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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 (approximate) 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[2] ($\phi_0 X_i^0$ and $\phi_f X_j^f$)

$$W_{0i,fj} = \frac{2\pi}{\hbar^2}|\langle \phi_0 X_i^0|\vec{E}\cdot\vec{r}|\phi_f X_j^f\rangle|^2 \delta[\omega - (\epsilon_j^f - \epsilon_i^0)/\hbar] \text{ s}^{-1} \quad (1)$$

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

$$W = \frac{2\pi}{\hbar}\langle X_i^0|\langle \phi_0|\vec{E}\cdot\vec{r}|\phi_f\rangle^2 \delta[\hbar\omega - E^f + E^0]|X_i^0\rangle \text{ s}^{-1} \quad (2)$$

In eq 1 ϵ_j^f and ϵ_i^0 are the total (electronic plus vibrational and rotational) energies of the final and initial states; $E^f(\vec{R})$ and $E^0(\vec{R})$ 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 $\epsilon_j^f - \epsilon_i^0$ 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 vibrational–rotational kinetic energy operator T and the potential energy functions $E^f(\vec{R})$ and $E^0(\vec{R})$.

More precisely, when the δ-function appearing in eq 1 is replaced by its Fourier representation

$$\delta[\omega - (\epsilon_j^f - \epsilon_i^0)/\hbar] = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp[i\omega t - it(\epsilon_j^f - \epsilon_i^0)/\hbar]\, dt \quad (3)$$

and the (Born–Oppenheimer) identities

$$\epsilon_j^f \phi_f X_j^f = (T + E^f)\phi_f X_j^f \quad (4a)$$

and

$$\epsilon_i^0 \phi_0 X_i^0 = (T + E^0)\phi_0 X_i^0 \quad (4b)$$

are used, eq 1 becomes

$$W = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} \exp(i\omega t)\langle X_i^0|\langle \phi_0|\exp(it(E^0 + T)/\hbar)\vec{E}\cdot\vec{r} \times \exp(-it(E^f + T)/\hbar)|\phi_f\rangle|X_j^f\rangle\langle X_j^f|\langle \phi_f|\vec{E}\cdot\vec{r}|\phi_0\rangle|X_i^0\rangle\, dt \quad (5)$$

Writing[3]

$$\exp\left[\frac{it}{\hbar}(E^0 + T)\right] = \exp\left\{\frac{it}{\hbar}E^0 - \tfrac{1}{2}\left(\frac{it}{\hbar}\right)^2[E^0,T] - ...\right\} \exp\left(\frac{itT}{\hbar}\right) \quad (6a)$$

$$\exp\left[\frac{-it}{\hbar}(E^f + T)\right] = \exp\left(\frac{-it}{\hbar}T\right) \exp\left\{\frac{-it}{\hbar}E^f + \tfrac{1}{2}\left(\frac{-it}{\hbar}\right)^2[E^f,T] + ...\right\} \quad (6b)$$

and ignoring the fact that T does not commute[4] with E^0 or E^f allow us to write

$$\exp(it(E^0 + T)/\hbar)\vec{E}\cdot\vec{r} \exp(-it(E^f + T)/\hbar) \cong \exp[it(E^0 - E^f)/\hbar]\vec{E}\cdot\vec{r} \quad (7)$$

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

$$W = \frac{2\pi}{\hbar^2}\langle X_i^0|\langle \phi_0|\vec{E}\cdot\vec{r}|\phi_f\rangle \delta[\omega - (E^f - E^0)/\hbar]|X_j^f\rangle \times \langle X_j^f|\langle \phi_f|\vec{E}\cdot\vec{r}|\phi_0\rangle|X_i^0\rangle \quad (8)$$

If we now restrict ourselves to evaluating eq 8 only at values of $\hbar\omega$ which match a particular energy difference $\epsilon_j^f - \epsilon_i^0$, the vibration–rotation quantum states $|X_j^f\rangle\langle X_j^f|$ appearing in eq 8 can actually be summed over; only those states whose energy ϵ_j^f matches $\epsilon_i^0 + \hbar\omega$ will contribute to the sum. The advantage to summing over these states is that the completeness relation

$$\sum_j |X_j^f\rangle\langle X_j^f| = 1 \quad (9)$$

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 picture[5] of the electronic transition process: (a) The photon's energy $\hbar\omega$ must match the state energy difference $\epsilon_j^f - \epsilon_i^0$. (b) Electronic selection rules arise from the electronic transition moment integral $\langle \phi_0|\vec{E}\cdot\vec{r}|\phi_f\rangle$. If the geometry dependence of this moment is ignored (Condon approximation), the familiar[5] Franck–Condon factors $|\langle X_i^0|X_j^f\rangle|^2$ arise. On the other hand, the approximation, eq 2, gives a different picture[1] of the electronic transition event: (a) Only at those molecular geometries where $\epsilon_j^f - E^f = \epsilon_i^0 - E^0$ is obeyed will photon absorption occur. It is precisely at these geometries where the classical vibration–rotation

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[1] J. Simons, *J. Phys. Chem.*, **86**, 3615 (1982).

[2] ϕ_0 and ϕ_f are the electronic wave functions, and X_i^0 and X_j^f are the vibration–rotation wave functions of the respective Born–Oppenheimer states.

[3] These equations are special cases of the operator identity $\exp(A)\exp(B) = \exp\{A + B + {}^1/_2[A,B] + {}^1/_{12}[A,[A,B]] + {}^1/_{12}[[A,B],B] + ...\}$ given in R. M. Wilcox, *J. Math. Phys.* (*N.Y.*), **8**, 962 (1967).

[4] This can be viewed either as treating the T operator classically or as making a short-time expansion of the terms appearing in eq 6. The short-time interpretation arises by noticing that the commutators on the right-hand sides of eq 6 give rise to t^2, t^3, etc., in the exponentials. Ignoring the t^2, t^3, etc., terms relative to the t term therefore amounts to making a short-time approximation. To our knowledge, the earliest developments along these lines were made by M. Lax, *J. Chem. Phys.*, **30**, 1752 (1952).

[5] G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand Reinhold, New York, 1966, p 148.

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kinetic energy ($\epsilon_i^0 - E^0$ = kinetic energy) remains unchanged[6] in going from $\phi_0 X_i^0$ to $\phi_f X_j^f$. (b) At each such "critical geometry" ($\vec{R}_c$), the rate of transition is proportional to the probability that the molecule experiences that geometry $|X_i^0(\vec{R}_c)|^2$ 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 $X_i^0(\vec{R})$ together with knowledge of those geometries $\vec{R}_c$ where the classical kinetic energy conservation condition is met. In the (quite common) case where ϕ_0 is the ground electronic state and X_i^0 corresponds to some low-energy vibration–rotation level, knowledge of X_i^0 and $E^0(\vec{R})$ in regions of geometry space where $|X_i^0|^2$ 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, $E^f(\vec{R})$ could be known for geometries where $|X_i^0|^2$ is significant. However, knowledge of the excited-state vibrational wave functions X_j^f may often be difficult to achieve, especially if X_j^f corresponds to a high-energy vibration–rotation state which spans geometries where $E^f(\vec{R})$ is highly anharmonic and/or mode coupled. Moreover, basis set or differential equation methods for generating X_j^f do not give these functions only where X_i^0 is appreciable; they generate X_j^f 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.[7] 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 subsurfaces 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

$$\epsilon_j^f - E^f(\vec{R}_c) = \epsilon_i^0 - E^0(\vec{R}_c) \tag{10}$$

is met. For a molecule containing N atoms, both E^f 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 $\hat{n}$ which is normal to the intersection subspace at $\vec{s}$:

$$\vec{R} = \vec{s} + d\hat{n} \tag{11}$$

Since $E^f - E^0$ is constant in the S subspace (equal to the transition energy $\hbar\omega$), the direction of $\hat{n}$ can easily be obtained; $\hat{n}$ is parallel to the gradient[8] $\vec{\nabla}(E^f - E^0)$ of $E^f - E^0$ 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_i^0 and X_j^f caused by a perturbation involving the electronic dipole matrix element $\mu_{0f} \equiv \langle\phi_0|\vec{E}\cdot\vec{r}|\phi_f\rangle$ which is $\vec{R}$ dependent. Landau,[9a] Zener,[9b] and others[9c] 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 $E^0(\vec{R}) + \hbar\omega$ and $E^f(\vec{R})$ can be viewed as intersecting diabatic surfaces which, via their interaction $\mu_{0f}(\vec{R})$, give rise to two adiabatic surfaces

$$E_{\pm}(\vec{R}) = \tfrac{1}{2}\{(E^0 + E^f + \hbar\omega) \pm [(E^f - E^0 - \hbar\omega)^2 + 4\mu_{0f}^2]^{1/2}\} \tag{12}$$

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

In regions of geometry space near where $E^f - E^0 - \hbar\omega = 0$, E_+ and E_- approach to within $2|\mu_{0f}|$. According to the LZ theory, it is near such geometries that transitions are most likely to occur.[9] 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 Δ varies with geometry for small d. We begin by expanding $E^f - E^0 - \hbar\omega$ about a point $\vec{s}$ in S (corresponding to $d = 0$)

$$E^f - E^0 - \hbar\omega = 0 + \frac{\partial}{\partial n}(E^f(\vec{s}) - E^0(\vec{s}))d + \ldots \tag{13}$$

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

$$\Delta \cong [(F^0 - F^f)_n^2 d^2 + 4\mu_{0f}^2]^{1/2} \tag{14}$$

The conventional LZ approach amounts to ignoring the d dependence of μ_{0f} and parametrizing the classical motion, causing a change in d as a linear function of time near $d = 0$

$$d(t) = v_n(\vec{s})(t - t_0) \tag{15}$$

where v_n is the velocity of the molecule's motion along $\hat{n}$ as it crosses the point $d = 0$ at $\vec{s}$. The probability of a transition from $E^0(\vec{R}) + \hbar\omega$ to $E^f(\vec{R})$ is then given by the LZ-like theory as[9b]

$$P = 1 - \exp[-2\pi\mu_{0f}^2/(\hbar v_n|F^0 - F^f|_n)] \tag{16}$$

Given this probability of transition from the $E^0 + \hbar\omega$ surface to the E^f 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. Thus, at 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^f) for the molecule to subsequently vibrate on.

[7] J. P. Bergsma, P. H. Berens, K. R. Wilson, D. R. Fredkin, and E. J. Heller, *J. Phys. Chem.*, **88**, 612 (1984).

[8] Recent developments in analytical evaluation of gradients of potential energy surfaces (see, for example, P. Jørgensen and J. Simons, *J. Chem. Phys.*, **79**, 334 (1983), and references therein) make it possible to systematically map out the S subspace and the $\hat{n}$ 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.

$d = 0$. The above Landau–Zener model only considers small deviations away from $d = 0$ so as to incorporate the effects of how fast (v_n) and with how much recoil ($|F^0 - F^f|_n$) the molecule passes through $d = 0$; v_n, $|F^0 - F^f|_n$, and μ_{0f}^2 are all evaluated at points $\vec{s}$ which lie in **S**.

To formulate the *rate* of transitions from $E^0 + \hbar\omega$ to E^f, we multiply the *rate* at which molecules pass through points $\vec{s}$ in the critical subspace **S** by the (LZ) *probability* of transition at point $\vec{s}$ and we then integrate over the space **S**. The molecule moves in a $(3N - 6)$-dimensional coordinate space; thus, it only passes *through* the $(3N - 7)$-dimensional subspace **S**. The rate (r) of molecules passing through **S** at $\vec{s}$ is equal to the total number of molecules (N) in the sample, multiplied by the probability of any one molecule being between ($\vec{s}$, $d = 0$) and ($\vec{s} + d\vec{s}$, $d = \delta$) and multiplied by the rate of passage of that one molecule through ($\vec{s}$, 0):

$$r(\vec{s}) = N|X_i^0(\vec{s},d)|^2 d\mathbf{S}\,\delta(v_n/\delta) \tag{17}$$

Here $|X_i^0(\vec{s},d)|^2$ is the square of the vibration–rotation wave function of the $E^0 + \hbar\omega$ energy surface, $d\mathbf{S}$ is the volume element for integration over **S**, and (v_n/δ) is the speed normal to **S** divided by the infinitesimal "thickness" δ of the region **S**. Since δ/v_n is the time the molecule spends within the region of thickness δ, its reciprocal can be thought of as a frequency of passage. Following through on the above analysis, we obtain the spatially averaged rate (s^{-1}) of photon-induced transitions per molecule given, via eq 16 and 17, by

$$W = \int N^{-1} r(\vec{s}) P \, \mathrm{d}\mathbf{S}$$

$$= \int |X_i^0|^2 v_n \{1 - \exp[-2\pi\mu_{0f}^2/(\hbar v_n |F^0 - F^f|_n)]\} \, \mathrm{d}\mathbf{S} \tag{18}$$

where the integration is only over the subspace **S**. This is our final expression[10] for W, which we view as a generalization of eq 2.

Connection between Eq 2 and 18. It is instructive to consider whether eq 18 and 2 can be shown to give identical rate expressions in some limiting case. It is well-known[9c] that the LZ expression for the probability of transition given in eq 16 is of "infinite order" in the perturbation strength μ_{0f}. In contrast, eq 2 was obtained[1] by using the first-order perturbation theory method. Therefore, let us examine the lowest order term in our LZ-based expression for W, which we obtain by expanding the exponential in P and keeping only the first nonzero term:

$$W \cong \int |X_i^0|^2 v_n 2\pi\mu_{0f}^2 (\hbar v_n |F^0 - F^f|_n)^{-1} \, \mathrm{d}\mathbf{S}$$

$$= \frac{2\pi}{\hbar} \int |X_i^0|^2 \mu_{0f}^2 |F^0 - F^f|_n^{-1} \, \mathrm{d}\mathbf{S} \tag{19}$$

Equations 19 and 2 are indeed very similar except that eq 2 involves integration over the entire $(3N - 6)$-dimensional space but constrained by the δ-function $\delta(\epsilon_j^f - \epsilon_i^0 - E^f + E^0)$, whereas eq 19 contains the $|F^0 - F^f|_n^{-1}$ factor. The energy-restricting δ-function of eq 2 can be recast as a δ-function in geometrical factors by expanding the energy difference about the point ($\vec{s}$, $d = 0$) in **S**:

$$\epsilon_j^f - \epsilon_i^0 - E^f(\vec{R}) + E^0(\vec{R}) = \\ \epsilon_j^f - \epsilon_i^0 + E^0(\vec{s},0) - E^f(\vec{s},0) + (F^0(\vec{s})_n - F^f(\vec{s})_n)d + \ldots \tag{20}$$

(the zeroth-order term in the expansion on the right-hand side of eq 20 vanishes) and using[11]

$$\delta[(F^0 - F^f)_n d] = |F^0 - F^f|_n^{-1} \delta(d) \tag{21}$$

With these substitutions, eq 2 becomes

$$W_{0i,fj} = \frac{2\pi}{\hbar} \int |X_i^0|^2 \mu_{0f}^2 |F^0 - F^f|_n^{-1} \delta(d) \, \mathrm{d}\vec{R}$$

$$= \frac{2\pi}{\hbar} \int |X_i^0|^2 \mu_{0f}^2 |F^0 - F^f|_n^{-1} \, \mathrm{d}\mathbf{S} \tag{22}$$

which is identical with eq 19. Therefore, we conclude that the LZ-based theory expressed in eq 18 is a generalization of our eq 2. Of course, eq 18 may be preferred in numerical calculations because it properly treats situations in which $\mu_{0f}^2[\hbar v_n |F^0 - F^f|_n]^{-1}$ is large; the first-order perturbative result (eq 22) cannot be used when $2\pi\mu_{0f}^2[|F^0 - F^f|_n \hbar v_n]^{-1}$ is large.

In summary, we have shown that one can view the photon absorption process and calculate its rate in either of two ways: as a state-to-state transition induced by the $\vec{\epsilon}\cdot\vec{r}$ perturbation or as a "hopping" from one energy surface[9] ($E^0 + \hbar\omega$) to another (E^f). It is our feeling that this analysis sheds new light on the connections between these two seemingly quite different means of viewing the same physical process. It should also be noted in closing this section that computational implementation of the result of eq 2 or the identical eq 19 does not require information about the classical momentum vector. Only the intersection surface **S**, the magnitude of the force change normal to **S**, the electronic dipole integral, and the initial-state vibration wave function are needed. In the work of ref 10, classical trajectories are actually run on the initial-state surface $E^0(\vec{R})$ as a means of calculating the rate of passage through **S**, which is given in eq 17. In our picture as well as that given in ref 7, the need for running classical trajectories is obviated when eq 19 is used.

III. Conclusions

In this paper we have shown that the view of molecular electronic transitions afforded by eq 2 is *identical* with the first-order Landau–Zener-based rate expression given in eq 19. Thus, the neglect of the noncommutation of the vibration–rotation kinetic energy operator and the potential energy functions $E^0(\vec{R})$ and $E^f(\vec{R})$ (which is the only approximation made in deriving eq 2) leads to the same final rate expression as does the Landau–Zener approximation within a surface hopping picture (involving the $E^0(\vec{R}) + \hbar\omega$ and $E^f(\vec{R})$ surfaces). We feel that this connection between eq 2 and the Landau–Zener picture gives us a better understanding of the limitations of our picture of photon absorption because of the extensive experience base which exists for the Landau–Zener method.

The numerical work of Heller and Brown,[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 quantal 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 within the bandwidth of the exciting light). The total rate of transitions to such a group of states should be less sensitive to phase information than the rate of transition to any single state. Thus, it is likely that our approximate eq 19 will be more useful relative to the exact eq 1 for larger molecules; this is, of course, a fortunate

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(10) Heller et al. (E. J. Heller and R. C. Brown, *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, Bergsma et al. have obtained a similar result in their treatment of electronic absorption profiles.

(11) L. I. Schiff, "Quantum Mechanics", 3rd ed., McGraw-Hill, New York, 1955, p 57.

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 ^{12}CO or ^{13}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 $S = {}^5/_2$. The bent form (^{6}A′) has an approximate configuration [$\mathrm{d}\pi^2\mathrm{d}\delta^2\mathrm{s}\sigma^{0.2}(\mathrm{p}\sigma + \mathrm{d}\sigma)^{0.8}$] and a zero-field splitting parameter $|D| = 0.45$ cm^{-1}. The electronic parameters changed considerably in the linear form. V(CO)$_2$ was observed only in a neon matrix and has a $S = {}^3/_2$ 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)$_3$ was also observed only in neon as an axial molecule with a ^{2}A$_1$′ or ^{2}A$_1$ 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, partially 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)$_4$, V(CO)$_5$,[1] V(CO)$_6$,[2-5] Mn(CO)$_5$,[6] Co(CO)$_3$, Co(CO)$_4$,[7,8] CuCO, Cu(CO)$_3$,[9,10] and AgCO, Ag(CO)$_3$.[11,12] (Ionic carbonyls have also been observed via ESR[13,14] but will not be explicitly discussed here.) Theoretical discussions of the geometries, ground states, and bonding in these types of molecules have been given by several authors beginning perhaps with Kettle[15] and then by DeKock,[16] Burdett,[17,18] Elian and Hoffmann,[19] and Hanlan, Huber, and Ozin.[20] Although a number of ab initio calculations have been made on such carbonyls, the vanadium molecules considered here apparently have not been treated in detail.

The background for the present investigation was provided by the matrix work of Hanlan, Huber, and Ozin[20] who observed the infrared spectra of V(CO)$_n$ where n = 1 to 5, in the solid rare gases. Most notably, those authours concluded, from experiment and theory, that (1) VCO is nonlinear, (2) V(CO)$_2$ exists in linear, cis, and trans forms in all three matrices, argon, krypton, and xenon, (3) V(CO)$_3$ is probably of D_{3h} trigonal planar geometry. It should be emphasized that the supporting theory usually assumed low-spin ground states.

Morton and Preston have prepared V(CO)$_4$ and V(CO)$_5$ in krypton matrices by γ irradiation of trapped V(CO)$_6$.[1] From ESR they assign V(CO)$_4$ as high-spin ^{6}A$_1$ in tetrahedral (T_d) symmetry and V(CO)$_5$ as ^{2}B$_2$ with distorted trigonal bipyramid (C_{2v}) symmetry. V(CO)$_6$ is a well-known stable free radical which has been rather thoroughly researched by infrared,[21] MCD,[22] ultraviolet,[23] electron, and X-ray diffraction,[24] and ESR. It is presumably a Jahn–Teller distorted octahedral (^{2}T$_{2g}$) molecule at low temperatures leading to a ^{2}B$_{2g}$ ground state.

Our ESR findings are only for V(CO)$_n$, where n = 1 to 3, and are not always in agreement with conclusions from optical work and semiempirical theory. The most explicit departure is in finding that VCO and V(CO)$_2$ are high-spin molecules.

Experimental Section

The vanadium carbonyls synthesized in this work were made in situ by co-condensing neon (Airco, 99.996% pure), argon (Airco, 99.999% pure), or krypton (Airco, 99.995% pure) doped to 0.1–5 mol % with ^{12}CO (Airco, 99.3% pure) or ^{13}CO (Merck, 99.8% pure) with vanadium metal [99% pure, 99.8% ^{51}V($I = {}^7/_2$)] onto a flat sapphire rod maintained at 4–6 K but capable of being annealed to higher temperatures.

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