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CHAOS IN A SEMICLASSICAL MODEL OF MULTIPHOTON EXCITATION OF SPHERICAL TOP MOLECULES

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INTRODUCTION AND CONCLUSIONS

We study the dynamical effects of vibration-rotation coupling in multiple photon excitation at lowest order. Our molecular model is the simplest possible: that of an oscillator (triply degenerate) and uncoupled rigid rotor. The molecule-field interactions introduce a vibration-rotation nonlinearity which gives rise to nonconservation of the molecular angular momentum and in some instances consequent chaotic dynamics. The chaos leads to incoherence (widely seen in experiments¹) in the time dependence of the photon absorption and is not treatable in an additive way as inhomogeneous broadening.^{2,4}

The nonconservation of the molecular angular momentum is due to the development with time of the molecular vibrational angular momentum. The degree of chaotic behavior is found to depend upon the relative size of the vibrational to pure rotational angular momenta as the excitation progresses, i.e., when vibrational angular momentum exceeds the pure rotational angular momentum we find chaos, conversely when J_0 is quite large the motion is gyroscopically stabilized and quasiperiodic. Therefore, the suggested "cold" experiments are perhaps not so desirable.

*Work performed while on leave from the Physics Department, University of Arkansas, Fayetteville, Arkansas.

MODEL AND EQUATIONS OF MOTION

Our model Hamiltonian is⁵⁻⁸

$$H = \Delta \hat{a}^+ \cdot \hat{a} + B_0 J^2 + \Omega \hat{\epsilon} \cdot C \cdot (\hat{a}^+ + \hat{a}) \quad (1)$$

where $\hat{a}^+$ ($\hat{a}$) is the vector creation (annihilation) operator for the IR-active normal mode of the molecule with components referred to body-fixed axes, J is the molecular angular momentum operator, C is the 3×3 orthogonal matrix relating the lab-body reference frames, $\hat{\epsilon}$ is the laser's polarization vector whose components are referred to the laboratory frame, Δ , B_0 and Ω are parameters representing the laser detuning, the inverse moment of inertia of the molecule in its equilibrium configuration and the laser-molecule Rabi frequency, respectively. If $\{\hat{l}_1, \hat{l}_2, \hat{l}_3\}$ are the lab-frame unit vectors and $\{\hat{f}_1, \hat{f}_2, \hat{f}_3\}$ are those of the body frame, then

$$C_{ij} = \hat{l}_i \cdot \hat{f}_j \quad (2)$$

and the body-fixed and lab-fixed components of the molecular angular momentum are respectively

$$J_i = i \sum_{s=1}^3 \left(C_{sj} \frac{\partial}{\partial C_{sk}} - C_{sk} \frac{\partial}{\partial C_{sj}} \right) \quad (3)$$

and

$$J_I = -i \sum_{s=1}^3 \left(C_{JS} \frac{\partial}{\partial C_{KS}} - C_{KS} \frac{\partial}{\partial C_{JS}} \right) \quad (4)$$

with i, j, k (I, J, K) cyclic in $\{1, 2, 3\}$.

The Heisenberg equations of motion are:

$$\dot{\hat{a}} = -i\Delta \hat{a} - i\Omega \hat{P} \quad (5)$$

$$\dot{\hat{P}} = -2B_0 (\hat{J} \times \hat{P}) \quad (6)$$

and

$$\dot{\hat{J}} = \Omega \hat{P} \times (\hat{a}^+ + \hat{a}) \quad (7)$$

In Eq.'s (5-7) we have introduced the body fixed components of the laser polarization vector (which we have supposed to be along the lab-fixed Z-axis)

$$\underline{p} = \hat{\epsilon} \cdot \underline{C} \quad . \quad (8)$$

In what follows we integrate the equations (5)-(7) (replacing $\underline{g}^+$ by $\underline{g}^*$ in (7)) subject to boundary conditions:

$$\underline{g}(0) = \text{col}(0,0,0) \quad , \quad (9)$$

$$\underline{J}(0) = \text{col}(0,0,J_0) \quad , \quad (10)$$

$$\underline{p}(0) = \text{col}(1/\sqrt{2}, 0, 1/\sqrt{2}) \quad . \quad (11)$$

These choices are quite arbitrary but convenient.

CALCULATIONS

We begin by noting that Eq. (6) represents a precession of the polarization (unit) vector about $\underline{J}$ at frequency $2B_0|\underline{J}|$. If $\underline{J}$ is taken to be a constant of the motion by removing Eq. (7) from the set of equations, then we can solve Eq. (5)-(6) analytically. (Clearly this system is linear and no chaos can occur.) We obtain

$$\underline{p}(t) = \text{col}\left(\frac{\cos 2B_0 J_0 t}{\sqrt{2}}, \frac{\sin 2B_0 J_0 t}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right) \quad . \quad (12)$$

Substituting this result into Eq. (5) shows that $\underline{g}$ is driven now at three frequencies, Δ and $\Delta \pm B_0 J_0$. In our calculations we have picked $B_0 = .1 \text{ cm}^{-1}$ and $\Omega = 1 \text{ cm}^{-1}$ with Δ arbitrarily taken as $.5 \text{ cm}^{-1}$. These values are realistic for molecules with large moments of inertia (like SF_6 , CF_4 , etc.) and substantial induced dipole moments. Using Eq. (12) gives

$$\begin{aligned} |\underline{g}(t)|^2 = \Omega^2 \left\{ \frac{1 - \cos(\Delta + 2B_0 J_0)t}{2(\Delta + 2B_0 J_0)^2} + \frac{1 - \cos(\Delta - 2B_0 J_0)t}{2(\Delta - 2B_0 J_0)^2} \right. \\ \left. + \frac{1 - \cos \Delta t}{\Delta^2} \right\} \quad . \quad (13) \end{aligned}$$

Equation (13) shows resonances at $\Delta = \pm 2B_0 J_0$ and $\Delta = 0$ giving the familiar P, Q, R branches of the spectrum.

Fig. (I.a) shows a plot of Eq. (13) vs. time for $J_0 = 5$. The plot shows simple oscillation at the detuning frequency.

Fig. (Ib) shows a Fourier transform of (I.a) showing peaks at Δ and $|\Delta \pm 2B_0 J_0|$, Eq. (13). The peak at zero is the net average absorption. Fig. (I.c) shows the phase plot P_1 vs. P_2 (body-fixed components) as given by Eq. (12).

Fig. (I.a) Dynamics of vibration-rotation model with J fixed; $\Delta = .5 \text{ cm}^{-1}$, $\Omega = 1 \text{ cm}^{-1}$ and $J_0 = 5$. Energy in vibrations vs. time.

Fig. (I.b) Fourier transform of Fig. (I.a).

We now solve the full system (5)-(7) again at $J_0 = 5$ and give the results in Fig's. (IIa-c) corresponding to Fig's. (Ia-c). Fig. (IIa) shows a more erratic energy deposition with greater peak absorption than Fig. (Ia). The spectrum of Fig. (IIb) is now the characteristic broadband indicative of chaotic dynamics. Fig. (II.c) shows the erratic motion of the polarization vector, attempting precession about the time dependent J . That true (technical) chaos has been observed has been confirmed by a calculation of the maximal Lyapunov exponent using the method of Bennetin and Galgani.⁹

Fig. (III) shows our results at $J_0 = 20$ for the phase plot of Case (II.b). Now the motion has been stabilized within a band. The Lyapunov exponent is now zero and the spectrum shows characteristic frequencies.

Fig. (I.c) P_1 vs. P_2 for Case I.

Fig. (II.a) Same as Fig's (I), but now $\dot{J} \neq 0$.

Fig. (II.b) Fourier spectrum of Fig. (II.a).

Fig. (II.c) P_1 vs. P_2 for Case II.

Fig. (III) P_1 vs. P_2 for $J_0 = 20$ with $\dot{J} \neq 0$.

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