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Interference Effects in the Optical Spectrum of Large Molecules

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Interference effects between intravalence and extravalence excitations in the optical spectrum of a large molecule are considered. The sharp antiresonances observed in the Rydberg spectrum of the naphthalene molecule are interpreted in terms of configuration interaction between zero-order Rydberg levels and an inhomogeneously broadened $\pi\rightarrow\pi^*$ transition.

It is now well established that in the excited electronic states of large molecules, the Born–Oppenheimer (BO) separability conditions for electronic and nuclear motion breakdown. The cause of this breakdown is the coupling (vibronic, spin–orbit, etc.), between isoenergetic BO vibronic states which correspond to different electronic configurations and the results are intramolecular radiationless transitions.[1–3] A phenomenon intimately related to intramolecular electronic relaxation processes is the occurrence of line broadening in the higher excited states of large molecules.[3–7] For an isolated resonance the line shape is expected to be Lorentzian, while the linewidth is given by $\Delta=2\pi v^2\rho$, where v is a mean vibronic coupling term and ρ corresponds to the mean density of vibronic states.[3] In view of spectral congestion due to rotational structure and sequence length in an "isolated" molecule in the gas phase,[6] extra line broadenings due to radiationless transitions are amenable to experimental observation only when the linewidth exceeds $\sim$0.5 cm^{-1} (which corresponds to nonradiative lifetimes,[3] $\tau=\hbar/\Delta$, shorter than 10^{-11} sec).

Intravalence transitions (e.g., $\pi\rightarrow\pi^*$ excitations) to the higher excited singlet states of large organic molecules (e.g., benzene, naphthalene, and anthracene) are diffuse.[4–7] The vibronic components in the optical spectrum have linewidths in the range 100–1000 cm^{-1}. In the case of these high, spin-allowed, intravalence excitations the large value of the density of vibronic states together with the appreciable size ($\sim10^{-2}$–10^{-4} cm^{-1}) of the vibronic coupling term[3] induces efficient intramolecular electronic relaxation. The situation is, of course, radically different when extravalence excitations, such as transitions to molecular Rydberg states, are considered. In the gas phase these absorption lines corresponding to the Rydberg levels are quite sharp compared with the absorption bands of the intravalence transitions almost isoenergetic with the Rydberg levels. For example, the linewidths of the $3R$ Rydberg states of benzene are of the order of a few cm^{-1},[8] i.e., about two orders of magnitude less than the linewidths of the π–π^* $^1A_{1g}\rightarrow{}^1E_{1u}$ transition.[9] For anthracene,[10] the corresponding values are about 30 cm^{-1} for the Rydberg states and about 2000 cm^{-1} for the π–π^* $^1A_{1g}\rightarrow{}^1B_{2u}$ transition. For naphthalene,[5–11] the Rydberg bands are sharper than in anthracene but the π–π^* $^1A_{1g}\rightarrow{}^1B_{2u}$ band still has a width of some 2000 cm^{-1}.[12] It is then possible to deduce that there is relatively weak vibronic coupling in these Rydberg states. This observation can be easily rationalized by noting that the vibronic coupling terms involve a one-electron operator of the form[3] $\sum_k\partial U/\partial Q_k$, where U is the molecular Coulomb potential energy while $\{Q_k\}$ correspond to the nuclear coordinates. Hence the coupling between the large-radius Rydberg orbital and the ground-state π orbital via the $\partial U/\partial Q_k$ terms is expected to be relatively weak.

An interesting situation is encountered when Rydberg levels overlap an inhomogeneously broadened $\pi\rightarrow\pi^*$ transition. Such a situation prevails for the $2R$ Rydberg state of benzene which in the gas phase is quasidegenerate with the $^1A_{1g}\rightarrow{}^1E_{1u}$ $\pi\rightarrow\pi^*$ transition.[8] It was pointed out by Hazi[13] that such a situation may result in interesting interference effects. However, the experimental data for benzene[8] do not unambiguously reveal this feature. In the case of the naphthalene molecule, the $n=5$ to $n=13$ Rydberg levels overlap a medium-intensity ($f\sim0.1$) $\pi\rightarrow\pi^*$ transition located near 62 000 cm^{-1}.[11] The gas-phase optical spectrum of naphthalene as reported recently by Angus, Christ, and Morris[11] reveals several sharp antiresonances, as demonstrated

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[1] G. W. Robinson, J. Chem. Phys. **47**, 1967 (1967).

[2] B. R. Henry and M. Kasha, Ann. Rev. Phys. Chem. **19**, 161 (1968).

[3] M. Bixon and J. Jortner, J. Chem. Phys. **48**, 715 (1968).

[4] G. R. Hunt and I. G. Ross, Proc. Chem. Soc. **1961**, 11; J. Mol. Spectry. **9**, 50 (1962).

[5] G. A. George and G. C. Morris, J. Mol. Spectry. **26**, 67 (1968).

[6] J. P. Byrne and I. G. Ross, Can. J. Chem. **43**, 3253 (1965).

[7] R. M. Hochstrasser, Accounts Chem. Res. **1**, 266 (1968).

[8] P. G. Wilkinson, Can. J. Phys. **34**, 596 (1956). We have used Wilkinson's nomenclature when referring to specific Rydberg bands of benzene.

[9] B. Katz, M. Brith, A. Ron, B. Sharf, and J. Jortner, Chem. Phys. Letters **2**, 189 (1968).

[10] J. G. Angus and G. C. Morris, J. Mol. Spectry. **21**, 310 (1966).

[11] J. G. Angus, B. J. Christ, and G. C. Morris, Aust. J. Chem. **21**, 2153 (1968).

[12] Because these π–π^* transitions are inhomogeneously broadened, we use the full-width at half-height as an approximate measure only of the bandwidth.

[13] A. Hazi (private communication, 1966).

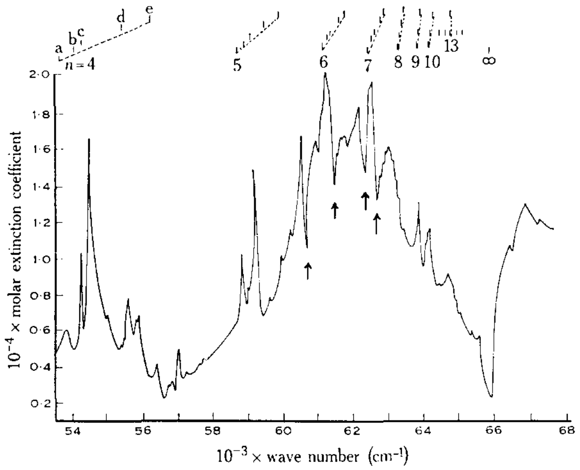

FIG. 1. The vacuum uv absorption spectrum of the naphthalene molecule in the gas phase as reported by Angus, Christ, and Morris (Ref. 11). a, b, c, d, e refer to Rydberg absorption bands of series characterized by different quantum defects and formed with increasing values of the principal quantum number (n). The positions of some of the more obvious antiresonances are indicated by the vertical arrows (↑).

in Fig. 1. Less pronounced but similar antiresonances are seen in the 56 000-cm^{-1} region of anthracene[10] and the 59 000-cm^{-1} region of pyrimidine.[14] We expect that other molecule systems would show similar phenomena, e.g., azulene, but the available spectra have been taken at too low resolution[15] or with too high gas pressure.[16] It is the purpose of this paper to discuss the nature of the interference effects which give rise to this unique behavior in the optical spectrum of an isolated large molecule. It is proposed that these effects arise from interference between resonance and potential scattering which is well known in atomic,[17] nuclear,[18] and solid-state,[19] physics.

In essence the situation is this: we assume that we know a set of zero-order Born–Oppenheimer states which consists of the following vibronic wavefunctions:

(a) A small set $\{\phi_s\}$, $s=1, 2, \cdots$, of the vibronic components of a highly excited $\pi\rightarrow\pi^*$ state each of which carries oscillator strengths from the ground state.

(b) A Rydberg ϕ_R which also carries oscillator strength from the ground state.

(c) A dense manifold of states $\{\phi_i\}$, corresponding to all lower electronic configurations, which are quasi-degenerate with $\{\phi_s\}$ and with ϕ_R. These $\{\phi_i\}$ states do not carry oscillator strength from the ground state. The molecular Hamiltonian is $H_{\mathrm{el}}=H_{\mathrm{BO}}+H_v$, where H_{BO} is the BO Hamiltonian while H_v corresponds to the intramolecular (vibronic, spin–orbit, etc.), coupling terms. The states $\{\phi_s\}$, ϕ_R, and ϕ_i are eigenfunctions of H_{BO}.

The optical properties of the system can now be elucidated by considering the molecular eigenstates $\{\Psi\}$ of the system which consist of superpositions of zero-order molecular states, i.e.,

$$\Psi_n=\sum_s a_s{}^n\phi_s+a_R{}^n\phi_R+\sum_i b_i{}^n\phi_i. \tag{1}$$

The off-diagonal matrix elements of the molecular Hamiltonian H_{el} in the Born–Oppenheimer representation are

$$\langle\phi_s \mid H_{\mathrm{el}} \mid \phi_R\rangle=v_{SR}, \tag{2a}$$

$$\langle\phi_s \mid H_{\mathrm{el}} \mid \phi_i\rangle=v_{si}, \tag{2b}$$

$$\langle\phi_R \mid H_{\mathrm{el}} \mid \phi_i\rangle=v_{Ri}. \tag{2c}$$

From the experimental observation of the narrow linewidths of Rydberg states we can safely assume that $v_{si}\gg v_{Ri}$ for all i. The problem can then be handled by the application of the Fano configuration-interactions scheme.[17] We first construct the superpositions $\{\psi_j\}$ of $\{\phi_s\}$ and $\{\phi_i\}$ which diagonalize the corresponding submatrix of the molecular Hamiltonian,

$$\psi_j=\sum_s \alpha_s{}^j\phi_s+\sum_i \beta_i{}^j\phi_i. \tag{3}$$

The molecular eigenstates are then given in the form

$$\Psi_n=A_R{}^n\phi_R+\sum_j B_j{}^n\psi_j. \tag{4}$$

The relevant coupling terms are

$$\langle\phi_R \mid H_{\mathrm{el}} \mid \phi_R\rangle=E_R, \tag{5a}$$

$$\langle\psi_j \mid H_{\mathrm{el}} \mid \psi_j\rangle=E_j\delta_{jj}, \tag{5b}$$

$$\langle\phi_R \mid H_{\mathrm{el}} \mid \psi_j\rangle=v_j. \tag{5c}$$

In the statistical limit, the manifold $\{\psi_j\}$ can be taken as an effective continuum. We can thus consider the Rydberg state as a closed channel interacting with an effective open channel $\{\psi_j\}$. The resonance width Γ_r obtained from Fano's theory[12] is given by

$$\Gamma_r=2\pi \mid v_j \mid^2 \rho_j, \tag{6}$$

where ρ_j is the density of states in the manifold $\{\psi_j\}$. The line-shape function $A(E)$ is given by[17]

$$A(E)=[(q+\epsilon)^2/(1+\epsilon^2)] \mid \langle\phi_0 \mid \boldsymbol{\mu} \mid \psi_j(E)\rangle \mid^2, \tag{7}$$

where $\langle\phi_0 \mid \boldsymbol{\mu} \mid \psi_j(E)\rangle$ is the dipole matrix element connecting the ground state ϕ_0 with the quasicontinuum states $\{\psi_j\}$ near E. The reduced energy parameter is[17]

$$\epsilon=(E-E_r-\gamma_1)/\tfrac{1}{2}\Gamma_r, \tag{8}$$

where γ_1 corresponds to the level shift (note that the assumption $v_j=$ const for all j implies that $\gamma_1=0$). The line-profile index[17] q is determined by the relative

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[14] J. E. Parkin and K. K. Innes, J. Mol. Spectry. **15**, 407 (1965).

[15] T. Kitagawa, Y. Harada, H. Inokuchi, and K. Kodera, J. Mol. Spectry. **19**, 1 (1966).

[16] L. B. Clark, J. Chem. Phys. **43**, 2566 (1965).

[17] U. Fano, Phys. Rev. **124**, 1868 (1961).

[18] M. A. Preston, *Physics of the Nucleus* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1962), p. 503.

[19] J. C. Phillips, Phys. Rev. Letters **12**, 447 (1964).

oscillator amplitudes of the states Ψ_n and ψ_j:

$$q=\langle\phi_0 \mid \mu \mid \Psi_n\rangle/\pi \mid v_j \mid \rho_j\langle\phi_0 \mid \mu \mid \psi_j\rangle. \tag{9}$$

The matrix elements v_j can be displayed by using Eqs. (2) and (3) in the form

$$v_j \approx \sum_s \alpha_s{}^j v_{SR}. \tag{10}$$

Now, for the sake of a rough estimate we shall consider only a single state ϕ_s contributing to Eq. (10). Furthermore, we shall make use of the Lorentzian distribution[20] of the amplitudes $|\alpha_s{}^j|^2$:

$$|\alpha_s{}^j|^2=v_{si}{}^2/[(E_j-E_s)^2+\Delta_i{}^2], \tag{11}$$

where $\Delta_i=2\pi v_{si}{}^2\rho_i$. The matrix element v_j can be thus written in the approximate form

$$v_j \approx \alpha_s{}^j v_{SR} \approx v_{si}v_{SR}/\Delta_i. \tag{12}$$

We can also safely assume that the densities of states in the manifolds $\{\phi_i\}$ and $\{\psi_j\}$ are about equal, i.e., $\rho_i=\rho_j$. From Eqs. (9) and (12) the following approximate relation results for the line profile index:

$$q \approx (\langle\phi_0 \mid \mu \mid \Psi_n\rangle/\langle\phi_0 \mid \mu \mid \psi_j\rangle)(v_{si}/v_{SR}). \tag{13}$$

The matrix elements v_{si} and v_{SR} both consist of a product of an electronic term $v^{(e)}$ and a vibrational overlap factor F, so that $v_{SR}=v_{SR}{}^{(e)}F_{SR}$ and $v_{si}=v_{si}{}^{(e)}F_{si}$. The electronic term $v_{si}{}^{(e)}$ for an intravalence excitation is expected to be of the order of 100–1000 cm^{-1}, as evident from the theory of vibronic coupling. On the other hand, for an intervalence Rydberg-type excitation, we expect a substantially smaller contribution to the electronic term of the order of $v_{SR}{}^{(e)} \lesssim 1\ \text{cm}^{-1}$. However, in the latter case, the Franck–Condon vibrational overlap factor is expected to be appreciable, i.e., $F_{SR}\sim 1$. In the case of an intravalence excitation, the corresponding F_{si} factor is very small. Thus, for example, for an electronic energy gap of 1 eV rough estimates[21] lead to $F_{si}\sim 10^{-4}$–10^{-6}. On the basis of these qualitative arguments we can assert that $v_{si}/v_{SR}\sim 1$. The following comments should be made at this point:

(a) Provided that the ratio of the transition moments

$$\langle\phi_0 \mid \mu \mid \Psi_n\rangle/\langle\phi_0 \mid \mu \mid \psi_j\rangle$$

is of the order of 1–10, the absolute value of the line profile index is expected to be of the order of unity and interference effects in absorption are expected to be revealed.

(b) A cursory examination of the absorption spectrum of naphthalene (Fig. 1) reveals that antiresonances in absorption are observed in the region where $\langle\phi_0 \mid \mu \mid \psi_j\rangle$ is large (i.e., strong background absorption), as expected on the basis of Fano's theory.

(c) The sign of the line profile index determines the assymmetry of the absorption line. In the case of the naphthalene Rydbergs the antiresonances are located on the high-energy side. Hence we may ascertain that $q<0$.

(d) The experimental linewidths of the Rydberg states consist of the following contributions:

(1) Interference effects discussed herein lead to a width Γ_r [see Eq. (6)].

(2) Inhomogenous broadening due to configuration interaction of the zero-order state ϕ_R with the background vibronic quasicontinuum $\{\phi_i\}$ leads to an additional contribution $\gamma=2\pi v_{Ri}{}^2\rho_i$. We should note in passing that $\gamma \ll \Delta_i$ and $\Gamma_R \ll \Delta_i$. From the experimental data displayed in Fig. 1, we notice that the linewidths of the Rydberg levels in the region 59 000 cm^{-1} (where no interference effects are observable) and in the range 60 000–63 000 cm^{-1} (where interference effects are of considerable importance), do not appreciably differ. We may thus ascertain that in the case under consideration $\gamma \gtrsim \Gamma_r$. Quantitative information concerning the relative contributions of the widths Γ_r and γ to the total resonance width can be obtained by following Phillips' recipe[19] folding the Fano line shape with a Lorentzian width γ. Such numerical calculations were performed by Jain[22] for a metastable exciton in solid xenon.

(e) When two Rydberg levels are closely spaced, i.e., their widths are comparable to their spacing, interference effects between these resonances are encountered. Such interference effects will lead to a "dip" in the intensity in the region between the two resonances. Such an effect is observed in the spectral region around 57 000 cm^{-1} (see Fig. 1) where the background absorption is weak.

The qualitative features of the line shapes of the naphthalene Rydberg states provide us with further insight into the nature of the breakdown of the Born–Oppenheimer approximation in the highly excited electronic states of an isolated large molecule. A quantitative analysis of the optical spectrum will yield valuable information concerning the vibronic coupling matrix elements and the density of effectively coupled vibronic states in such systems.

ACKNOWLEDGMENTS

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[20] Equation (11) is approximate as overlap between the inhomogeneously broadened vibrational components of the π–π^* state has to be considered.

[21] G. W. Robinson and R. P. Frosch, J. Chem. Phys. 38, 1187 (1963).

[22] K. P. Jain, Phys. Rev. 139, A544 (1965).