On Observing "New" States in Small Molecules

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In this paper we consider the general problem of a discrete state interacting with a continuum which is bounded below in energy. We investigate the optical properties of the new state which splits off below the threshold and determine its energy and oscillator strength in terms of the transition moments of the zero-order states and the matrix elements of the level shift operator. We study in particular the case of predissociation in diatomic molecules and provide numerical estimates and experimental criteria for the observation of this new effect. Finally, we discuss certain more general situations in which this phenomenon is expected to arise and suggest appropriate extensions of the present, semiempirical, treatment.

I. INTRODUCTION

It has been noted recently that the breakdown of the Born–Oppenheimer approximation in molecular systems can lead in principle to the appearance of "new" states.[1,2] This general phenomenon is a direct consequence of configuration interaction within a manifold of zero-order states which are bounded below in energy. Simple examples with which we shall be concerned involve a discrete vibronic level (energy $E_s > 0$) of a bound electron state mixing (through nonadiabatic terms, e.g., the nuclear kinetic energy and spin–orbit coupling in the case of predissociation, or by Coulomb terms in the case of autoionization) with the nearly degenerate continuum levels of a lower electronic state whose threshold is taken as the zero of energy. In these cases it can be shown that the spectrum of the exact eigenstates consists of a new continuum plus a new discrete state lying below the zero-order threshold.

Riess[1] has investigated several models of the coupling of zero-order molecular states and has complemented earlier work on the theory of nonradiative processes[3] by taking into account the role played by the bottom of the continuum in determining the properties of the new spectrum. Similarly Rosenfield, Voigt, and Mead[2] have considered in detail the breakdown of the adiabatic separability conditions in small molecules and have demonstrated certain mathematical features of the splitting off of new states. They discuss general conditions on the zero-order continuum wavefunctions and the coupling energy, etc., which must be satisfied in order for these new effects to arise.

In the more familiar case of configuration interaction involving discrete levels, one simply finds a stabilization of the lowest zero-order state. This situation is commonly observed in γ-ray spectroscopy, where for example, in the case of the oxygen nucleus, the onset of excited Hartree–Fock states is calculated to be at ≈ 12 MeV, whereas a single state (carrying most of the zero-order oscillator strength) is observed at ≈ 6 MeV.[4] Here, of course, the dramatic level shifts are due to the strong, short range, nuclear forces. Nevertheless, a completely analogous situation arises in small molecules such as NO_2 and SO_2[5] even though one is dealing only

with the weaker nonadiabatic interaction. In these triatomic systems there is configuration mixing between discrete singlet and triplet vibronic levels due to spin–orbit coupling terms and to favorable Franck–Condon overlap integrals (large geometry changes). This spreading out of oscillator strength and shifting of zero-order states is directly observable since it leads to anomalously long radiative lifetimes and many new lines in the absorption spectrum.[5,3b,c]

While the effects of configuration interaction within a manifold of zero-order discrete levels are well understood, it is interesting to inquire under what circumstances a "new" discrete state, resulting from the coupling of a zero-order level with a bounded zero-order continuum, is amenable to experimental observation. In this paper we choose to depart from the more formal, phenomenological, analyses of Riess[1] and Rosenfield *et al.*[2] We feel that a semiempirical treatment of the possibility of observing new states is desirable and that numerical estimates for particular diatomic molecules can lead to convenient experimental criteria relevant to this new effect.

We shall focus attention on the case of predissociation in which a bound electronic state is crossed by a lower lying repulsive state [Herzberg[6] type I(c)]. We use order of magnitude estimates appropriate to this problem in order to make quantitative predictions on the observable properties of the new states, i.e., do their energies and oscillator strengths satisfy the basic criteria which will be specified in the following sections.

II. GENERAL THEORY

We consider a system which can be described in zeroth order by a Hamiltonian H_0 with a discrete state $|s\rangle$, $E_s > 0$, lying in a continuum $\{|E'\rangle\}$, $E' \geq 0$, all E'. Let V denote the set of interaction terms coupling these zero-order states and let $H = H_0 + V$ be the total Hamiltonian of the system. In order to determine the manifold of new eigenstates, $\{|E\rangle\}$, of H we define the resolvent operator

$$G(E) \equiv (E - H)^{-1}. \qquad (1)$$

The matrix elements of $G(E)$ in, say, the zero-order

basis have the convenient property that they are analytic everywhere in the complex energy plane except for poles and a branch cut corresponding to the discrete and continuous portions of the spectrum of H. More explicitly, the eigenvalues of H are given by those values of E at which the function

$$G_{ss}(E) \equiv \langle s \mid (E-H)^{-1} \mid s \rangle \qquad (2)$$

is not regular. Equivalently, to find the new discrete energies we need only determine the isolated zeros of $[G_{ss}(E)]^{-1}$. Now, it is completely straightforward to show that

$$G_{ss}(E) = (E-E_s - \langle s \mid R(E) \mid s \rangle)^{-1}, \qquad (3)$$

where

$$R(E) \mid s \rangle \equiv V \mid s \rangle + V Q_s (E - Q_s H Q_s)^{-1} Q_s V \mid s \rangle, \qquad (4)$$

with $Q_s (\equiv 1 - \mid s \rangle \langle s \mid)$ projecting onto all zero-order states except $\mid s \rangle$. Thus we have simply that the eigenvalues $\{E\}$ of H are solutions of the algebraic equation

$$E - E_s = \langle s \mid R(E) \mid s \rangle \equiv R_{ss}(E). \qquad (5)$$

This fundamental equation of infinite-order perturbation theory allows us to interpret R as the "level shift" operator.

$R_{ss}(E)$, as is well known, can be shown[7] to be analytic everywhere in the complex energy plane, except for a branch cut running along the positive real axis. Accordingly, it satisfies the usual dispersion relation:

$$R_{ss}(E) = \pi^{-1} \int_0^\infty \frac{\mathrm{Im} R_{ss}(E'+i0^+)}{E'-E} \, dE'. \qquad (6)$$

Equation (6) defines the level shift function for all $0 < \arg(E) < 2\pi$ in terms of the values assumed on the upper lip of the cut. This result is convenient since one can demonstrate that[7]

$$\mathrm{Im} R_{ss}(E' \pm i0^+) = \mp \pi \mid v(E') \mid^2 \rho(E') \equiv \mp \Gamma(E'), \qquad (7)$$

where $\rho(E')$ denotes the density of zero-order states at E', and $v(E') \equiv \langle s \mid V \mid E' \rangle$ is the interaction energy coupling the discrete state $\mid s \rangle$ and the continuum state $\mid E' \rangle$. We note that (7) is exact only in the case where H has been prediagonalized in the space spanned by $\{\mid E' \rangle\}$, i.e., where the only nonvanishing matrix elements of V are those involving the coupling of $\mid s \rangle$ to the continuum. In the case of the breakdown of the Born–Oppenheimer approximation this situation obtains since the exact Hamiltonian H can be shown to be diagonal in any basis composed of vibronic levels belonging to the same electronic state.

Substituting (7) for $\mathrm{Im} R_{ss}(E'+i0^+)$ in (6) and returning to (5) we have that the discrete eigenvalues of H are given by the roots of

$$E_s - E = \int_0^\infty \frac{\Gamma(E') dE'}{E'-E} \equiv \int_0^\infty \frac{\mid v(E') \mid^2 \rho(E') dE'}{E'-E}. \qquad (8)$$

Now, the "new" states in which we are interested cor-respond to those solutions of (8) whose real part is negative (since they will then lie below the threshold of the continuum). Let the energy of the "new" state be $-E_0$. Writing $E = -E_0 + iI_0$, $E_0 > 0$, and equating the real and imaginary parts of the two sides of (8) we find that I_0 must vanish identically and that E_0 satisfies the relation

$$E_s + E_0 = \int_0^\infty \frac{\Gamma(E') dE'}{E'+E_0} \equiv \int_0^\infty \frac{\mid v(E') \mid^2 \rho(E') dE'}{E'+E_0}$$
$$\equiv F(E_0). \qquad (9)$$

Note that $F(E_0)$ is a positive, monotonically decreasing function of E_0 and that therefore, in general, (9) can be satisfied for at most one value of E_0 (>0). Only two cases can arise: (a) $\lim_{E_0 \to 0} F(E_0)$ exists, i.e., is finite—then (9) has a solution if and only if $E_s < F(E_0 = 0)$; (b) $F(E_0)$ diverges at $E_0 = 0$—then there exists a solution for all E_s. These conclusions have been formulated before[1,2]; we now follow up these results by quantitatively investigating the observable properties of the new states.

In addition to the energy of the "new" state, it is also important to determine its optical absorption cross section. In treating general radiationless decomposition processes (viz., predissociation and auto-ionization) we need to allow for the fact that in many cases the zero-order discrete state and the zero-order continuum can both carry oscillator strength from the ground state $\mid g \rangle$. Then the transition dipole matrix element with the state $\mid s \rangle$, $\mu_{gs} = \langle s \mid \mu \mid g \rangle$, and those with the manifold $\{\mid E' \rangle\}$, $\{\mu(E') = \langle g \mid \mu \mid E' \rangle\}$, must all be properly taken into account in the calculation of the line shape. The dipole strength per unit energy, $d(E)$, can be written as

$$d(E) = \mathrm{Im} \langle g \mid \mu G(E) \mu \mid g \rangle \qquad (10)$$

and can be simply evaluated in terms of the matrix elements of $G(E)$ in, say, the zero-order representation. We recall that the exact and approximate resolvent operators are related by the Dyson equation,

$$G(E) = G_0(E) + G_0(E) V G(E), \qquad (11)$$

and that the interaction V satisfies the convenient condition,

$$\langle s \mid v \mid s \rangle \equiv \langle E' \mid v \mid E'' \rangle \equiv 0, \qquad \text{all } E', E''. \qquad (12)$$

It follows directly from (11) and (12) that

$$\langle s \mid G(E) \mid s \rangle = [E - E_s - \Delta(E) - i\Gamma(E)]^{-1}, \qquad (13)$$

where

$$\Delta(E) \equiv P \int_0^\infty \frac{\Gamma(E') dE'}{E-E'} \quad \text{and} \quad \Gamma(E) \equiv \mid v(E) \mid^2 \rho(E)$$

are the real and imaginary parts of $\langle s \mid R(E-i0^+) \mid s \rangle$;

$$\langle s \mid G(E) \mid E' \rangle = G_{ss}(E) v(E') [1/(E-E')]; \qquad (14)$$
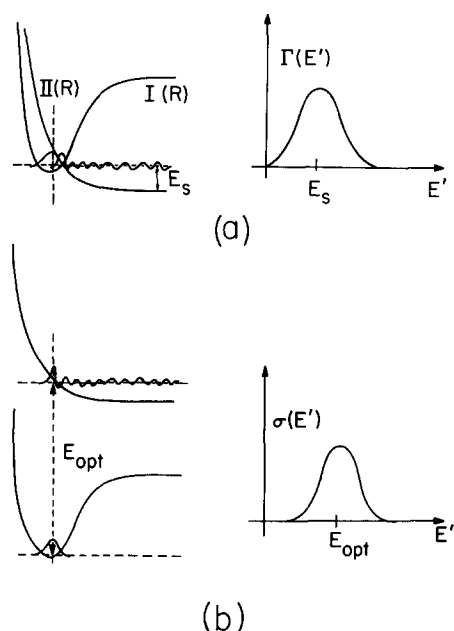
FIG. 1. Curve crossing geometries and line shapes for predissociation (a) and photodissociation (b) in diatomic molecules.

and

$$\langle E' \mid G(E) \mid E''\rangle = [1/(E-E')]$$
$$+ [1/(E-E')]v(E')G_{ss}(E)v(E'')[1/(E-E'')], \quad (15)$$

the first term contributing only for $E'=E''$. Then, provided that a new state exists at $E=-E_0$, it is straightforward to derive the following expression for the dipole strength in the negative energy region:

$$d(E) = \mid 1 + (\partial F/\partial E)_{E=-E_0} \mid^{-1} \mid \mu_{gs} + J \mid^2 \delta(E+E_0),$$
$$E<0. \quad (16)$$

Here

$$J \equiv P \int_0^\infty \frac{\mu(E')v(E')\rho(E')dE'}{E-E'}, \quad (17)$$

having the appearance of a "transition level shift" operator. Thus the absorption line shape for $E<0$ is seen to have zero width[8] (we have not yet included radiative damping) and to be characterized by a strength determined by the weight factor $1/\mid 1+F'(-E_0) \mid$ and the effective transition moment $\mu_{gs}+J$. The physical significance of this result becomes even more transparent since it can be shown that the amplitude squared, $\mid \langle s \mid -E_0 \rangle \mid^2$, of the discrete state $\mid s \rangle$ in the "new" state $\mid -E_0 \rangle$ is exactly equal to $1/\mid 1+F'(-E_0) \mid$.

In the case where the zero-order continuum does not carry oscillator strength from the ground state, (16) reduces to the simple form ($\{\mu(E')=0\}$)

$$d(E) = \mid \langle s \mid -E_0 \rangle \mid^2 \mid \mu_{gs} \mid^2 \delta(E+E_0). \quad (18)$$

In general, however, the dipole strength of the "new" state is determined by the effective transition moment,

$\mu_{gs}+J$, which may either enhance or decrease the absorption coefficient relative to the situation encountered for an optically inactive continuum. This interference effect (for the negative energy line of "zero width") is complementary to Fano's[9] configuration interaction ("antiresonance") effects which occur in the positive energy region.

Equations (9) and (16)–(18) provide us with the basic relations for the energy and oscillator strength of the "new" state of interest: $\mid -E_0 \rangle$ will be observable if and only if its negative energy exceeds its radiative width and its dipole strength is not too small compared with that of the zero-order discrete state (the magnitude of $\mid \langle s \mid -E_0 \rangle \mid^2$ being used as an index of photo-excitation cross section).

We have shown that the optical properties of the discrete level split from the bottom of the zero-order continuum are determined completely by the level shift operator and by the transition dipole moments of the zero-order states. This is a common feature of the generalized (infinite order) perturbation schemes which have been used extensively in the theory of impurity effects on the energy spectrum of elementary excitations in solids (e.g., phonons and excitons),[10] where the zero-order density of states is bounded from below (and from above).

III. SEMIEMPIRICAL TREATMENT: PREDISSOCIATION

Rather than consider properties of $\rho(E')$ and $\mid v(E') \mid^2$ which follow from a formal treatment of translational wavefunctions and the breakdown of the adiabatic approximation, we proceed from Eqs. (9) and (16) in a decidedly different manner. Our discussion derives from recognizing that the function $\Gamma(E')$ corresponds to an optical line shape and that $\mid v(E') \mid^2$ can be written in the usual way as a product of an electronic factor and the square of a vibrational overlap integral. For example, consider the case depicted in Fig. 1(a) where $\mid s \rangle$ corresponds to the vibrationless level of a bound electronic state I, and $\{\mid E'\rangle\}$ to the continuum levels of a repulsive state II which crosses I at E_s. Then since the Franck Condon factors do not depend upon vertical displacement of the oscillators (adiabatic curves), $\Gamma(E')$ will have the form of the photodissociation line shape observed in Fig. 1(b). The latter (modified Gaussian in this case) has been studied both experimentally[6] and theoretically[11,12] (numerical computation) in great detail. The electronic matrix elements (which we assume to be independent of nuclear coordinates[13]) enter as proportionality constants, or scale factors, which determine the absorption peak normalization.

For the case of a predissociating curve which crosses the bound electronic state higher than a few thousand wavenumbers above the vibrationless level, one can still appeal to the optical line shape. The semiempirical treatment is considerably complicated, however, in two

important ways. First, one must contend with absorption coefficients [and hence $\Gamma(E')$'s], which show oscillatory behavior[14] and which, as a result, are more difficult to parameterize. Secondly, and more importantly, one must properly take into account the fact that there are in effect several curve crossings and, accordingly, the possibility of more than one "new" state splitting off.[15] For example, in high resolution studies of the ultraviolet bands of P_2, breaking off of rotational structure in the emission spectrum has been observed, at different J, in several vibrational states.[16] In the semiempirical treatment which follows, then, we shall for simplicity's sake consider the case where the predissosiation occurs only in the 0–0 band, i.e., where the repulsive curve crosses the bound electronic state within a few thousand wavenumbers of its vibrationless level. We shall investigate particular systems (diatomic molecules) of this kind which give rise to "new" states of the sort discussed in Sec. II and shall provide numerical estimates of their energies and oscillator strengths. It will be recognized that these arguments can easily be generalized to other predissociation, as well as autoionization, etc., situations.

We begin by considering an approximate sum rule for $\Gamma(E')$ which derives from its normalization. Let $\psi_I(r, R)$ and $\chi_{I0}(R)$, and $\psi_{II}(r, R)$ and $\chi_{IIE'}(R)$, denote the electronic and nuclear wavefunctions corresponding to the zero-order states $|s\rangle$ and $|E'\rangle$, respectively. Then in a Condon-like approximation we write

$$|v(E')|^2$$
$$\equiv \left| \int_r \int_R \psi_I(r, R)\chi_{I0}(R)V(r, R)\psi_{II}(r, R)\chi_{IIE'}(R)drdR \right|^2$$
$$\approx |v|^2 |a(E')|^2, \qquad (19)$$

where $|v|^2$ is the usual, R-independent,[13] "electronic factor" (e.g., in diatomics, the matrix element squared of the spin–orbit and orbit–rotational coupling terms), and

$$a(E') = \int_R \chi_{I0}(R)\chi_{IIE'}(R)dR \qquad (20)$$

is the energy-dependent vibrational overlap. But with (19) we have immediately that

$$\int_0^\infty \Gamma(E')dE' \approx |v|^2 \int_0^\infty |a(E')|^2\rho(E')dE' = |v|^2 \qquad (21)$$

since the integral over $|a(E')|^2$ is just the sum of the

squares of the projections of $\chi_{I0}(R)$ onto the complete set $\{\chi_{IIE'}(R)\}$, $E' \in [0, \infty]$. This sum rule for $\Gamma(E')$ obtains even in the case where the configuration mixing is due to vibronic coupling effects.[3a] More explicitly, the generalized Franck–Condon factors, viz., the scalar products of the derivative of the bound state nuclear wavefunction and the continuum states, can simply be interpreted as the squares of the projections of $d\chi_{I0}(R)/dR$ on the complete set $\{\chi_{IIE'}(R)\}$, $E' \in [0, \infty]$. The electronic factor $|v|^2$ has been deduced for certain predissociation situations and in the case of the $^3\Sigma_U^- - ^3\Pi_U$ crossing in O_2, for example, is of the order of $10^4(cm^{-1})^2$.[17] We shall demonstrate below that, for purposes of predicting the observable properties of "new" states in diatomics, the actual shape of $\Gamma(E')$ is in no way critical. Rather the line shape can be essentially specified by its (i) area, (ii) width, and (iii) peak position relative to E_s and the threshold.

The first $\Gamma(E')$ we consider is shown in Fig. 2 and is defined by

$$\Gamma(E') \equiv (2|v|^2/\pi W^2)[W^2 - (E'-W)^2]^{1/2},$$
$$0 \leq E' \leq 2W,$$
$$\equiv 0, \qquad E' > 2W. \qquad (22)$$

Even though this line shape describes only symmetrical intensity distributions, it is of particular interest for the following simple reason. If any feature at all of the line shape were critical in determining the observable properties of the new states, it would be the asymptotic behavior of $\Gamma(E')$ near the threshold $(E' \rightarrow 0)$—for this directly determines whether or not $F(E_0)$ diverges at $E_0 = 0$. Now, from simple arguments applied to the one dimensional case (viz., diatomics) of curve crossing between bound and repulsive potential curves, it can be demonstrated that the square of the vibrational overlap integral, $|a(E')|^2$, weighted by the density of states, $\rho(E')$, behaves as $(E')^{1/2}$ for small E': this is precisely the asymptotic property shown by the $\Gamma(E')$ defined by (22).

Evaluating the integral in (9) for this "squashed circle" line shape we find that E_0, the energy of the "new" state below the threshold $(E' = 0)$, is given by the positive solution of $B(E_0) \equiv F(E_0) - (E_s + E_0) = 0$, or

$$B(E_0) \equiv 2|v|^2/W^2\{W + E_0 - [(W + E_0)^2 - W^2]^{1/2}\}$$
$$- (E_s + E_0) = 0. \qquad (23)$$

Note that $\lim_{E_0 \rightarrow 0}F(E_0)$ exists and is finite. More explicitly, $B(E_0)$ will admit of a positive zero ("new" state energy $= -E_0$) if and only if $E_s < F(E_0 = 0) = 2|v|^2/W$. For $|v|^2 \approx 10^4(cm^{-1})^2$ and $W \approx 10^3 cm^{-1}$ for example, we have that the zero-order state $|s\rangle$ must lie within 20 cm^{-1} of the continuum threshold. However, as emphasized earlier, even for values of E_s satisfying this condition it remains to prove that the new states formed will be observable. We have solved (23) [and
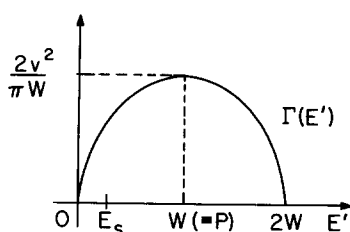

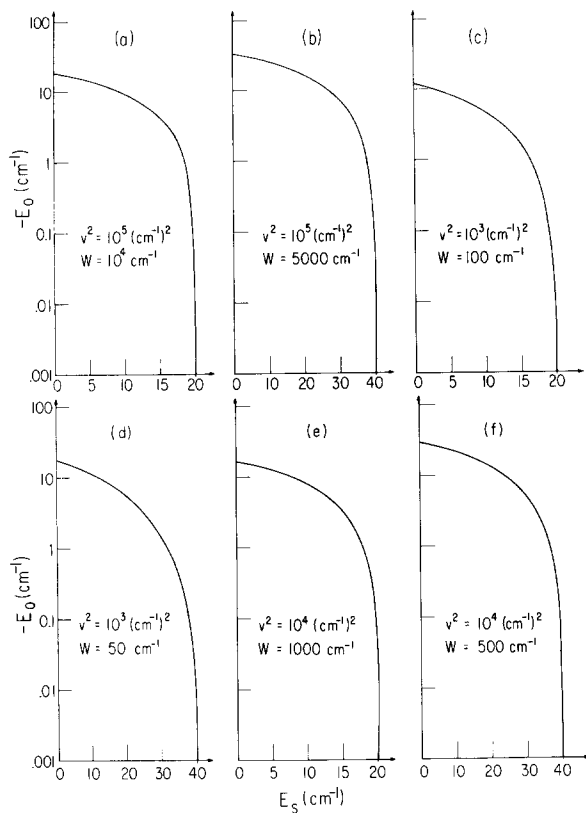FIG. 2. "Squashed-circle" line shape as defined by Eq. (22) of text.

FIG. 3. Semilogarithmic plots of the new state energy, $-E_0$, as a function of the zero-order energy, E_s, for the "squashed-circle" line shape defined in Eq. (22) of text. Results are displayed for six "physical" choices of the parameters $|v|^2$ (area) and W (width).

(16)] for the new state energy and oscillator strength and have displayed typical results in Fig. 3 as functions of $|v|^2$, W, and the zero-order energy of $|s\rangle$. The values of $|\langle s | -E_0 \rangle|^2$ were found to be sensibly constant for all choices of the line shape parameters—they ranged from ≈ 0.1 to ≈ 0.9 and, accordingly, it was not deemed instructive to include them in the semilog plots. We defer a full discussion of these results until after we have presented those for a rather different line shape.

To demonstrate that the actual shape of $\Gamma(E')$ is not important to our discussion we consider the following
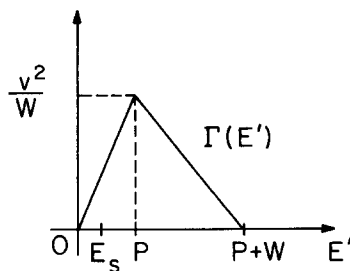

FIG. 4. Asymmetrical line shape as defined by Eq. (24) of text.

case (Fig. 4):

$$\Gamma(E') \equiv (|v|^2/WP)E', \qquad\qquad 0 \leq E' < P,$$
$$\equiv -(|v|^2/W^2)[E'-(P+W)], \qquad P \leq E' < P+W,$$
$$\equiv 0, \qquad\qquad E' > P+W.$$
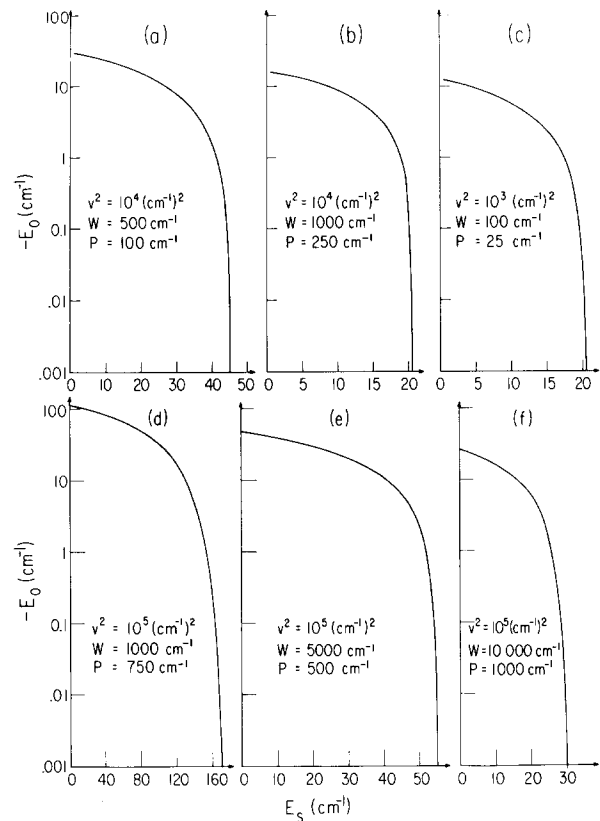$$(24)$$

This line shape can be made as asymmetrical as one

FIG. 5. $-E_0$ plotted as a function of E_s for representative values of $|v|^2$, W, and P (peak position) defining the triangular line shape [see Eq. (24) of text].

chooses ($P \neq W$). Evaluating the integral in (9) for the approximate $\Gamma(E')$ given by (24) we find that E_0 must now satisfy $B(E_0) = F(E_0) - (E_s + E_0) = 0$, or

$$B(E_0) \equiv |v|^2/W^2\{(E_0 W/P)[\ln(E_0) - \ln(E_0+P)]$$
$$+ (E_0+P+W)[\ln(E_0+P+W) - \ln(E_0+P)]\}$$
$$- (E_s+E_0) = 0. \quad (25)$$

Furthermore, since $F(E_0)$ diverges at E_0 for this line shape we are assured that $B(E_0)$ will in fact have a positive zero for all values of E_s and the parameters $|v|^2$ and W (unlike the "squashed circle" case where solutions existed only for $E_s < 2 |v|^2/W$). Equivalently, if we visualize the graphical solution of (25),

$\lim_{E_0 \to 0} F(E_0) = \infty$ guarantees [cf. (9)] that the straight line $E_s + E_0$ will always cross the monotonically decreasing curve $F(E_0)$ at some value of $E_0 > 0$. In order to determine which of these solutions correspond to observable new states, we have solved Eqs. (25) and (16) numerically for E_0 and $| \langle s | -E_0 \rangle |^2$ as functions of the line shape parameters $| v |^2$ (area), W (width), and P (peak position), and the zero-order energy E_s. Representative results are displayed in Fig. 5: $| \langle s | -E_0 \rangle |^2$ was again found to vary between ≈ 0.1 and ≈ 0.9. $E_0 = 0.001$ cm^{-1} is taken as the effective zero since those states lying closer to the threshold are masked by their radiative width and hence are not observable. Comparison with Fig. 3 shows clearly that the actual shape of $\Gamma(E')$ has no sensible effect on the observable properties of the new states.

IV. DISCUSSION

We have considered the general problem of configuration interaction of a discrete state with a continuum which is bounded below. This situation arises in all radiationless decomposition processes in molecular systems, i.e., in the cases of autoionization and predissociation. Essentially the same phenomena occur in electronic relaxation[3] and photochemical rearrangements[18] in larger molecules—one considers the quasi-continua of bound vibronic levels (characterized by wavefunctions which decay to zero at large distances) which are mixed (through nonadiabatic terms) with the discrete vibrational levels of higher electronic states. However, since we were primarily concerned there with the case of large energy gaps (cf. the statistical limit), the bottom of the manifold of closely spaced states played no critical role in the theory of radiationless transitions.

In this paper we have treated in detail the case of predissociation corresponding to the crossing of a bound electronic state by a lower repulsive curve. This situation serves as a convenient prototype of the general phenomenon of the formation of "new" states in small molecules. We have departed from the formal treatments developed by previous workers[1,2] insofar as we have set about to provide numerical estimates of the observable properties of these new states. We have demonstrated that one need not be concerned with the details of the predissociation line shape other than specifying its area $| v |^2$ (which derives from the "electronic factor"), width W (determined by the shape of the repulsive curve in the crossing region) and peak position P. The energy and oscillator strength of the new state can then be expressed simply in terms of these parameters and the energy E_s of the zero-order discrete state.

The numerical results obtained in Sec. III suggest that the new states arising from type I(c) predissociation effects will be amenable to observation only in diatomic molecules which satisfy a number of severely restrictive conditions. It is improbable that these "new" states can be detected experimentally since we have demonstrated that: the bound and repulsive states must cross in a manner which is highly unlikely; destructive interference effects may reduce the magnitude of the effective transition moment; and vib-rotational substructure may mask the new state. More explicitly, one must contend simultaneously with the following facts (necessary conditions):

(A) The crossing point must lie within ≈ 50 cm^{-1} of the threshold of the repulsive state (for $E_s > 50$ cm^{-1} the "new" state collapses into the continuum, as demonstrated in Figs. 3 and 5).

(B) Rotational fine structure may mask the appearance of the new state. We should consider the "real life" situation where there is more than a single vib-rotational level which can be optically excited from the ground state and which interacts strongly with continuum states. For molecules characterized by a small rotational constant a large number of rotational states will be excited and the dipole strength in the negative energy region will consist of a superposition of the δ functions, (26), each characterized by a slightly different energy and effective transition moment. This effect serves to smear out the lines of "zero width" and further undermines the chance of observing the new states.

(C) Vibrational–rotational fine structure, e.g., band heads present in the "negative energy region" due to sequence structure, may obscure the "new" state.

(D) We have shown that the optical cross section in the negative energy region (i.e., below the threshold) assumes the simple form

$$d(E) = | \langle s | -E_0 \rangle |^2 | \mu_{sg} + J |^2 \delta(E + E_0), \qquad E < 0, \tag{26}$$

where

$$J = -\int_0^\infty \frac{\mu(E') v(E') \rho(E') dE'}{E' + E_0} \tag{27}$$

describes the contribution of the zero-order continuum to the effective transition moment of the new state. Note that J may be either positive or negative, real or complex. $| \langle s | -E_0 \rangle |^2$, the square of the amplitude of the discrete state $| s \rangle$ in $| -E_0 \rangle$, has been calculated to be of the order 0.1–0.9. Then, in the simple case for which the states $\{| E' \rangle\}$ do not carry oscillator strength, $\mu(E') = 0$ for all E' and we can conclude that the absorption coefficient of the new state is comparable with that of $| s \rangle$. In general, however, J does not vanish and one must contend with the possibility of a destructive interference effect between the two contributions to the transition moment $| \mu_{sg} + J |$ whose magnitude and sign will depend on the details of the energy dependence of $\mu(E')$ and $v(E')$.

From the foregoing discussion we conclude that new

states arising from predissociation effects in diatomic molecules may be observable if the curve crossing lies sufficiently close to the threshold of the repulsive state and within the first vibrational band of the bound state. Furthermore, because of the complicating presence of spectral fine structure, a likely system to give rise to experimentally detectable new states would be some diatomic hydride (characterized by a large rotational constant).[19]

Throughout the above we have implicitly taken the absorption band shape in the negative energy region to be characterized by radiative damping only. We have shown that, except under rather restrictive (and unlikely) conditions, the "new" state will lie too close to the zero energy threshold and will hence be masked by its natural linewidth. We have neglected, of course, both Doppler and pressure broadening; also, since the "new" state is embedded in the continua of lower electronic states, it can be metastable against decay into these new channels. These additive contributions to the linewidth serve simply to further frustrate any chance of observing the "new" state which has split off from the repulsive state threshold. Recall that the basic idea behind the present semiempirical treatment has been to demonstrate that it is most difficult to detect these effects experimentally, even under ideal conditions. Accordingly, it appeared inappropriate to us to include, say, the higher-order effects arising from more than one bound vib–rotational level interacting strongly with the continuum states. For, as argued in the last two sections, the severe problems of observation (already manifest in the idealized case) are only propounded in the "real life" situation.

The approach described in Secs. II and III for elucidating the properties of new states in small molecules is quite general insofar as we have: (1) developed the underlying theory in terms of the "physical" properties of the level shift operator; and (2) exploited the known features of the appropriate line shapes. Thus, for example, one can treat the case of autoionization in the same semiempirical way as we have done here for predissociation. $\Gamma(E')$ will, of course, have different asymptotic behavior near the threshold (e.g., a step function dependence on energy) and will be normalized to a new "electronic factor" (viz., the matrix element squared of the Coulomb interaction terms). Insofar as the present discussion treats only a rather specific (albeit important) case of configuration interaction, it will be of interest to learn the results of similar quantitative calculations of "new" state effects in several different physical situations.

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$$\rho_e(E) = \pi^{-1}\mathrm{Im}[\mathrm{Tr}G(E-i0^+)]$$

$$= \pi^{-1}\mathrm{Im}\left[G_{ss}(E-i0^+) + \int_0^\infty \langle E' \mid G(E-i0^+) \mid E' \rangle \rho(E')dE' \right],$$

and using relations (13) and (15) for the diagonal matrix elements of the resolvent, it is simple to show that

$$\rho_e(E) = \delta(E+E_0), \qquad E<0,$$

provided that $F(E)-(E+E_s)$ has a zero at $E=-E_0(E_0>0)$.
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[19] The present semiempirical treatment also provides numerical estimates for the spatial extent of the new state. The wavefunction describing the new state can be written as

$$\mid -E_0 \rangle \equiv a(-E_0) \mid s \rangle$$

$$+ \int_0^\infty b(-E_0; E') \mid E' \rangle \rho(E')dE' \equiv G_0(-E_0)V \mid -E_0 \rangle,$$

where $G_0(E) = (E-H_0)^{-1}$ is the zero-order resolvent operator

$(H_0 = II - V)$. It is then straightforward to show that

$$P(E')dE' \equiv |\,b(-E_0;\,E')|^2 \rho(E')dE'$$
$$= [\Gamma(E')/(E'+E_0)^2] |\langle s | -E_0 \rangle|^2 dE'$$

is the probability of finding the continuum state $|\,E'\,\rangle$ in $|\,-E_0\,\rangle$. For the "squashed-circle" line shape with $|\,v^2\,| = 10^4 (\text{cm}^{-1})^2$, $W = 500$ cm^{-1}, and $E_s \approx 20$ cm^{-1} [implying $E_0 \approx 10$cm^{-1}—see Fig. 3(f)], this weighting function rises from zero at $E'=0$ to a maximum at $E' \approx 4$ cm^{-1} and then decreases monotoncially,

becoming negligible long before $E' \approx 1000$ cm^{-1}. Thus the spread in zero-order energy is of the order of, say, 50 cm^{-1}. For the diatomic hydrides (reduced mass ≈ 1 amu) this wave packet implies that the momentum (k) range of the continuum states which contribute significantly to $|\,-E_0\,\rangle$ is roughly 10^8 cm^{-1}. The spatial extent (vibrational amplitude) of the same molecules ($\omega_{\text{hydrides}} \approx 3000$ cm^{-1}) in the $v=0$ level of a pure bound state is about 0.1 Å. Thus the uncertainty in coordinate space of the new state arising from predissociation effects is roughly an order of magnitude greater than that for familiar vibrational bound states.

Optical and Magnetic Studies of Tripositive Thulium in Hydrated Chloride Crystals*

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The optical absorption spectra of single crystal TmCl$_3$·6H$_2$O and Tm^{3+} in YCl$_3$·6H$_2$O have been investigated between 2500 and 8000 Å at 4.2 and 77°K. The spectra were studied as a function of magnetic field strength and as a function of crystal orientation relative to the magnetic field. Both optical and EPR data indicate a nearly accidental degeneracy in the ground state of tripositive thulium in the hydrated chloride salts. The magnetic moment is found to be perpendicular to the twofold axis of symmetry and the zero field splitting is found to be 1.12 cm^{-1}. The observed splitting factor is 14.00±0.05 LU.

INTRODUCTION

This investigation is concerned with the study of the energy level scheme and magnetic properties of trivalent thulium in the low symmetry crystals YCl$_3$·6H$_2$O and TmCl$_3$·6H$_2$O. The detailed interpretation of the electronic and vibronic states is of interest not only to the spectroscopist, but also to those performing Mössbauer experiments, magnetic susceptibility, microwave resonance, and heat capacity measurements on this particular salt.

Although optical studies have been made on this crystal previously, a reinterpretation of the spectrum is of interest since the existing experimental information for thulium trichloride hexahydrate is incomplete. Gruber and Conway[1] investigated the optical spectrum of TmCl$_3$·6H$_2$O. However, their work was mainly to show the agreement between "free-ion" J-level energy calculations and the center of gravity of each crystal-field-split J level. Harrop[2] used the experimental results of several investigators to calculate the crystal field splitting of several rare earth chlorides including TmCl$_3$·6H$_2$O. The fit he obtained for Tm^{3+} and, in fact, for all rare earths with an even number of electrons does not appear to be in very good agreement with the observed levels. To quote Harrop, "The experimental situation for this crystal is very confused and the comparison given in Figs. 11–13 [of Harrop's paper] may be a guide to the correct assignment."

The most interesting feature of Harrop's crystal field calculation is the prediction that the two lowest Stark levels of the $^3H_6$ ground level are nearly degenerate. Harrop claims these levels should split in a magnetic field with splitting factors $S_1 = 13.7$ LU (Lorentz Unit)

and $S_2 = S_3 = 0$. According to Harrop, this splitting has never been observed because all the absorption lines are broad and diffuse.

Recoilless nuclear resonance spectra experiments performed by Clauser and Mössbauer[3] on TmCl$_3$·6H$_2$O have also suggested that several levels may be nearly accidentally degenerate with the ground level. These investigators were forced to this conclusion by the observation of large temperature-dependent line shifts and asymmetric line broadening in the RNR spectrum of TmCl$_3$·6H$_2$O. They concluded that these temperature-dependent shifts result from unequal thermal population of a nearly degenerate ground electronic level in the 0.5–4.2°K temperature range.

We have carried the work of Gruber and Conway[1] and Harrop[2] further with this investigation. In particular, we have identified the experimental details of the optical spectrum and have verified optically and by EPR experiments that a nearly accidental degeneracy does exist in the electronic ground level of TmCl$_3$·6H$_2$O.

CRYSTAL PREPARATION AND STRUCTURE

Single crystals of TmCl$_3$·6H$_2$O and various concentrations of Tm^{3+} in YCl$_3$·6H$_2$O were supplied by Mössbauer.[4] The remainder of the crystals were grown from solution in our laboratory by dissolving Tm$_2$O$_3$ in HCl and allowing the resulting solution to evaporate until single crystals of the desired size were obtained. Single crystals of TmCl$_3$·6D$_2$O were also grown by dissolving anhydrous TmCl$_3$ in D$_2$O.

The crystal structure of the rare earth hydrated chlorides has been investigated by several crystallographers.[5–7] Pabst[5] has made optical reflection measurements on PrCl$_3$·6H$_2$O, ErCl$_3$·6H$_2$O, GdCl$_3$·6H$_2$O,