one surface at a time and adding the spectra obtained for both surfaces. The wave packet that develops amplitude on a given surface due to coupling will be different from a wave packet $\phi(t=0)$ which is placed directly on the surface. From just this qualitative point of view it is to be expected that the autocorrelation functions and hence the spectra will be different.

A commonly encountered disposition of potential surfaces is that illustrated by the examples in Fig. 3, where the minima are displaced both in energy and in normal coordinate space from each other. In order to illustrate the effects of coupling on vibronic progressions, the spectra resulting from transitions to the surfaces in Fig. 3(b) will be discussed. The absorption spectra are shown in Fig. 6 as a function of the magnitude of the coupling between the surfaces. The relative intensities of the vibronic features from each individual state change as a function of coupling. The vibronic structure is not simply a progression multiplied by a constant related to the coupling strength. In the ‘forbidden’ state, for example, significant intensity appears in the $v=1$ quantum line even though the diabatic potential surface for this state is undisplaced and there is no force constant change between the ground and excited states. Likewise, the relative intensities between the vibronic peaks in the allowed transition change as the coupling is changed.

The numerical values of the vibronic intensities can readily be calculated by using the split-operator method. However, the trends in the relative intensities in a

![Absorption spectra](image)

Fig. 5. Absorption spectra calculated for the potentials in Fig. 3(a) with damping factors $\Gamma = 15 \text{ cm}^{-1}$ (solid lines) and $250 \text{ cm}^{-1}$ (dotted lines) at three different coupling strengths. The coupling constants are 0, 400 and 700 cm$^{-1}$ from top to bottom. Vibronic bands that gain intensity with increasing coupling are denoted by arrows.
progression do not necessarily follow a simple pattern. The vibronic intensities must be calculated on a case by case basis. The spectra that have been interpreted by using the theory include K₂NiO₃ [42], Ti²⁺ and V³⁺ in chloride lattices [43,44], and Cr³⁺ and Mn⁴⁺ in fluoride lattices [45–48].

4.4. Vibronic structure in emission spectra

To calculate the emission spectra of molecules in condensed media at low temperature, the initial wave packet is the vibrational eigenfunction corresponding to the lowest eigenvalue of the coupled excited state surfaces. The eigenvalue can be found by calculating the absorption spectrum. Once the eigenvalue is known, the eigenfunction is calculated by using Eq. (15) [23]:

\[
\Psi_i(E_i) = \int_0^\tau \phi(t)w(t) \exp\left(\frac{iE_i}{\hbar} t\right) dt
\]

where \( \Psi_i \) denotes the eigenfunction corresponding to the eigenvalue \( E_i \), \( \phi(t) \) is the time-dependent (propagating) wavefunction and \( w(t) \) is a Hanning window function. The eigenfunction is multiplied by the transition dipole moment and propagated on the ground state potential surface. The emission spectrum is calculated by using Eq. (7). For coupled potentials, each eigenfunction \( \Psi_i \) is an array with two components corresponding to the two diabatic potentials which form the basis in the calculations. The concept of the eigenfunction of the lowest vibrational level of the coupled excited electronic states being expressed in terms of its projection on the two diabatic potential surfaces is not immediately intuitive. This is true especially when the minimum of one of the diabatic states is much higher in energy than that of the eigenvalue corresponding to the eigenfunction.
For spin–orbit coupled excited states shown in Fig. 3(b), the eigenfunction of the lowest vibrational state of the coupled excited state system has two components, one from the lowest energy diabatic potential and the other from the highest energy diabatic potential. The lowest energy excited state surface is the forbidden surface and the highest energy surface is the allowed surface. As selection rules dictate, the components of the wave function are multiplied by their respective transition dipole moments. The transition dipole moment \( \mu = 0 \) for a forbidden transition and \( \mu \neq 0 \) for an allowed transition. Therefore, only the component from state 2 makes the transition to the ground electronic state. The emission spectrum will show a progression in the ground electronic state frequency because the component of the wave packet from state 2 is displaced away from the minimum of the ground state. No progression would be observed if the transition originated purely from the lowest uncoupled surface (assuming that the transition dipole were non zero) because that surface is not displaced relative to the ground state.

In a detailed spectroscopic study of Mn(V) ions doped in tetrahedral sites in a variety of oxide lattices, Güdel and co-workers measured the intensities of the components of the vibronic progressions in the emission spectra [49–51]. All of the quantities necessary to define the theoretical model are known. These spectra provide a stringent test of the calculations of the intensities of the vibronic components of the emission spectra. The diabatic potential surfaces shown in Fig. 3(b) provide the model for the relevant electronic states of Mn(V) in the oxide lattices (MnO_4^-). For the Mn(V) ion in tetrahedral symmetry, the ground state corresponds to \( 3A_2 \), surface 1 corresponds to \( 1E \) and surface 2 corresponds to \( 3T_2 \). The point group of the MnO_4^- ion can be distorted to \( C_{3v} \) in the apatite host lattice or to \( D_{2d} \) in the spodiosite host lattice. These perturbations of the \( T_d \) point group allow the transition to the \( 3T_2 \) state to become allowed. It is assumed that the nearby \( 3T_1 \) state (~5000 cm\(^{-1}\) higher in energy) does not play a role in the emission process. This assumption is valid because the separation in energy between the \( 3T_2 \) and \( 3T_1 \) excited states is on the order of 10^3 cm\(^{-1}\). In the perturbed system, surface 1 represents the emitting state and surface 2 is the allowed triplet state to which it is coupled. For crystals with a \( D_{2d} \) distortion, the relevant states are \( 3B_2, 1A_1 \) and \( 3E \), respectively. For crystals with a \( C_{3v} \) distortion, the relevant states are \( 3A_2, 1E \) and \( 3E \), respectively. The normal coordinate is the totally symmetric Mn–O stretch.

The experimental quantity that provides the rigorous test of the theory is the ratio of the intensity of the first side band (\( v = 1 \)) to that of the emission origin (\( v = 0 \)), \( R_{10} \).

\[
R_{10} = \frac{\text{Emission intensity } (v = 1)}{\text{Emission intensity } (v = 0)}
\]  

(16)

Experimentally determined \( R_{10} \) values in the emission spectra of Mn(V) range from 0.031 for Mn in a Li_3PO_4 lattice to 0.13 for Mn in a Sr_2VO_4Cl lattice. For an electronic state produced by a purely intraconfigurational transition with no coupling to other states, the \( R_{10} \) values should be zero because there is no change in either the force constant or the position of the minimum of the excited state
potential surface relative to those of the ground state. The calculated $R_{10}$ ratios are in excellent (but not exact) agreement with experimental results. A sample calculated spectrum is shown in Fig. 7. The $R_{10}$ ratio is calculated directly from the $v = 0$ and $v = 1$ peaks in the emission spectrum. Because of the excellent agreement between theory and experiment, the model is a good representation of the excited state properties.

4.5. *Interference dips in absorption spectra* [17]

A third spectroscopic manifestation of amplitude transfer between two potential surfaces is interference dips, sharp losses of intensity in broad, unresolved bands in absorption spectra, a little-known but not uncommon phenomenon observed in transition metal spectra. Precedent for dips in intensity in broad bands is found in atomic spectroscopy. Atomic states whose energies lie within a dissociation continuum can give rise to sharp dips in the continuum band. These dips were interpreted by Fano et al. and are known as ‘Fano antiresonances’ [52]. Fano’s equation has been adopted in its entirety to treat the dips arising from molecular states involved in the transition metal spectra, and these molecular spectroscopic features have also been called Fano antiresonances. Examples include complexes of V$^{2+}$, Cr$^{3+}$, and Eu$^{2+}$ [53–56]. The antiresonances are unexpected; absorption spectra arising from transitions to two or more nearby electronic states are commonly assumed to be the superposition of the bands arising from transitions to each state individually.

The model which will be used to illustrate interference effects in absorption spectra is based on the three potential surfaces shown in Fig. 3(b). The two excited state surfaces are coupled by spin–orbit coupling. Typical magnitudes of the coupling are $10^2 \text{ cm}^{-1}$. The calculations in the following are based on a coupling

![Fig. 7. Calculated electronic spectra of Mn(V) doped in a Sr$_2$VO$_4$Cl lattice. The emission and absorption spectra are shown (normalized to one) with solid lines and are labeled appropriately. The dashed line is the absorption spectrum calculated with a $\Gamma = 25 \text{ cm}^{-1}$ damping factor so that the vibronic structure is resolved.](image)
The calculation of the absorption spectra follows the procedure described in the theory section. For the model illustrated in Fig. 3(b), the transition dipole moment to diabatic surface 1 (the doublet state) is chosen to be zero for this spin-forbidden transition. Thus the initial wave packet is placed only on diabatic surface 2, corresponding to the spin-allowed quartet–quartet transition in an octahedral $d^3$ complex.

The electronic absorption spectrum is calculated by using the potential surfaces discussed above with the following properties. The ground state surface is a harmonic potential surface with its minimum at zero along a totally symmetric normal coordinate. In this example the mass is 16 g mol$^{-1}$ and the vibrational frequency is 500 cm$^{-1}$. The first diabatic excited state potential surface is constructed to be representative of an undisplaced ligand-field excited-state of a transition metal complex with a vibrational frequency of 500 cm$^{-1}$ with its minimum at 14 000 cm$^{-1}$ above that of the ground state surface. The second diabatic excited state potential surface represents a ligand-field excited-state displaced by 0.2 Å along the metal–ligand stretching coordinate. It is constructed to represent an excited state vibrational frequency of 450 cm$^{-1}$. Its lowest energy level is 11 000 cm$^{-1}$ above that of the ground state surface. The two diabatic surfaces cross at an energy of 13 930 cm$^{-1}$ and a value of $-0.057$ Å along the normal coordinate.

The spectrum shown by the solid line in Fig. 8 was calculated with a damping factor $\Gamma$ of 15 cm$^{-1}$ and shows the individual vibronic peaks. The spectrum shown by the dotted line was calculated with a damping factor of 180 cm$^{-1}$ and shows the envelope of the absorption band. The most important feature of the spectra is the dip in the envelope at about 14 000 cm$^{-1}$. The more highly resolved spectrum shows that the dip is caused by a decrease in the intensity of the vibronic feature at 13 900 cm$^{-1}$ and an increase in the intensity of the band at 14 420 cm$^{-1}$. This dip has been observed in the absorption spectra of $d^3$ transition metal complexes and has been called a Fano antiresonance. It is a consequence of interference between the two excited electronic states.

The presence of the interference effect can be most clearly observed by comparing the spectrum calculated from the coupled potential surfaces with that calculated from the uncoupled surfaces shown in Fig. 8. The spectrum calculated with zero coupling consists of a Poisson distribution of equally spaced vibronic bands originating from the harmonic potential surface 2. No bands are observed from surface 1 because the transition dipole is zero.

The dip is caused by the interference between the two electronic states and is not a result of the anharmonic nature of the adiabatic surfaces. The spectrum calculated by propagating the wave packet on the lowest adiabatic surface is shown in Fig. 8. This spectrum does not contain the dip in the envelope or the decrease in the intensity of the seventh vibronic band as is observed in the complete spectrum. The spectrum which arises from the two coupled potential surfaces is not the sum of the spectra, which can be calculated by propagating the wave packet individually on the two adiabatic surfaces.
Fig. 8. Absorption spectra calculated for the potentials described in the text with damping factors $\Gamma = 15$ cm$^{-1}$ (solid line) and $\Gamma = 180$ cm$^{-1}$ (dashed line). (a) Absorption spectrum with transition moments of 0 and 1 for diabatic states 1 and 2, respectively, and $V_{12} = 300$ cm$^{-1}$. (b) Absorption spectrum for uncoupled diabatic potentials ($V_{12} = 0$ cm$^{-1}$). (c) Absorption spectrum for a transition to the lower adiabatic surface only.

4.6. **Time-domain explanation of the interference**

The origins of the dip in the absorption spectrum as well as the other features in the spectrum discussed above can be interpreted by examining the wave packet in the time domain. The time dependence of the absolute value of the overlap is shown in Fig. 9(a). The dashed line shows the overlap for the case of zero coupling between the surfaces and the solid line shows it for a coupling of 300 cm$^{-1}$. The damping factor is 15 cm$^{-1}$ in both cases. The difference between the two cases is shown in Fig. 9(b). The features which will play an important part in the following discussions are the faster initial decrease in the overlap, the non-zero overlap between the major recurrences, the smaller magnitude of the recurrences, and the unequal time intervals of the recurrences for the coupled surfaces compared to the uncoupled surfaces. The Fourier transform of the overlap difference is shown in Fig. 9(c). This figure shows the difference between the spectra calculated from the coupled and uncoupled surfaces (Fig. 8(a and b)). Note that for the highly resolved difference spectrum (solid line), each peak consists of a positive and a negative component of unequal magnitude. The positive and negative components of a given peak (the ‘derivative-like’ shape) correspond to the energy shift of the vibronic
bands in the coupled versus the uncoupled spectra. The difference between the magnitudes of the positive and negative components of a given peak correspond to the gain or loss of intensity of that peak. The 'envelope' of the difference, calculated by using a damping factor of 180 cm\(^{-1}\) (dotted line) clearly shows the region where the interference 'dip' in the envelope is observed as well as the region where intensity borrowing results in features associated with the forbidden diabatic state.

The time-domain explanation of the interference dip in the absorption spectrum is contained in the short-time overlaps shown in Fig. 10. When the two surfaces are coupled, the total overlap rapidly decreases but does not decrease to zero, as shown by the solid line. In the case of a coupling of 600 cm\(^{-1}\) shown in Fig. 10, the overlap reaches a local minimum at about 10 fs, increases to give a small recurrence at about 13 fs, and then slowly decreases. In contrast, the overlap for the uncoupled surfaces decreases smoothly to zero. The initial decrease is less rapid than that calculated with coupling. The more complicated behavior of the overlap with
coupling is explained by the population changes which take place. The population of diabatic surface 2 is shown by the dotted line on the same time scale as the overlaps in Fig. 10. The population is one at $t = 0$ fs, then it decreases rapidly, reaches a local minimum at about 10 fs, and increases to reach a local maximum at about 15 fs. The initial decrease corresponds to loss of population to diabatic surface 1 followed by net back-transfer of some population. The overlap roughly follows the population, although its magnitude is not simply proportional to the population because the properties of the wavefunction are changed when the population changes. When compared to the overlap for the uncoupled case, the decrease is more rapid at shorter times but a recurrence is also observed. When transformed to the frequency domain, the more rapid decrease results in a broader spectrum, i.e. in more intensity at higher energies and less intensity at lower energies in the spectrum relative to that in the uncoupled case. The small recurrence at about 13 fs corresponds to a separation between bands in the frequency domain of $c^{-1}t_{\text{recurrence}}^{-1} = 2600$ cm$^{-1}$. The net result of these two effects is to produce a spectrum for the coupled case, in which an interference dip is observed in the envelope as shown in the spectrum in Fig. 8(a) and in the difference spectrum in Fig. 9(c). Again, it is easily rationalized from the calculations in the time domain.

Interference effects, large or small, always occur between two potential surfaces when the surfaces are coupled. The interference dips discussed above are prize examples of cases where calculations and interpretation in the time domain are very powerful. If we were to limit ourselves to the clamped nuclei picture where the energy levels are rungs on a ladder, then the total spectrum would be the sum of the spectra caused by transitions to each of the individual rungs and dips in the total spectrum would not occur. In the time domain, many types of intensity effects including borrowing, vibronic structure and dips can be understood.
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