

The Electronic Quasicontinuum

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High n ($=50$ – 250) molecular Rydberg states are characterized by a high density ($\rho \propto n^3/2Ry$) of electronic states and by unique intramolecular couplings (V) which involve long-range Rydberg electron–core multipole interactions. We explore spectroscopic and dynamic implications of the dipole coupling $V = C_D(nm')^{-3/2}$ of a doorway Rydberg state $|n, l, N^+, N\rangle$ with a dense $|\{n', l', N^+ - 1, N\}\rangle$ manifold ($n' > n$) of bound Rydberg states, which are described by Hund coupling case (d). We establish the conditions for the realization of the statistical limit ($V\rho \gg 1$ and $\gamma\rho > 1$) and of the sparse mixed level structure ($V\rho \gg 1$ and $\gamma\rho < 1$) within the mixed electronic manifold (where $\gamma = \Gamma_0/n^3$ are the nonradiative decay widths). The statistical limit for an electronic quasicontinuum is realized for the coupling strength domain $1.109Ry(B/Ry)^{3/8} < C_D < (\Gamma_0Ry/\pi)^{1/2}$, establishing how the characteristics of the level structure and dynamics are determined by the rotational constant B , by the molecular dipole moment ($C_D \propto \mu$), by the decay width constant Γ_0 , and by l (where $C_D \propto l^{-7}$). The statistical limit within an electronic quasicontinuum is expected to be amenable for experimental observation in polar large molecules, while the $np(N^+=0) - n'd(N^+=1)$ coupling in H_2O (Gilbert, R. D.; Child, M. S. *Chem. Phys. Lett.* **1991**, *187*, 153) corresponds to the sparse mixed level structure. Our analysis provides a generalization and unification of the theory of intramolecular coupling and dynamics for an electronic quasicontinuum.

I. Introduction

The spectroscopy and dynamics^{1–16} of high n ($=50$ – 250 , where n is the principal quantum number) Rydberg states of molecules are being explored by time-resolved zero electron kinetic energy (ZEKE) spectroscopy^{1–7,10–13} and by pulsed field ionization (PFI) ion counting spectroscopy.^{8,9} Of considerable interest is the nature of radiationless transitions of high n molecular bound Rydberg states below the lowest ionization potential, which correspond to predissociation for diatomics and for polyatomics and/or internal conversion for large molecules.^{8,9,17–30} The nonradiative decay channels for high Rydbergs, which involve the conventional dissociative continuum (for predissociation) and vibrational quasicontinuum (for internal conversion), are identical to those for the intramolecular dynamics of intravalence excitations and of low n Rydbergs. These radiationless transitions pertain to intramolecular relaxation to conventional decay channels in microsystems (mean radius $\langle r \rangle = (3/2)n^2a_0$, e.g., $r = 1\mu$ for $n = 112$), which occur from core-penetrating low electron angular momentum l states in the spatial region close to the nucleus (range A in Fano's terminology³¹). Very high n molecular Rydberg states are characterized by two novel features:

(1) High density of electronic states in a bound level structure (i.e., below IP(0)), which is $\rho(n) = n^3/2Ry$.³² This dense nl electronic manifold can serve in intramolecular coupling and even in intramolecular relaxation of a doorway Rydberg state.

(2) Unique intramolecular couplings. These involve long-range Rydberg electron–core multipole^{28,29,33} and/or anisotropic polarizability^{28,29,33} interactions, e.g., Rydberg electron–core dipole and quadrupole coupling for polar molecules (NO,^{8,9,23} HCl,³⁰ and H_2O ^{15,16}) or Rydberg electron–core quadrupole and anisotropic polarizability in homonuclear diatomics (H_2 ^{28,29} and N_2 ¹⁴).

These novel aspects of level structure and intramolecular coupling of high Rydberg states will be manifested in spectro-

scopic and time-resolved dynamic observables. It was established^{23,34,35–37} that these intramolecular couplings (in the absence of weak external fields^{18–23}) can be important only for low l (≤ 3) core-penetrating states. Two classes of such intramolecular coupling effects subjected to the appropriate selection rules between high Rydberg states can prevail:

(1) The coupling between pairs of near-resonant low l (≤ 3) Rydbergs.^{8,9,23} Such accidental near-degeneracies will result in the redistribution of the decay widths between pairs of states. This effect constitutes the electronic analogue to Fermi resonances for vibrational motion.

(2) The coupling of a doorway n Rydberg state to a manifold of dense n' electronic Rydbergs. Gilbert and Child¹⁶ and Lee *et al.*¹⁵ have explained the anomalous (type A) transitions in the ZEKE spectrum of H_2O in terms of intramolecular Rydberg electron interactions, which mix an nd ($n \approx 50$) state from a “sparse” electronic manifold with a dense $n'p$ ($n' \approx 330$) electronic manifold.

In this paper, we examine the spectroscopic and dynamic implications of the intramolecular coupling of a high n Rydberg state to a manifold of very high n' Rydbergs, addressing the question: Can a dense Rydberg manifold serve as an electronic quasicontinuum for a Lorentzian line broadening and for intramolecular dynamics? Intramolecular coupling to a vibrational manifold (or quasicontinuum) is well established,^{38–47} providing the conceptual framework for the dynamics and spectroscopy of large isolated molecules. In this paper, we generalize the concept of intramolecular coupling and dynamics, addressing the features of an electronic manifold (or quasicontinuum) of Rydberg states.

II. Intramolecular Vibrational and Electronic Manifolds

The concept of coupling and relaxation in a manifold of a bound level structure of large molecules played a central role in the theory of intramolecular dynamics.³⁹ Interstate (nuclear momentum and/or spin–orbit) coupling, which involves two electronic states with a vibrational quasicontinuum (correspond-

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ing to one of these electronic states), results in internal conversion or intersystem crossing,^{38–47} while intrastate (anharmonic or Coriolis) coupling within one electronic state with a vibrational quasicontinuum (corresponding to this electronic configuration) results in intramolecular vibrational relaxation in large molecules.^{44–47} When a doorway state (for excitation) is coupled to a bound manifold, this manifold is characterized as an intramolecular quasicontinuum for intramolecular relaxation of the doorway state and for Lorentzian spectral line broadening, provided that the following two conditions are satisfied:

(1) Strong coupling

$$V\rho > 1 \quad (\text{II.1})$$

where V is the (interstate or intrastate) coupling strength and ρ the density of states within the manifold. An equivalent (and more transparent) condition for the strong coupling is obtained from the condition of a sufficiently large number of coupled states within the line width of coupled states

$$\eta = 2\pi V^2 \rho^2 \gg 1 \quad (\text{II.1a})$$

(2) Overlapping resonances

$$\gamma\rho \gg 1 \quad (\text{II.2})$$

where γ is the decay width of a state within the manifold, which originates from intramolecular decay.

When both conditions (II.1) and (II.2) are satisfied, the vibronic level structure involves an intramolecular quasicontinuum corresponding to the statistical limit of intramolecular radiationless transitions in large molecules. When condition (II.1) only is satisfied while condition (II.2) is not fulfilled, the system corresponds to the sparse mixed level structure.^{38–47}

In analogy to the bound vibronic intramolecular manifold, we shall explore the features of an electronic manifold of bound high n Rydberg states below the first ionization potential. Using the high Rydbergs of a diatomic molecule as a generic example, the electronic angular momentum \vec{l} is weakly coupled to the rotational angular momentum \vec{N}^+ of the molecular ion core, so that the system is characterized by Hund's coupling case (d).^{17,28,29} The total angular momentum (excluding the spin) is $\vec{N} = \vec{l} + \vec{N}^+$ with a projection M_N . The Rydberg electron-core states of a definite N for a single vibrational state of the core are

$$|\kappa\rangle = |n, l, N^+, N, M_N\rangle \quad (\text{II.3})$$

The energies are

$$E(\kappa) = \text{IP}(N^+) - \text{Ry}/[n - \delta(l, N, N^+)]^2 \quad (\text{II.4})$$

where $\delta(l, N, N^+)$ is the quantum defect, which depends on l and also weakly on N^+ and N . The ionization potential for the formation of the N^+ state of the ion core is

$$\text{IP}(N^+) = \text{IP}(0) + BN^+(N^+ + 1) \quad (\text{II.5})$$

where B is the rotational constant of the ion core. In our analysis, vibrational excitations of the core will not be considered. We proceed to explore the intramolecular coupling and dynamics of an electronic manifold of high n' Rydbergs.

We consider the molecular system in the absence of an electric field ($F = 0$). The zero-order manifold $\{| \kappa \rangle\}$ of the high Rydberg in the Hund coupling case (d) is subdivided into

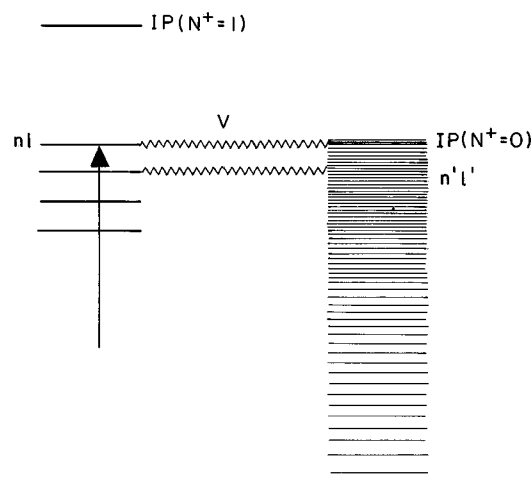


Figure 1. Energy levels scheme for the coupling of the doorway Rydberg state(s) $|n, l, N^+ = 1, N\rangle$ to the background Rydberg manifold $\{|n', l', N^+ = 0, N\rangle\}$. V denotes the intramolecular core multipole (or anisotropic polarizability)–Rydberg electron coupling.

three submanifolds: (i) Doorway state(s). A subset of low ($l = 0-3$) core-penetrating states constitutes the doorway state(s) for excitation. These doorway states are determined by the optical selection conditions and selection rules, i.e., one-photon excitation, two-photon excitation, or excitation from an intermediate state. (ii) Escape states. The doorway state(s) and a few additional low l (≤ 3) states, which are coupled to it by near-resonant intramolecular interactions, constitute the escape states for the decay. The decay widths $\Gamma_{l, N^+, N}(n)$ (for autoionization and predissociation for diatomics and/or internal conversion in polyatomics) of a $|n, l, N^+, N\rangle$ state are given by the n^3 scaling law^{20–22,48–53}

$$\Gamma_{l, N^+, N}^{(n)} = \Gamma_0(l, N^+, N)/[n - \delta(l, N^+)]^3 \quad (\text{II.6})$$

where $\Gamma_0(l, N^+, N)$ is the decay constant, which depends on l , N^+ , and N . (iii) The inactive states. The high l (≥ 4) nonpenetrating hydrogenic states (denoted by $\{|L\rangle\}$) are inactive in excitation and in decay. For these states $\delta(L) \rightarrow 0$ and $\Gamma_0(L) = 0$.

We consider the intramolecular coupling scheme of a single $|n, l, N^+, N\rangle$ Rydberg to a dense $\{|n', l', N^+, N\rangle\}$ Rydberg manifold (Figure 1). The energy difference between $|n', l', N^+, N\rangle$ and $|n, l, N^+, N\rangle$ is determined by the rotational energies which appear in eq II.5. To consider the coupling with a nonautoionizing $|n', l', N^+, N\rangle$ Rydberg manifold, we take $N^+ = 0$. The intramolecular couplings between the quasidegenerate (proximal) zero-order n and n' Rydberg states can be well described for nonpenetrating ($l \geq 2$) high n, n' Rydberg states in terms of Rydberg electron–core multipoles and polarizability couplings.^{26,28–30,33} This description of long-range interactions is borne out by the work of Eyler and Pipkin^{28,29} on the energetics of the 3d Rydberg complexes of H_2 and by Herzberg and Jungen^{33b} for the 4f Rydberg states of He_2 . For lower ($l = 0, 1$) Rydbergs, these long-range interactions provide only an approximate description for the intramolecular coupling, while for $l = 0$ Rydbergs, e.g., the $ns-nd$ coupling in NO ,²⁵ where core penetration effects are crucial, this scheme is inapplicable. In what follows, we shall consider an approximate description of the coupling between high $n \geq 1$ Rydbergs in terms of the long-range interactions. We proceed to explore the characteristics of the dense $\{|n', l', N^+, N\rangle\}$ electronic manifold in terms of conditions (II.1) and (II.2). To establish the characteristics of the dense electronic manifold (Figure 1), we have to consider the intramolecular coupling V and the density of states $\rho(n')$.

III. Intramolecular Coupling

The Hamiltonian of the diatomic molecule (in the absence of an external field) is

$$H_M = H_0 + H_{\text{INT}} \quad (\text{III.1})$$

where the zero-order molecular Hamiltonian is

$$H_0 = \sum_{\kappa} \langle |\kappa\rangle E_{\kappa} \langle \kappa| \quad (\text{III.2})$$

being expressed in terms of eqs II.3 and II.4. The Rydberg electron–core interaction is $H_{\text{INT}} = H_{\text{DIPOLE}} + H_{\text{QUAD}} + H_{\text{POL}}$, with the interactions between the Rydberg electron and the core dipole (H_{DIPOLE}), the core quadrupole (H_{QUAD}), and the core polarizability (H_{POL}) being known from the work of Eyler and Pipkin^{28,29} and Herzberg and Jungen.³³ For a typical polar ion core with a dipole moment $\mu = 1$ D (a quadrupole moment of $Q = 10^{-26}$ esu cm² and an isotropic polarizability of $\gamma \approx 0.5 \times 10^{-24}$ cm³), the dominating contribution to H_{INT} arises from the dipole coupling^{23,29,30} and we set

$$H_M = H_0 + H_{\text{DIPOLE}} \quad (\text{III.3})$$

with

$$H_{\text{DIPOLE}} = (e/r^2) \vec{C}^{(1)}(\theta, \phi) \cdot \vec{\mu} \quad (\text{III.4})$$

where r, θ, ϕ are the Rydberg electron coordinates in the molecule-fixed coordinate system, $\vec{C}^{(1)}(\theta, \phi)$ is the angular vector,⁵⁴ and $\vec{\mu}$ is the (electronic origin independent) dipole moment of the ion core.

The matrix elements for the Rydberg electron–core dipole coupling are²⁹

$$\langle n, l, N^+, N, M_N | H_{\text{DIPOLE}} | n', l', N^{+'}, N', M'_N \rangle = -e\mu \langle \nu l | r^{-2} | \nu' l' \rangle f(l, N^+, N, M_N; l', N^{+'}, N', M'_N) \quad (\text{III.5})$$

where $\nu = n - \delta(l)$, while the angular part is²⁹

$$f(l, N^+, N, M_N; l', N^{+'}, N', M'_N) = (-1)^{l'+l+N'} \begin{Bmatrix} N' & N^+ & l \\ 1 & l' & N^{+'} \end{Bmatrix} \otimes \delta_{N, N'} \delta_{M_N, M'_N} [(2l+1)(2l'+1)]^{1/2} \begin{bmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{bmatrix} \otimes [(2N^+ + 1)(2N^{+'} + 1)]^{1/2} \begin{bmatrix} N^+ & 1 & N^{+'} \\ 0 & 0 & 0 \end{bmatrix} \quad (\text{III.6})$$

with the selection rules

$$\Delta l = \pm 1, \quad \Delta N^+ = \pm 1, \quad \Delta N = 0, \quad \Delta M_N = 0 \quad (\text{III.7})$$

A semiquantitative estimate of the radial integral in eq III.5 for high n, n' states was obtained utilizing the Gilbert–Child¹⁶ near-threshold approximation with a finite quantum defect

$$\langle \nu l | r^{-2} | \nu' l' \rangle = 2(\nu\nu')^{-3/2} (\lambda + \lambda' + 1) \frac{\sin[\pi(\lambda - \lambda')]}{\pi(\lambda - \lambda')} \quad (\text{III.8})$$

where $\lambda = l - \delta(l)$ is the effective azimuthal quantum number and $\nu = n - \delta(l)$. Equation III.8 is based on the asymptotic form of the phase-shifted radial wave function.¹⁶ A major contribution to the radial integral, eq III.8, for high n and n' states originates from very short distances (e.g., $r \leq 4$ au for

$np-n'd$ interaction, $n, n' = 80-100$), in accord with Berry's classical studies of molecular autoionization.⁴⁸ The utilization of eq III.8 constitutes only an approximate description, which is, however, sufficient for our purposes.

We consider the coupling scheme in Figure 1. The (absolute) values of the matrix elements V for the dipole coupling, eqs III.5, III.6, and III.8, are

$$V = C_D (nn')^{-3/2} \quad (\text{III.9})$$

where

$$C_D = (2\mu e^2/a_0^2)(\lambda + \lambda' + 1)^{-1} [\sin[\pi(\lambda - \lambda')]/\pi(\lambda - \lambda')] \otimes f(l, N^+, N; (l \pm 1), (N^+ \pm 1), N) \quad (\text{III.10})$$

For a polar molecule, we take $\mu = 0.4-2.5$ D (0.16–1.0 au). Then for the lower $np(N^+=0)-n'd(N^+=1)$ dipole coupling with $f(\cdot) \approx 0.3$ and with typical quantum defects data for the NO molecule $\delta(p) = 0.723$ and $\delta(d) = -0.05$,^{9,25} we estimate C_D in the range $C_D = 1 \times 10^3 - 12 \times 10^3$ cm⁻¹. For high values of l (≥ 3), we estimated²³ for NO $V \approx C_D (nm')^{-3/2}$, where $C_D \approx 3 \times 10^6$ cm⁻¹/ l , which increases fast ($\propto l^{-7}$) with decreasing l .

IV. Characterization of the Dense Electronic Manifold

The density of states in the $\{|n', l', N^{+'}, N\rangle\}$ ($N^{+'} = 0$) manifold in the proximity of $|n, l, N^+, N\rangle$ is

$$\rho(n') = (n')^3/2Ry \quad (\text{IV.1})$$

Making use of eq III.9 for the weighted coupling parameter, eq III.1 is

$$V\rho(n') = (C_D/2Ry)(n'/n)^{3/2} \quad (\text{IV.2})$$

Neglecting the contribution of the quantum defects for large values of n and n' , we estimate from eqs II.4 and II.5

$$(n'/n) = n_{\text{MAX}}/(n_{\text{MAX}}^2 - n^2)^{1/2} \quad (\text{IV.3})$$

for $n < n_{\text{MAX}}$, where

$$n_{\text{MAX}} = (Ry/2B)^{1/2}(N^+ + 1)^{-1/2} \quad (\text{IV.4})$$

is the highest value of n below the ionization threshold IP(0) of the n' manifold. Taking $n = n_{\text{MAX}} - 1$, we readily estimate $n'/n = (n_{\text{MAX}}/2)^{1/2} = [Ry/8B(N^+ + 1)]^{1/4}$. It is useful to apply a scaling of the rotational constant setting $B_{\text{eff}} = B(N^+ + 1)$, so that

$$(n'/n) = (Ry/8B_{\text{eff}})^{1/4} \quad (\text{IV.5})$$

The ratio (n'/n) increases with decreasing B_{eff} . For a “light” diatomic molecule with $B_{\text{eff}} = 10$ cm⁻¹, $(n'/n) = 6$, in accord with the estimate of Gilbert and Child¹⁶ for H₂O ($n = 50$ and $n' = 330$), while for a heavy molecule with $B_{\text{eff}} = 0.1$, $(n'/n) = 19$.

The weighted coupling strength, eq IV.2, is

$$V\rho(n') = (C_D/2Ry)(Ry/8B_{\text{eff}})^{3/8} \quad (\text{IV.6})$$

The onset of strong coupling $V\rho \geq 1$ (for a given molecule with a fixed B) is marked by the condition $C_D > C_D^{(C)}$, where the value of $C_D^{(C)}$ is inferred from eq IV.6 by setting $(C_D^{(C)}/Ry) = 4.36(B_{\text{eff}}/Ry)^{3/8}$. As is apparent from Figure 2, this condition is realized for a “heavy” model molecule ($B_{\text{eff}} = 0.1$ cm⁻¹) for $C_D^{(C)} = 2.6 \times 10^3$ cm⁻¹. For the NO molecule

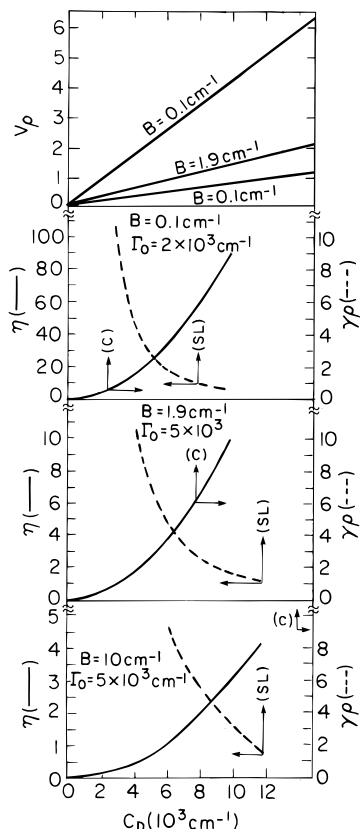


Figure 2. Dependence of the coupling parameters $V\rho$ and $\eta = 2\pi V^2\rho^2$ and of the line width parameter $\gamma\rho$ on the strength C_D of the dipole coupling. The vertical arrow marked (C) denotes the onset of strong coupling for $C_D > C_D^{(C)}$. The vertical arrow marked (SL) denotes the upper limit $C_D < C_D^{(SL)}$ for the statistical limit.

($B_{\text{eff}} = 1.9 \text{ cm}^{-1}$), strong coupling can be accomplished only for $C_D^{(C)} = 7.8 \times 10^3 \text{ cm}^{-1}$, which is higher by a numerical factor of 2 than our estimate $C_D = 3.7 \times 10^3 \text{ cm}^{-1}$ for the $np(N^+=1) - nd(N^+=1)$ interaction in this molecule.³⁴ For a “light” model molecule ($B_{\text{eff}} = 10$) strong coupling can set in only at the large value of $C_D^{(C)} = 1.5 \times 10^4 \text{ cm}^{-1}$.

Equivalent information regarding the coupling strength is obtained from the coupling width

$$\Delta = 2\pi V^2\rho = \pi C_D^2/n^3 \text{Ry} \quad (\text{IV.7a})$$

which is independent of n' . Taking $n \approx n_{\text{MAX}} = (\text{Ry}/2B_{\text{eff}})^{1/2}$ results in $\Delta = \pi C_D(C_D/\text{Ry})(2B_{\text{eff}}/\text{Ry})^{3/2}$. The number of states within the coupling width is defined by

$$\eta = \rho(n')\Delta = (\pi/2)(C_D/\text{Ry})^2(\text{Ry}/8B_{\text{eff}})^{3/4} \quad (\text{IV.7b})$$

Figure 2 presents the dependence $\eta \propto C_D^2$ for the “light” model molecule, for the “heavy” model molecule, and for NO, where we mark the onset $C_D^{(C)}$ of strong coupling $\eta \geq 6$ (which is equivalent to $V\rho \geq 1$). From this analysis we infer the following:

(1) Strong $|n, l, N^+, N\rangle - \{|n', l', N^+, N\rangle\}$ coupling can be realized for a moderately low value of l , e.g., for the p–d coupling. For higher values of l (≥ 3), the coupling is $V \propto l^{-7}$, eq III.10, i.e., $C_D \approx 10^3 \text{ cm}^{-1}$ for typical f–g coupling (with $\mu = 1 \text{ D}$) and $C_D < 10^3 \text{ cm}^{-1}$ for $l > 3$, which is too weak to warrant strong coupling.

(2) The onset of strong coupling, as marked by the values $C_D^{(C)}$, is determined by the rotational constant B_{eff} . For a

“heavy” model molecule ($B_{\text{eff}} = 0.1 \text{ cm}^{-1}$) $C_D^{(C)} = 2.6 \times 10^3 \text{ cm}^{-1}$ (being in the reasonable range of $\mu \approx 1 \text{ D}$), while for a “light” model molecule ($B_{\text{eff}} = 10 \text{ cm}^{-1}$) $C_D^{(C)} \approx 1.5 \times 10^4 \text{ cm}^{-1}$.

(3) For “light” molecules, the realization of strong coupling requires a large value of C_D ($> C_D^{(C)} \approx 1.5 \times 10^4 \text{ cm}^{-1}$). Such a situation is realized for H_2O ,¹⁶ which is characterized by a large value of μ . Of course, a complete treatment of the Rydberg electron–core dipole coupling in H_2O requires an extension of the diatomic molecule formalism used herein, but this will not change the gross features of our conclusions.

(4) For “heavy” polar model molecules ($B_{\text{eff}} \approx 0.1 \text{ cm}^{-1}$) with a reasonable value of $\mu \approx 1 \text{ D}$, strong coupling can prevail for moderately low values of C_D ($\geq 2.6 \times 10^3 \text{ cm}^{-1}$). Thus strong coupling with an electronic Rydberg quasicontinuum (for moderately low values of l) is expected to be realized in the Rydberg spectra of large molecules, e.g., large aromatic polar molecules, which are expected to be characterized by small values ($B = 0.05\text{--}0.1 \text{ cm}^{-1}$) of the rotational constants.

We have established the conditions for the realization of strong intramolecular coupling of a $|n, l, N^+, N\rangle$ Rydberg with a $|n', (l+1), (N^+\pm 1), N\rangle$ manifold. Such a strong coupling situation can correspond either to the sparse (strongly) mixed level structure, i.e., $\gamma\rho \lesssim 1$, or to the statistical limit, i.e., $\gamma\rho \gg 1$, according to eq II.2. We now consider the width of the mixed $|n, l, N^+, N\rangle + \{|n', (l+1), (N^+\pm 1), N\rangle\}$ states in the strong coupling limit ($\eta \geq 6$). A “democratic” mixing of the width $\Gamma_0(l)/n^3$ of the doorway state $|n, l, N^+, N\rangle$ among η $|n', (l+1), (N^+\pm 1), N\rangle$ states, which are characterized by the widths $\Gamma_0(l+1)/(n')^3$, results in the widths of a mixed state

$$\gamma = \frac{\Gamma_0(l)}{\eta n^3} + \frac{\Gamma_0(l+1)}{(n')^3} \quad (\eta \gg 1) \quad (\text{IV.8})$$

Setting the decay widths parameter of the n doorway state and of the n' manifold states to be equal, i.e., $\Gamma_0(l) = \Gamma_0(l+1) = \Gamma_0$, we then estimate

$$\gamma = \frac{\Gamma_0}{(n')^3} [1 + \eta^{-1}(n'/n)^3] \quad (\text{IV.9})$$

Making use of eqs IV.1, IV.5, IV.7b, and IV.9, we get

$$\gamma\rho(n') = (\Gamma_0/2\text{Ry})[1 + 2\text{Ry}^2/\pi C_D^2] \approx \Gamma_0\text{Ry}/\pi C_D^2 \quad (\text{IV.10})$$

Equation IV.10 implies that the parameter $\gamma\rho(n')$ ($\propto C_D^{-2}$), which determines the overlap of resonances, is independent of n' and of n . Furthermore, $\gamma\rho$ is independent of B_{eff} , as expected.

The condition for the onset of the statistical limit, eq II.2, sets a lower limit $C_D^{(SL)}$ on C_D , according to eq IV.10. When $C_D < C_D^{(SL)} = (\Gamma_0\text{Ry}/\pi)^{1/2}$ and concurrently strong coupling prevails, i.e., $C_D > C_D^{(C)}$, the mixed Rydberg level structure corresponds to the statistical limit. The $C_D^{(SL)}$ parameters are determined by the decay width parameter, which (for moderate values of $l = 1\text{--}3$) for molecular systems, falls in the range $\Gamma_0 = (1\text{--}8) \times 10^3 \text{ cm}^{-1}$.^{20–25} In Figure 2 we present typical values of $C_D^{(SL)}$ (for $\Gamma_0 = 2 \times 10^3 \text{ cm}^{-1}$ and $\Gamma_0 = 5 \times 10^3 \text{ cm}^{-1}$), which mark the upper limit of the coupling (for $\eta \gg 1$) which corresponds to the statistical limit.

From this analysis we conclude the following:

(1) The statistical limit for the coupling with a Rydberg doorway state n with a Rydberg electronic quasicontinuum is realized when

$$C_D^{(C)} < C_D < C_D^{(SL)} \quad (IV.11)$$

where $C_D^{(C)} = 4.36Ry(B_{\text{eff}}/Ry)^{3/8}$ and $C_D^{(SL)} = (\Gamma_0 Ry/\pi)^{1/2}$.

(2) The prevalence of the statistical limit, eq IV.11, can be realized over a reasonable domain of the interaction strength C_D for a “heavy” model molecule with a small value of $B_{\text{eff}} = 0.1 \text{ cm}^{-1}$ and for a molecule with a moderate value of $B_{\text{eff}} = 1.9 \text{ cm}^{-1}$ (Figure 2).

(3) The statistical limit for coupling with an electronic quasicontinuum is expected to be amenable to experimental observation in polar large molecules with a small value of B_{eff} .

(4) For a model “light” molecule with a large value of $B_{\text{eff}} = 10 \text{ cm}^{-1}$ we expect that for the reasonable values of $\Gamma_0 = 10^3\text{--}8 \times 10^3 \text{ cm}^{-1}$, we have $C_D^{(SL)} \lesssim C_D^{(C)}$, so that the statistical limit cannot be realized. For a “light” model molecule strong coupling resulting in a sparse mixed level structure can prevail for a coupling strength $C_D > C_D^{(C)} \gtrsim C_D^{(SL)}$. This situation requires a strong intramolecular interaction, characterized by a large value of μ . The $np(N^+=1)\text{--}n'd(N^+=1)$ ($n = 50$, $n' = 330$) level structure in H_2O studied by Gilbert and Child¹⁶ corresponds to the sparse mixed level structure.

(5) For molecular Rydbergs, where the statistical limit can be realized in the C_D domain $C_D^{(C)} < C_D < C_D^{(SL)}$, a sparse strongly mixed level structure can be realized for larger C_D values, i.e., $C_D > C_D^{(SL)} > C_D^{(C)}$ (Figure 2). In this large C_D domain η is very large, but the resonances do not overlap.

(6) For molecular systems characterized by $C_D < C_D^{(C)}$ “global” level mixing does not occur and the n' Rydberg background manifold does not exhibit the effects of strong mixing. In this C_D domain accidental near-resonances between a small number of n, n' pairs of states can be exhibited. These near-resonances between pairs (or a small number) of states (which are equivalent to Fermi resonances in a vibrational level structure) will result in local redistribution of intensities and lifetimes. This situation requires the treatment of individual energy gaps and couplings between proximal energy levels.

It should be realized that our analysis of the characteristics of the n' electronic manifold rests on the strength of the intramolecular interaction. The n and n' dependence of the intramolecular electronic interactions is, of course, determined by the Rydberg state normalization constants ($\propto n^{-3/2}, (n')^{-3/2}$), but these wash out for the reduced parameters $V\rho$ and $\gamma\rho$, which determine the level structure and dynamics. The reduced parameters for a given molecule are dominated by the C_D parameter, which, for weakly penetrating orbitals, is determined by l , $\delta(l)$, and μ . In any case, for the realization of the statistical limit or of the strongly mixed level structure, the C_D parameter (which constitutes an intrinsic molecular property for $l\text{--}l'$ coupling) has to be large (Figure 2) and this situation can be accomplished only for lower l Rydbergs. For higher ($l \geq 3$) nonpenetrating Rydbergs, e.g., for $l = 3 - l = 4$ coupling, the coupling strength $C_D = (1\text{--}2) \times 10^3 \text{ cm}^{-1}$ (for $\mu = 1\text{--}2 \text{ D}$) is already rather weak to warrant the realization of the onset of strong coupling.

V. Concluding Remarks

We have established the characteristics of a bound $n'l'$ ($N^+ = 0$) Rydberg manifold below the lowest ionization potential, establishing the conditions for the realization of a strongly mixed level structure and of the statistical limit for an electronic quasicontinuum. In this case, intramolecular coupling and relaxation can be realized within an electronic manifold. Our analysis provides a generalization of previous work on intramolecular coupling and intramolecular dynamics within a vibra-

tional–electronic (or vibrational) manifold of triatomic and large molecules^{38–47} to encompass the isomorphous features of a pure electronic Rydberg manifold. There is, however, a basic qualitative difference between the manifold of Rydberg states (the electric quasicontinuum) and the manifold of vibronic (or vibrational) states (the vibronic quasicontinuum). The coupling of a vibronic doorway state $|s\rangle$ to the vibronic quasicontinuum $\{|\alpha\rangle\}$ exhibits a large variation of the matrix elements $V_{s\alpha} = s|\hat{H}|\alpha\rangle$ for different α states, i.e., the correlation function of the couplings is $\langle V_{s\alpha}V_{s\alpha'}\rangle \ll \langle V_{s\alpha}^2\rangle$ for $\alpha' \neq \alpha$. On the other hand, the couplings $V_{s\alpha}$ of a Rydberg doorway state $|s\rangle$ with an electronic quasicontinuum $\{|\alpha\rangle\}$ exhibit a smooth and slow variation for different α states, i.e., $\langle V_{s\alpha}V_{s\alpha'}\rangle \approx \langle V_{s\alpha}^2\rangle$. This difference between the electronic and the vibronic quasicontinua is important for interference between several doorway states but does not affect the gross features of the level structure and dynamics of mixed states, which have their parentage in a single doorway state coupled with a quasicontinuum.

The experimental spectroscopic implications of intramolecular coupling and relaxation within an electronic manifold are then identical to those within the well-known vibrational–electronic (or vibrational) manifold.^{38–47} In the statistical limit of overlapping resonances, a Lorentzian line shape will be exhibited whose width is given by Δ , eq IV.7a. In the sparse strong mixing limit, a manifold of a large number ($\eta \gg 1$) of resolved states will be exhibited in the spectrum. These states are characterized by the average lifetimes \hbar/γ with $\gamma \approx [\Gamma_0/(n')^3](2Ry^2/\pi C_D^2)$, according to eqs IV.2, IV.7, and IV.9. With increasing strength of the intramolecular interaction for $C_D > C_D^{(SL)}$, the individual decay widths decrease, becoming smaller than the decay width Γ_0/n^3 of the doorway n Rydberg. This is the spectroscopic manifestation of the “dilution” effect for coupling in the electronic manifold, which is analogous to the Douglas effect^{42,44–47,55} for lifetime “dilution” as a consequence of strong mixing in the sparse level structure of the vibrational manifolds. Regarding the dynamic implications of the intramolecular coupling and relaxation within the electronic manifold, these are determined by the autocorrelation function of the light pulse and by the experimental interrogation method as previously discussed.²⁰ The time-resolved population of the entire mixed electronic manifold in a given energy domain (as conducted by ZEKE and PFI experiments^{1–14}) will be given by a superposition of exponential decay terms of the form²⁰ $\sum_j |a_j^{(s)}|^2 \exp(-\gamma_j t/\hbar)$, where $|a_j^{(s)}|^2$ are the mixing coefficients of the doorway state and the reciprocal lifetimes are $\gamma_j \approx \gamma$. No quantum beats are exhibited in the time-resolved interrogation of the total population. When the population of the doorway state is interrogated, the time-resolved decay in the limit of a sparse strongly mixed level structure will exhibit quantum beats (which reflect the energy spacings) and decay lifetimes of $\hbar\gamma_j^{-1} \approx \hbar\gamma^{-1}$. In the statistical limit, the time-resolved population of the doorway state (under optical excitation conditions with a light pulse with a coherent width $> \Delta$) will exhibit a decay lifetime of \hbar/Δ , as appropriate for a giant resonance.²⁰ Our analysis provides the generalization and unification of the concepts of intramolecular coupling and dynamics for a vibrational^{38–47} and for a purely electronic quasicontinuum.

Finally, we would like to point out that the present analysis focused on the spectroscopic and dynamic implications of intramolecular coupling between high n (and moderately low l) Rydberg states in the absence of external electric fields. Such external weak electric fields ($F = 0.02\text{--}0.1 \text{ V/cm}$), inevitably present in a ZEKE or PFI-ion counting system, induce l (or lm_i) mixing.^{18,19} The field-induced coupling and mixing model^{8,9,18–23} provides a semiquantitative account of the “global”

l mixing, which results in the breakdown of the n^3 scaling law for the nonradiative lifetimes (for predissociation and/or autoionization or diatomics,¹⁷ internal conversion and/or predissociation and/or autoionization for large molecules^{17,20,27}), which results in a dramatic lifetime lengthening (by 2–4 orders of magnitude) of these states. In the context of the characteristics of the electronic quasicontinuum within a high n, n' Rydberg manifold, electric field effects will dramatically increase the density of states within the mixed manifold and result in the lengthening (dilution) of the lifetimes of the mixed states. These interesting effects of field mixing were already semiquantitatively explored in the context of the time-resolved dynamics of the entire population of the autoionizing $^2P_{1/2}np^3[3/2]_1$ ($n = 100$ – 280) Rydbergs of Ar^{13,22} and of the predissociation dynamics of the $nf(N^+=2)$ ($n = 40$ – 95) and $np(N^+=0)$ ($n = 70$ – 125) Rydberg series of NO^{1,8,9,23} and deserve further study in the context of the exploration of the electronic quasicontinuum.

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