MOLECULAR PHYSICS, 1974, VOL. 27, No. 6, 1543–1552

Sequential decay involving multiple continua

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(*Received* 3 *September* 1973)

We have utilized the Green's function method to derive an explicit solution for the problem of sequential decay involving multiple continua with constant coupling between adjacent continua. This model system is applicable for theoretical studies of dynamics of photodissociation, predissociation and electronic quenching of polyatomic molecules.

Theoretical studies of photochemical fragmentation have considered a sequential decay process [1, 2], where an initial state is coupled to a manifold of intermediate levels, which in turn are coupled to a common dissipative continuum. Problems related to sequential decay involving two continua were recently explored in some detail [3–5], bringing up interesting manifestations of interference effects, such as the retardation of the decay rate of the initial state and the simultaneous population of these continua. Application of the Green's function method [5] resulted in a formal solution for the problem of sequential decay involving multiple unbound continua, all characterized by constant coupling. This problem is relevant for the elucidation of several interesting processes in excited electronic states of polyatomic molecules, such as

(*a*) Dynamics of direct photodissociation of polyatomic molecules [6–8]. One can consider the decay of an initial (zero order) state consisting of the ground state and a photon wave packet into a (zero photon) manifold of coupled dissociative continua, each corresponding to a different vibrational state of the fragments.

(*b*) Predissociation of polyatomic molecules [8]. In this case the ' initially excited ' zero-order state (resulting from ' short-time ' excitation) decays into a manifold of coupled dissociative continua.

(*c*) Electronic quenching of an excited atom by a diatomic molecule [9, 10]. This collision process can be described in terms of an initial (continuum state) of the electronically excited atom and the ground-state molecule which is coupled to a set of continua each corresponding to a different vibrational level of the molecule and to the ground state of the atom.

(*d*) Another possible application involves the vibrational excitation of diatomics by electron impact which proceeds via the formation of an intermediate negative ion [11].

The relevant physical observables are

(1) The distribution of the final vibrational states of the products in experiments (*a*), (*b*), (*c*) and (*d*). (2) The optical absorption lineshape and cross sections for ' resonance fluorescence ' [12] in experiments (*a*) and (*b*). (3) The decay rate of the ' initially excited ' state in experiment (*b*). (4) Cross sections for electronic quenching in experiment (*c*).

The nature of the final vibrational states of the products in experiments (*a*) and (*c*) was considered by Holdy *et al.* [7] and by Levine and Bernstein [13] in terms of a semiclassical ' half collision ' model while Shapiro and Levine [14] have handled experiment (*a*) by collision theory. We propose a quantum mechanical model for photodissociation, predissociation, electronic quenching and vibrational excitation in terms of sequential decay involving multiple continuua. We consider the case of photodissociation and predissociation of a triatomic molecule, when rotational effects are disregarded and the vibration of the diatomic fragment is considered to be harmonic. Then coupling occurs between dissociative continua where the vibrational levels of the diatomic fragment differ just by one vibrational quantum number [14]. A similar situation prevails for electronic quenching of an atom by a harmonic diatomic molecule. Thus experiments (*a*) and (*b*) for a triatomic molecule and experiment (*c*) for a diatomic can be handled in terms of sequential decay process with coupling between adjacent continua. It is our purpose to present a general solution to this problem for a simplified but useful model system.

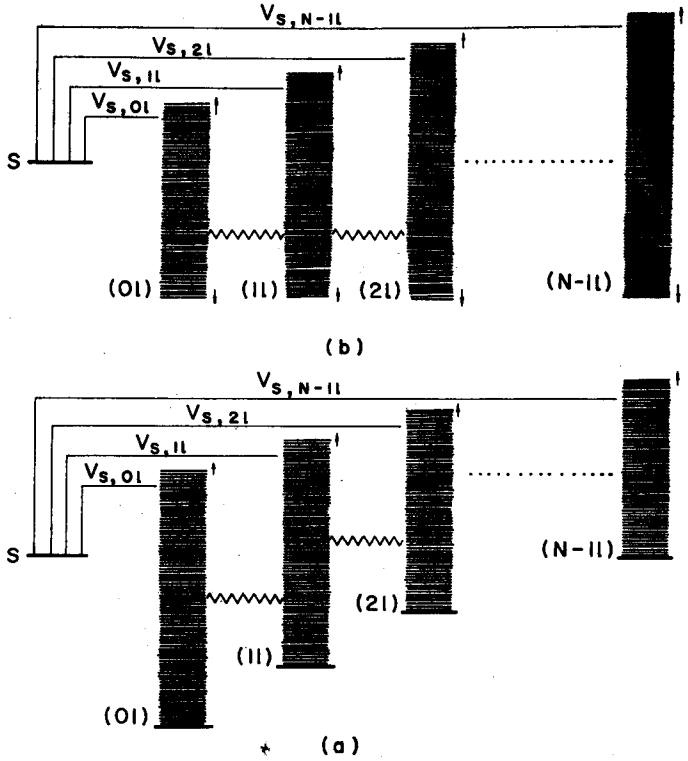

Figure 1. The coupling scheme. (*a*) The physical model where the $|s\rangle$ state is coupled to N continua ($|vl\rangle$, $v=0, 1, \ldots, N-1$), each of which is bound below. (*b*) A simplified model neglecting threshold effects.

The simplest physical model for photodissociation or predissociation of a triatomic molecule ABC is portrayed in figure 1. The zero-order state $|s\rangle$ (which for photodissociation corresponds to a wave packet of one photon states $(\sum_{\mathbf{ke}} \alpha_{\mathbf{ke}}|g, \mathbf{ke}\rangle)$ while for predissociation is given by a zero photon state $|s, \text{vac}\rangle$) is coupled to a set of continua which we label $\{|vl\rangle\}$. Here v is the vibrational quantum number of the diatomic fragments while l labels the relative translational energy in the dissociative mode. $|s\rangle$ and $\{|vl\rangle\}$ correspond to the eigenstates of a zero-order hamiltonian H_0. Assuming a collinear fragmentation process, we may choose the reduced distances R_{AB} and R_{BC} [14 b] as our internal coordinates for nuclear motion. Our zeroth-order hamiltonian, H_0, may be defined as follows :

$$H_0 = H_{BO} + \frac{1}{m}\frac{\partial^2}{\partial R_{AB}\partial R_{BC}} + H_{rad}, \tag{1 a}$$

where H_{BO} is the Born–Oppenheimer hamiltonian for the molecule, H_{rad} is the hamiltonian for the free radiation field and m is a reduced mass parameter introduced by Secret and Johnson [15] $m = (m_A m_C)/[m_B(m_A + m_B + m_C)]$.

The total hamiltonian, H, specifying the nuclear motion is given by [14 b]

$$H = H_0 + V, \tag{1 b}$$

where

$$V = -\frac{1}{m}\frac{\partial^2}{\partial R_{AB}\partial R_{BC}} + H_{ad} + H_{int}. \tag{1 c}$$

Here H_{ad} is the usual non-adiabatic term resembling deviations from the Born–Oppenheimer approximation and H_{int} is the interaction term between the molecule and the radiation field. For the sake of convenience we define a kinetic energy term

$$H_k = -\frac{1}{m}\frac{\partial^2}{\partial R_{AB}\partial R_{BC}} \tag{1 d}$$

which involves the product of the momenta in the internal and the relative coordinates of the fragments. Thus we have

$$V = H_k + H_{ad} + H_{int}. \tag{1 e}$$

The coupling matrix elements $\langle s|V|v_1\rangle = V_{s,\,vl}$ corresponds to $\langle s|H_{int}|vl\rangle$ in experiment (a) and to $\langle s|H_{ad}|vl\rangle$ in experiment (b). This matrix element can be taken to be proportional to the Franck–Condon vibrational overlap integral, FC, in the internal mode

$$V_{s,\,vl} = \mathscr{E}_l \mathrm{FC}(s, v). \tag{2}$$

The matrix elements for intercontinuum coupling can be factorized into a contribution of the internal mode and the translational states of the fragments

$$\langle vl|V|v'l'\rangle = \langle vl|H_k|v'l'\rangle = \alpha_{ll'}{}^{(v+1)}\delta_{v,\,v'-1} + \alpha_{ll'}{}^{v}\delta_{v,\,v'+1}, \tag{3}$$

whereupon coupling occurs only between adjacent continua.

The time evolution of the system is now handled by the Green's function method [16]. The time-dependent state of the system is represented by the superposition

$$\psi(t)=C_s(t)|s\rangle+\sum_v\sum_l C_{vl}(t)|vl\rangle \tag{4}$$

with $C_s(0)=1$. The amplitudes in equation (4) are given by the Fourier transforms of the Green's function

$$\left.\begin{aligned} C_s(t)&=\frac{1}{2\pi i}\int_{-\infty}^{\infty}\exp(-iEt)G_{ss}{}^{+}(E)\,dE,\\ C_{vl}(t)&=\frac{1}{2\pi i}\int_{-\infty}^{\infty}\exp(-iEt)G_{vl,\,s}{}^{+}(E)\,dE, \end{aligned}\right\} \tag{5}$$

where the Green's operator is $G^{+}(E)=\lim_{\eta\to 0^{+}}(E-H+i\eta)^{-1}$. The probability to find the system in the initial state is

$$P_s(t)=|C_s(t)|^2, \tag{6}$$

while the probability of decay into the v continuum is obtained by summation over all the states in this continuum

$$P_v(t)=\sum_l|C_{vl}(t)|^2. \tag{7}$$

Application of the Dyson equation results in the general form of the matrix elements

$$G_{ss}{}^{+}=\frac{1}{E-E_s+i\eta}+\frac{1}{E-E_s+i\eta}\sum_v\sum_l V_{s,\,vl}G^{+}{}_{vl,\,s} \tag{8}$$

and

$$G^{+}{}_{vl,\,s}=\frac{1}{E-E_{vl}+i\eta}\sum_{v'}\sum_{l'}V_{vl,\,v'l'}G^{+}{}_{v'l',\,s}+\frac{1}{E-E_{vl}+i\eta}V_{vl,\,s}G_{ss}{}^{+} \tag{9}$$

for each v and l. In order to obtain manageable results the following approximations are introduced :

(A) The coupling matrix elements $V_{s,\,vl}$ between the 'initial' state $|s\rangle$ and each of the continua are independent of the translational state, so that $\mathscr{E}_l=\mathscr{E}$ in equation (2) and $V_{s,\,vl}=V_{s,\,v}$.

(B) The number, (N) of the continua is determined by the highest continuum accessible by resonance coupling from $|s\rangle$ (see figure 1).

(C) The matrix elements between adjacent continua (equation (3)) are constant and we set $V_{vl,\,(v\pm1)l'}=\overline{V}$, being independent both of l and l' and of v.

(D) The continua are unbounded.

It should be noted that the constant coupling assumption (C), for different states in v and in the $v+1$ continua is consistent with assumption (D) and will result in the vanishing of level shift terms.

Equations (8) and (9) now take the form

$$G^{+}_{vl,\,s}=\frac{1}{E-E_{vl}+i\eta}\,[\overline{V}\sum_{l'}(G^{+}_{(v+1)l',\,s}+G^{+}_{(v-1)l',\,s})+V_{v,\,s}G_{ss}{}^{+}]\,;$$

$$v=0\ \ldots\ N-1\,;\quad -\infty<l<\infty, \tag{10}$$

$$G^{+}_{ss}=\frac{1}{E-E_s+i\eta}\,(1+\sum_{v}\sum_{l}V_{s,\,v}G^{+}_{vl,\,s}). \tag{11}$$

Performing an integration $\sum_{l}\to\int dE_l\rho_l$ (where ρ_l in the density of states in the continua) equation (10) results in

$$a_v=\beta a_{v+1}-\beta^{*}a_{v-1}-\gamma_v\,;\quad v=0,\,1,\,\ldots,\,N-1 \tag{12}$$

$$G_{ss}{}^{+}=(E-E_s+i\eta)^{-1}(1+\sum_{v}V_{s,\,v}a_v), \tag{13}$$

where the auxiliary functions for the sum of the matrix elements are

$$a_v=\sum_{l}G^{+}_{vl,\,s}=\int dE_l\rho_l G^{+}_{vl,\,s} \tag{14}$$

with $a_{-1}=a_N=0$.

We have also defined

$$\gamma_v=i\pi V_{v,\,s}\rho_l G_{ss}{}^{+} \tag{15}$$

and the reduced intercontinuum coupling parameter

$$\beta=-i\pi\overline{V}\rho_l. \tag{16}$$

The general set of $N+1$ (equations (12), (13) (for $a_0\ \ldots\ a_{N-1}$ and $G_{ss}{}^{+}$) can be readily solved. We shall consider herein the simple case of 'initial' coupling to a single continuum $\{|kl\rangle\}$, whereupon $V_{s,\,v}=V_{s,\,k}\delta_{v,\,k}$.

The solutions of equation (12) can be recast in the form

$$a_v=-F(v,\,k)\,.\,\gamma_k \tag{17}$$

where the auxiliary function

$$F(v,\,k)=\frac{Q_vQ_{N-1-k}}{Q_N}\,\beta^{k-v}\,;\quad v\leqslant k, \tag{18 a}$$

$$F(v,\,k)=\frac{Q_{N-1-v}Q_k}{Q_N}\,(-\beta^{*})^{v-k}\,;\quad v\geqslant k \tag{18 b}$$

is expressed in terms of the polynomials Q_v, which are given by the recurrence formulae

$$Q_0=Q_1=1,$$

$$Q_{v+1}=Q_v+|\beta|^2Q_{v-1},\quad v>0. \tag{19}$$

The matrix elements of the Green's function are explicitly expressed using equations (10), (11) and (17) in the form

$$G_{ss}^{+}=\frac{1}{E-E_s+\frac{i\Gamma_s}{2}} \tag{20}$$

which is characterized by the width

$$\Gamma_s=\Gamma_s^0F(k,k)\,;\quad \Gamma_s^0=2\pi|V_{ks}|^2\rho_k \tag{21}$$

and

$$G_{vl,\,s}^{+}=\frac{F(v,k)V_{k,\,s}}{(E-E_{vl}+i\eta)\left(E-E_s+\frac{i\Gamma_s}{2}\right)}. \tag{22}$$

Equations (20)–(22) together with the general relations (5)–(7) determine the time evolution of the system. The decay of the ' initial ' state is exponential, being characterized by the decay rate $\Gamma_s/\hbar$ (equation (21)), which is given by the zero-order width Γ_s^0 multiplied by the diagonal element $F(k,k)=(Q_kQ_{N-1-k}/Q_N)$. The population of the $\{|vl\rangle\}$ continuum at $t\to\infty$ is obtained from equations (7) and (22) in the form

$$P_v(\infty)=\sum_l\frac{|F(v,k)V_{k,\,s}|^2}{(E_{vl}-E_s)^2+(\Gamma_s/2)^2}=|F(v,k)|^2. \tag{23}$$

We note in passing that the matrix $F(v,k)$ (equation (18)) obeys the unitary relation $\sum_v|F(v,k)|^2=1$ and contains all the relevant information regarding the vibrational partitioning of the fragments. This matrix is related to the level shift operator R, by $R_{s,\,v}=F(v,k)V_{k,\,s}$. It is important to notice that a general form of equation (22) is

$$G^{+}{}_{vl,\,s}=\frac{R_{vl,\,s}}{(E-E_{vl}+i\eta)(E-E_s-D_s(E)+i\Gamma_s(E)/2)} \tag{22 a}$$

(where $D_s(E)$ is the real part of $R_{ss}(E)$). This result is independent of assumptions (A)–(D), being the consequence of the partitioning of Hilbert space into $\hat{P}+\hat{Q}=1$, where $\hat{P}=|s\rangle\langle s|$, contains a single state [16]. Equation (22 *a*) together with equation (5) imply that all the continua are simultaneously populated.

The predictions of the present model can be summarized as follows :

(1) In the case of weak intercontinuum coupling, $|\beta|\ll1$, the vibrational distribution is a smoothly varying function of v, as demonstrated in figure 2 for $k=0$. This is evident from equations (18) and (19) as for $|\beta|\ll1$ the polynomials Q_v are close to unity for all v.

(2) In the limit of strong intercontinuum coupling when $|\beta|\gg1$ the final vibrational distribution, $P_v(\infty)$, exhibits a steplike structure (figure 2). This effect originates from the significant contribution of the Q_v polynomials to

equation (18). As is evident from equation (19) these polynomials include even powers of $|\beta|$, being of the same degree in $|\beta|$ for Q_{2n} and for Q_{2n+1} (where $n<N/2$ is an integer). The increase in an even power of $|\beta|$ for every second polynomial results in the ' oscillatory ' distribution in the strong coupling situation.

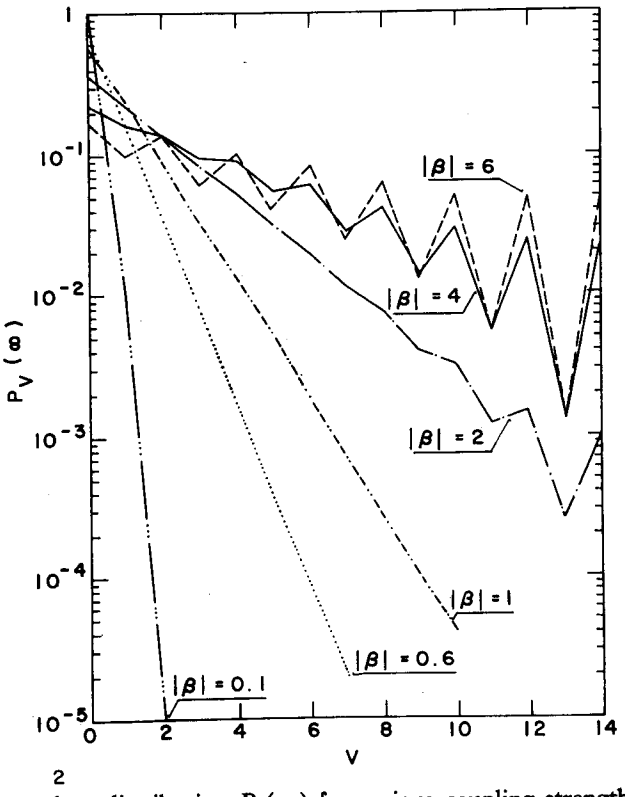

Figure 2. The product distribution $P_v(\infty)$ for various coupling strengths $|\beta|$. $N=15$, $k=0$.

(3) The k dependence of the distribution in the weak coupling situation exhibits a maximum at $v=k$ followed by a sharp decrease (as $|\beta|^{2|v-k|}$, for increasing $|v-k|$. In the strong coupling case the distribution is less regular.

(4) The dependence of $P_v(\infty)$ on N is weak for $|\beta|\ll 1$ (when v is not too close to N) and also for $|\beta|\gg 1$ for either even or for odd N values. However, changing N by unity in the strong coupling case shifts the maxima and the minima in $P_v(\infty)$ from v to $v+1$ (see figure 3). In this case the average $(P_v^{(N)}(\infty)+P_v^{(N+1)}(\infty))/2$ is a smooth function of v (see figure 3). This averaged distribution exhibits a weak dependence on N.

(5) The width Γ_s of the initial state decreases with increasing $|\beta|$ (figures 4 and 5) and exhibits oscillations with k for $|\beta|>1$. Note that for the present model of constant, v independent, coupling, equations (18) and (21) imply that $\Gamma_s(k)=\Gamma_s(N-1-k)$. From equation (21) it is evident that $\Gamma_s\to\Gamma_s^0$ for $|\beta|\to 0$

and $\Gamma_s \to 0$ for $|\beta| \to \infty$. The decrease of Γ_s with increasing the inter-continuum coupling strength exhibits a retardation effect on the decay of the internal state due to interference effects†.

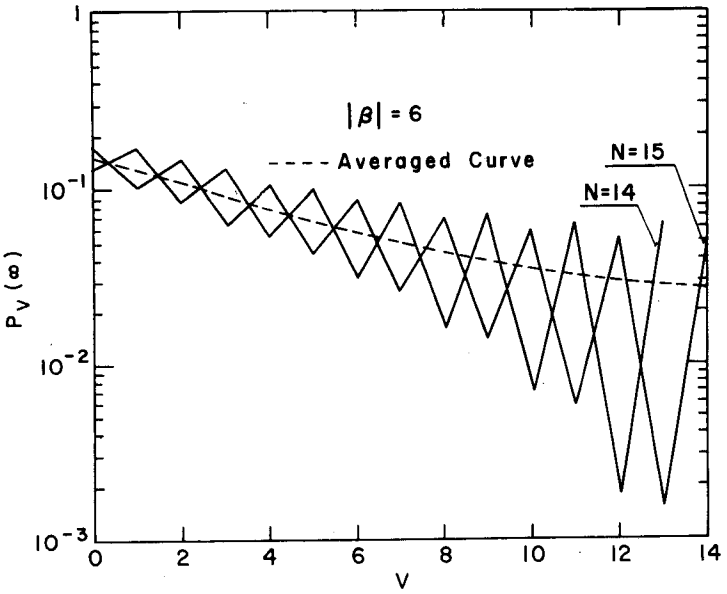

Figure 3. Oscillations of the distribution $P_v(\infty)$ in the strong coupling limit $|\beta|=6$, $k=0$. The dashed curve is the average of the $N=14$ and $N=15$ curves.

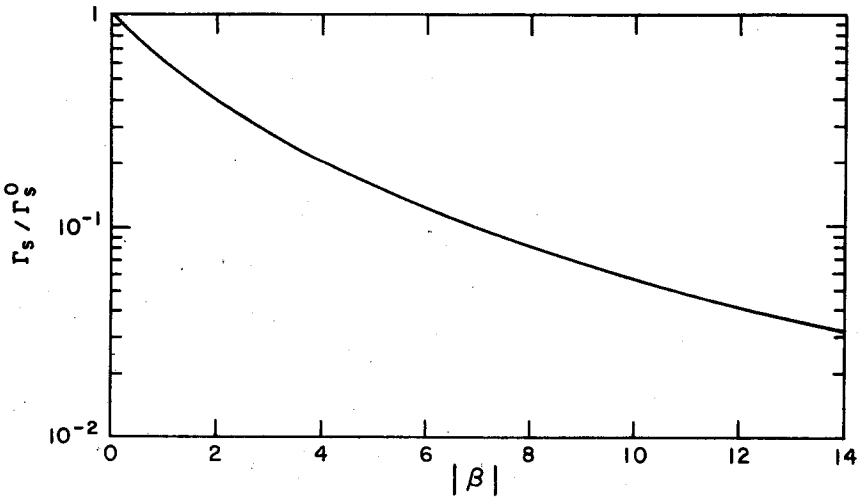

Figure 4. The dependence of Γ_s on the coupling strength. $N=14$, $k=0$.

† Conclusion (5) is valid for the case of predissociation, while for direct photodissociation a proper averaging over the photon wave packet has to be performed.

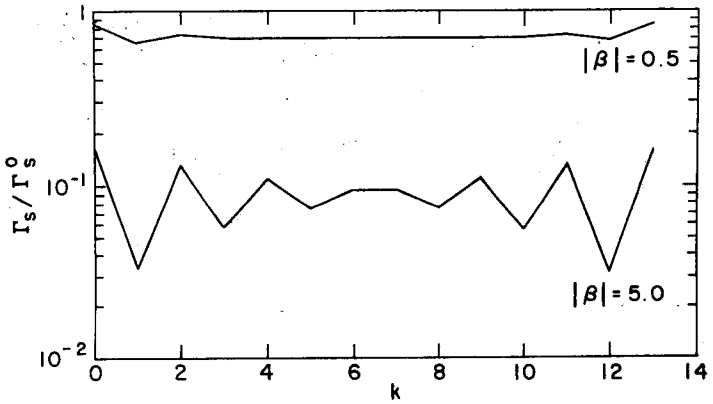

Figure 5. The dependence of Γ_s on the initially populated level k in the weak and in the strong coupling limits, $N=13$.

The present results obtained for a simple model system provide us with guidelines for the understanding of some interesting photofragmentation and electronic quenching processes. Before applying this model to a real life situation several modifications have to be introduced :

(1) We have explicitly considered the $|s\rangle$ state coupled to a single $\{|kl\rangle\}$ continuum. It is a straightforward matter to extend this formalism to include the coupling of $|s\rangle$ to all continua. These results will be presented elsewhere [17].

(2) The coupling matrix elements between adjacent continua were taken to be independent of the vibrational quantum number v. It can be demonstrated [17] that the coefficients in equation (2) can be factored out as

$$\alpha_{ll'}{}^{v} = (v)^{1/2v}(l, l'). \tag{25}$$

We have solved the problem incorporating the v dependence of the matrix elements, which resulted only in a qualitative modification of the results. In the weak coupling limit $P_v(\infty) \propto (k!/v!)|1/\beta|^{2(k-v)}$ for $v \leqslant k$ and

$$P_v(\infty) \propto (v!/k!)|\beta|^{2(v-k)}$$

for $v \geqslant k$, which is reminiscent of, but quantitatively different from a Poissonian distribution obtained from the semi classical model [7]. In the strong coupling situation the oscillating behaviour of the distribution is retained.

(3) The assumption regarding the independence of the intercontinuum coupling on the quantum numbers l and l' (i.e. $f(l, l') = \text{const}$ in equation (25) and the related assumption which disregards the effect of the lower bound of the continua involve gross oversimplifications of the problem. Simple models for the continua indicate that resonance coupling around the energy $E_s \sim E_{vl} \sim E_{v\,l'}$, will decrease with increasing v. In the weak coupling situation the general features of the solution are not expected to be grossly modified. On the other hand, the oscillations exhibited for $P_v(\infty)$ in the strong coupling limit will be considerably damped.

In conclusion, we would like to point out that the results of the present quantum mechanical model considerably differ from the predictions of the semi-classical 'half collision' approach. The experimental data for direct photodissociation [8] and for predissociation from Rydberg states [8] of XCN molecules results in $P_v(\infty)$ distributions of $CN(B^2\Sigma)$ where high v values are populated. This result is incompatible with a Poisson type distribution but concurs with predictions of our model. The occurrence of a non smooth distribution of $P_v(\infty)$ versus v of the vibrational levels resulting from electronic quenching was observed [10] in the case of $Hg(^3P_1)+HF$, which is in qualitative agreement with our model for $|\beta| > 1$.

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