VOLUME 53, NUMBER 25 PHYSICAL REVIEW LETTERS 17 DECEMBER 1984

Unified Treatment of Dissociation and Ionization Processes in Molecular Hydrogen

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(Received 20 August 1984)

A theoretical procedure is introduced which yields eigenvalues and eigenvectors of the reactance matrix pertaining to competing dissociation and ionization processes in molecular Rydberg states. A calculation is set up in terms of adiabatic (nuclear-coordinate dependent) quantum defects $\mu(R)$ which contain the essence of the physics of the excited molecular complex at short range. The application to preionized and predissociated resonances in the H_2 spectrum yields good agreement with experiment.

PACS numbers: 33.10.Cs, 33.80.Eh, 33.80.Gj, 34.10.+x

Four years ago Dill and I[1] used multichannel quantum defect theory to calculate the photoionization spectrum of molecular hydrogen near threshold. The calculation included effects of vibrational-rotational preionization and reproduced very closely the complicated resonance structure observed by Dehmer and Chupka[2] in a high-resolution experiment. The calculation was straightforward because of a greatly simplifying physical circumstance whose importance had been stressed by Fano some years earlier. Fano[3] had suggested that even a highly excited bound or continuum electron conforms to the Born-Oppenheimer approximation so long as it is moving inside or near the molecular core. The Born-Oppenheimer separation of rovibrational and electronic motion breaks down only when the outer electron roams far from the core where its motion is comparable to or slower than the nuclear motion. This picture implies that nuclear-coordinate–dependent (body-frame) electron phase shifts $\pi\mu(R)$ [or the equivalent quantum defects $\mu(R)$ in the discrete range] provide all that is needed to calculate preionization, which involves a transfer of rovibrational energy from the core to the excited electron. The nondiagonal reactance or scattering matrices which account for this process can be constructed from the adiabatic phase shifts by means of an analytic transformation to the laboratory frame, which is applied to the wave function at some point outside the core, in a zone which one may term the "recoupling" zone.

In this Letter I show how this concept can be extended further to include *molecular dissociation* and *predissociation* occurring within a molecular Rydberg channel. Indeed, predissociation may be regarded[4] as the counterpart of vibrational-rotational preionization since here energy is transferred from the Rydberg electron to the nuclei, enabling the system to dissociate into atomic fragments. An analogous problem is encountered in dissociative attachment or associative detachment collisions involving hydrogen-halides.[5] The present extension aims at calculating the *competition* between preionization and predissociation, a problem which hitherto has been solved only for cases where weakly avoided crossings occur between Rydberg states and a dissociating valence state, i.e., where there is electronic rearrangement in the core.[6] The present work is still based on adiabatic quantum defects as the only dynamical parameters. It demonstrates that quantum defects, familiar from atomic physics, have a relevance far beyond their original context: Here they serve for the description of the *chemical transformation of matter* in a half-collision.

Figure 1 shows a prototype set of molecular Rydberg potential energy curves, namely, the lowest states of molecular hydrogen which can be excited by photoabsorption. The curves can be represented

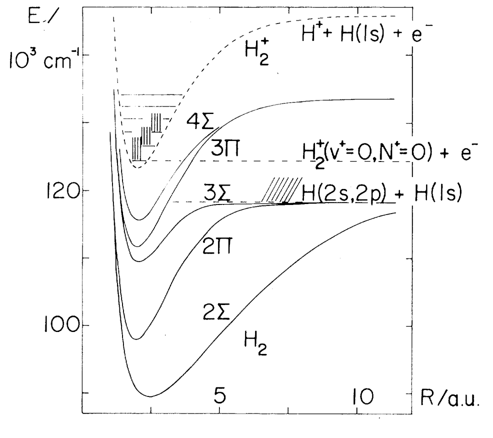


FIG. 1. Potential energy curves of singlet *ungerade* symmetry for H_2 (solid lines). The curve for H_2^+ $(X^2\Sigma_g^+)$ is also shown (dashed line). Continua are indicated by hatching.

by the Rydberg equation

$$U_{n\Lambda}(R) = U^{+}(R) - \{2[n-\mu_{\Lambda}(R)]^{2}\}^{-1} \text{ a.u.} \qquad (1)$$

with a *single* quantum defect function $\mu_{\Lambda}(R)$ for each symmetry Λ. (An exception is the large-R portion of the lowest curve whose associated quantum defect function differs significantly from that representing the other Σ states.) $U^{+}(R)$ is the potential function of the ion and n is the principal quantum number. The set of curves represents the lower discrete portion of a molecular p-wave *ionization channel* associated with the electronic ground state of the ion. (s and d electrons yield *gerade* states which do not appear in the dipole absorption spectrum.) Upon ionization the core remains in a particular vibration-rotation level $v^{+}N^{+}$. Dissociation and predissociation may take place *within* the Rydberg series because for energies higher than the first dissociation limit each of the lowest states $n\Lambda$ acts simultaneously as a *dissociation channel.*

In order to analyze the alternative fragmentation processes consider the two-dimensional configuration space spanned by the radial coordinate r of the Rydberg electron and the internuclear distance R (Fig. 2). Several zones are defined by the following critical values of r and R: r_0 corresponds to the boundary of the ion core, r_1 is the distance where the Born-Oppenheimer approximation is beginning to break down, and r_2 is the distance where all relevant bound Rydberg components have fallen exponentially to a negligibly small value. R_0 is the nuclear separation beyond which all relevant bound vibrational wave functions have become negligibly small. Typical values of r_0, r_1, r_2, and R_0 are, respectively, 4, 6, 30, and 7 a.u. Consider now a close-coupling expansion of the total wave function Ψ outside the reaction zone with components of general form $|i\rangle[f_i(r)\cos\delta - g_i(r)\sin\delta]$. The specific form of the expansion terms appropriate to each zone is indicated in Fig. 2. The kets $|i\rangle$ are the wave functions for all degrees of freedom of the system except the radial coordinate corresponding to fragmentation. They include the angular and spin wave functions of the escaping particle (electron or atom), coupled so as to yield a given total angular momentum J, space-fixed component M, and parity. The f_i and g_i are regular and irregular radial functions for the relative motion of the fragments, i.e., Coulomb functions (f,g) or vibrational continuum functions (F,G). The scattering phase shift δ represents the net effect of the short-range interactions in each channel. Note that in the inner part of region I each expansion term is a Born-Oppenheimer product with a core function $|v^{+}\Lambda\rangle$ characterized by a well-defined electronic angular momentum component Λ in the body frame. Accordingly δ is set equal to the adiabatic electron phase shift $\pi\mu_{\Lambda}(R)$. In region IV Ψ is set equal to zero and thereby the method is at present limited to the range below the threshold for dissociative ionization.

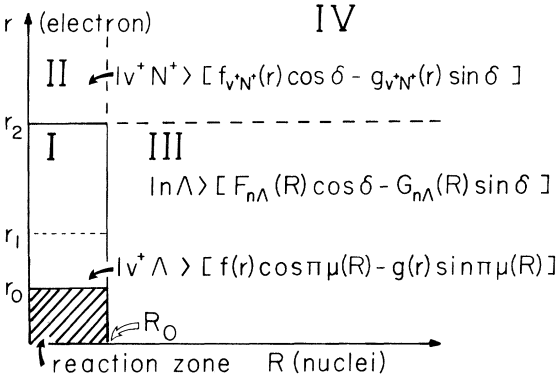


FIG. 2. Close-coupling expansion terms appropriate in different regions of configuration space.

The three forms of the close-coupling expansion indicated in Fig. 2 are equivalent to boundary conditions imposed on Ψ along the boundary of region I. Thereby attention is focused on the recoupling zone in which the dynamics of the system changes drastically from adiabatic to entirely nonadiabatic motion.

In this finite volume a multichannel rovibronic wave function Ψ_E is set up for a given total energy E, similar to the expansion used in Ref. 1, and which satisfies the specific boundary conditions just outlined. The difference from the earlier work is, firstly, that the truncated set of vibrational wave functions, $\{\chi_{v^+}(R)\}$, included in the calculation is extended to contain numerous functions reaching out to the boundary R_0. Secondly, a *common* phase shift $\pi\tau_\rho$ is imposed on both the various electronic radial components at $r=r_2$ and the vibrational radial components at $R=R_0$. Thereby an eigenchannel R-matrix problem of the type introduced by Fano and Lee[7] is defined, in which a multiparticle Schrödinger equation is to be solved within a finite volume. More specifically, the rovibronic multichannel quantum defect treatment in the recoupling zone leads to an eigenvalue problem of the type described first by Seaton,[8] namely,

$$\textstyle\sum_{i'}[\sin\beta_i(E)\mathscr{C}_{ii'}(E) + \cos\beta_i(E)\mathscr{S}_{ii'}(E)]B_{i'} = 0. \qquad (2)$$

Here i is an index for asymptotic channels which now may be closed or open. The β_i express the condition imposed on each asymptotic component at large distance, while the matrices $\mathscr{C}$ and $\mathscr{S}$ reflect the conditions imposed on the wave function at the boundary of the reaction zone.

Consider now for simplicity a situation where a single dissociation channel, $d = n\Lambda$, is open and molecular rotation can be disregarded. In the first stage of the calculation the dissociation channel does not appear explicitly. Instead, three classes of ionization channels $|v^+\rangle$ are distinguished, P, Q_1, and Q_2, respectively, which correspond to low, medium, and high vibrational excitation of the ion core. P contains the n_p open ionization channels. Q_1 contains n_{q_1} "weakly" closed ionization channels, namely, those which yield Rydberg resonances in the range of interest near E. Q_2 contains n_{q_2} "strongly" closed ionization channels corresponding to vibrational wave functions with a nonnegligible amplitude at R_0. This third set represents the dissociation continuum. The linear system (2) is then set up by putting $i = v^+$, $i' = v^{+\prime}$. At this stage open-channel boundary conditions are applied to P and Q_1 and closed-channel conditions to Q_2, respectively. The choice of the unphysical condition for Q_1 at this point takes advantage of the flexibility of quantum defect theory, in which the physical conditions need be applied only in the final stage. The present choice eliminates the resonances arising from Q_1 and is tantamount to reducing the radius r_2. As a result, a reactance matrix is obtained which varies smoothly with energy. (I am indebted to Ch. H. Greene for suggesting this procedure.) One puts

$$\beta_{v^+}(E) = -\pi\tau_\rho, \quad v^+ \in P, Q_1, \tag{3a}$$

$$\beta_{v^+}(E) = \pi\nu_{v^+}(\tau_\rho), \quad v^+ \in Q_2. \tag{3b}$$

The $\pi\tau_\rho$ are the eigenphases on the boundary of zone I to be determined. The $\nu_{v^+}(\tau_\rho)$ are the effective principal quantum numbers relating to the ionization limits v^+, viz., $\nu_{v^+}(\tau_\rho) = \{-2[E - E(v^+, \tau_\rho)]\}^{-1/2}$. The key elements here are the following: (i) the energy spectrum $E(v^+)$ of the vibrational wave functions calculated in the finite range $0 < R < R_0$ is *discrete*, because of imposition of a definite value of the logarithmic derivative on the functions $\chi_{v^+}(R)$ at $R = R_0$; (ii) this spectrum, and hence the effective principal quantum numbers ν in Eq. (3b), *depends on the phase* $\pi\tau_\rho$ since the corresponding logarithmic derivative $-b(\tau_\rho)$ is chosen. The coupling matrices $\mathscr{C}$ and $\mathscr{S}$ also depend on the phase since their elements are vibrational integrals of the type

$$\mathscr{C}_{v^+v^{+\prime}}(\tau_\rho) = \int_0^{R_0} dR\, \chi_{v^+}(R, \tau_\rho) \cos\pi\mu(R) \chi_{v^{+\prime}}(R, \tau_\rho) \tag{3c}$$

(and an analogous expression for $\mathscr{S}$ with $\sin\pi\mu$) familiar from the theory of vibrational preionization.[1]

In the R-matrix procedure of Fano and Lee τ_ρ is varied until an eigenvalue of the Hamiltonian in the finite volume coincides with the desired total energy E. The condition (3a) together with the linear system (2) generates $n_p + n_{q_1}$ such solutions. An additional eigenvalue arises through Eq. (3b), namely, when a low-n Rydberg level associated with the set Q_2 passes through E because of the variation of the ionization energies $E(v^+, \tau_\rho)$ as functions of τ_ρ. This level represents the dissociation continuum, and its mixing with vibrationally bound components through the linear system (2) provides the mechanism for the *conversion of energy*.

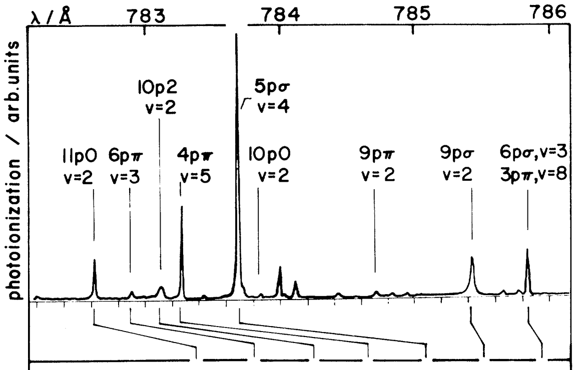
Each of the $n_p + n_{q_1} + 1$ eigenfunctions $\Psi^{(\rho)}(r_0 < r < r_2, R < R_0)$ thus found finally has to be projected at the surface of the recoupling zone onto the energy-normalized asymptotic channel functions outside. Following Refs. 1 and 7 one finds

$$\langle\rho|v^+\rangle = \sum\nolimits_{v^{+\prime}} [\mathscr{C}_{v^+v^{+\prime}}(\tau_\rho)\cos\pi\tau_\rho + \mathscr{S}_{v^+v^{+\prime}}(\tau_\rho)\sin\pi\tau_\rho] B^{(\rho)}_{v^{+\prime}}, \tag{4a}$$

$$\langle\rho|d\rangle = \frac{\sum_{v^{+\prime}} \chi_{v^{+\prime}}(R_0, \tau_\rho) B^{(\rho)}_{v^{+\prime}}}{[n - \mu(R_0)]^{-3/2} [F_{n\Lambda}(R_0)\cos\pi\tau_\rho - G_{n\Lambda}(R_0)\sin\pi\tau_\rho]}. \tag{4b}$$

Equation (4) yields the eigenvectors of the desired reactance matrix. Its nondiagonal form is

$$\mathscr{R}_{ii'} = \sum\nolimits_\rho \langle i|\rho\rangle \tan\pi\tau_\rho \langle\rho|i'\rangle, \quad i = v^+ \in P, Q_1 \quad \text{or} \quad i = d. \tag{5}$$



ion yield	obs.	100	>90	-	85	77	100	11
	calc.	100	99	98	81	96	99	7
diss. yield	obs.	-	-	-	18±5	10±10	-	95±5
	calc.	0	1	2	19	4	1	93
width (cm^{-1})	obs.	-	-	5.6	-	-	4.2	3.4
	calc.	0.6	1.1	5.5	0.07	0.3	4.0	3.3

FIG. 3. Top: Photoionization efficiency curve [$J'=1$ (negative parity) $\leftarrow J''=0$] of parahydrogen near 784 Å (Ref. 2). The unassigned peaks correspond to $J''=1$ transitions. Bottom: Observed (Refs. 2 and 9) and calculated ionization and dissociation yields and resonance widths for the individual resonances.

This matrix now has dimension $n_p + n_{q_1} + 1$ and includes the dissociation channel *explicitly*, condensed into a *single* row and column. In a final stage, then, the photodissociation and photoionization cross sections including resonances can be calculated from this reactance-type matrix by applying the physical boundary conditions at infinity, with use of standard quantum defect methods.[1,8]

Figure 3 illustrates the application of the method to photoabsorption by H_2. At the top of the figure is shown a section of the high-resolution photoionization efficiency curve obtained by Dehmer and Chupka from cold parahydrogen. Complementary photodissociation excitation spectra have been recorded by Guyon, Breton, and Glass-Maujean[9] but are not shown here. The spectrum is quite perturbed because of multiple interactions between the various Rydberg levels. This is revealed by the irregular intensity pattern and is confirmed by the calculations. In this range the $H_2^+(v^+=0$ and 1, $N^+=0$ and 2) $+e$ and $H(1s)+H(2s,2p)$ channels are open and accessible by dipole absorption from $H_2(J''=0)$. The multichannel quantum defect calculation yielded directly all seven partial-cross-section spectra evaluated point by point on a convenient energy mesh. In the lower part of the figure are given the total dissociation and ionization yields obtained by integration over each Rydberg resonance, and also the resonance width, along with the available experimental data from Refs. 2 and 9. Experiment and theory agree quite well. The observed yields for $5p\sigma, v=4$ are inconsistent since their sum is less than 100% depsite the fact that the molecular fluorescence decay channel is inactive.[10] The calculation agrees with Ref. 9 in this case. A more detailed account of this work will be given elsewhere.

I am greatly indebted to Dr. Dan Dill for participating in the early stages of this work, and to Dr. Ch. H. Greene and Dr. A. Giusti-Suzor for many discussions and for their comments on the manuscript.

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[1] Ch. Jungen and Dan Dill, J. Chem. Phys. **73**, 3338 (1980).

[2] P. M. Dehmer and W. A. Chupka, J. Chem. Phys. **65**, 2243 (1976), and private communication.

[3] U. Fano, Phys. Rev. A **2**, 353 (1970).

[4] E. S. Chang, Dan Dill, and U. Fano, in *Abstracts of Papers, Proceedings of the Eighth International Conference on the Physics of Electronic and Atomic Collisions,* edited by B. C. Cobic and M. V. Kurepa (Institute of Physics, Belgrade, 1973), p. 536.

[5] J. P. Gauyacq, J. Phys. B **15**, 2721 (1982).

[6] A. Giusti-Suzor and Ch. Jungen, J. Chem. Phys. **80**, 986 (1984).

[7] U. Fano and C. M. Lee, Phys. Rev. Lett. **31**, 1573 (1973).

[8] M. J. Seaton, Proc. Phys. Soc., London **88**, 801, 815 (1966), and Rep. Prog. Phys. **46**, 167 (1983).

[9] P. M. Guyon, J. Breton, and M. Glass-Maujean, Chem. Phys. Lett. **68**, 314 (1979), and **63**, 591 (1979), and private communication.

[10] J. Breton, P. M. Guyon, and M. Glass-Maujean, Phys. Rev. A **21**, 1909 (1980).