LINE SHAPE ANALYSIS OF INTENSE FIELD MOLECULAR MULTIPHOTON ABSORPTION SPECTRA

James V. Tietz
Department of Chemistry, University of Kansas, Lawrence, Kansas 66045

Shih-I Chu*
Department of Chemistry, University of Kansas, Lawrence, Kansas 66045† and Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, Boulder, Colorado 80309

I. Introduction

The interaction of intense electromagnetic fields with multi-level atoms and molecules has been the subject of intensive theoretical and experimental investigations in recent years [1,2]. Recently we have developed a non-perturbative quasi-energy method [3] for the treatment of collisionless high-order multiphoton excitation dynamics of vibration-rotational states of molecules in intense laser and static electric fields. Nonlinear effects such as power broadening, dynamic Stark shift, Autler-Townes multiplet splitting, hole burning and S-hump behaviors, etc., are observed. It is found that many of the salient features in the spectral line shapes may be understood in terms of an analytical three-level quasi-energy model. In this paper we shall present a more detailed spectral line shape analysis based on the three and four quasi-level models. Comparison of the model calculations with the 'exact' Floquet analysis for the HF and CO systems will be discussed, and the usefulness of the analytical models for extracting the nonlinear multiphoton dynamics will be pointed out.

*Alfred P. Sloan Foundation Fellow.
†Permanent address.
II. Floquet Theory and Quasi-Energy Method for Molecular Multiphoton Excitation

As details of the quasi-energy method have been described in a previous paper [3], only an outline of the method will be presented here to serve to define notations.

Consider the vibrational-rotational motion of a heteronuclear diatomic molecule in the presence of a monochromatic electric field $\varepsilon_{\text{AC}}$ of an IR laser as well as a static electric field $\varepsilon_{\text{DC}}$. (The following discussion is still applicable for the special case of $\varepsilon_{\text{DC}} = 0$.) The Schrödinger equation for the system in the electric-dipole approximation is

$$i\hbar \frac{\partial \Psi (r,t)}{\partial t} = H(r,t)\Psi (r,t) \quad ,$$

where

$$H(r,t) = H_0 (r) + V(r,t) \quad ,$$

$$H_0 (r) = H^{(0)} (r) - \mu (r) \cdot \varepsilon_{\text{DC}} \quad ,$$

and

$$V(r,t) = -\mu (r) \cdot \varepsilon_{\text{AC}} (t) \quad .$$

Here $\mu (r)$ is the electric dipole moment of the diatom, $\varepsilon_{\text{AC}} (t) = \varepsilon_{\text{AC}} \cos \omega t$, and $H^{(0)}$ is the Hamiltonian of the free molecule, with

$$[H^{(0)} (r) - E_{\text{vj}}^{(0)}] \chi_{\text{vjm}} (r) = 0 \quad ,$$

where $\chi_{\text{vjm}} (r = r\theta \phi)$ is the molecular vibration-rotational wave function, with $(v,j,m_j)$ being the vibrational, rotational and angular momentum projection quantum number, respectively.

We shall assume that $\varepsilon_{\text{AC}} \parallel \varepsilon_{\text{DC}} \parallel \hat{z}$, so that the electric dipole interactions have the form

$$\mu (r) \cdot \varepsilon (\text{a.c. or d.c.}) = \mu (r) \varepsilon \cos \theta \quad ,$$

which is independent of the azimuthal angle $\phi$. Thus when fields are
turned on, the angular momentum projection quantum number \( m_j \) remains a good quantum number (although \( v \) and \( j \) are no longer constants of motion).

Now that \( H(\vec{r}, t) = H(\vec{r}, t+T) \), \( T = 2\pi/\omega \), the Floquet theorem [4, 5] admits the solution of Eq. (1) in the following form:

\[
\psi_\varepsilon(\vec{r}, t) = e^{-i\varepsilon t} \phi_\varepsilon(\vec{r}, t) ,
\]

(7)

where \( \psi_\varepsilon \) is called the quasi-energy state (QES) corresponding to the quasi-energy \( \varepsilon \) (in this case the quasi-vibration-rotational energy \( \varepsilon_{v_j} \)) and \( \phi_\varepsilon \) is a periodic function of time, viz., \( \phi_\varepsilon(\vec{r}, t) = \phi_\varepsilon(\vec{r}, t+T) \). Following the Floquet Hamiltonian method [3-6], one can reduce the dynamic problem into an equivalent static problem. Thus the QES \( \psi_\varepsilon \) can be expanded into a Fourier series,

\[
\psi_\varepsilon(\vec{r}, t) = e^{-i\varepsilon t} \sum_{n=-\infty}^{\infty} e^{-in\omega t} \phi_\varepsilon^{(n)}(\vec{r}) ,
\]

(8)

where \( \alpha = (v_j) \) and \( \phi_\varepsilon^{(n)}(\vec{r}) \) is the quasi-energy harmonics which is independent of time. To solve the quasi-energy spectrum [6], we further expand the quasi-energy harmonics over an orthonormalized molecular-field basis \( |\beta m\rangle \), where \( \beta \) runs over all (unperturbed) vibration-rotational states \( \chi_{vjm}(\vec{r}) \) (with \( m_j \) fixed) and \( m \) is a Fourier index which steps from \( -\infty \) to \( +\infty \):

\[
\phi_\varepsilon^{(n)}(\vec{r}) \equiv |\lambda_{\alpha n}\rangle = \sum_{\beta} \sum_{m} |\beta m\rangle \langle \beta m|\lambda_{\alpha n}\rangle.
\]

(9)

Substituting Eqs. (8) and (9) in Eq. (1), we obtain the following set of linear homogeneous equations (the Floquet matrix) [3-6],

\[
\sum_{\gamma k} \langle \gamma n|H_F|\gamma k\rangle F_{\gamma \beta}^{k} = \varepsilon_{\beta} f_{\alpha \beta}^{n} .
\]

(10)

The quasi-vibration-rotational Floquet matrix so obtained possesses a block tridiagonal form as shown in Fig. 1 [3]. The determination of the vibration-rotational quasi-energy and QES thus reduces to the solution of a time-independent Floquet matrix eigenproblem. Figure 1 shows that \( H_F \) has a periodic structure with only the number of \( \omega \)'s in the diagonal elements varying from block to block. The structure endows the quasi-energy eigenvalues and eigenvectors of \( H_F \) with periodic properties.
\[
\begin{array}{cccccc}
 n = 2 & n = 1 & n = 0 & n = -1 & n = -2 \\
 A + 2\omega & B & 0 & 0 & 0 & n' = 2 \\
 B & A + \omega & B & 0 & 0 & n' = 1 \\
 0 & B & A & B & 0 & n' = 0 \\
 0 & 0 & B & A - \omega & B & n' = -1 \\
 0 & 0 & 0 & B & A - 2\omega & n' = -2
\end{array}
\]

\[\begin{bmatrix}
[H_r] = 
\end{bmatrix}\]

Where

\[
A =
\]

and

\[
B =
\]

**Fig. 1.** Structure of the dc/ac Floquet Hamiltonian. The Hamiltonian is composed of the diagonal Floquet blocks, of type A, and off-diagonal blocks of type B. \(E^{(0)}_{\nu j}\) are the unperturbed molecular energies and \(a_{\nu j, \nu' j'}\) and \(b_{\nu j, \nu' j'}\) are respectively the dc and ac coupling matrix elements.

Finally the time-averaged transition probability from the initial state \(\alpha(=\nu j)\) to the final state \(\beta(=\nu' j')\) can be computed from the eigenvectors of the QES:

\[
P^{(m_j)}_{\alpha+\beta} = \sum_k \sum_{\gamma \lambda} |\langle \beta_k | \lambda_{\gamma \lambda} \rangle|^2 \cdot |\langle \lambda_{\gamma \lambda} | \alpha 0 \rangle|^2 ,
\]

(11)

where \(m_j\) is the rotational angular momentum projection quantum number which is conserved before and after multiphoton excitation.
III. Multiphoton Excitation and Quasi-Energy Spectra of HF -- Exact Results

In this section we shall focus our discussion on the process
\[ \text{HF}(v=j=m_j=0) + n\hbar\omega + \text{d.c. field} \rightarrow \text{HF}(v',j',m_j' = 0), \]
which is sufficient to illustrate the salient features of the underlying mechanism in the MPE process. The molecular parameters of HF are given in Ref. [3].

Shown in Fig. 2 are the time averaged MPE transition probabilities \( P_{00\rightarrow v',j'} \) for \( \varepsilon_{DC} = 1.0 \) TW/cm\(^2\) and several dc strengths: (a) \( \varepsilon_{DC} = 0.0 \) a.u., (b) \( \varepsilon_{DC} = 10^{-4} \) a.u., (c) \( \varepsilon_{DC} = 5 \times 10^{-4} \) a.u., and (d) \( \varepsilon_{DC} = 5 \times 10^{-4} \) a.u. (1 a.u. d.c. field strength = \( 5.14 \times 10^9 \) V/cm). Figures 2a-2c are 'exact' numerical results obtained by including the seven Floquet cycles (\( A\pm 3\omega I, A\pm 2\omega I, A\pm \omega I, A \)) in Fig. 1, whereas Fig. 2d is the Floquet matrix rotating wave approximation (RWA) results (including only \( A\pm 3\omega I, A\pm 2\omega I, A\pm \omega I, A \) cycles) with coarser resolution. For these computations on HF, the number of molecular vibrator basis states (which is the dimension of the matrix \( A \) in Fig. 1) used is 28, distributed (7,7,7,7) (seven rotational states in \( v = 0, 1, 2, \) and 3 vibrational levels), which was found to be sufficient to obtain converged results to within 5%. (Note that for the case of \( \varepsilon_{DC} \neq 0 \), the Floquet A block was prediagonalized to obtain the dc-shifted molecular levels. The quasi-energies and transition probabilities were then computed for these dc-perturbed levels subject to strong IR laser field.) The line patterns in Fig. 2 are as follows: dot-dash lines indicate one-photon peaks, dashed lines indicate two-photon peaks, and solid lines show three-photon peaks. The triangles on top of (a) indicate the zero-field transition energies.

The multiphoton spectra are generally much narrower than the one-photon peaks. In our data, the mesh spacing along the frequency axis was adjusted to give accurate peak representations. The mesh attained in our data is at least as good as that needed for comparison with experimental data.
Fig. 2. Time-averaged MPE transition probabilities $\bar{P}_{00-v'j'}$ for $\varepsilon_{\text{AC}} = 1.0$ TW/cm$^2$ and various dc strengths (for HF): (a) $\varepsilon_{\text{DC}} = 0.0$ a.u., (b) $\varepsilon_{\text{DC}} = 10^{-4}$ a.u., (c) $\varepsilon_{\text{DC}} = 5 \times 10^{-4}$ a.u., and (d) $\varepsilon_{\text{DC}} = 5 \times 10^{-4}$ a.u. See text for detailed explanation.
Many nonlinear effects are present in the data. Power broadening by the ac field is quite pronounced. Also evident in the data are dynamic Stark shifts. This effect is most pronounced for the three-photon transitions. Several authors have reported Autler-Townes splitting under the influence of intense fields [7]. Previously, observed splitting has been primarily limited to the doublet case. We have observed multiplet splitting in much of our data.

Other nonlinear features in the spectra seem to form a loosely related group. The phenomenon of hole-burning has been widely reported and many examples may be found in these data. In some cases, however, the hole does not seem to be exactly matched in position or shape with the peak responsible for its presence (e.g. Fig. 2c, the 0,0 - 1,0 - 2,1 system). In many instances, the situation is even more complicated with a region of enhancement side-by-side with the attenuation or hole (e.g. Fig. 2a, the 0,0 - 1,1 - 2,2 system). In these cases, a characteristic S-hump is observed. If the situation is taken a step further, the enhancement becomes the major effect and little attenuation is noticed (e.g. Fig. 2b, the 0,0 - 1,0 - 2,1 system).

Figures 3a and 3b show that by using quasi-energy graphs, virtually all of the features of the transition probability plots can be explained. In particular, as will be shown later, most of the nonlinear line shape effects such as hole-burning, S-hump, multiplet splitting and enhancement behaviors, etc., are all similar effects stemming from the relative coupling strengths as well as detunings of three (or at most four) effective quasi-energy levels involved.

The addition of a dc electric field removes the restriction of the rotational dipole selection rule and causes significant intermixing of the bare molecular vibrator states. Due to the greater number of strongly coupled nearby states in the dc field, nonlinear effects such as those mentioned above appear at a much lower ac field strength than they would in the absence of the dc field. The introduction of an external dc field therefore strongly enhances the multiphoton excitation probabilities and results in a much richer spectrum [8].
Fig. 3. Quasi-energy plot (a) and 'exact' time-averaged MPE transition probabilities (b) for HF for the case of $\varepsilon_{AC} = 1$ TW/cm$^2$ and $\varepsilon_{DC} = 10^{-4}$ a.u. In (a), the quasi-energy (in cm$^{-1}$) line patterns are as follows: solid lines refer to $v=0$ states, dashed lines to $v=1$ states, dot-dash lines to $v=2$ states, and dotted lines to $v=3$ states. Since $\varepsilon_{DC} \neq 0$, all line encounters are avoided crossings.

IV. Three-Level Line Shape analysis

Although the MPE spectra discussed in Sec. III are rather complicated, many of the salient features of spectral line shapes may be qualitatively understood by means of three- or four-level analytic solutions. Appendix A of Ref. [3] gives a brief discussion of the three-level analytic solutions of QES and transition probabilities within the RWA. Figure 4 shows an example in which the three quasi-energy level approximation correctly mimics real behavior within the RWA.

Plotted in Fig. 5 are the transition probabilities between the lowest energy level and each of the upper levels of a three-level model system.
Fig. 4. Comparison of the 'exact' RWA data (Fig. 4a) with the three-level-approximation data (Fig. 4b) for HF for the time-averaged MPE peaks 0,0 $\rightarrow$ 1,1 and 0,0 $\rightarrow$ 2,2 at $\varepsilon_{AC} = 1$ TW/cm$^2$ and $\varepsilon_{DC} = 0$.

Transitions between the 0 and 1 levels are plotted with solid lines while the 0$\rightarrow$2 transitions are dashed. The energy levels used to produce this graph were $E_0 = 0$ cm$^{-1}$, $E_1 = 4004$ cm$^{-1}$, and $E_2 = 8008$ cm$^{-1}$ or 7958 cm$^{-1}$ for columns A and B, respectively. Couplings between the states were arbitrarily picked to give informative graphs. In row a, $\langle 0|\mu|1 \rangle = 0.0223$ a.u. and $\langle 1|\mu|2 \rangle = 0.00446$ a.u. In row b, $\langle 0|\mu|1 \rangle = \langle 1|\mu|2 \rangle = 0.0223$ a.u. In row c, $\langle 0|\mu|1 \rangle = 0.00446$ a.u. and $\langle 1|\mu|2 \rangle = 0.0223$ a.u. These coupling values approximate those typically found in real systems. The value of 0.0223 a.u. corresponds to that of the real HF 0,0 $\rightarrow$ 1,1 coupling.

In the upper portion of each section of Fig. 5, the quasi-energies of the three-level system have been depicted. The energy scale for these graphs is arbitrary, since the topography of the quasi-energies is what is important here. The unperturbed state most closely associated with a particular
Fig. 5. Line shape analysis of MEP spectra using the three-level approximation. See text for detailed explanation.

Quasi-energy state is used as a label for that QES. At each closest approach (avoided-crossing) of a pair of quasi-energies, the corresponding QES's "exchange" labels, i.e., they take on the unperturbed character of the other state. By noting which two unperturbed states are involved in the exchange, one can assign a mechanism to the corresponding peaks in the transition probability spectrum. Following is a summary of these mechanisms for each section of Fig. 5.
Column A: $|E_2 - E_1| = |E_1 - E_0|$

Row a: $V_{01} > V_{12}$ — "Normal Autler-Townes Splitting"
This case gives rise to the normally observed Autler-Townes splitting. There exists a large 0-1 interaction. Symmetrically distributed on either side of this peak are induced two-photon peaks due to the resonance between state 1 and 2. Since the induced two-photon peaks come from transitions out of state 1, the 0-1 transition drops. This leads to the hole-burning effect in the 0-1 transition at precisely the locations of the 0-2 transitions.

Row b: $V_{01} = V_{12}$ — "Symmetric S-hump"
Here again there is a large 0-1 transition. At the same frequency, however, there is a 1-2 interaction of equal magnitude. The 0-2 transition which arises from these interactions is narrower than the 0-1 transition present. Therefore, there is a 0-2 transition burning a hole in the center of the broader 0-1 peak. This gives rise to a 0-1 transition which has the appearance of being split.

Row c: $V_{01} < V_{12}$ — "Inverted Autler-Townes Splitting"
The primary interaction in this case is the coupling between the states 1 and 2. As can be seen from the diagram, there is a pair of 0-1 interactions symmetrically placed about the center of the 1-2 interaction. Since the upper two states are strongly coupled, wherever there is a one-photon transition, a two-photon transition will be induced. This causes the 0-1 peaks to be reduced in intensity and the 0-2 peaks to appear under the one-photon transitions.

Column B: $|E_2 - E_1| < |E_1 - E_0|$

Row a: $V_{01} > V_{12}$ — "Asymmetric Autler-Townes Splitting"
The main feature in this spectrum is a large 0-1 transition peak. The two-photon peaks arise from two different mechanisms. The higher frequency peak comes from a direct 0-2 transition. A hole is burnt in the 0-1 peak at this location due to the shared initial state. The lower
frequency peak is an induced transition due to the strong 0-1 transition followed by 1-2 coupling. Again a hole is burnt in the 0-1 peak, but in this case it is due to the continuation of some of the model molecular systems through state 1 on to state 2.

Row b: \( V_{01} = V_{12} \) - "S-hump"
Again there is a large 0-1 transition and a 0-2 transition downfield from it. It is the effect of the 0-2 transition on the 0-1 peak which is of interest here. On the low-frequency side of the 0-2 peak, the significant 1-2 coupling causes induced enhancement of the 0-1 transition from a 0\,+\,2\,+\,1 emission process. On the high-frequency side, the 0-1 peak is depleted by competition with the 0-2 peak for the initial state population. The intensity and location of the 0-2 transition are affected a small amount by these interactions. Taken all together, these effects lead to a pronounced "S-hump" in the 0-1 transition.

Row c: \( V_{01} < V_{12} \) - "Induced Transitions"
Here, there are independent 0-1 and 0-2 transitions. The strong 1-2 coupling, however, causes induced peaks to appear under those already present. Under the 0-2 peak there is an induced 0-1 transition from a 0\,+\,2\,+\,1 emission process. Under the 0-1 peak there is an induced 0-2 transition from a 0\,\,+\,1\,+\,2 continuation process. Both primary peaks are somewhat reduced in intensity by their participation in the creation of the induced peaks. The induced transitions, on the other hand, are less intense than the primary peaks due to the more involved process leading to their existence.

Each of the sections explained above represents a limiting case. As the parameters involved are changed, one may move from one case to another via gradual steps. The mechanisms of transitions in these intermediate cases are not as well defined and should not be referred to in absolute terms. However, by resorting to these six quasi-energy diagrams, one can explain many of the features found in intense field, multiphoton spectra. Likewise, by examining the features found experimentally, one can obtain qualitative information about the relative coupling strengths and detunings of the levels involved.
V. Four-Level Line Shape Analysis

As shown in the last section and in Ref. [3], most of the MPE line shapes in weak and medium strong field strengths can be accounted for by invoking a three quasi-energy level interaction model. As field strength becomes even higher, more than three levels may be required to explain the line shape change.

An example is provided by the $\nu j = (0,0), (1,1), (2,0)$ and $(2,2)$ system of CO. Figure 6 shows this system at $\varepsilon_{AC} = 35 \text{ GW/cm}^2$ and $\varepsilon_{DC} = 0$. As can be seen, the system behaves like two nearly independent S-humps and the line shapes encountered can still be explained by the three-level model. However, as field strength goes higher ($\varepsilon_{AC} = 320 \text{ GW/cm}^2$), the line shapes diverge from those expected in the three-level case (Fig. 7). In this case, a four-level model is required to account for the line shape change.

![Graph showing line shapes and quasi-energy plot](image_url)

**Fig. 6.** Quasi-energy plot and time-averaged MPE transition probabilities $P_{00\rightarrow 11,20,22}$ for CO for $\varepsilon_{AC} = 35 \text{ GW/cm}^2$ and $\varepsilon_{DC} = 0$. 
Fig. 7. Same as Fig. 6 except $\varepsilon_{AC} = 320$ GW/cm$^2$.

VI. Conclusions

It has been shown that the three- and four-level analytical models can mimic the behavior, specifically the line shapes, of some diatomic molecular systems under the influence of strong monochromatic radiation fields. In this paper we have presented some mechanistic processes which lead to specific line shapes. The three-level model can account for nearly all of the line shapes encountered in MPE spectra at weak and medium strong field strengths. In particular, two mechanisms were found for the enhancement of transition probability, and two mechanisms were found for the attenuation (hole burning). At very strong fields, more than three quasi-energy levels may be required to account for the line shapes. A specific case in which four-level interactions are taking place has been found for CO.

While the three-level model can explain the line shapes of MPE spectra over a wide range of conditions, four-level interactions in real molecular
systems are much less common. The limited application of both of these models is offset by the better understanding of the dynamics of MPE processes involved. This knowledge can be applied in a qualitative and intuitive way to much more complicated molecular systems and spectral line shapes.

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References