A Different View of Molecular Electronic Transitions

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The conventional Fermi golden rule expression for the rate of transitions between vibration-rotation states of two electronic states is shown to reduce, under a single specified approximation, to an expression which contains only the initial-state vibration-rotation wave function, the upper and lower electronic energy surfaces, and the electronic transition moment integral. This result affords a new picture of the photon absorption process, which is shown to be equivalent to a Landau–Zener surface hopping picture. Potential conceptual and computational advantages and disadvantages of this new picture are discussed.

I. Introduction

In an earlier publication,1 we demonstrated how the conventional first-order perturbation theory based Fermi golden rule expression for the rate of transitions between initial and final Born–Oppenheimer states \( \psi \) and \( \phi \) can be rewritten (approximately) as follows:

\[
W = \frac{2\pi}{\hbar} \langle X_0^f | \psi \rangle \delta \left( \omega - \left( \epsilon_f^j - \epsilon_i^j \right) / \hbar \right) \text{s}^{-1} \tag{1}
\]

induced by electric dipole \( \langle \vec{E} \cdot \vec{r} \rangle \) interaction with light of energy \( \hbar \omega \) can be rewritten (approximately) as follows:

\[
W = \frac{2\pi}{\hbar} \langle X_0^f | \psi \rangle \delta \left( \omega - \left( \epsilon_f^j - \epsilon_i^j \right) / \hbar \right) \text{s}^{-1} \tag{2}
\]

In eq 1 \( \epsilon_f^j \) and \( \epsilon_i^j \) are the Born–Oppenheimer potential energy surfaces of the final and initial electronic states. In eq 2, it is intended that \( \hbar \omega \) be set equal to a specific energy difference \( \epsilon_f^j - \epsilon_i^j \) to obtain the rate of transitions between these states. That is, eq 2 still contains all of the state-specific information of eq 1 because it is to be evaluated only for values of \( \hbar \omega \) which match specific transition energies. The only approximation made in deriving eq 2 from eq 1 involved neglecting the noncommutation of the vibration-rotational genetic energy operator \( T \) and the potential energy functions \( E(R) \) and \( E'(R) \).

More precisely, when the \( \delta \)-function appearing in eq 1 is replaced by its Fourier representation

\[
\delta \left( \omega - \left( \epsilon_f^j - \epsilon_i^j \right) / \hbar \right) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp \left( i \omega t - i \left( \epsilon_f^j - \epsilon_i^j \right) t / \hbar \right) dt \tag{3}
\]

and the (Born–Oppenheimer) identities

\[
e_i \psi_i \phi_i = (T + E^0) \phi_i \psi_i \tag{4a}
\]

and

\[
e_i \phi_i \psi_i = (T + E^0) \phi_i \psi_i \tag{4b}
\]

are used, eq 1 becomes

\[
W = \frac{1}{\hbar} \int_{-\infty}^{\infty} \exp \left( i \omega t \right) \langle X_0^f | \psi \rangle \exp \left( -i \left( E^0 + T \right) / \hbar \right) \langle X_0^f | \psi \rangle \text{d}t \tag{5}
\]

Writing3

\[
\exp \left( \frac{iT}{\hbar} \right) = \exp \left( \frac{iT}{\hbar} \right) \exp \left( \frac{iE^0}{\hbar} \right) = \exp \left( \frac{iT}{\hbar} \right) \exp \left( \frac{iE^0}{\hbar} \right) \left( \frac{iT}{\hbar} \right)^2 (E^0, T) + ... \tag{6a}
\]

and ignoring the fact that \( T \) does not commute with \( E^0 \) or \( E' \) allow us to write

\[
\exp \left( it \left( E^0 + T / \hbar \right) \right) \frac{E'}{\hbar} \exp \left( -it \left( E^0 + T / \hbar \right) \right) = \exp \left( it \left( E^0 + E' / \hbar \right) \right) \frac{E'}{\hbar} \tag{7}
\]

which then allows us to rewrite eq 5 using eq 3, again, as

\[
W = \frac{2\pi}{\hbar^2} \langle X_0^f | \psi \rangle \exp \left( i \left( E^0 + E' \right) / \hbar \right) \langle X_0^f | \psi \rangle \tag{8}
\]

If we now restrict ourselves to evaluating eq 8 only at values of \( \hbar \omega \) which match a particular energy difference \( \epsilon_f^j - \epsilon_i^j \), the vibration-rotation quantum states \( |X_0^f \rangle \langle X_0^f| \) appearing in eq 8 can actually be summed over; only those states whose energy \( \epsilon_f^j \) matches \( \epsilon_i^j + \hbar \omega \) will contribute to the sum. The advantage to summing over these states is that the completeness relation

\[
\sum |X_0^f \rangle \langle X_0^f| = 1 \tag{9}
\]

can be used, as a result of which eq 8 then reduces to eq 2. Before moving on to address the accuracy of the approximations contained in eq 2, let us reflect upon the physical content and possible merits of eq 2 and 1. Equation 1 expresses the conventional picture3 of the electronic transition process: (a) The photon's energy \( \hbar \omega \) must match the state energy difference \( \epsilon_f^j - \epsilon_i^j \). (b) Electronic selection rules arise from the electronic transition moment integral \( \langle \phi_f \vec{E} \cdot \vec{r} \psi_i \rangle \). If the geometry dependence of this moment is ignored (Condon approximation), the familiar Franck–Condon factors \( |X_0^f \rangle \langle X_0^f| \) arise. On the other hand, the approximation, eq 2, gives a different picture4 of the electronic transition event: (a) Only at those molecular geometries where \( \epsilon_f^j - \epsilon_i^j - E' \) is obeyed will photon absorption occur. It is precisely at these geometries where the classical vibration-rotation

\[
\begin{align}
(1) & \text{J. Simons, } J. \text{Phys. Chem., 86, 3615 (1982).} \\
(2) & \phi_i \text{ and } \phi_f \text{ are the electronic wave functions, and } X_0^f \text{ and } X_0^f \text{ are the vibration-rotation wave functions of the respective Born–Oppenheimer states.}
\end{align}
\]
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kinetic energy \( (\varepsilon^0 - E^0) \) = kinetic energy remains unchanged in going from \( \phi_0 \chi_0^2 \) to \( \phi_0 \chi_1^2 \). (b) At each such "critical geometry" \( \vec{R}_c \), the rate of transition is proportional to the probability that the molecule experiences that geometry \( X^i(\vec{R}_c) \) multiplied by the square of the electronic transition moment at \( \vec{R}_c \).

Clearly, eq 2 is an approximation to eq 1. However, on conceptual grounds and even in certain quantitative calculations, eq 2 may be preferred. Application of eq 1 requires knowledge of the vibration-rotation wave functions of both states, whereas eq 2 needs the initial-state functions \( X^i(\vec{R}) \) together with knowledge of those geometries \( \vec{R}_c \), where the classical kinetic energy conservation condition is met. In the (quite common) case where \( \phi_0 \) is the ground electronic state and \( X^0 \) corresponds to some low-energy vibration-rotation level, knowledge of \( X^0 \) in regions of geometry space where \( X^1 \) is appreciable is quite likely to be available. It is even reasonable to expect that, either through ab initio quantum calculations or cruder semiempirical estimates, \( E^i(\vec{R}) \) could be known for geometries where \( X^1 \) is significant. However, knowledge of the excited-state vibrational wave functions \( X^1 \) may often be difficult to achieve, especially if \( X^1 \) corresponds to a high-energy vibration-rotation state which spans geometries where \( E^0(\vec{R}) \) is highly anharmonic and/or mode coupled. Moreover, basis set or differential equation methods for generating \( X^1 \) do not give these functions only where \( X^1 \) is appreciable; they generate \( X^1 \) at many geometries which are not needed for computing the Franck-Condon factors.

The above summary of the developments made in ref 1 makes it clear that eq 2 may provide new insights into the electronic transition process and has potential utility as a computational tool. The purpose of the present paper is to further explore the implications of eq 2. In section II we reexamine the derivation of eq 2 with an eye toward making improvements which preserve its pedagogical value and computational utility. Section III contains our concluding remarks. Our analysis is quite similar to that carried out by Bergsma et al. 9 In that we focus on connections between the classical picture afforded by eq 2 and a Landau-Zener-like reinterpretation. However, we feel that our treatment of the multidimensional nature of the energy surfaces and of their intersection subspaces is more explicit than Bergsma’s. We therefore feel that our treatment offers additional clarity and potential for understanding.

II. Further Reflections on the Partly Classical Model

The Critical Geometries. Let us consider the geometries \( \vec{R}_c \) at which the classical kinetic energy conservation condition

\[
\varepsilon^i - E^i(\vec{R}_c) = \varepsilon^0 - E^0(\vec{R}_c) \tag{10}
\]

is met. For a molecule containing \( N \) atoms, both \( E^i \) and \( E^0 \) are functions of \( 3N - 6 \) \((3N - 5) \) for a linear molecule internal degrees of freedom. The geometry subspace \( S \) in which eq 10 is satisfied is of dimension \( 3N - 7 \) \((3N - 6) \). Any geometrical arrangement of the molecule can be described by specifying a point \( \vec{S} \) in \( S \) and a distance \( d \) along the vector \( \vec{d} \) which is normal to the intersection subspace at \( \vec{S} \):

\[
\vec{R} = \vec{S} + d\vec{d} \tag{11}
\]

Since \( E^i - E^0 \) is constant in the \( S \) subspace (equal to the transition energy \( \hbar \omega \)), the direction of \( \vec{d} \) can easily be obtained; \( \vec{d} \) is parallel to the gradient \( \vec{\nabla} (E^i - E^0) \) of \( E^i - E^0 \) and is dependent on the value of \( \vec{S} \). Clearly, the critical geometries \( \vec{R}_c \) correspond to points with \( d = 0 \) in eq 11.

As we demonstrated above, the picture developed in ref 1 gives rise to the concepts of "critical geometries" at which the electronic transition takes place. To further explore the original formalism, let us reexamine eq 1 with a focus on regions of geometry space near to the, presumably most important, critical geometry space \( S \).

Rate of Photon Absorption. The transition rate given in eq 1 can be viewed as relating to transitions between \( X^0 \) and \( X^1 \) caused by a perturbation involving the electronic dipole matrix element \( \mu_{ij} = \langle \phi_0 | \vec{E} \cdot \vec{r} | \phi_i \rangle \) which is \( \vec{R} \) dependent. Landau, Zener, and others have shown how to evaluate transition probabilities relating to such processes semiclassically. We can make use of the Landau-Zener \((LZ)\) type developments by recognizing that the potential energy surfaces \( E^i(\vec{R}) + \hbar \omega \) and \( E^0(\vec{R}) \) can be viewed as intersecting diabatic surfaces which, via their interaction \( \mu_{ij}(\vec{R}) \), give rise to two adiabatic surfaces

\[
E_\pm(\vec{R}) = \frac{1}{2}\left[(E^i + E^0 + \hbar \omega) \pm \sqrt{(E^i - E^0 - \hbar \omega)^2 + 4\mu_{ij}(\vec{R})^2}\right] \tag{12}
\]

differing by \( [(E^i - E^0 - \hbar \omega)^2 + 4\mu_{ij}(\vec{R})^2]^{1/2} = \Delta \) in energy. In writing \( E^i + \hbar \omega \) as a potential energy surface, we are identifying the total electronic-plus-photon energy as our unperturbed energy. Of course, the shape of \( E^i + \hbar \omega \) is identical with that of \( E^i \); the former is simply \( E^i \) shifted by the constant energy \( \hbar \omega \).

In regions of geometry space near where \( E^i - E^0 - \hbar \omega = 0 \), \( E_+ \) and \( E_- \) approach to within \( 2\Delta \). According to the LZ theory, it is near such geometries that transitions are most likely to occur. 10 From our earlier discussion, we recognize these geometries as those corresponding to small \( d \) values in eq 11. Let us consider how the energy splitting \( \Delta \) varies with geometry for small \( d \). We begin by expanding \( E^i - E^0 - \hbar \omega \) about a point \( \vec{S} \) in \( S \) (corresponding to \( d = 0 \))

\[
E^i - E^0 - \hbar \omega = 0 + \frac{\partial}{\partial n}(E^i(\vec{S}) - E^0(\vec{S}))d + ... \tag{13}
\]

In writing eq 13, we used the fact that the components of the gradient of \( E^i - E^0 - \hbar \omega \) along directions lying within \( S \) vanish; only the gradient along \( \vec{d} \) is nonzero. Noting that \( (\partial \Delta / \partial n) \) \( E^i - E^0 \) is the force difference \( (F^i - F^0)(\vec{S}) \) along \( \vec{d} \) for the two surfaces at the point \( \vec{S} \), we have (for small \( d \))

\[
\Delta \simeq (F^i - F^0)^2d^2 + 4\mu_{ij}(\vec{R})^2 \tag{14}
\]

The conventional LZ approach amounts to ignoring the \( d \) dependence of \( \mu_{ij} \) and parametrizing the classical motion, causing a change in \( d \) as a linear function of time near \( d = 0 \)

\[
d(t) = v_d(\vec{S})(t - t_0) \tag{15}
\]

where \( v_d(\vec{S}) \) is the velocity of the molecule's motion along \( \vec{d} \) as it crosses the point \( d = 0 \) at \( \vec{S} \). The probability of a transition from \( E^i(\vec{R}) + \hbar \omega \) to \( E^0(\vec{R}) \) is then given by the LZ-like theory as

\[
P = 1 - \exp(-2\pi \mu_{ij}^2/(\hbar v_d(\vec{S}) - F^0)) \tag{16}
\]

Given this probability of transition of from \( E^i + \hbar \omega \) to \( E^0 \) surface to the \( E^i \) surface as the molecule passes through \( d = 0 \) at \( \vec{S} \), we must now incorporate it into the overall electronic transition rate in order to achieve a comparison with eq 2. Recall that, in deriving eq 2 from eq 1, the concept of the critical geometry subspace \( S \) gave rise to considering only those molecular geometries where

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(6) In this interpretation, we view the molecule as vibrating in the presence of the photon's time-varying electric field. As the molecule vibrates through these special geometries, the photon can be absorbed; at other geometries the photon cannot be absorbed because doing so would violate the conservation of vibration-rotation kinetic energy condition. The critical geometries are special in that they allow the molecule's vibration-rotation kinetic energy to remain unchanged. This means that all of the photon's energy goes into vibration-rotation potential energy. This potential energy is nothing but the Born-Oppenheimer electronic energy. Through the critical geometries, we see that all of the photon's energy is absorbed into the electronic degrees of freedom which then, of course, give rise to a new potential energy surface \( E^i \) for the molecule to subsequently vibrate on.


(8) Recent developments in analytical evaluation of gradients of potential energy surfaces (see, for example, P. Jorgensen and J. Simons, J. Chem. Phys., 79, 334 (1983), and references therein) make it possible to systematically map out the \( S \) subspace and the \( \vec{d} \) vector at each point in \( S \).

(9) (a) L. Landau, Phys. Z. Sowjetunion, 1, 88 (1932); (b) C. Zener, Proc. R. Soc. London, A 137, 696 (1932); (c) For an excellent overview and for a discussion of various workers' contributions to this area, see M. S. Child, "Molecular Collision Theory", Academic Press, London, 1974.
The numerical work of Heller and Brown,\textsuperscript{10} who developed a similar picture for use on radiationless transition processes, shows that such semiclassical approximations can indeed reproduce some of the trends seen in the exact quantum results of eq 1. We have also carried out numerical investigations comparing eq 1 and 19 for several two-dimensional model potentials (harmonic and anharmonic) chosen to realistically simulate geometrical degrees of freedom in actual molecules. We find substantial differences between the exact results of eq 1 and the approximate results of eq 2 in cases where the quasistatic Franck–Condon factors are small because of destructive interference between the upper and lower state wave functions. The approximate eq 2 contains no direct wave function phase information; thus, it cannot accurately predict such rates. We also observed that eq 2 tends to overestimate all transition rates; again, this is due to the lack of phase information which could lead to cancellation in the exact eq 1. It is likely that the picture provided by eq 2 will be most useful in quantitative calculations when the total rate of transitions is considered to a collection of vibration–rotation states within a narrow energy range (e.g., in a polyatomic molecule in which there are many states (e.g., in a polyatomic molecule in which there are many states)

\textsuperscript{10} Heller \textit{et al.} (E. J. Heller and R. C. Brown, \textit{J. Chem. Phys.}, 79, 3336 (1983)) showed that radiationless transition rates could also be formulated in terms of a Landau–Zener probability factor combined with a rate of passage through a subsurface of intersection between the two relevant surfaces. Also, as mentioned earlier, Bergama et al. have obtained a similar result in their treatment of electronic absorption profiles.

situation. Although it is our plan to further explore the utility of eq 2 within a polyatomic molecule framework, we feel that the observations relating eq 2 to the Landau-Zener picture as well as the physically clear picture or photon absorption afforded by eq 2 or 19 constitute the essential results of this paper.

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ESR of V(CO)$_n$ ($n = 1$ to 3) Molecules in Rare-Gas Matrices


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Three vanadium carbonyls, two with high spin, were observed and partially identified from hyperfine interactions with $^{51}$V ($I = 7/2$) and $^{13}$C ($I = 1/2$). They were formed by the reaction of vanadium metal vapor with low concentrations of $^{13}$CO or $^{14}$CO in rare gases and condensed at 4 K. VCO is trapped in two conformations of almost equal stability, one linear and the other presumed to be slightly bent; both have $S = 7/2$. The bent form ($^4I_A$) has an approximate configuration [d$^5$sp$^2$(pe + de)$^1$] and a zero-field splitting parameter $D = 0.45$ cm$^{-1}$. The electronic parameters changed considerably in the linear form. V(CO)$_3$ was observed only in a neon matrix and has a $S = 1/2$ ground state with $|D| = 0.30$ cm$^{-1}$. It is probably slightly bent, but the ESR spectrum provided no definite evidence of nonlinearity. V(CO)$_7$ was observed only in neon as an axial molecule with a $^2A'$ or $^2I_2$ ground state depending upon whether it has planar D$_{3h}$ (considered more probable) or pyramidal C$_3v$ symmetry.

Introduction

Transition-metal carbonyl molecules continue to be of great interest, particularly because of their relevance to catalysis. The simplest molecules, those containing only one metal atom, have been studied spectroscopically, and electron spin resonance (ESR) has been applied successfully in some cases, specifically to V(CO)$_3$, V(CO)$_5$, $^{18}$Mn(CO)$_3$, $^{13}$Co(CO)$_3$, $^{15}$Cu(CO)$_3$, $^{10}$AgCO, and Ag(CO)$_3$.


