

## **A THEORETICAL STUDY OF TWO-COLOR PHOTOIONIZATION AND AUTOIONIZATION OF MOLECULES**

S. H. LIN and A. BOEGLIN

*Department of Chemistry, Arizona State University, Tempe, AZ 85287 (U.S.A.)*

S. M. LIN

*Institute of Atomic and Molecular Science, Academia Sinica (Taiwan)*

(Received January 22, 1987)

### **Summary**

The main purpose of this paper is to apply the density matrix formalism for treating multiphoton ionization of multivibronic level systems. Both direct photoionization and photoionization through autoionization states are taken into account. Numerical results will be presented for demonstrating the effect of the interference resulting from the neighboring rovibronic levels. The theoretical results are applied to interpret two sets of experimental data on two-color photoionization of molecules; one set is for two-color threshold photoionization spectra of jet-cooled aniline which exhibit autoionizing Rydberg structures and the other is for high resolution Rydberg spectra of  $H_2$  by stepwise resonance two-photon ion-pair ( $H^+ + H^-$ ) production.

---

### **1. Introduction**

Two-color photoionization studies have provided important insights into studies of the properties of highly excited states of molecules, such as the precise determination of ionization energies and lifetimes of excited states, the detection of autoionizing states and the investigation of photo-fragmentation phenomena [1]. By using resonant two-photon excitation, the weak transition probabilities due to small Franck-Condon factors for single-photon excitation can be greatly improved. New excited states whose transitions cannot be easily reached from the ground state can be studied. For small molecules, the spectrum can also be simplified by selective labelling of the rotational states.

In previous papers [2, 3], we have developed a density matrix formalism for treating one-photon ionization and two-photon ionization of molecules. We have shown that Fano's results [4] for one-photon autoionization can be reproduced by this formalism. It has also been shown that this density matrix method can treat two-color photoionization spectroscopy and the

measurement of excited state lifetimes by the multiphoton ionization technique.

In this paper, we shall extend this density matrix method to take into account the multilevel effect on one-photon and two-photon ionization of molecules and apply the theoretical results to the analysis of some recent experimental data. It should be noted that in our previous papers [2, 3] for one-photon ionization we considered only two discrete levels and for two-photon ionization we considered only three discrete levels. In this paper, the effect of the existence of multivibronic levels in the ground and excited electronic states is taken into account.

## 2. Theory

It has been shown that the master equations (MEs) for the photoionization of molecules in the Markoff approximation can be expressed as [2, 3]

$$\frac{\partial \rho_{mn}}{\partial t} + \frac{i}{\hbar} \sum_m (V_{mn} \rho_{mn} - \rho_{mn} V_{mn}) + \sum_m \Gamma_{mn}^{mm} \rho_{mn} + \sum_m \sum_{m'} R_{mn}^{mm'} \rho_{mm'} = 0 \quad (2-1)$$

and

$$\begin{aligned} \frac{\partial \rho_{m'n'}}{\partial t} + (i\omega_{m'n'} + \Gamma_{m'n'}^{m'n'}) \rho_{m'n'} + \frac{i}{\hbar} \sum_{m'} (V_{m'n'} \rho_{m'n'} - \rho_{m'n'} V_{m'n'}) \\ + \sum_{m'} \sum_{n'} R_{m'n'}^{m'n'} \rho_{m'n'} = 0 \end{aligned} \quad (2-2)$$

where

$$R_{mn}^{m'n'} = \delta_{m'n'} J_{mn} + \delta_{mm'} J_{nn'}^* \quad (2-3)$$

$$J_{mn} = \frac{1}{\hbar^2} \sum_c \int_0^\infty d\tau V_{mc}(t) V_{cm'}(t-\tau) \exp \left\{ -i \int_{t-\tau}^t dt_1 \omega_{cm'}(t_1) \right\} \quad (2-4)$$

and

$$\hat{V} = \hat{D} + \hat{U} \quad (2-5)$$

Here  $\hat{U}$  represents the perturbation for inducing autoionization and  $\hat{D}$  denotes the interaction hamiltonian between the system and the radiation field. In eqns. (2-1) and (2-2), the  $\Gamma_{mn}^{mn}$  are the relaxation rate constants and  $\Gamma_{m'n'}^{m'n'}$  represents the dephasing rate constant. In eqn. (2-4), the summation over  $c$  refers to the continuum states above the ionization threshold.

For convenience, we shall present the theoretical treatment of one-photon ionization and two-photon ionization of multilevel systems separately.

### 2.1. One-photon ionization

We shall let  $n$  denote a vibronic (or a rovibronic) level in the ground electronic state  $g$  and  $m$  represent a vibronic (or a rovibronic) level in the excited electronic state  $a$  (see Fig. 1). The MEs in this case are

$$\begin{aligned} \frac{\partial \rho_{mm}}{\partial t} + \sum_n \left\{ \frac{1}{\hbar} (V_{nm} \rho_{nn} - \rho_{mm} V_{nm}) + R_{nm}^{mn} \rho_{nn} + R_{nm}^{nm} \rho_{nm} \right\} \\ + R_{nm}^{mn} \rho_{mm} + \sum_k \Gamma_{nm}^{kk} \rho_{kk} = 0 \end{aligned} \quad (2-6)$$

$$\begin{aligned} \frac{\partial \rho_{nn}}{\partial t} + \sum_m \left\{ \frac{1}{\hbar} (V_{nm} \rho_{mm} - \rho_{nn} V_{nm}) + R_{nm}^{mn} \rho_{mm} + R_{nm}^{nm} \rho_{nm} \right\} \\ + R_{nm}^{nn} \rho_{nn} + \sum_k \Gamma_{nn}^{kk} \rho_{kk} = 0 \end{aligned} \quad (2-7)$$

and

$$\begin{aligned} \frac{\partial \rho_{mn}}{\partial t} + (i\omega_{nm} + \Gamma_{nm}^{mn} + R_{nm}^{mn}) \rho_{mn} + \frac{1}{\hbar} V_{nm} (\rho_{nn} - \rho_{mm}) \\ + R_{nm}^{nn} \rho_{nn} + R_{nm}^{mm} \rho_{mm} = 0 \end{aligned} \quad (2-8)$$

where  $\sum_k \Gamma_{nm}^{kk} \rho_{kk}$  and  $\sum_k \Gamma_{nn}^{kk} \rho_{kk}$  include both electronic relaxation and vibrational relaxation. For convenience we shall ignore the inverse electronic relaxation.

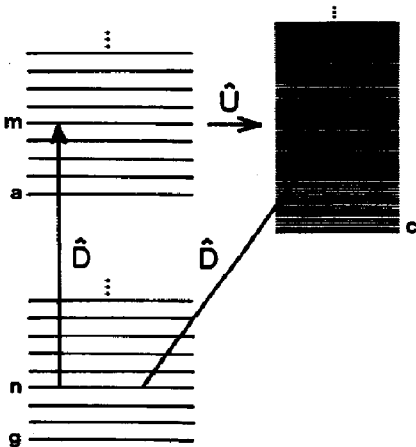


Fig. 1. One-photon ionization.

Applying the steady state approximation to eqn. (2-8) yields (Appendix A)

$$\frac{\partial \rho_{nn}}{\partial t} + (R_{nn}^{nn} + A_{nn})\rho_{nn} + \sum_m A_{nm}\rho_{mn} + \sum_m \Gamma_{nn}^{mm}\rho_{mm} + \sum_{n'} \Gamma_{nn}^{n'n'}\rho_{n'n'} = 0 \quad (2-9)$$

and

$$\frac{\partial \rho_{mm}}{\partial t} + (R_{mm}^{mm} + A_{mm})\rho_{mm} + \sum_n A_{mn}\rho_{nn} + \sum_{m'} \Gamma_{mm}^{m'm'}\rho_{m'm'} - \sum_n \Gamma_{nn}^{mm}\rho_{mm} = 0 \quad (2-10)$$

where the  $\Gamma_{nn}^{mm}$  represent electronic relaxation rate constants, while  $\Gamma_{mm}^{m'm'}$ ,  $\Gamma_{nn}^{n'n'}$  etc. denote vibrational relaxation constants. Other quantities in eqns. (2-9) and (2-10) are defined as follows:

$$A_{nn} = \frac{2}{\hbar^2} \sum_m \text{Im} \left\{ \frac{i |\langle n | \hat{D}(-\omega) | \phi_m \rangle|^2 (1 - i/q_{nm})^2}{i(\omega_{mn} - \omega) + \Gamma_{nn}^{mm} + R_{nn}^{mm}} \right\} \quad (2-11)$$

$$A_{nm} = A_{mn} = -\frac{2}{\hbar^2} \text{Im} \left\{ \frac{i |\langle n | \hat{D}(-\omega) | \phi_m \rangle|^2 (1 + 1/q_{nm}^2)}{i(\omega_{mn} - \omega) + \Gamma_{nn}^{mm} + R_{nn}^{mm}} \right\} \quad (2-12)$$

$$A_{mm} = \frac{2}{\hbar^2} \sum_n \text{Im} \left\{ \frac{i |\langle \phi_m | \hat{D}(\omega) | n \rangle|^2 (1 + i/q_{nm})^2}{i(\omega_{mn} - \omega) + \Gamma_{nn}^{mm} + R_{nn}^{mm}} \right\} \quad (2-13)$$

$$|\phi_m\rangle = |m\rangle + \frac{P}{\hbar} \sum_c \frac{U_{cm}}{\omega_{mc}} |c\rangle \quad (2-14)$$

and

$$q_{nm} = \frac{\langle n | \hat{D}(-\omega) | \phi_m \rangle}{(\pi/\hbar) \sum_c D_{nc}(-\omega) U_{cm} \delta(\omega_{mc})} \quad (2-15)$$

In this case, the photoionization yield  $Y(t)$  is given by

$$\begin{aligned} Y(t) &= -\sum_n \frac{\partial \rho_{nn}}{\partial t} - \sum_m \frac{\partial \rho_{mm}}{\partial t} \\ &= \sum_n \left( R_{nn}^{nn} + A_{nn} + \sum_m A_{nm} \right) \rho_{nn} + \sum_m \left( R_{mm}^{mm} + A_{mm} + \sum_n A_{nm} \right) \rho_{mm} \end{aligned} \quad (2-16)$$

The integrated yield (or efficiency) is defined by

$$I(t) = 1 - \sum_n \rho_{nn} - \sum_m \rho_{mm} \quad (2-16A)$$

In the weak intensity and short time regime, we can ignore the excited state distributions  $\rho_{mm}$

$$Y = \sum_n \left[ R_{nn}^{nn} - \frac{4}{\hbar^2} \sum_m \frac{(1/q_{nm})(\omega'_{nm} - \omega) + (1/q_{nm}^2)\{R_{nn}^{mn}(\mathbf{r}) + \Gamma_{nn}^{mn}(\mathbf{r})\}}{(\omega'_{nm} - \omega)^2 + \{\Gamma_{nn}^{mn}(\mathbf{r}) + R_{nn}^{mn}(\mathbf{r})\}^2} \right. \\ \left. \times |\langle n | \hat{D}(\omega) | \phi_m \rangle|^2 \right] \rho_{nn} \quad (2-17)$$

where  $\Gamma_{nn}^{mn}(\mathbf{r})$  and  $R_{nn}^{mn}(\mathbf{r})$  represent the real parts of  $\Gamma_{nn}^{mn}$  and  $R_{nn}^{mn}$  respectively, and determine the bandwidth of  $Y$  vs.  $\omega$ ; the imaginary portions of  $\Gamma_{nn}^{mn}$  and  $R_{nn}^{mn}$  which determine the band shift of  $Y$  vs.  $\omega$  have been included in  $\omega'_{nm}$  (see Appendix A).

For the weak field case, if we can apply the steady state approximation to  $\rho_{mm}$  given by eqn. (2-10), then substituting the resulting  $\rho_{mm}$  into eqn. (2-16) we obtain

$$Y = \sum_n \left( R_{nn}^{nn} + A_{nn} + \sum_m \frac{W_{nm}}{R_{nm}^{mn} + W_{nm}} A_{mn} \right) \rho_{nn} \quad (2-17A)$$

where  $W_{nm} = -\sum_n \Gamma_{nn}^{mn}$  represents the electronic relaxation of the  $m$ th level. Here the vibrational relaxation terms  $\sum_m \Gamma_{nn}^{m'm'}$   $\rho_{m'm'}$  have been ignored; this approximation is valid only when the vibrational relaxation is very slow or when the vibrational equilibrium is established. When  $W_{nm} \gg R_{nm}^{mn}$  eqn. (2-17A) reduces to eqn. (2-17) and when  $W_{nm} \ll R_{nm}^{mn}$  eqn. (2-17A) reduces to

$$Y = \sum_n (R_{nn}^{nn} + A_{nn}) \rho_{nn} \quad (2-17B)$$

which exhibits the Fano-type bandshape (*cf.* eqn. (2-20)).

According to the theoretical analysis of the two-discrete-level model of one-photon ionization of molecules, for the weak-field case, and in the short time region [3], the approximate expression for  $Y$  given by eqn. (2-17) is more accurate than that given by eqn. (2-17A).

Notice that  $R_{nn}^{nn}$  and  $R_{nn}^{mn}$  denote the direct photoionization rate and the autoionization rate respectively, that is

$$R_{nn}^{nn} = \frac{2\pi}{\hbar^2} \sum_c |\langle c | \hat{D}(\omega) | n \rangle|^2 \delta(\omega - \omega_{cn}) \quad (2-18)$$

and

$$R_{nn}^{mn} = \frac{2\pi}{\hbar^2} \sum_c |U_{cn}|^2 \delta(\omega_{cn}) \quad (2-19)$$

Equation (2-17) shows that the photoionization yield consists of two parts, the contribution from the direct photoionization  $R_{nn}^{nn}$  and the contribution through autoionization  $A_{nn} + \sum_m A_{mn}$  (or  $A_{nn}$  if eqn. (2-17B) is valid). The

latter contribution gives us the Beutler-Fano asymmetric bandshape of photoionization. From eqn. (2-9), we can see that the rate constant

$$K_n = R_{nn}^{nn} + A_{nn} \quad (2-9A)$$

represents the depletion rate of the  $n$ th level of the ground electronic state through the ionization channel, and again  $K_n$  consists of the contributions from the direct photoionization and from autoionization  $A_{nn}$ . Notice that  $A_{nn}$  can be rewritten as

$$A_{nn} = \frac{2}{\hbar^2} \sum_m \frac{(1 - 1/q_{nm}^2) \{ \Gamma_{nn}^{mn}(\mathbf{r}) + R_{nn}^{mn}(\mathbf{r}) \} - (2/q_{nm}) (\omega'_{mn} - \omega)}{(\omega'_{mn} - \omega)^2 + \{ \Gamma_{nn}^{mn}(\mathbf{r}) + R_{nn}^{mn}(\mathbf{r}) \}^2} \times |\langle n | \hat{D}(-\omega) | \phi_m \rangle|^2 \quad (2-11A)$$

where  $\omega'_{mn} = \omega_{mn} + R_{nn}^{mn}(\mathbf{r}) + \Gamma_{nn}^{mn}(\mathbf{r})$ . Defining the detuning

$$\epsilon_{mn} = \frac{\omega - \omega'_{mn}}{\Gamma_{nn}^{mn}(\mathbf{r}) + R_{nn}^{mn}(\mathbf{r})} \quad (2-11B)$$

eqn. (2-11A) becomes

$$A_{nn} = \frac{2}{\hbar^2} \sum_m \frac{q_{nm}^2 - 1 + 2q_{nm}\epsilon_{mn}}{1 + \epsilon_{mn}^2} \frac{|\langle n | \hat{D}(-\omega) | \phi_m \rangle|^2}{q_{nm}^2 \{ \Gamma_{nn}^{mn}(\mathbf{r}) + R_{nn}^{mn}(\mathbf{r}) \}} \quad (2-20)$$

Notice that  $(q_{nm}^2 - 1 + 2q_{nm}\epsilon_{mn})/(1 + \epsilon_{mn}^2)$  is the lineshape expression derived by Fano [4]. However, the physical meanings of Fano's expression and ours are somewhat different. In Fano's case, the spectral linewidth is due to autoionization only while in our case the spectral linewidth consists of the contribution from the lifetimes of the  $n$ -level and the  $m$ -level and pure dephasing through  $\Gamma_{nn}^{mn}(\mathbf{r})$  and the contribution from the rates of direct photoionization and autoionization through  $R_{nn}^{mn}(\mathbf{r})$ .

## 2.2. Two-photon ionization

Figure 2 shows the energy level scheme for two-color two-photon ionization of molecules. That is, we let  $l$ ,  $n$  and  $m$  represent the rovibronic (or vibronic) levels of the ground electronic state, first excited state and second excited state respectively. The equations of motion for the diagonal elements  $\rho_{ll}$ ,  $\rho_{nn}$  and  $\rho_{mm}$  are given by

$$\frac{\partial \rho_{ll}}{\partial t} + \frac{i}{\hbar} \sum_n (V_{ln} \rho_{nl} - \rho_{ln} V_{ln}) + \sum_k \Gamma_{ll}^{kk} \rho_{kk} = 0 \quad (2-21)$$

$$\begin{aligned} \frac{\partial \rho_{nn}}{\partial t} + \frac{i}{\hbar} \sum_l (V_{nl} \rho_{ln} - \rho_{nl} V_{ln}) + \frac{i}{\hbar} \sum_m (V_{nm} \rho_{mn} - \rho_{nm} V_{nm}) \\ + R_{nn}^{nn} \rho_{nn} + \sum_m (R_{nn}^{mn} \rho_{mn} + R_{nn}^{mn} \rho_{nm}) + \sum_k \Gamma_{nn}^{kk} \rho_{kk} = 0 \end{aligned} \quad (2-22)$$

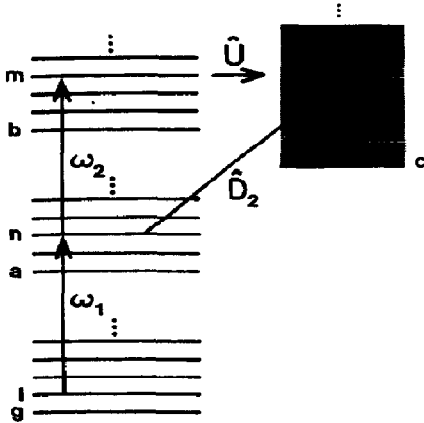


Fig. 2. Two-color, two-photon ionization.

and

$$\begin{aligned} \frac{\partial \rho_{mm}}{\partial t} + \frac{i}{\hbar} \sum_n (V_{mn} \rho_{nm} - \rho_{mn} V_{nm}) + R_{mm}^{mm} \rho_{mm} + \sum_n (R_{mm}^{nn} \rho_{mn} + R_{mm}^{nn} \rho_{nm}) \\ + \sum_k \Gamma_{mm}^{kk} \rho_{kk} = 0 \end{aligned} \quad (2-23)$$

Using eqns. (2-3) - (2-5) and eqn. (A-2) of Appendix A, eqns. (2-21) - (2-23) become

$$\frac{\partial \rho_{ii}}{\partial t} - \frac{2}{\hbar} \sum_n \text{Im}\{D_{in}(-\omega_1)_1 \rho_{ni}(\omega_1)\} + \sum_n \Gamma_{ii}^{nn} \rho_{nn} + \sum_{i'} \Gamma_{ii}^{i'i'} \rho_{i'i'} = 0 \quad (2-24)$$

$$\begin{aligned} \frac{\partial \rho_{nn}}{\partial t} + \frac{2}{\hbar} \sum_l \text{Im}\{D_{ln}(-\omega_1)_1 \rho_{nl}(\omega_1)\} \\ - \frac{2}{\hbar} \sum_m \text{Im}\left\{ \langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle \left( 1 - \frac{i}{q_{nm}} \right) \rho_{mn}(\omega_2) \right\} \\ + R_{nn}^{nn} \rho_{nn} + \sum_m \Gamma_{nn}^{mm} \rho_{mm} - \sum_l \Gamma_{nn}^{ll} \rho_{ll} + \sum_{n'} \Gamma_{nn}^{n'n'} \rho_{n'n'} = 0 \end{aligned} \quad (2-25)$$

and

$$\begin{aligned} \frac{\partial \rho_{mm}}{\partial t} + \frac{2}{\hbar} \sum_n \text{Im}\left\{ \langle n | \hat{D}(-\omega_2)_2 | \psi_m \rangle \left( 1 + \frac{i}{q_{nm}} \right) \rho_{mn}(\omega_2) \right\} \\ + R_{mm}^{mm} \rho_{mm} + \sum_{m'} \Gamma_{mm}^{m'm'} \rho_{m'm'} - \sum_n \Gamma_{mm}^{nn} \rho_{nn} = 0 \end{aligned} \quad (2-26)$$

where

$$|\phi_m\rangle = |m\rangle + \frac{P}{\hbar} \sum_c \frac{U_{cm}}{\omega_{mc}} |c\rangle \quad (2-27)$$

$$|\psi_m\rangle = |m\rangle + \frac{P}{\hbar} \sum_c \frac{U_{cm}}{\omega_2 - \omega_{cn}} |c\rangle \quad (2-28)$$

$$q'_{mn} = \frac{\langle n | \hat{D}(-\omega_2)_2 | \psi_m \rangle}{(\pi/\hbar) \sum_c D_{nc}(-\omega_2)_2 U_{cm} \delta(\omega_2 - \omega_{cn})} \quad (2-29)$$

and

$$q_{mn} = \frac{\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle}{(\pi/\hbar) \sum_c D_{nc}(-\omega_2)_2 U_{cm} \delta(\omega_{cm})} \quad (2-30)$$

The derivation of eqns. (2-24) - (2-26) is similar to that for the one-photon ionization case given in Appendix A.

Next we consider the equations of motion for the off-diagonal density matrix elements

$$\begin{aligned} \frac{\partial \rho_{nl}}{\partial t} + (i\omega_{nl} + \Gamma_{nl}^{nl} + R_{nl}^{nl})\rho_{nl} + \frac{i}{\hbar} V_{nl}(\rho_{ll} - \rho_{nn}) \\ + \frac{i}{\hbar} \sum_m V_{nm}\rho_{ml} + \sum_m R_{nl}^{ml}\rho_{ml} = 0 \end{aligned} \quad (2-31)$$

$$\begin{aligned} \frac{\partial \rho_{ml}}{\partial t} + (i\omega_{ml} + \Gamma_{ml}^{ml} + R_{ml}^{ml})\rho_{ml} + \frac{i}{\hbar} \sum_n (V_{mn}\rho_{nl} - \rho_{mn}V_{nl}) \\ + \sum_n R_{ml}^{nl}\rho_{nl} = 0 \end{aligned} \quad (2-32)$$

and

$$\begin{aligned} \frac{\partial \rho_{mn}}{\partial t} + (i\omega_{mn} + \Gamma_{mn}^{mn} + R_{mn}^{mn})\rho_{mn} + \frac{i}{\hbar} V_{mn}(\rho_{nn} - \rho_{mm}) \\ - \frac{i}{\hbar} \sum_l \rho_{ml} V_{ln} + (R_{mn}^{ml}\rho_{mm} + R_{mn}^{nn}\rho_{nn}) = 0 \end{aligned} \quad (2-33)$$

These expressions can be simplified (see Appendix B) as

$$\begin{aligned} \frac{\partial \rho_{nl}(\omega_1)}{\partial t} + \{i(\omega_{nl} - \omega_1) + \Gamma_{nl}^{nl} + R_{nl}^{nl}\}\rho_{nl}(\omega_1) + \frac{i}{\hbar} D_{nl}(\omega_1)_1(\rho_{ll} - \rho_{nn}) \\ + \frac{i}{\hbar} \sum_m \langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle \left\{ \left( 1 - \frac{i}{q_{mn}} \right) \rho_{ml}(\omega_1 + \omega_2) \right\} = 0 \end{aligned} \quad (2-34)$$



$$\begin{aligned} & \frac{\partial \rho_{ml}(\omega_1 + \omega_2)}{\partial t} + \{i(\omega_{ml} - \omega_1 - \omega_2) + \Gamma_{ml}^{ml} + R_{ml}^{ml}\} \rho_{ml}(\omega_1 + \omega_2) \\ & - \frac{i}{\hbar} \sum_n \rho_{mn}(\omega_2) D_{nl}(\omega_1)_1 + \frac{i}{\hbar} \sum_n \langle \psi_m | \hat{D}(\omega_2)_2 | n \rangle \left(1 - \frac{i}{q'_{nm}}\right) \rho_{nl}(\omega_1) = 0 \end{aligned} \quad (2-35)$$

and

$$\begin{aligned} & \frac{\partial \rho_{mn}(\omega_2)}{\partial t} + \{i(\omega_{mn} - \omega_2) + \Gamma_{mn}^{mn} + R_{mn}^{mn}\} \rho_{mn}(\omega_2) \\ & - \frac{i}{\hbar} \sum_l D_{ln}(-\omega_1)_1 \rho_{ml}(\omega_1 + \omega_2) + \frac{i}{\hbar} \langle \psi_m | \hat{D}(\omega_2)_2 | n \rangle \left(1 - \frac{i}{q'_{nm}}\right) \rho_{mn} \\ & - \frac{i}{\hbar} \langle \phi_m | \hat{D}(\omega_2)_2 | n \rangle \left(1 + \frac{i}{q_{nm}}\right) \rho_{mn} = 0 \end{aligned} \quad (2-36)$$

where, for example,  $D_{nl}(\omega_1)_1 = \langle n | \hat{D}(\omega_1)_1 | l \rangle$ . This completes the derivation of the generalized MEs for two-photon ionization of molecules. Here the only main approximation that has been introduced is the rotating wave approximation.

A computer program for solving these generalized MEs has been developed by us. In the following we shall present the analytical results for an important case. Applying the steady state approximation to  $\rho_{mn}(\omega_2)$ ,  $\rho_{nl}(\omega_1)$  and  $\rho_{ml}(\omega_1 + \omega_2)$ , we find

$$\begin{aligned} \rho_{mn}(\omega_2) = & \frac{i}{\hbar} \left\{ \langle \phi_m | \hat{D}(\omega_2)_2 | n \rangle \left(1 + \frac{i}{q_{nm}}\right) \rho_{mn} \right. \\ & \left. - \langle \psi_m | \hat{D}(\omega_2)_2 | n \rangle \left(1 - \frac{i}{q'_{nm}}\right) \rho_{nn} \right\} F_{mn}(\omega_2) \end{aligned} \quad (2-37)$$

$$\rho_{nl}(\omega_1) = \frac{i}{\hbar} D_{nl}(\omega_1)_1 (\rho_{nn} - \rho_{ll}) F_{nl}(\omega_1) \quad (2-38)$$

and

$$\begin{aligned} \rho_{ml}(\omega_1 + \omega_2) = & \frac{i}{\hbar} F_{ml}(\omega_1 + \omega_2) \sum_n \left\{ \rho_{mn}(\omega_2) D_{nl}(\omega_1)_1 \right. \\ & \left. - \langle \psi_m | \hat{D}(\omega_2)_2 | n \rangle \left(1 - \frac{i}{q'_{nm}}\right) \rho_{nl}(\omega) \right\} \end{aligned} \quad (2-39)$$

where for example

$$F_{mn}(\omega_2) = \frac{1}{i(\omega_{mn} - \omega_2) + \Gamma_{mn}^{mn} + R_{mn}^{mn}} \quad (2-40)$$

In obtaining eqn. (2-37), off-diagonal terms such as  $D_{ln}(-\omega_1)_1 \rho_{ml}(\omega_1 + \omega_2)$  were neglected and in obtaining eqn. (2-38) the off-diagonal terms such as  $\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle \rho_{ml}(\omega_1 + \omega_2)$  were neglected. Substituting eqns. (2-37) and (2-38) into eqn. (2-39) yields

$$\begin{aligned} \rho_{ml}(\omega_1 + \omega_2) = & \left( \frac{i}{\hbar} \right)^2 F_{ml}(\omega_1 + \omega_2) \sum_n \left[ F_{nm}(\omega_2) D_{nl}(\omega_1)_1 \langle \phi_m | \hat{D}(\omega_2)_2 | n \rangle \right. \\ & \times \left( 1 + \frac{i}{q_{nm}} \right) \rho_{mm} - \rho_{nn} \{ F_{nm}(\omega_2) + F_{nl}(\omega_1) \} \langle \psi_m | \hat{D}(\omega_2)_2 | n \rangle \\ & \times \left( 1 - \frac{i}{q'_{nm}} \right) D_{nl}(\omega_1)_1 + F_{nl}(\omega_1) \langle \psi_m | \hat{D}(\omega_2)_2 | n \rangle \\ & \left. \times \left( 1 - \frac{i}{q'_{nm}} \right) D_{nl}(\omega_1)_1 \rho_{ll} \right] \end{aligned} \quad (2-41)$$

The validity of this approximation is examined in Appendix C.

By using eqns. (2-37) - (2-41), we obtain the MEs for  $\rho_{ll}$ ,  $\rho_{nn}$  and  $\rho_{mm}$  as

$$\frac{\partial \rho_{ll}}{\partial t} - \sum_n A_{nl}(\omega_1) (\rho_{nn} - \rho_{ll}) + \sum_n \Gamma_{ll}^{nn} \rho_{nn} + \sum_{l'} \Gamma_{ll'}^{l'l'} \rho_{l'l'} = 0 \quad (2-42)$$

$$\begin{aligned} \frac{\partial \rho_{nn}}{\partial t} + \sum_l A_{nl}(\omega_1) (\rho_{nn} - \rho_{ll}) + \sum_m A'_{nm}(\omega_2) \rho_{mm} + \{ A'_{nn}(\omega_2) + R_{nn}^{nn} \} \rho_{nn} \\ + \sum_m \Gamma_{nn}^{mm} \rho_{mm} - \sum_l \Gamma_{ll}^{nn} \rho_{nn} + \sum_{n'} \Gamma_{nn'}^{n'n'} \rho_{n'n'} = 0 \end{aligned} \quad (2-43)$$

and

$$\begin{aligned} \frac{\partial \rho_{mm}}{\partial t} + \{ R_{mm}^{mm} + A'_{mm}(\omega_2) \} \rho_{mm} + \sum_n A'_{mn}(\omega_2) \rho_{nn} - \sum_n \Gamma_{nn}^{mm} \rho_{mm} \\ + \sum_{m'} \Gamma_{mm'}^{m'm'} \rho_{m'm'} = 0 \end{aligned} \quad (2-44)$$

where

$$\begin{aligned} A_{nl}(\omega_1) &= \frac{2}{\hbar^2} |D_{nl}(\omega_1)_1|^2 \operatorname{Re}\{F_{nl}(\omega_1)\} \\ &= \frac{2}{\hbar^2} |D_{nl}(\omega_1)_1|^2 \frac{\Gamma_{ni}^{nl}(\mathbf{r}) + R_{ni}^{nl}(\mathbf{r})}{(\omega'_{ni} - \omega)^2 + \{ \Gamma_{ni}^{nl}(\mathbf{r}) + R_{ni}^{nl}(\mathbf{r}) \}^2} \end{aligned} \quad (2-45)$$

$$\begin{aligned}
A'_{nm}(\omega_2) &= -\frac{2}{\hbar^2} \text{Im}\{iF_{mn}(\omega_2)\} |\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle|^2 \left(1 + \frac{1}{q_{nm}^2}\right) \\
&= -\frac{2}{\hbar^2} |\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle|^2 \left(1 + \frac{1}{q_{nm}^2}\right) \\
&\quad \times \frac{\Gamma_{nm}^{nn}(\mathbf{r}) + R_{nm}^{nn}(\mathbf{r})}{(\omega'_{nm} - \omega_2)^2 + \{\Gamma_{nm}^{nn}(\mathbf{r}) + R_{nm}^{nn}(\mathbf{r})\}^2}
\end{aligned} \tag{2-46}$$

$$\begin{aligned}
A'_{nn}(\omega_2) &= \frac{2}{\hbar^2} \sum_m \text{Im}\left\{iF_{mn}(\omega_2) \left(1 - \frac{i}{q_{nm}}\right)^2\right\} |\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle|^2 \\
&= \frac{2}{\hbar^2} \sum_m |\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle|^2 \\
&\quad \times \frac{(1 - 1/q_{nm}^2)\{\Gamma_{nm}^{nn}(\mathbf{r}) + R_{nm}^{nn}(\mathbf{r})\} + (2/q_{nm})(\omega_2 - \omega'_{mn})}{(\omega'_{nm} - \omega_2)^2 + \{\Gamma_{nm}^{nn}(\mathbf{r}) + R_{nm}^{nn}(\mathbf{r})\}^2}
\end{aligned} \tag{2-47}$$

$$\begin{aligned}
A'_{mn}(\omega_2) &= \frac{2}{\hbar^2} \sum_n |\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle|^2 \text{Im}\left\{iF_{mn}(\omega_2) \left(1 + \frac{i}{q_{nm}}\right)^2\right\} \\
&= \frac{2}{\hbar^2} \sum_n |\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle|^2 \\
&\quad \times \frac{(1 - 1/q_{nm}^2)\{\Gamma_{nm}^{nn}(\mathbf{r}) + R_{nm}^{nn}(\mathbf{r})\} - (2/q_{nm})(\omega_2 - \omega'_{mn})}{(\omega'_{nm} - \omega_2)^2 + \{\Gamma_{nm}^{nn}(\mathbf{r}) + R_{nm}^{nn}(\mathbf{r})\}^2}
\end{aligned} \tag{2-48}$$

From eqns. (2-42) - (2-44) we obtain the differential yield of photo-ionization as

$$\begin{aligned}
Y(t) &= -\left(\sum_l \frac{\partial \rho_{ll}}{\partial t} + \sum_n \frac{\partial \rho_{nn}}{\partial t} + \sum_m \frac{\partial \rho_{mm}}{\partial t}\right) \\
&= \sum_n \left\{R_{nn}^{nn} + A'_{nn}(\omega_2) + \sum_m A'_{mn}(\omega_2)\right\} \rho_{nn} \\
&\quad + \sum_m \left\{R_{mm}^{mm} + A'_{mm}(\omega_2) + \sum_n A'_{nm}(\omega_2)\right\} \rho_{mm}
\end{aligned} \tag{2-49}$$

For the weak field-weak field case [3], we can apply the steady state approximation to eqns. (2-43) and (2-44) to obtain  $\rho_{nn}$  and  $\rho_{mm}$  as

$$\rho_{nn} = \frac{\sum_l A_{nl}(\omega_1) \rho_{ll}}{R_{nn}^{nn} + W_{nn} + A'_{nn}(\omega_2) + \sum_l A_{nl}(\omega_1)} \tag{2-50}$$

and

$$\rho_{mm} = \frac{-\sum_n A'_{mn}(\omega_2)\rho_{nn}}{R_{mm}^{mm} + W_{mm}} \quad (2-51)$$

where  $W_{nn} = -\sum_l \Gamma_{ll}^{nn}$  and  $W_{mm} = -\sum_n \Gamma_{nn}^{mm}$  represent the electronic relaxation rates of the  $n$ -level and the  $m$ -level respectively. Here the vibrational relaxation  $\sum_n \Gamma_{nn}^{n'n'}\rho_{n'n'}$  and  $\sum_m \Gamma_{mm}^{m'm'}\rho_{m'm'}$  have been neglected. This means that either the vibrational relaxation is fast so that the vibrational equilibrium is established or the vibrational relaxation is so slow that it can be ignored. Substituting eqn. (2-51) into eqn. (2-49) yields

$$Y = \sum_n \left\{ R_{nn}^{nn} + A'_{nn}(\omega_2) + \sum_m A'_{mn}(\omega_2) \frac{W_{mm}}{R_{mm}^{mm} + W_{mm}} \right\} \rho_{nn} \quad (2-52)$$

where  $R_{nn}$  denotes the rate of direct photoionization due to the  $\omega_2$  photon originating from the  $n$ -level of the intermediate electronic excited state.

For the case  $W_{mm} \gg R_{mm}^{mm}$  (*i.e.* the case in which the electronic relaxation is much faster than the autoionization), eqn. (2-52) reduces to

$$\begin{aligned} Y &= \sum_n \left\{ R_{nn} + A'_{nn}(\omega_2) + \sum_m A'_{mn}(\omega_2) \right\} \rho_{nn} \\ &= \sum_n \left[ R_{nn}^{nn} + \frac{4}{\hbar^2} \sum_m \frac{1}{q_{nm}^2} |\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle|^2 \right. \\ &\quad \left. \times \frac{q_{nm}(\omega_2 - \omega'_{mn}) - \{\Gamma_{mn}^{mn}(\mathbf{r}) + R_{mn}^{mn}(\mathbf{r})\}}{(\omega_2 - \omega'_{mn})^2 + \{\Gamma_{mn}^{mn}(\mathbf{r}) + R_{mn}^{mn}(\mathbf{r})\}^2} \right] \rho_{nn} \end{aligned} \quad (2-53)$$

These results for the photoionization yield are similar to the one-photon ionization case (comparing with eqns. (2-16) and (2-17)). However, for the case  $W_{mm} \ll R_{mm}^{mm}$  (*i.e.* the case in which the electronic relaxation is much slower than the autoionization), we have

$$\begin{aligned} Y &= \sum_n \{ R_{nn}^{nn} + A'_{nn}(\omega_2) \} \rho_{nn} \\ &= \sum_n \left[ R_{nn}^{nn} + \frac{2}{\hbar^2} \sum_m \frac{1}{q_{nm}^2} |\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle|^2 \right. \\ &\quad \left. \times \frac{(q_{nm}^2 - 1)\{\Gamma_{mn}^{mn}(\mathbf{r}) + R_{mn}^{mn}(\mathbf{r})\} + 2q_{nm}(\omega_2 - \omega'_{mn})}{(\omega'_{mn} - \omega_2)^2 + \{\Gamma_{mn}^{mn}(\mathbf{r}) + R_{mn}^{mn}(\mathbf{r})\}^2} \right] \rho_{nn} \end{aligned} \quad (2-54)$$

The asymmetric bandshapes in these two cases are somewhat different; the second case shows the Fano bandshape [4].

Other cases such as the strong field-weak field case, the weak field-strong field case, the strong field-strong field case etc. [3] can be considered similarly and will not be given here.

It should be noted that, although  $l$ ,  $m$  and  $n$  in this section and in Figs. 1 and 2 have been referred to as representing vibronic or robronic levels of a molecule, they can of course also be referred to as higher electronic states (such as Rydberg states). In other words, by reinterpreting the models shown in Figs. 1 and 2, the theoretical results presented in this section have quite a wide range of applications. For example, they can be applied to photo-dissociation of van der Waals complexes or laser-stimulated desorption of adsorbed molecules.

### 3. Discussion

From Sections 2.1 and 2.2 for one-photon ionization and two-photon ionization of molecules, we see that the Beutler-Fano-type asymmetric bandshape will be observed provided  $U_{mc} \neq 0$  (autoionization matrix element) and  $D_{nc} \neq 0$  (direct photoionization matrix element). In other words, Fano's  $q$  parameter is finite. The Beutler-Fano-type bandshape disappears if  $q \rightarrow \infty$ ; this can happen if either  $U_{mc} = 0$  or  $D_{nc} = 0$ , but  $D_{nm} \neq 0$ . To see the consequence of these conditions, let us consider the one-photon ionization case. For the case  $U_{mc} = 0$ , we have  $R_{mm}^{mm} = 0$ , *i.e.* autoionization does not take place, and eqns. (2-9) and (2-10) become

$$\frac{\partial \rho_{nn}}{\partial t} + (R_{nn}^{nn} + A_{nn})\rho_{nn} + \sum_m A_{nm}\rho_{mm} + \sum_m \Gamma_{nn}^{mm} \rho_{mm} + \sum_{n'} \Gamma_{nn}^{n'n'} \rho_{n'n'} = 0 \quad (3-1)$$

and

$$\frac{\partial \rho_{mm}}{\partial t} + A_{mm}\rho_{mm} + \sum_n A_{mn}\rho_{nn} + \sum_{m'} \Gamma_{mm}^{m'm'} \rho_{m'm'} - \sum_n \Gamma_{nn}^{mm} \rho_{mm} = 0 \quad (3-2)$$

where

$$A_{nm} = A_{mn} = -\frac{2}{\hbar^2} \frac{\Gamma_{nn}^{mm}(\mathbf{r}) + R_{nn}^{mm}(\mathbf{r})}{(\omega'_{mn} - \omega)^2 + \{\Gamma_{nn}^{mm}(\mathbf{r}) + R_{nn}^{mm}(\mathbf{r})\}^2} |\langle n | \hat{D}(-\omega) | m \rangle|^2 \quad (3-3)$$

and

$$A_{nn} = -\sum_m A_{mn} \quad (3-4)$$

$$A_{mm} = -\sum_n A_{nm}$$

As expected, the photoionization yield is dependent only on direct photoionization, *i.e.*

$$Y(t) = \sum_n R_{nn}^{nn} \rho_{nn} \quad (3-5)$$

Similarly, for the case  $D_{nc} = 0$  we have  $R_{nn}^{mm} = 0$ , *i.e.* direct photoionization does not take place. In this case, the MEs are given by

$$\frac{\partial \rho_{nn}}{\partial t} + A_{nn} \rho_{nn} + \sum_m A_{nm} \rho_{mm} + \sum_m \Gamma_{nn}^{mm} \rho_{mm} + \sum_{n'} \Gamma_{nn}^{n'n'} \rho_{n'n'} = 0 \quad (3-6)$$

and

$$\frac{\partial \rho_{mm}}{\partial t} + (R_{nn}^{mm} + A_{mm}) \rho_{mm} + \sum_n A_{mn} \rho_{nn} - \sum_n \Gamma_{nn}^{mm} \rho_{mm} + \sum_{m'} \Gamma_{mm}^{m'm'} \rho_{m'm'} = 0 \quad (3-7)$$

In this case, the relations given by eqns. (3-3) and (3-4) still hold and the photoionization yield is dependent only on autoionization:

$$Y(t) = \sum_m R_{nn}^{mm} \rho_{mm} \quad (3-8)$$

It should be noted that for the case  $q \rightarrow \infty$  the MEs given by eqns. (3-2), (3-6) and (3-7) are the conventional rate equations [5, 6] and that the conventional rate equation approach usually cannot provide the Beutler-Fano-type bandshape for photoionization. Similar conclusions for  $q \rightarrow \infty$  can be obtained for the two-photon ionization case and will not be discussed here.

The continuum shown in Figs. 1 and 2 does not have to represent only the ionization continuum; it can represent any other type of continuum (e.g. a dissociation continuum or separate ion-pair formation continuum etc.). In other words, the theoretical results presented in Sections 2.1 and 2.2 can also be applied to other multiphoton processes with the excited electronic state coupled to a continuum.

Several types of autoionization appear in molecular photoionization spectra [7 - 9]. The kinetic energy of the ejected electron may come from the autoionization state by conversion of either the rotational energy or the vibrational energy of the ion core [7]. Another common type of autoionization involves the conversion of the electronic energy of the core and is called electrostatic autoionization [8]. One other type of autoionization, which can be called the spin-orbit autoionization, results from a transfer of the spin-orbit energy of the ion core to the photoelectron kinetic energy [9].

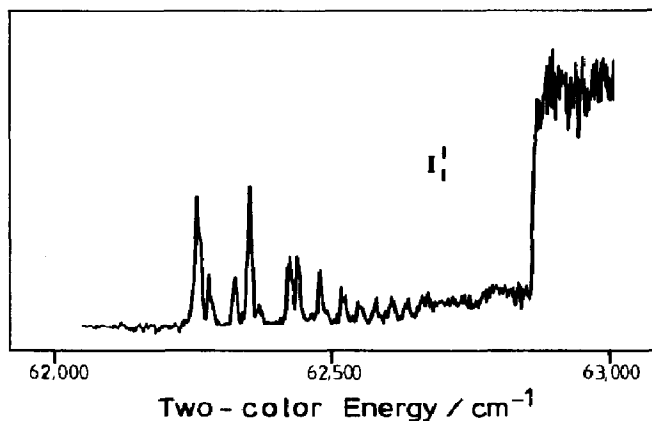


Fig. 3. The two-color PIE spectrum of the aniline  $I_1^1 B_2$  band.

Recently, Hager *et al.* [10] have measured the two-color, threshold photoionization spectra of jet-cooled aniline, and observed vibrationally selective autoionizing Rydberg structures in these spectra, containing quanta of the non-totally symmetric vibrational modes 10b, I and 15. Figure 3 shows the photoionization efficiency (PIE) spectrum for aniline photoionized from the  $I_1^1 \ ^1B_2$  transition [10]. We shall qualitatively interpret this PIE spectrum by using the theoretical results presented in this paper as follows.

Depending on whether  $W_{mm} \gg R_{mm}^{mn}$  or  $W_{mm} \ll R_{mm}^{mn}$ , the two-color photoionization yield can be expressed by eqn. (2-53) or eqn. (2-34). For example, for the  $W_{mm} \ll R_{mm}^{mn}$  case, we have

$$Y = \sum_n \left[ R_{nn}^{mn} + \frac{2}{\hbar^2} \sum_m |\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle|^2 \frac{1}{q_{nm}^2} \times \frac{2q_{nm}(\omega_2 - \omega_{mn}') + (q_{nm}^2 - 1)\{\Gamma_{mn}^{mn}(\mathbf{r}) + R_{mn}^{mn}(\mathbf{r})\}}{(\omega_2 - \omega_{mn}')^2 + \{\Gamma_{mn}^{mn}(\mathbf{r}) + R_{mn}^{mn}(\mathbf{r})\}^2} \right] \rho_{mn} \quad (3-9)$$

where  $R_{nn}^{mn}$  denotes the direct photoionization rate

$$R_{nn}^{mn} = \frac{2\pi}{\hbar^2} \sum_c |\langle c | \hat{D}(\omega_2)_2 | n \rangle|^2 \delta(\omega_2 - \omega_{cn}) \quad (3-10)$$

and

$$\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle = \langle n | \hat{D}(-\omega_2)_2 | m \rangle + \frac{P}{\hbar} \sum_c \frac{U_{cm}}{\omega_{mc}} \langle n | \hat{D}(-\omega_2)_2 | c \rangle \quad (3-11)$$

Equation (3-9) shows that the photoionization yield consists of two parts, one from the direct photoionization which determines the adiabatic ionization threshold, and the other from the contribution through autoionizing states  $|m\rangle$ . Notice that the autoionization contribution to the photoionization yield is determined by the matrix element  $\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle$  given by eqn. (3-11). If the autoionization state  $|m\rangle$  is a Rydberg state of high principal quantum number, then  $\langle n | \hat{D}(-\omega_2)_2 | m \rangle$  is usually much smaller than  $\langle n | \hat{D}(-\omega_2)_2 | c \rangle$  if  $c$  is the lowest ionic state. In this case, the direct photoionization  $R_{nn}^{mn}$  makes more contribution to  $Y$  than that through autoionization given by the second term on the right-hand side of eqn. (3-9). This is the reason why one observes a sharp adiabatic ionization threshold due to  $R_{nn}^{mn}$ . In this case, the second term on the right-hand side of eqn. (3-11) becomes important and we see that the autoionization matrix element  $U_{cm}$  plays an important role in determining the Rydberg structures of the PIE spectra near the threshold [10].

To interpret the  $I_1^1 \ ^1B_2$  PIE spectrum of aniline, we use the adiabatic approximation as a basis set:

$$|n\rangle = \Phi_a X_1(Q_I) \theta_{av} \quad (3-12)$$

$$|m\rangle = \Phi_b X_1(Q_I) \theta_{bv} \quad (3-13)$$

and

$$|c\rangle = \Phi_c X_w(Q_I) \theta_{cv''} \quad (3-14)$$

where  $\Phi_a$ ,  $\Phi_b$  and  $\Phi_c$  represent the electronic wavefunctions (see Fig. 2),  $X_1(Q_I)$  and  $X_w(Q_I)$  denote the vibrational wavefunctions of the inversion mode  $Q_I$  and  $\theta_{av}$ ,  $\theta_{bv'}$  and  $\theta_{cv''}$  are the vibrational wavefunctions of all other vibrational modes. Thus for direct photoionization

$$\begin{aligned} R_{nm}^{nn} &= \frac{2\pi}{\hbar^2} \sum_c |\langle X_w \theta_{cv''} | \langle \Phi_c | \hat{D}(-\omega_2)_2 | \Phi_a \rangle | X_1 \theta_{av} \rangle|^2 \delta(\omega_2 - \omega_{c w v'', a 1 v}) \\ &= \frac{2\pi}{\hbar^2} \sum_c |\langle \Phi_c | \hat{D}(-\omega_2) | \Phi_a \rangle|^2 |\langle X_w | X_1 \rangle|^2 |\langle \theta_{cv''} | \theta_{av} \rangle|^2 \delta(\omega_2 - \omega_{c w v'', a 1 v}) \end{aligned} \quad (3-15)$$

where, in the second step, the Condon approximation has been introduced. Owing to the fact that the inversion mode is not totally symmetric, we can see that the most probable transition is  $w = 1$  and  $v' = v$  provided there is no big change in geometry between the  ${}^1B_2$  state and the ground state of the ion. In other words, the direct photoionization yields the step-function ionization behavior shown in Fig. 3 for the high resolution measurement.

Next we consider the autoionization contribution to the  $I_1^1 {}^1B_2$  PIE spectrum. From eqn. (3-9), we can see that it is determined by the matrix elements  $U_{cm}$  and  $\langle n | \hat{D}(-\omega_2)_2 | c \rangle$ . Note that for vibrational autoionization we have

$$\begin{aligned} U_{cm} &= -\hbar^2 \langle X_w \theta_{cv''} | \langle \Phi_c | \frac{\partial}{\partial Q_I} | \Phi_b \rangle \frac{\partial}{\partial Q_I} | X_1 \theta_{bv'} \rangle \\ &= -\hbar^2 \langle \Phi_c | \frac{\partial \Phi_b}{\partial Q_I} \rangle \langle X_w | \frac{\partial X_1}{\partial Q_I} \rangle \langle \theta_{cv''} | \theta_{bv'} \rangle \end{aligned} \quad (3-16)$$

Here again the Condon approximation has been introduced. From eqn. (3-16) we can see that the dominant transitions are  $w = 0$ ,  $v'' = v'$  and  $w = 2$ ,  $v'' = v'$ . However, the latter transition takes place above the threshold. Thus, the Rydberg structures shown in Fig. 3 are due to the  $w = 0$ ,  $v'' = v'$  transition. In this case, we have

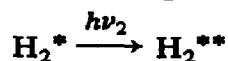
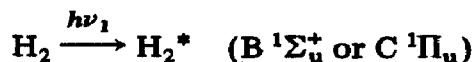
$$\begin{aligned} \langle n | \hat{D}(-\omega_2)_2 | c \rangle &= \langle X_1 \theta_{av} | \langle \Phi_a | \hat{D}(-\omega_2)_2 | \Phi_c \rangle | X_w \theta_{cv''} \rangle \\ &= \left\{ \frac{\partial \langle \Phi_a | \hat{D}(-\omega_2)_2 | \Phi_c \rangle}{\partial Q_I} \right\}_0 \langle X_1 | Q_I | X_w \rangle \langle \theta_{av} | \theta_{cv''} \rangle \end{aligned} \quad (3-17)$$

Here the vibronic coupling is introduced. In other words, in this case the vibronic coupling plays an important role in the Rydberg structures of the  $I_1^1 {}^1B_2$  PIE spectrum.

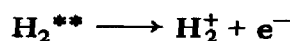


More recently, Kung *et al.* [11] have obtained the high resolution spectra of new Rydberg states of  $H_2$  in the extreme UV region by two-step doubly resonant excitation (*i.e.* stepwise resonant two-photon ion-pair ( $H^+ + H^-$ ) production) followed by  $H^-$  ion detection. In other words, their experiment can be described by the following scheme:

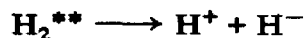
*Excitation*



*Autoionization*



*Ion-pair formation*



For convenience of discussion, we reproduce their ion-pair production spectrum of  $H_2$  and the fitted Beutler-Fano bandshapes in Fig. 4.

Kung *et al.* [11] have fitted the observed Beutler-Fano asymmetric bandshapes by using Fano's equation (see eqn. (2-54)). As shown in Section 2, Fano's equation can be used only when we have the weak field-weak field case and  $W_{nm} \ll R_{nm}^{mn}$ . For comparison, we consider the  $W_{nm} \gg R_{nm}^{mn}$  case

$$Y = \sum_n \left[ R_{nm}^{mn} + \frac{4}{\hbar^2} \sum_m \frac{|\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle|^2}{q_{nm}^2 \{ \Gamma_{nm}^{mn}(\mathbf{r}) + R_{nm}^{mn}(\mathbf{r}) \}} \frac{q_{nm} \epsilon_{nm} - 1}{\epsilon_{nm}^2 + 1} \right] \rho_{nm} \quad (3-18)$$

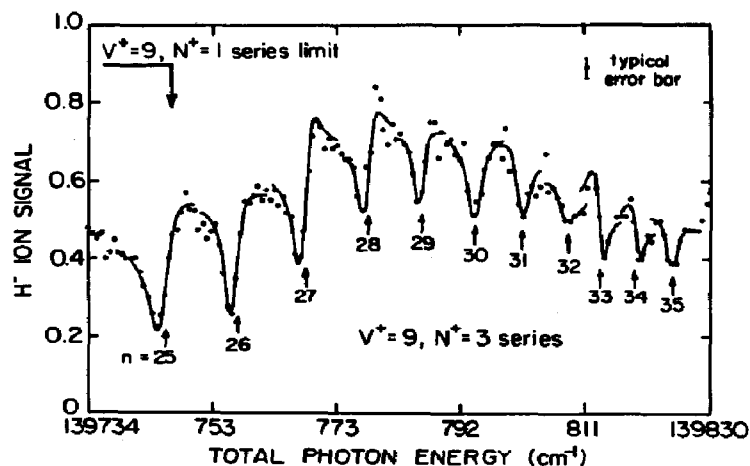


Fig. 4. Ion-pair production spectrum of  $H_2$  and the fitted Beutler-Fano bandshapes: —, calculated; ···, experimental.

in terms of the detunings  $\epsilon_{nm}$  defined by eqn. (2-19). As was pointed out in Section 2, the asymmetric bandshape function given by eqn. (3-18) is somewhat different from Fano's bandshape function (see eqn. (2-20)). However, both expressions can be made to exhibit the same asymmetric bandshape by choosing the two  $q_{nm}$  values as follows:

$$q_{nm}(Y) = \frac{2q_{nm}(F)}{1 - q_{nm}(F)^2} \quad (3-19)$$

where  $q_{nm}(Y)$  represents the  $q_{nm}$  value given by eqn. (3-18) while  $q_{nm}(F)$  denotes the  $q_{nm}$  value for Fano's bandshape function. For comparison these two sets of  $q_{nm}$  values for the ion-pair production spectrum of  $H_2$  are given in Table 1. Note that the widths determined from the Beutler-Fano bandshapes consist of  $\Gamma_{mn}^{mn}(r)$  and  $R_{mn}^{mn}(r)$  from both  $m$  and  $n$  levels (see Appendix A).

Also, from eqn. (3-18) (or eqn. (2-52) for the Fano case), we can see that, within a small wavelength range, we can assume that the contribution from the direct process  $R_{mn}^{mn}$  is relatively constant. In this case we can determine the ratio of the two neighboring  $|\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle|^2$  values (Fig. 5). For  $n = 25$  and  $n = 26$  we find

$$\frac{|\langle n | \hat{D}(-\omega_2)_2 | \phi_m(26) \rangle|^2}{|\langle n | \hat{D}(-\omega_2)_2 | \phi_m(25) \rangle|^2} = 0.32 \quad (3-20)$$

Note that

$$\frac{q_{nm}}{q_{nm'}} = \frac{\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle \sum_c D_{nc}(-\omega_2)_2 U_{cm'} \delta(\omega_{m'c})}{\langle n | \hat{D}(-\omega_2)_2 | \phi_{m'} \rangle \sum_c D_{nc}(-\omega_2) U_{cm} \delta(\omega_{mc})} \quad (3-21)$$

TABLE 1

Comparison of  $q_{nm}(F)$  and  $q_{nm}(Y)$  values of the ion-pair production spectrum of  $H_2$

$n$	$R_{mn}^{mn}(r) + \Gamma_{mn}^{mn}(r)$	$q_{nm}(F)^a$	$q_{nm}(Y)^b$
25	1.75	0.40	0.95
26	0.95	0.20	0.40
27	1.25	0.60	1.75
28	1.10	0.55	1.60
29	0.85	0.10	0.35
30	1.00	0.00	0.00
31	1.20	-0.30	-0.35
32	1.50	-0.30	-0.50
33	0.90	-0.80	-4.50
34	0.70	-0.80	-4.50
35	1.00	-0.15	-0.45

<sup>a</sup> From ref. 13.

<sup>b</sup> Our results.

In this way we can determine the ratio

$$\frac{\left\{ \sum_c D_{nc}(-\omega_2)_2 U_{cm} \delta(\omega_{mc}) \right\}_{26}^2}{\left\{ \sum_c D_{nc}(-\omega_2) U_{cm} \delta(\omega_{mc}) \right\}_{25}^2} = 0.21 \quad (3-22)$$

and estimate the relative magnitude of the terms  $\langle n | \hat{D}(-\omega_c)_2 | m \rangle$  and

$$\frac{P}{\hbar} \sum_c \frac{U_{cm}}{\omega_{mc}} \langle n | \hat{D}(-\omega_2)_2 | c \rangle$$

involved in  $q_{nm}$ .

It should be mentioned that in Fig. 5, in order to fit the experimental data, the values of  $q_{nm}$  and  $R_{nm}^{mn}(\mathbf{r}) + \Gamma_{nm}^{mn}(\mathbf{r})$  for  $n = 26$  have been modified slightly from those given in Table 1 to take the values of 0.67 and 1.00 respectively. This is due to the interference between the two neighboring bands, and indicates that it is important to know the behavior of the contribution from the direct photodissociation (or photoionization) and to take into account the interference effect in order to obtain accurate  $q_{nm}$  and  $|\langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle|^2$  values. The widths  $\Gamma_{nm}^{mn}(\mathbf{r}) + R_{nm}^{mn}(\mathbf{r})$  are relatively insensitive to the interference effect however.

In conclusion, in this paper we have generalized our previous density formalism for the treatment of multiphoton ionization of molecules by including the effect of multivibronic levels and have shown how to apply this theory to analyze the experimental data. It should be noted that the Green's function formalism for multiphoton ionization of atoms has been developed by Lambropoulos and coworkers [12]. A main feature of the density matrix method is that it can properly take into account the heat bath effect represented by  $\Gamma_{nm}^{m'n'}$  in this paper. Thus the theoretical results obtained in this paper can also be applied to study photoionization of

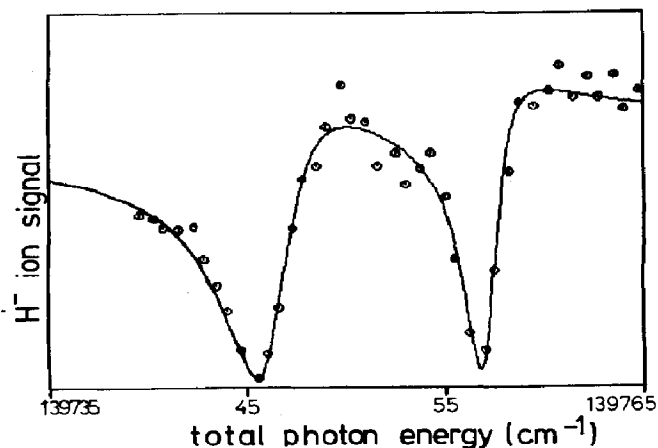


Fig. 5. Calculated ion-pair production spectrum of  $H_2$  for  $n = 25$  and  $n = 26$ .

molecules in dense media. In this case, vibrational relaxation is often much faster than other rate processes so that the vibrational equilibrium is established. Then, for one-photon ionization, we may set  $\rho_{nm} = \rho_g P_n$  and  $\rho_{mn} = \rho_a P_m$  where  $P_n$  and  $P_m$  represent the equilibrium distributions in the ground electronic state and the excited electronic state respectively,  $\sum_n P_n = 1$  and  $\sum_n P_m = 1$ . Equations (2-9) and (2-10) yield

$$\frac{\partial \rho_g}{\partial t} + a \rho_g + b \rho_a = 0 \quad (3-23)$$

and

$$\frac{\partial \rho_a}{\partial t} + a' \rho_g + b' \rho_a = 0 \quad (3-24)$$

where

$$a = \sum_n P_n (R_{nn}^{mm} + A_{nn}) \quad (3-25)$$

$$b = \sum_n \sum_m P_m (A_{nm} + \Gamma_{nm}^{mm}) \quad (3-26)$$

$$a' = \sum_n \sum_m A_{mn} P_n \quad (3-27)$$

and

$$b' = \sum_m P_m \left( R_{mm}^{mm} + A_{mm} - \sum_n \Gamma_{nn}^{mm} \right) \quad (3-28)$$

In this case, all the rate constants are weighted by the equilibrium distributions  $P_n$  and  $P_m$ , and the time-dependent behaviors can be obtained by solving eqns. (3-23) and (3-24). The two-photon ionization case can be treated similarly and will not be discussed here.

Another feature of the density matrix formalism of multiphoton ionization of molecules is that the competing processes other than photoionization can be taken into account. Work is in progress to apply this formalism to study the photoionization of liquids and solids.

### Acknowledgments

This work was supported by the National Science Foundation and Arizona State University. Two of us (A.B. and S.H.L.) wish to thank Professor Hofacker of the Technical University of Munich for his gracious hospitality.

### References

- 1 C. Y. Ng, *Adv. Chem. Phys.*, 52 (1983) 263.  
Y. Fujimura, in S. H. Lin (ed.), *Advances in Multiphoton Processes and Spectroscopy*, Vol. 2, World Scientific, 1986, pp. 1 - 75.

- H. Kühlewind, H. J. Neusser and E. W. Schlag, *J. Phys. Chem.*, **89** (1985) 5600.  
 W. Dietz, H. J. Neusser, U. Boesl, E. W. Schlag and S. H. Lin, *Chem. Phys.*, **66** (1982) 105.
- 2 B. Fain, H. Kono, S. H. Lin, W. E. Henke, H. L. Selzle and E. W. Schlag, *J. Chin. Chem. Soc.*, **32** (1985) 187.  
 Y. Fujimura and S. H. Lin, *J. Chem. Phys.*, **75** (1981) 5110.
- 3 A. Boeglin, B. Fain and S. H. Lin, *J. Chem. Phys.*, **84** (1986) 4838.
- 4 U. Fano, *Phys. Rev.*, **124** (1961) 1866.
- 5 H. Rottke and H. Zacharias, *J. Chem. Phys.*, **83** (1985) 4831.
- 6 D. S. Zakheim and P. M. Johnson, *Chem. Phys.*, **46** (1980) 263.  
 V. S. Letokhov, V. I. Mishin and A. A. Puretzky, *Prog. Quantum Electron.*, **5** (1977) 139.
- 7 R. S. Berry, *J. Chem. Phys.*, **45** (1966) 1228.  
 U. Fano, *Phys. Rev. A*, **2** (1970) 353.
- 8 M. Raoult, H. Le Rouzo, G. Raseev and H. Lefebvre-Brion, *J. Phys. B*, **16** (1983) 4601.
- 9 H. Lefebvre-Brion, A. Giusti-Suzon and G. Raseev, *J. Chem. Phys.*, **83** (1985) 1557.
- 10 J. Hager, M. A. Smith and S. C. Wallace, *J. Chem. Phys.*, **83** (1985) 4820; **84** (1986) 6771.
- 11 A. H. Kung, R. H. Page, R. J. Larkin, Y. R. Shen and Y. T. Lee, *Phys. Rev. Lett.*, **56** (1986) 328.
- 12 P. Lambropoulos and P. Zoller, *Phys. Rev. A*, **24** (1981) 379.  
 Y. S. Kim and P. Lambropoulos, *Phys. Rev. A*, **29** (1984) 3159.

#### Appendix A: Derivation of eqns. (2-1) - (2-20)

Consider  $\rho_{mn}$  given by eqn. (2-7). Notice that

$$\begin{aligned}
 & \frac{i}{\hbar} (V_{nm}\rho_{mn} - \rho_{nm}V_{mn}) + R_{nn}^{mn}\rho_{mn} + R_{nn}^{nm}\rho_{nm} \\
 &= 2\text{Im} \left\{ \left( \frac{i}{\hbar} V_{nm} + R_{nn}^{mn} \right) \rho_{mn} \right\} \\
 &= 2\text{Re} \left\{ \left( \frac{i}{\hbar} V_{nm} + J_{nm} \right) \rho_{mn} \right\} \tag{A-1}
 \end{aligned}$$

Here eqn. (2-3) has been used. Writing  $\rho_{mn}(t)$  as

$$\rho_{mn}(t) = \rho_{mn}(\omega) \exp(-it\omega) + \rho_{mn}(-\omega) \exp(it\omega) \tag{A-2}$$

and using eqn. (2-4) and the rotating wave approximation, we obtain

$$\begin{aligned}
 2\text{Re} \left\{ \left( \frac{i}{\hbar} V_{nm} + J_{nm} \right) \rho_{mn} \right\} &= 2\text{Re} \left[ \left\{ \frac{i}{\hbar} D_{nm}(-\omega) + \frac{i}{\hbar^2} \sum_c D_{nc}(-\omega) U_{cm} \frac{P}{\omega_{mc}} \right. \right. \\
 &\quad \left. \left. + \frac{\pi}{\hbar^2} \sum_c D_{nc}(-\omega) U_{cm} \delta(\omega_{cm}) \right\} \rho_{mn}(\omega) \right] \\
 &= 2\text{Re} \left[ \left\{ \frac{i}{\hbar} \langle n | \hat{D}(-\omega) | \phi_m \rangle \right. \right. \\
 &\quad \left. \left. + \frac{\pi}{\hbar^2} \sum_c D_{nc}(-\omega) U_{cm} \delta(\omega_{cm}) \right\} \rho_{mn}(\omega) \right] \tag{A-3}
 \end{aligned}$$

where

$$|\phi_m\rangle = |m\rangle + \frac{P}{\hbar} \sum_c \frac{U_{cm}}{\omega_{mc}} |c\rangle \quad (\text{A-4})$$

Equation (A-3) can be written as

$$2\text{Re} \left\{ \left( \frac{i}{\hbar} V_{nm} + J_{nm} \right) \rho_{mn}(t) \right\} = \text{Re} \left\{ \frac{i}{\hbar} \langle n | \hat{D}(-\omega) | \phi_m \rangle \left( 1 - \frac{i}{q_{nm}} \right) \rho_{mn}(\omega) \right\} \quad (\text{A-5})$$

where

$$\frac{1}{q_{nm}} = \frac{(\pi/\hbar) \sum_c D_{nc}(-\omega) U_{cm} \delta(\omega_{cm})}{\langle n | \hat{D}(-\omega) | \phi_m \rangle} \quad (\text{A-6})$$

Substituting eqn. (A-5) into eqn. (2-7) yields

$$\frac{\partial \rho_{nn}}{\partial t} - \frac{2}{\hbar} \sum_m \text{Im} \left\{ \langle n | \hat{D}(-\omega) | \phi_m \rangle \left( 1 - \frac{i}{q_{nm}} \right) \rho_{mn}(\omega) \right\} + R_{nn}^{nn} \rho_{nn} + \sum_k \Gamma_{nn}^{kk} \rho_{kk} = 0 \quad (\text{A-7})$$

Similarly, eqn. (2-6) becomes

$$\begin{aligned} \frac{\partial \rho_{mm}}{\partial t} + \frac{2}{\hbar} \sum_n \text{Im} \left\{ \langle n | \hat{D}(-\omega) | \psi_m \rangle \left( 1 + \frac{i}{q'_{nm}} \right) \rho_{mn}(\omega) \right\} \\ + R_{mm}^{mm} \rho_{mm} + \sum_k \Gamma_{mm}^{kk} \rho_{kk} = 0 \end{aligned} \quad (\text{A-8})$$

where

$$|\psi_m\rangle = |m\rangle + \frac{P}{\hbar} \sum_c \frac{U_{cm}}{\omega - \omega_{cn}} |c\rangle \quad (\text{A-9})$$

and

$$\frac{1}{q'_{nm}} = \frac{(\pi/\hbar) \sum_c D_{nc}(-\omega) U_{cm} \delta(\omega - \omega_{cn})}{\langle n | \hat{D}(-\omega) | \psi_m \rangle} \quad (\text{A-10})$$

It is commonly assumed that  $q_{nm} = q'_{nm}$  and  $\langle n | \hat{D}(-\omega) | \psi_m \rangle = \langle n | \hat{D}(-\omega) | \phi_m \rangle$  and that  $q_{nm}$  is a real number. This assumption will be examined in a future investigation.

Using the relations

$$\exp(it\omega) \left( \frac{i}{\hbar} V_{mn} + R_{mn}^{nn} \right) = \frac{i}{\hbar} \langle \psi_m | \hat{D}(\omega) | n \rangle \left( 1 - \frac{i}{q'_{nm}} \right) \quad (\text{A-11})$$

and

$$\exp(it\omega) \left( -\frac{i}{\hbar} V_{mn} + R_{mn}^{mn} \right) = -\frac{i}{\hbar} \langle \phi_m | \hat{D}(\omega) | n \rangle \left( 1 + \frac{i}{q_{nm}} \right) \quad (\text{A-12})$$

we can rewrite eqn. (2-8) as

$$\begin{aligned} \frac{\partial \rho_{mn}(\omega)}{\partial t} + \{i(\omega_{mn} - \omega) + R_{mn}^{mn} + \Gamma_{mn}^{mn}\} \rho_{mn}(\omega) \\ + \frac{i}{\hbar} \langle \psi_m | \hat{D}(\omega) | n \rangle \left( 1 - \frac{i}{q'_{nm}} \right) \rho_{nn} - \frac{i}{\hbar} \langle \phi_m | \hat{D}(\omega) | n \rangle \left( 1 + \frac{i}{q_{nm}} \right) \rho_{mm} = 0 \end{aligned} \quad (\text{A-13})$$

Applying the steady state approximation to  $\rho_{mn}(\omega)$  yields

$$\rho_{mn}(\omega) = \frac{(i/\hbar) \langle \phi_m | \hat{D}(\omega) | n \rangle (1 + i/q_{nm}) \rho_{mm} - (i/\hbar) \langle \psi_m | \hat{D}(\omega) | n \rangle (1 - i/q'_{nm}) \rho_{nn}}{i(\omega_{mn} - \omega) + R_{mn}^{mn} + \Gamma_{mn}^{mn}} \quad (\text{A-14})$$

Equations (2-9) and (2-10) are obtained by substituting eqn. (A-14) into eqns. (A-7) and (A-8). Notice that

$$A_{nn} = \frac{2}{\hbar^2} \sum_m \text{Im} \left\{ \frac{i \langle n | \hat{D}(-\omega) | \phi_m \rangle \langle \psi_m | \hat{D}(\omega) | n \rangle (1 - i/q_{nm}) (1 - i/q'_{nm})}{i(\omega_{mn} - \omega) + R_{mn}^{mn} + \Gamma_{mn}^{mn}} \right\} \quad (\text{A-15})$$

$$A_{nm} = -\frac{2}{\hbar^2} \text{Im} \left\{ \frac{i |\langle \phi_m | \hat{D}(\omega) | n \rangle|^2 (1 + 1/q_{nm}^2)}{i(\omega_{mn} - \omega) + R_{mn}^{mn} + \Gamma_{mn}^{mn}} \right\} \quad (\text{A-16})$$

$$A_{mn} = -\frac{2}{\hbar^2} \text{Im} \left\{ \frac{i |\langle \psi_m | \hat{D}(\omega) | n \rangle|^2 (1 + 1/q'_{nm}{}^2)}{i(\omega_{mn} - \omega) + R_{mn}^{mn} + \Gamma_{mn}^{mn}} \right\} \quad (\text{A-17})$$

and

$$A_{mm} = \frac{2}{\hbar^2} \sum_n \text{Im} \left\{ \frac{i \langle n | \hat{D}(-\omega) | \psi_m \rangle \langle \phi_m | \hat{D}(\omega) | n \rangle (1 + i/q'_{nm}) (1 + i/q_{nm})}{i(\omega_{mn} - \omega) + R_{mn}^{mn} + \Gamma_{mn}^{mn}} \right\} \quad (\text{A-18})$$

Here the only assumption introduced is that  $q_{nm}$  and  $q'_{nm}$  are real. Further assumptions of  $\phi_m = \psi_m$  and  $q_{nm} = q'_{nm}$  will reduce the above expressions for  $A_{nn}$ ,  $A_{nm}$ ,  $A_{mn}$  and  $A_{mm}$  to those given in Section 2.

Next we consider the calculation of  $R_{mn}^{mn}$ . Using eqn. (2-3) we find

$$R_{mn}^{mn} = J_{mn} + J_{nr}^* = R_{mn}^{mn}(r) + iR_{mn}^{mn}(i) \quad (\text{A-19})$$

and from eqn. (2-4) we obtain

$$J_{mn} = \frac{\pi}{\hbar^2} \sum_c |U_{mc}|^2 \delta(\omega_{mc}) + i \frac{P}{\hbar^2} \sum_c \frac{|U_{mc}|^2}{\omega_{mc}} \quad (\text{A-20})$$

and

$$J_{nm} = \frac{\pi}{\hbar^2} \sum_c |D_{cn}(\omega)|^2 \delta(\omega - \omega_{cn}) + i \frac{P}{\hbar^2} \sum_c \frac{|D_{cn}(\omega)|^2}{\omega - \omega_{cn}} \quad (\text{A-21})$$

Substituting eqns. (A-20) and (A-21) into eqn. (A-19) yields

$$R_{mn}^{mn}(\mathbf{r}) = \frac{1}{2} (R_{mn}^{mn} + R_{nn}^{nn}) \quad (\text{A-22})$$

and

$$R_{mn}^{mn}(i) = \frac{P}{\hbar^2} \sum_c \frac{|U_{mc}|^2}{\omega_{mc}} - \frac{P}{\hbar^2} \sum_c \frac{|D_{cn}(\omega)|^2}{\omega - \omega_{cn}} \quad (\text{A-23})$$

In other words,  $R_{mn}^{mn}(\mathbf{r})$  and  $R_{mn}^{mn}(i)$  represent the level width and level shift due to autoionization and direct photoionization. Similarly, it has been shown that the dephasing constant  $\Gamma_{mn}^{mn}$  due to the coupling between the system and the heat bath can also be written as [A1, A2]

$$\Gamma_{mn}^{mn} = \Gamma_{mn}^{mn}(\mathbf{r}) + i\Gamma_{mn}^{mn}(i) \quad (\text{A-24})$$

That is, it can also be written as the summation of the level width and the level shift. It should be noted that

$$\Gamma_{mn}^{mn}(\mathbf{r}) = \frac{1}{2} (\Gamma_{nn}^{nn} + \Gamma_{nn}^{nn}) + \Gamma_{mn}^{mn}(d) \quad (\text{A-25})$$

where  $\Gamma_{mn}^{mn}(d)$  denotes the pure dephasing. Equation (A-25) indicates that  $\Gamma_{mn}^{mn}(\mathbf{r})$  has contributions not only from the lifetimes of the  $m$ -level and the  $n$ -level but also from the pure dephasing.

Next we consider an important case,  $q_{nm} = 0$ . We find

$$\langle n | \hat{D}(-\omega) | \phi_m \rangle \frac{1}{q_{nm}} = \frac{\pi}{\hbar} \sum_c D_{nc}(-\omega) U_{cm} \delta(\omega_{mc}) = r_{nm} \quad (\text{A})$$

$$\langle n | \hat{D}(-\omega) | \psi_m \rangle \frac{1}{q'_{nm}} = \frac{\pi}{\hbar} \sum_c D_{nc}(-\omega) U_{cm} \delta(\omega - \omega_{cn}) = r'_{nm} \quad (\text{B})$$

$$A_{nm} = A_{mn} = - \frac{2}{\hbar^2} \frac{r_{nm}^2 \{ \Gamma_{mn}^{mn}(\mathbf{r}) + R_{mn}^{mn}(\mathbf{r}) \}}{(\omega'_{nm} - \omega)^2 + \{ R_{nn}^{nn}(\mathbf{r}) + \Gamma_{nn}^{nn}(\mathbf{r}) \}^2} \quad (\text{C})$$

$$A_{nn} = \sum_m A_{nm} \quad (\text{D})$$

and

$$A_{mm} = \sum_n A_{nm} \quad (\text{E})$$

Here for convenience we have assumed that  $r_{nm} = r'_{nm}$ . The above results show that for this particular transition  $n \rightarrow m$  the bandshape is lorentzian:

$$Y = \sum_n (R_{nn}^{nn} + 2A_{nn}) \rho_{nn} + \sum_m (R_{mm}^{mm} + 2A_{mm}) \rho_{mm} \quad (\text{F})$$



### References for Appendix A

- A1 S. H. Lin and H. Eyring, *Proc. Natl. Acad. Sci. U.S.A.*, 74 (1977) 3623.  
 A2 B. Fain and S. H. Lin, *Surf. Sci.*, 147 (1984) 497.  
 B. Fain, A. R. Ziv, G. S. Wu and S. H. Lin, in S. H. Lin (ed.), *Advances in Multi-photon Processes and Spectroscopy*, Vol. 1, World Scientific, 1984, pp. 420 - 500.

### Appendix B: Derivation of eqns. (2-21) - (2-54)

First we consider  $\rho_{ni}(t)$  given by eqn. (2-31). Notice that

$$\rho_{ni}(t) = \rho_{ni}(\omega_1) \exp(-it\omega_1) + \rho_n(-\omega) \exp(it\omega_1) \quad (\text{B-1})$$

$$\rho_{mi}(t) = \rho_{mi}(\omega_2) \exp(-it\omega_2) + \rho_{mn}(-\omega_2) \exp(it\omega_2) \quad (\text{B-2})$$

and

$$\rho_{mi}(t) = \rho_{mi}(\omega_1 + \omega_2) \exp[-it(\omega_1 + \omega_2)] + \rho_{mi}(-\omega_1 - \omega_2) \exp[it(\omega_1 + \omega_2)] \quad (\text{B-3})$$

Substituting eqns. (B-1) and (B-3) into eqn. (2-31) and using the rotating wave approximation, we find

$$\begin{aligned} \frac{\partial \rho_{ni}(\omega_1)}{\partial t} + \{i(\omega_{ni} - \omega_1) + \Gamma_{ni}^{ni} + R_{ni}^{ni}\} \rho_{ni}(\omega_1) + \frac{i}{\hbar} D_{ni}(\omega_1)_1 (\rho_{ii} - \rho_{nn}) \\ + \sum_m \left( \frac{i}{\hbar} V_{nm} + R_{ni}^{mi} \right) \exp(-it\omega_2) \rho_{mi}(\omega_1 + \omega_2) = 0 \end{aligned} \quad (\text{B-4})$$

Notice that

$$\left( \frac{i}{\hbar} V_{nm} + R_{ni}^{mi} \right) \exp(-it\omega_2) = \frac{i}{\hbar} D_{nm}(-\omega_2)_2 J_{nm} \exp(-it\omega_2) \quad (\text{B-5})$$

and

$$\begin{aligned} J_{nm} \exp(-it\omega_2) = \frac{\exp(-it\omega_2)}{\hbar^2} \sum_c \int_0^\infty d\tau V_{nc}(t) V_{cm}(t - \tau) \exp(-i\tau\omega_{cm}) \\ = \frac{1}{\hbar^2} \sum_c D_{nc}(-\omega_2)_2 U_{cm} \left\{ -i \frac{P}{\omega_{cm}} + \pi \delta(\omega_{cm}) \right\} \end{aligned} \quad (\text{B-6})$$

where

$$\begin{aligned} \hat{D} = \hat{D}(\omega_1)_1 \exp(-it\omega_1) + \hat{D}(-\omega_1)_1 \exp(it\omega_1) + \hat{D}(\omega_2)_2 \exp(-it\omega_2) \\ + \hat{D}(-\omega_2)_2 \exp(it\omega_2) \end{aligned} \quad (\text{B-7})$$

Substituting eqn. (B-6) into eqn. (B-5) yields

$$\left( \frac{i}{\hbar} V_{nm} + R_{ni}^{mi} \right) \exp(-it\omega_2) = \frac{i}{\hbar} \langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle \left( 1 - \frac{i}{q_{nm}} \right) \quad (\text{B-8})$$

and eqn. (2-34) is obtained by introducing eqn. (B-8) into eqn. (B-4).

Next we consider  $\rho_{mi}(t)$  given by eqn. (2-32). Again substituting eqns. (B-1) - (B-3) into eqn. (2-32) and using the rotating wave approximation, we obtain

$$\frac{\partial \rho_{mi}(\omega_1 + \omega_2)}{\partial t} + \{i(\omega_{mi} - \omega_1 - \omega_2) + \Gamma_{mi}^m + R_{mi}^m\} \rho_i(\omega_1 + \omega_2) + \sum_n \left[ \left\{ \frac{i}{\hbar} D_{mn}(\omega_2)_2 + J_{nm} \exp(it\omega_2) \right\} \rho_{ni}(\omega_1) - \frac{i}{\hbar} \rho_{mn}(\omega_2) D_{ni}(\omega_1)_1 \right] = 0 \quad (\text{B-9})$$

where we have

$$J_{nm} \exp(it\omega_2) = \frac{i}{\hbar^2} \sum_c U_{mc} D_{cn}(\omega_2)_2 \left\{ i \frac{P}{\omega_2 - \omega_{cn}} + \pi \delta(\omega_2 - \omega_{cn}) \right\} \quad (\text{B-10})$$

It follows that

$$\frac{i}{\hbar} D_{nm}(\omega_2)_2 + J_{nm} \exp(it\omega_2) = \frac{i}{\hbar} \langle \psi_m | \hat{D}(\omega_2)_2 | n \rangle \left( 1 - \frac{i}{q'_{nm}} \right) \quad (\text{B-11})$$

where

$$|\psi_m\rangle = |m\rangle + \frac{P}{\hbar} \sum_c \frac{U_{cm}}{\omega_2 - \omega_{cn}} |c\rangle \quad (\text{B-12})$$

and

$$\frac{1}{q'_{nm}} = \frac{(\pi/\hbar) \sum_c U_{mc} D_{cn}(\omega_2)_2 \delta(\omega_2 - \omega_{cn})}{\langle \psi_m | \hat{D}(\omega_2)_2 | n \rangle} \quad (\text{B-13})$$

Equation (2-35) for  $\rho_{mi}(\omega_1 + \omega_2)$  is obtained by substituting eqn. (B-11) into eqn. (B-9).

Finally we consider  $\rho_{mn}(t)$  given by eqn. (2-33). Substituting eqns. (B-2) and (B-3) into eqn. (2-33) yields

$$\frac{\partial \rho_{mn}(\omega_2)}{\partial t} + \{i(\omega_{mn} - \omega_2) + \Gamma_{mn}^m + R_{mn}^m\} \rho_{mn}(\omega_2) - \frac{i}{\hbar} \sum_l D_{ln}(-\omega_1)_1 \rho_{ml}(\omega_1 + \omega_2) + \rho_{nn} \left\{ \frac{i}{\hbar} D_{mn}(\omega_2)_2 + \exp(it\omega_2) J_{mn} \right\} + \rho_{mm} \left\{ - \frac{i}{\hbar} D_{mn}(\omega_2)_2 + \exp(it\omega_2) J_{nm}^* \right\} = 0 \quad (\text{B-14})$$

where

$$\exp(it\omega_2) J_{nm} = \frac{i}{\hbar^2} \sum_c D_{mc} D_{cn}(\omega_2) \left\{ i \frac{P}{\omega_2 - \omega_{cn}} + \pi \sum_c U_{mc} D_{cn}(\omega_2) \delta(\omega_2 - \omega_{cn}) \right\} \quad (\text{B-15})$$

and

$$\exp(it\omega_2)J_{nm}^* = \frac{1}{\hbar^2} \sum_c U_{mc} D_{cn}(\omega_2)_2 \left\{ i \frac{P}{\omega_{cm}} + \pi \delta(\omega_{cm}) \right\} \quad (\text{B-16})$$

It follows that

$$\frac{i}{\hbar} D_{mn}(\omega_2)_2 + \exp(it\omega_2)J_{mn} = \frac{i}{\hbar} \langle \psi_m | \hat{D}(\omega_2)_2 | n \rangle \left( 1 - \frac{i}{q_{nm}} \right) \quad (\text{B-17})$$

and

$$-\frac{i}{\hbar} D_{mn}(\omega_2)_2 + \exp(it\omega_2)J_{nm}^* = -\frac{i}{\hbar} \langle \phi_m | \hat{D}(\omega_2)_2 | n \rangle \left( 1 + \frac{i}{q_{nm}} \right) \quad (\text{B-18})$$

Substituting eqns. (B-17) and (B-18) we obtain eqn. (2-36).

### Appendix C: Validity of eqn. (2-41)

The performance of the steady state approximation applied to  $\rho_{ni}(\omega_1)$ ,  $\rho_{mi}(\omega_1 + \omega_2)$  and  $\rho_{mn}(\omega_2)$  has been examined in a previous paper [C1]. Here we shall study the additional approximation associated with the multilevel system. Using eqn. (2-41), we obtain the improved expressions for  $\rho_{ni}(\omega_1)$  and  $\rho_{mn}(\omega_2)$  as

$$\rho_{ni}(\omega_1) = \frac{i}{\hbar} F_{ni}(\omega_1) D_{ni}(\omega_1)_1 (\rho_{nn} - \rho_{ii}) + \Delta\rho_{ni}(\omega_1) \quad (\text{C-1})$$

and

$$\begin{aligned} \rho_{mn}(\omega_2) = & \frac{i}{\hbar} F_{mn}(\omega_2) \left\{ \langle \phi_m | \hat{D}(\omega_2) | n \rangle \left( 1 + \frac{i}{q_{nm}} \right) \rho_{mn} \right. \\ & \left. - \langle \psi_m | \hat{D}(\omega_2)_2 | n \rangle \left( 1 - \frac{i}{q_{nm}} \right) \rho_{nn} \right\} + \Delta\rho_{mn}(\omega_2) \end{aligned} \quad (\text{C-2})$$

where  $\Delta\rho_{ni}(\omega_1)$  and  $\Delta\rho_{mn}(\omega_2)$  represent the correction terms for  $\rho_{ni}(\omega_1)$  and  $\rho_{mn}(\omega_2)$  respectively, and they are given by

$$\begin{aligned} \Delta\rho_{ni}(\omega_1) = & -\frac{i}{\hbar} F_{ni}(\omega_1) \sum_m \langle n | \hat{D}(-\omega_2)_2 | \phi_m \rangle \left( 1 - \frac{i}{q_{nm}} \right) \rho_{mi}(\omega_1 + \omega_2) \\ = & -\left( \frac{i}{\hbar} \right)^3 F_{ni}(\omega_1) \sum_m \langle n | \hat{D}(-\omega_2) | \phi_m \rangle \left( 1 - \frac{i}{q_{nm}} \right) F_{mi}(\omega_1 + \omega_2) \\ & \times \sum_{n'} \left[ F_{n'm'}(\omega_2) D_{n'i}(\omega_1)_1 \langle \phi_m | \hat{D}(\omega_2)_2 | n' \rangle \left( 1 + \frac{i}{q_{n'm}} \right) \rho_{mn} - \rho_{n'n'} \right] \end{aligned}$$

$$\begin{aligned} & \times \{F_{mm'}(\omega_2) + F_{n'l}(\omega_1)\} \langle \phi_m | \hat{D}(\omega_2)_2 | n' \rangle \left( 1 - \frac{i}{q_{n'm}} \right) D_{n'l}(\omega_1)_1 \\ & + F_{n'l}(\omega_1) \langle \phi_m | \hat{D}(\omega_2)_2 | n' \rangle \left( 1 - \frac{i}{q_{n'm}} \right) D_{n'l}(\omega_1)_1 \rho_{ll} \end{aligned} \quad (\text{C-3})$$

and

$$\begin{aligned} \Delta \rho_{mn}(\omega_2) &= \frac{i}{\hbar} F_{mm}(\omega_2) \sum_l D_{ln}(-\omega_1) \rho_{ml}(\omega_1 + \omega_2) \\ &= \left( \frac{i}{\hbar} \right)^3 F_{mm}(\omega_2) \sum_l D_{ln}(-\omega_1)_1 F_{ml}(\omega_1 + \omega_2) \sum_{n'} \left[ F_{mm'}(\omega_2) D_{n'l}(\omega_1)_1 \right. \\ & \quad \times \langle \phi_m | \hat{D}(\omega_2)_2 | n' \rangle \left( 1 + \frac{i}{q_{n'm}} \right) \rho_{mm} - \rho_{n'n'} \{ F_{mm'}(\omega_2) \\ & \quad + F_{n'l}(\omega_1) \} \langle \phi_m | \hat{D}(\omega_2)_2 | n' \rangle \left( 1 - \frac{i}{q_{n'm}} \right) D_{n'l}(\omega_1)_1 \\ & \quad \left. + F_{n'l}(\omega_1) \langle \phi_m | \hat{D}(\omega_2)_2 | n' \rangle \left( 1 - \frac{i}{q_{n'm}} \right) D_{n'l}(\omega_1) \rho_{ll} \right] \end{aligned} \quad (\text{C-4})$$

These correction terms are indeed higher order terms.

#### Reference for Appendix C

C1 A. Boeglin, B. Fain and S. H. Lin, *J. Chem. Phys.*, 84 (1986) 4838.