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Interaction of electromagnetic field with the OH radical: A non-perturbative approach

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Abstract. A non-perturbative approach for the study of the interaction of a hydroxyl (OH) radical with infra-red radiation is presented. The dressed states and vibrational transition probability of OH radical are defined by a quasi-energy approach (non-perturbative).

Keywords. Electromagnetic field; dressed states; quasi-energies.

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1. Introduction

Considerable attention has been paid recently in the study of multiphoton excitation of atoms and molecules in an intense laser beam (Cantrell *et al* 1978; Néel 1979; Mohan *et al* 1983; 1985; Sharma and Mohan 1985). Important processes such as multiphoton ionization of atoms (Cantrell *et al* 1978) and multiphoton collisionless dissociation of polyatomic molecules (Berry 1982) have been studied extensively. In this paper we study the vibrational excitation of hydroxyl (OH) radical in the presence of IR laser beam. The hydroxyl (OH) radical is one of the most thoroughly studied free radical owing to its importance in atmospheric chemistry (McEwan and Philips 1975), combustion processes (Gaydon 1948), and the interstellar medium (Watson 1976).

Here we assume the OH to be non-rotating, and its lowest quantized vibrational levels are assumed to be interacting with a classical, single-mode laser beam. The dressed states and absorption spectrum of this radical are obtained by using the quasi-energy approach (Ritus 1967; Zel'dovich 1967). Using this approach we obtain the analytic solutions of the quasi-energy states. Interesting cases near resonant frequencies, that is, when the detunings are small, are discussed in detail. Further, the effect of intensity and frequency on the infinite and time-averaged transition probability from one vibrational level to another, the power-broadening and the Stark-effect are discussed.

2. Theory

The quasi-energy approach provides a simple and elegant non-perturbative method to calculate the dressed state wave-functions and hence the dynamics of the molecular

system when it is placed in an intense electromagnetic field (Ritus 1967; Zel'dovich 1967). The laser field is characterized by a plane monochromatic electric wavevector i.e.

$$\mathbf{E}(t) = \hat{\varepsilon} E_0 \cos(\omega t), \tag{1}$$

where $\hat{\varepsilon}$ is a unit polarization vector, $|\mathbf{E}_0|$ the amplitude of the electromagnetic field and ω its frequency. The molecular Hamiltonian for such a system is

$$H = H_0 + H'(t)$$

where, within the framework of semiclassical radiation theory, the perturbation $H'(t)$ is

$$H'(t) = -\mu(\hat{r}) \cdot \hat{\varepsilon} E_0 \cos(\omega t). \tag{2}$$

Here $\mu(\hat{r})$ is the dipole moment of the molecule and H_0 is the unperturbed Hamiltonian of the molecule.

The wavefunction Ψ, which is the solution of the time-dependent Schrödinger equation, may be expanded into a series

$$\Psi(\mathbf{r}, t) = \sum_k C_k(t) \Phi_k(\mathbf{r}, t), \tag{3}$$

where $\{\Phi_k(\mathbf{r}, t)\}$ are the dressed states of the molecule and according to the quasi-energy approach (Ritus 1967; Zel'dovich 1967)

$$\Phi_k(\mathbf{r}, t) = \exp[-i(E_1 + \lambda_k)t] \sum_{m=1}^{3} a_m^{(k)} u_m \exp[-i(m-1)\omega t]. \tag{4}$$

The unperturbed wavefunction u_m satisfies

$$H_0 u_m = E_m u_m.$$

In (4), $\{a_m^{(k)}\}$ are the amplitudes corresponding to bare states $\{u_m\}$ and $\{\lambda_k\}$ are the eigenvalues corresponding to quasi-energy states $\{\Phi_k\}$. Substituting (4) and (3) into time-dependent Schrödinger equation and using the orthogonality relations for the dressed states, we obtain the following algebraic equations

$$-\lambda_k a_1 + v_{12} a_2 = 0, \tag{5a}$$

$$v_{21} a_1 + (\varepsilon_{21} - \lambda_k) a_2 + v_{23} a_3 = 0, \tag{5b}$$

$$v_{32} a_2 + (\varepsilon_{31} - \lambda_k) a_3 = 0, \tag{5c}$$

where $v_{ij} = -E_0/2 \langle u_i | \mu | u_j \rangle$ are the off-diagonal dipole matrix elements, and $\varepsilon_{pq} = E_p - E_q - (p-1)\omega$ is the field detuning term. Equations (5a) to (5c) can easily be solved for three unknowns a_1, a_2 and a_3 by solving the third order algebraic equation, namely

$$\lambda_k^3 - (\varepsilon_{21} + \varepsilon_{31})\lambda_k^2 - (v_{23} v_{32} - \varepsilon_{21}\varepsilon_{31} + v_{12} v_{21})\lambda_k + v_{12} v_{21} \varepsilon_{31} = 0. \tag{6}$$

Further, as the matrix corresponding to (5a) to (5c) is hermitian, the roots correspond-

ing to (6) must be real. The solutions obtained are given by (Abramowitz and Stegun 1964)

$$\lambda_1 = -\tfrac{1}{3}a_2' - 2q\cos(\theta/3), \tag{7}$$

$$\lambda_2 = \tfrac{1}{3}a_2' + 2q\cos(\theta/3 + 2\pi/3), \tag{8}$$

$$\lambda_3 = -\tfrac{1}{3}a_2' + 2q\cos(\theta/3 + 4\pi/3), \tag{9}$$

where

$$a_2' = -(\varepsilon_{21} + \varepsilon_{31}), \tag{10a}$$

$$q = \tfrac{1}{3}a_1' - \tfrac{1}{9}a_2'^2, \tag{10b}$$

$$a_1' = -\{v_{23}v_{32} - \varepsilon_{21}\varepsilon_{31} + v_{21}v_{12}\}, \tag{10c}$$

$$\theta = \cos^{-1}(R'/q^3), \tag{10d}$$

$$R' = \tfrac{1}{6}(a_1'a_2' - 3a_0') - \tfrac{1}{27}a_2'^3, \tag{10e}$$

$$a_0' = v_{21}v_{12}\varepsilon_{31}. \tag{10f}$$

For each eigenvalue we can find the corresponding eigenvector. For example, when $\lambda_k = \lambda_1$, we obtain from (5a) to (5c), the following normalized eigenvectors:

$$a_1(1) = v_{12}(\lambda_1 - \varepsilon_{31})/\{v_{12}^2(\lambda_1 - \varepsilon_{31})^2 + \lambda_1^2(\lambda_1 - \varepsilon_{31})^2 + v_{32}^2\lambda_1^2\}^{1/2}, \tag{11}$$

$$a_2(1) = v_{32}\lambda_1/\{v_{12}^2(\lambda_1 - \varepsilon_{31})^2 + \lambda_1^2(\lambda_1 - \varepsilon_{31})^2 + v_{32}^2\lambda_1^2\}^{1/2}, \tag{12}$$

$$a_3(1) = \lambda_1(\lambda_1 - \varepsilon_{31})/\{v_{12}^2(\lambda_1 - \varepsilon_{31})^2 + \lambda_1^2(\lambda_1 - \varepsilon_{31})^2 + v_{32}^2\lambda_1^2\}^{1/2}. \tag{13}$$

Thus the dressed states $\{\Phi_k\}$ can be written out by substituting eigenvalues from (7) to (9) and eigenvectors from (11) to (13) into (4). When the intensity is quite weak the quasi-energy states reduce to the following expression

$$\Phi_1(1) \to \exp[-i(E_1 + \lambda_1)t]a_1(1)u_1, \tag{14}$$

$$\Phi_2(1) \to \exp[-i(E_1 + \lambda_1 + \omega)t]a_2(1)u_2, \tag{15}$$

$$\Phi_3(1) \to \exp[-i(E_1 + \lambda_1 + 2\omega)t]a_3(1)u_3, \tag{16}$$

where $\omega_1 = E_1 + \lambda_1$, $\omega_2 = E_1 + \lambda_1 + \omega$ and $\omega_3 = E_1 + \lambda_1 + 2\omega$ play the role of quasi-energies. Instead of $\omega_{1,2,3}$; $\lambda_{1,2,3}$ are widely used and are called the quasi-energies.

3. Dynamical behaviour of the radical in the presence of laser beam

In this section we first discuss the behaviour of quasi-energies with the variation of the laser field for some interesting physical situations and discuss some interesting cases near resonances where analytic solutions are possible:

(i) $\varepsilon_{31} = 0$; $\varepsilon_{21} \neq 0$

This type of situation is shown in figure 1a and corresponds to the case when there is an exact resonance between the vibrational levels $v = 0$ and $v = 2$ due to two-photon absorption at weak-fields. Under the above condition, we obtain

$$\lambda_1 \approx 0, \lambda_{2,3} \approx \tfrac{1}{2}\varepsilon_{21} \pm \tfrac{1}{2}[|\varepsilon_{21}|^2 + 4(v_{23} + v_{12})^2]^{1/2}. \tag{17}$$

When the field is very weak we have the Rabi-frequencies, for example, when v_{12} and v_{23} are less than the detuning ε_{21}, we obtain from (17) $\lambda_1 \approx 0, \lambda_2 \approx \varepsilon_{21}$ and $\lambda_3 \approx 0$. For this transition, the resonant frequency is $\omega = 3484\ \text{cm}^{-1}$. The numerical calculation at this resonant frequency, show that for the electric field strength $|\mathbf{E}_0| = 2{\cdot}1 \times 10^{-6}$ (in a.u), $\lambda_1 = -0{\cdot}387 \times 10^{-12}$; $\lambda_2 = 0{\cdot}378 \times 10^{-3}$ and $\lambda_3 = 0{\cdot}74 \times 10^{-8}$ (all in a.u). At higher field, i.e., at $|\mathbf{E}_0| = 2{\cdot}1 \times 10^{-2}$ (a.u), we find $\lambda_1 = 0{\cdot}618 \times 10^{-8}$; $\lambda_2 = 0{\cdot}377 \times 10^{-3}$ and $\lambda_3 = 0{\cdot}312 \times 10^{-5}$. As the field is increased the Rabi-frequencies become quite appreciable as compared to detuning and we obtain from (17), $\lambda_1 \approx 0; \lambda_{2,3} \approx \varepsilon_{21} \pm [|v_{23}|^2 + |v_{12}|^2]$, which show the shifting of the levels at high fields.

(ii) $\varepsilon_{21} = 0; \varepsilon_{31} \neq 0.$

This type of situation is shown in figure 1b and corresponds to the case when the frequency of the laser beam is such that there is an exact resonance condition between the vibrational levels $v = 0$ and $v = 1$. For weak fields, as the detuning ε_{31} is greater than that of the Rabi-frequency, we obtain from (10a) to (10e) $q \approx \frac{1}{9}\varepsilon_{31}^2$ and $R' = \frac{1}{27}\varepsilon_{31}^2$, so that we have $q^3 + R'^2 \approx 0$. When the condition $q^3 + R'^2 \approx 0$ is satisfied for the cubic equation, the two roots must be nearly equal in magnitude i.e. $|\lambda_1| \approx |\lambda_2|$, and the third root $\lambda_3 \approx \varepsilon_{31}$. The numerical results for the electric-field strength $|\mathbf{E}_0| = 2{\cdot}1 \times 10^{-6}$ a.u., show that $\lambda_1 = 0{\cdot}103 \times 10^{-7}$; $\lambda_2 = 0{\cdot}141 \times 10^{-7}$ and $\lambda_3 = 0{\cdot}756 \times 10^{-3}$. For higher field, that is, for $|\mathbf{E}_0| = 2{\cdot}1 \times 10^{-2}$ a.u., we find $\lambda_1 = 0{\cdot}120 \times 10^{-5}$; $\lambda_2 = 0{\cdot}120 \times 10^{-5}$ and $\lambda_3 = 0{\cdot}751 \times 10^{-3}$. Thus at low field we find $|\lambda_1| \approx |\lambda_2|$ and $|\lambda_3| \approx \varepsilon_{21}$.

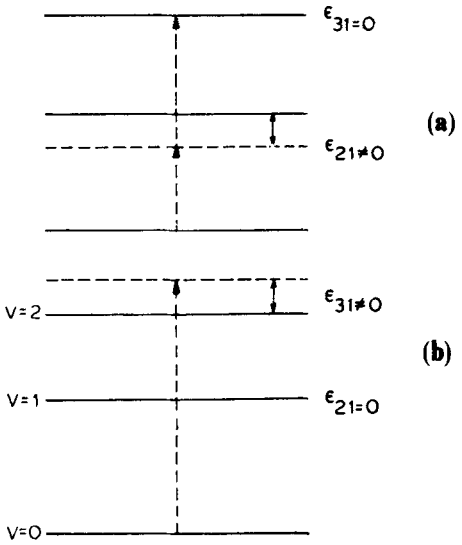

Figure 1. **a.** Two-photon absorption diagram showing $\varepsilon_{31} = 0$ but $\varepsilon_{21} \neq 0$. **b.** one-photon absorption diagram showing $\varepsilon_{21} = 0$ but $\varepsilon_{31} \neq 0$

Knowing eigenfunctions $\{a_m^k\}$ for a given eigenvalue, one can calculate the vibrational excitation transition probability. In fact, the transition probability that the system will be found in the vibrational state $|n\rangle$ at time t_f if it was in the state $|m\rangle$ at time t_i, can be shown to be

$$P(m, t_i; n, t_f) = \left| \sum_{\lambda=1}^{3} a_n(\lambda) a_m(\lambda) \exp[-i\lambda(t_f - t_i)] \right|^2.$$

However for a continuous operation of a laser, the infinite time-averaged transition probability is observed, that is

$$\bar{P}_{m \to n} = \sum_{\lambda=1}^{3} |a_n(\lambda) a_m(\lambda)|^2. \tag{18}$$

In figure 2 we have shown the variation of the transition probability $\bar{P}_{0 \to 1}$ for the transition from $v = 0$ to $v = 1$ with frequency ω of the e.m. field. As the frequency is increased from $\omega = 3540\ \text{cm}^{-1}$ to $3567\ \text{cm}^{-1}$, the probability $\bar{P}_{0 \to 1}$ increases steadily upto a maximum of 0·4987. This behaviour is quite expected (Crance and Stenholm 1980; Leasure and Wyatt 1979) as there exists one-photon resonance between $v = 0$ and $v = 1$ levels for $\omega = 3567\ \text{cm}^{-1}$. The two-photon absorption spectrum shows (not shown here) two peaks corresponding to two resonant frequencies, i.e., $\omega = 3484\ \text{cm}^{-1}$ ($\varepsilon_{31} = 0$) and $\omega = 3567\ \text{cm}^{-1}$ ($\varepsilon_{21} = 0$). It can be interpreted that for the transition from $v = 0$ to $v = 2$, the transition from $v = 0$ to $v = 1$ is also effective and hence causes an additional line on the spectrum.

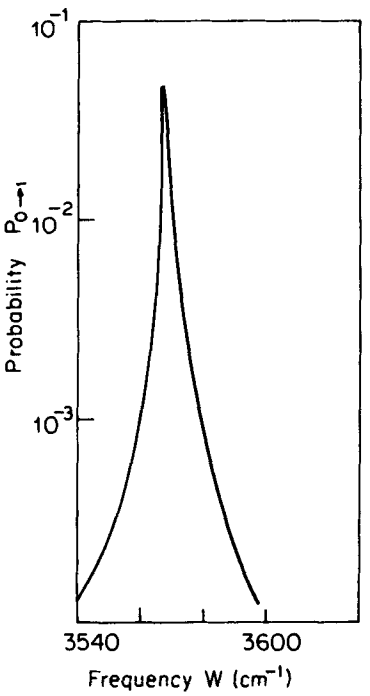

Figure 2. Time-average transition probability $\bar{P}_{0 \to 1}$ vs ω, frequency of the IR laser beam.

The multiphoton absorption line show that the lines get broadened as the intensity of the laser beam is increased e.g.; FWHM $\propto I^{1/2}$. According to Shirley (1965), the power-broadening and dynamic Stark shift are given by

$$\text{FWHM} = 4b,$$

and
$$(\omega_{\text{res}} - \omega_0) = b^2/\omega_0 = (\text{FWHM})^2/16\omega_0, \tag{19}$$

where ω_0 is the fundamental frequency of the molecule and

$$b = -\frac{E_0}{2}\langle u_1|\mu|u_2\rangle,$$

$\langle u_1|\mu|u_2\rangle$ is the one-photon dipole transition matrix element. In figures 3 and 4 we have shown the variation of FWHM and the dynamic Stark shift with the electric field strength. This type of variation was also shown by Leasure and Wyatt (1979) for the HF molecule.

4. Summary

We have discussed here the dynamical behaviour of the OH radical subjected to IR laser beam using the non-perturbative quasi-energy approach. We have derived analytic expressions for the quasi-energies and quasi-energy states of the three-level radical and have shown the variation of long time-averaged transition probability with the frequency of the laser beam.

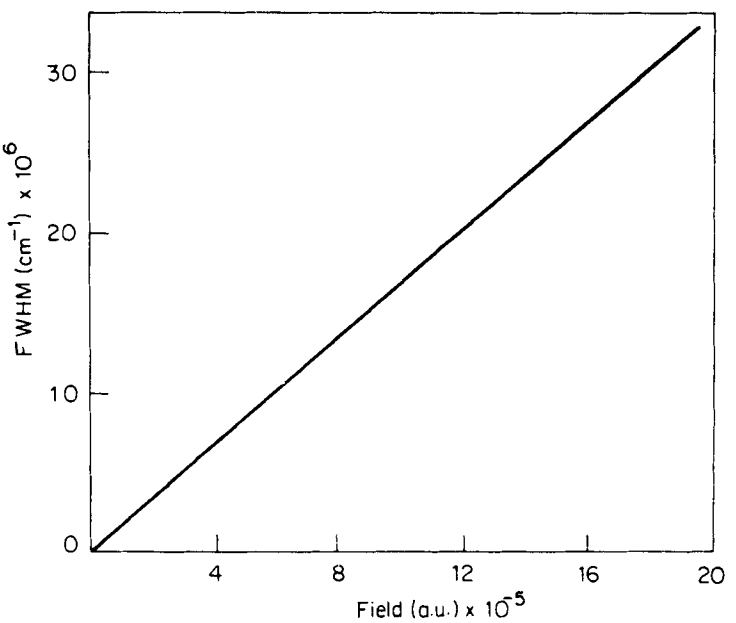

Figure 3. Power-induced resonance frequency shift vs laser intensity for $v = 0 \rightarrow v = 1$ transition.

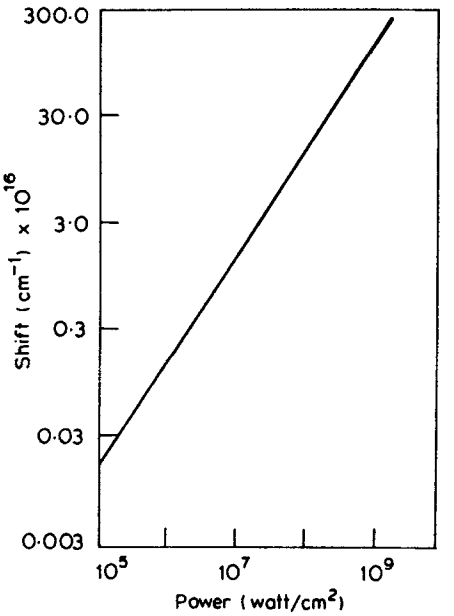

Figure 4. FWHM power-broadening vs electric field strength for $v = 0 \rightarrow v = 1$ transition.

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