Eur. Phys. J. D **21**, 293–298 (2002)
DOI: 10.1140/epjd/e2002-00223-y

**THE EUROPEAN
PHYSICAL JOURNAL D**

Role of electric field polarisation in rotational transitions

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Received 22 March 2002 / Received in final form 15 July 2002

Abstract. The molecular dynamics of polar diatomic molecule, interacting with linearly and circularly polarised laser field is studied. Non-perturbative quasi-energy technique is used to determine the rotational field surfaces. Degeneracy in different M-levels is found to be removed in the presence of circularly polarised electromagnetic radiation. In this paper, we present the calculations exhibiting the dynamics of rotational excitation of a linear molecule and characteristic features of spectra which become observable in considered fields.

PACS. 33. Molecular properties and interactions with photons

1 Introduction

The development and further improvement of high power laser technology elicits increasing interest in a theoretical description of the phenomena involved in the effect of intense electromagnetic radiation on matter. This has led to the discovery of nonlinear, non-perturbative effects such as above-threshold dissociation, collisionless multiphoton excitation and dissociation of polyatomic molecules [1–3]. The molecular dynamics with respect to the laser electric field polarisation vector can lead to an enhancement of detection signals in experiments and is useful in permitting reduced-dimension model in theoretical calculations [4]. It has been suggested as a tool to control laser induced isomerisation [5] and collisional cross-sections in study of chemical reactivity [6].

The theory of multiphoton processes can be formulated in a fully quantum-mechanical or semiclassical formalism [7]. Indeed much recent multiphoton research is couched in terms of semiclassical theory, particularly the quasi-energy approach. When laser photon energy is quite close to the transition frequency between the initial and final states of the interaction process, quasi-energy formalism [8–10] which makes use of the periodicity of applied field in time and a generalisation of the stationary states is most convenient to describe laser-molecule interaction. While, in the theoretical study of various non-resonant multiphoton processes perturbation theory proved to be a powerful method [11,12]. This quasi-energy method not only reduces the computer time on a realistic scale but also provides a simple and elegant picture of the non-perturbative treatment of resonant multiphoton absorption dynamics in intense laser fields [10,13].

The great importance of rotations for the multiphoton absorption mechanism has, however, not been overlooked. Already it has been concluded by Galbraith that "rotation cannot be treated as simple homogeneous broadening mechanism and molecule-field interactions which intrinsically couple rotation cannot be treated in casual manner". It presupposes that it is easier to turn a molecule than to stretch it. In the weak laser-field case, this approximation is based on the smallness of rotational energies as compared to vibrational. In the strong laser-field case, the approximation is based on the assumption that the typical times of molecular rotations are much shorter that the characteristic times of dissociation [14]. The problem of rotational excitation of diatomic molecule in strong laser fields depends on the peculiarities of molecular system and also on the laser radiation parameters. The effect of anharmonicity of rotational spectrum of diatomic molecule on multiphoton absorption mechanism is also studied [1]. Work demonstrating the feasibility of orienting rotationally cooled polar molecules in a uniform electric field has also come in to the limelight [15].

In this paper, we examine the effect of polarisation on the rotational transition of HF molecule in its ground electronic and lowest vibrational level ($v = 0$) in a complete dynamical treatment that will include resonant and nonresonant excitations of molecule with the use of quasi-energy method [10]. We have taken here the example of HF molecule because the most important parameter in the rotational excitation of a polar diatomic molecule is the permanent molecular dipole moment and HF molecule is one of the very few molecules for which accurate value of dipole

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moment is known [16]. We have compared the transition probabilities for rotational excitation of HF molecule in the presence of circularly polarised laser field with those for linearly polarised field.

Further, the effect of laser parameters *e.g.* intensity, frequency on rotational transitions of the molecule is also studied.

2 Theory

Let us consider quantum system of a molecule in presence of spatially homogeneous electromagnetic radiation. The target molecule is represented as rigid rotator, specified by rotational and projection quantum numbers j and m_j respectively.

The semiclassical time dependent Hamiltonian of such a molecule in the presence of laser under electric dipole approximation can be written as

$$H = H_0 + H_M^L \tag{1}$$

where H_0 is Hamiltonian of isolated molecule. Here, $H_0(\hat{r}) = H_{RR}(\hat{r})$ is the rigid rotator Hamiltonian (with spherical harmonic eigenfunctions $Y_{jm_j}(\hat{r})$ ($\hat{r} = \theta\phi$) and eigenvalues $Bj(j+1)$ where B is rotational constant. The interaction Hamiltonian between the molecule and classical field is given by

$$\begin{aligned} H_M^L &= -\mathbf{D}(\hat{r}) \cdot \mathbf{E} \\ &= -D(\hat{r}) E_0 \cos[\omega t(x + \mathrm{i}\eta y)] \end{aligned} \tag{2}$$

where $\eta = +1$ (-1) correspond to the left (right) circularly polarised light and $\eta = 0$ for linearly polarised light. $D(\hat{r})$ being the permanent molecular dipole moment, $\mathbf{E}$ is electric field propagating in the Z-axis and E_0 is the electric field amplitude. Because of considered field, the effect of electric field on molecular polarisability is not pronounced.

The time dependent Schrödinger equation for the system can be written as

$$\mathrm{i}\frac{\partial \phi(\hat{r},t)}{\partial t} = \left[H_0(\hat{r}) + H_M^L\right] \phi(\hat{r},t) \tag{3}$$

where $\phi(\hat{r},t)$ are rotational dressed states of the target molecule in the presence of classical field.

As a Hamiltonian is periodic in time with the period τ: $H(r,t+\tau) = H(r,t)$, the solution of Schrödinger equation can be written in the quasi-energy formulation as [8,17]

$$\begin{aligned} \phi_n(\hat{r}) = \sum_j \sum_{m_j=-j}^{+j} & a_{jm_j}(\lambda_n) \psi_{jm_j}(\hat{r}) \\ & \times \exp(-\mathrm{i}\lambda_n t) \exp(-\mathrm{i}j\omega t) \end{aligned} \tag{4}$$

where $a_{jm_j}(\lambda_n)$ are eigenvectors corresponding to quasi-energies (λ_n) and $\psi_{jm_j}(\hat{r})$ are molecular rotational eigenfunctions. In equation (4), for particular j summations are carried out for all values of m_j considered from $-j$ to $+j$ ($m_j = -j, -j+1, ..., +j$). Here n is running index to distinguish different solutions of the eigenvalues λ_n. We define the quasi-energy matrix in equation (5) (*see below*) by substituting equation (4) in (3). The structure of matrix is such that it follows the rotational selection rule $\Delta j = \pm 1$; $\Delta m_j = \pm 1$ for the circularly polarised field and $\Delta j = \pm 1$; $\Delta m_j = 0$ for the linearly polarised field, although weakly allowed overtone coupling $\Delta j = (\pm 2, \pm 3, \pm 4, ...)$ can also be included resulting in a dense

$$\left|\begin{array}{c|ccc|ccccc|ccccccc}
j=0 & \multicolumn{3}{c|}{j=1} & \multicolumn{5}{c|}{j=2} & \multicolumn{7}{c}{j=3} \\
\hline
E_{00} & V_{001-1} & 0 & V_{0011} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
V_{1-100} & E_{1-1} & 0 & 0 & V_{1-12-2} & 0 & V_{1-120} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & E_{10} & 0 & 0 & V_{102-1} & 0 & V_{1021} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
V_{1100} & 0 & 0 & E_{11} & 0 & 0 & V_{1120} & 0 & V_{1122} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
0 & V_{2-21-1} & 0 & 0 & E_{2-2} & 0 & 0 & 0 & 0 & V_{2-23-3} & 0 & V_{2-23-1} & 0 & 0 & 0 & 0 \\
0 & 0 & V_{2-110} & 0 & 0 & E_{2-1} & 0 & 0 & 0 & 0 & V_{2-13-2} & 0 & V_{2-130} & 0 & 0 & 0 \\
0 & V_{201-1} & 0 & V_{2011} & 0 & 0 & E_{20} & 0 & 0 & 0 & 0 & V_{203-1} & 0 & V_{2031} & 0 & 0 \\
0 & 0 & V_{2110} & & 0 & 0 & 0 & E_{21} & 0 & 0 & 0 & 0 & V_{2130} & 0 & V_{2132} & 0 \\
0 & 0 & 0 & V_{2211} & 0 & 0 & 0 & 0 & E_{22} & 0 & 0 & 0 & 0 & V_{2231} & 0 & V_{2233} \\
\hline
0 & 0 & 0 & 0 & V_{3-32-2} & 0 & 0 & 0 & 0 & E_{3-3} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & V_{3-22-1} & 0 & 0 & 0 & 0 & E_{3-2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & V_{3-12-2} & 0 & V_{3-120} & 0 & 0 & 0 & 0 & E_{3-1} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & V_{302-1} & 0 & V_{3021} & 0 & 0 & 0 & 0 & E_{30} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & V_{3120} & 0 & V_{3122} & 0 & 0 & 0 & 0 & E_{31} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & V_{3221} & 0 & 0 & 0 & 0 & 0 & 0 & E_{32} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & V_{3322} & 0 & 0 & 0 & 0 & 0 & 0 & E_{33}
\end{array}\right| = 0 \tag{5}$$

quasi-energy matrix [17]. Equation (5) provides an example for $j = 0, 1, 2, 3$ in the ground vibrational and electronic level with $m_j = -j$ to $+j$ with each j satisfying

$$V_{jm_j;j'm'_j} = \frac{-DE_0}{2}\langle jm_j|d|j'm'_j\rangle \tag{6}$$

where $d = \mathbf{e}_c \cdot \mathbf{r}$ is the interaction operator. For circularly polarised electromagnetic field it is given by

$$d = -\sqrt{\frac{4\pi}{3}}rY_{11}(\theta, \phi). \tag{7}$$

The matrix elements for the initial and the final states with the intermediate states can be separated into radial and angular parts. Integrating these matrix elements over the angular part and using the properties of 3J Wigner symbols, we have

$$V_{jm_j;j'm'_j} = -\frac{DE_0}{2}F_{jm_jj'm'_j} \tag{8}$$

where $F_{jm_jj'm'_j}$ are Herman Wall's rotational factors defined as

$$\begin{aligned}
F_{jm_jj'm'_j} &= (-1)^{2j+m_j+1}\left[\frac{(j+m_j+1)(j+m_j+2)}{2(2j+3)(2j+1)}\right]^{\frac{1}{2}}, \\
&\qquad j' = j+1;\ m'_j = m_j+1, \\
&= (-1)^{6j-4-m_j}\left[\frac{(j-m_j-1)(j-m_j)}{2(2j+1)(2j-1)}\right]^{\frac{1}{2}}, \\
&\qquad j' = j-1;\ m'_j = m_j+1, \\
&= (-1)^{4j-m_j}\left[\frac{(j-m_j+1)(j-m_j+2)}{(2j+3)2(2j+1)}\right]^{\frac{1}{2}}, \\
&\qquad j' = j+1;\ m'_j = m_j-1, \\
&= (-1)^{8j-3+m_j}\left[\frac{(j-1+m_j)(j+m_j)}{2(2j+1)(2j-1)}\right]^{\frac{1}{2}}, \\
&\qquad j' = j-1;\ m'_j = m_j-1.
\end{aligned} \tag{9}$$

The quasi-energies λ_n and the corresponding eigenvectors $a_{jm_j}(\lambda_n)$ are calculated by diagonalizing the quasi-energy matrix (Eq. (5)) by using standard diagonalization method. Once the eigenvectors and corresponding eigenvalues λ_n are found, the transition probability from initial rotational state $|j\, m_j\rangle$ to final state $|j'\, m'_j\rangle$ is given by

$$P_{jm_j\to j'm'_j} = \left|a_{jm_j}\, a_{j'm'_j}\right|^2. \tag{10}$$

3 Results and discussion

Under most experimental conditions (*i.e.* at or below room temperature) the molecules are populated only among the rotational states of the ground vibrational state. Also studies of the dynamics of transitions envolved from various j states are essential to many spectroscopic investigations.

Here, we have studied the laser-assisted rotational excitation of the HF molecule initially prepared in a specific $|v = 0, j = 0, m_j = 0\rangle$ state. The quasi-energy states of the HF molecule are calculated as described in Section 2. The rotational excitation of polar molecule by linearly and circularly polarised light is influenced greatly by the dipole moment of the molecule, fortunately HF is an example where an accurate dipole moment plus reliable molecular parameters are available. Although we have investigated results of the lowest five rotational states ($j = 0{-}4$) and all $m_j = -j$ to $+j$ in vibrational and electronic ground state of the HF molecule but in actual calculations we have taken lowest fifteen rotation levels.

In Figure 1 we have shown the variation of transition probability $P_{0\to1}$ for the transition from $|j = 0, m_j = 0\rangle$ to $|j = 1, m_j = 1\rangle$ with laser frequency ω (in eV) at laser intensities I (in W/cm^2) namely $I = 10^7$ W/cm^2 (series 1) and $I = 10^9$ W/cm^2 (series 2). It is clearly seen that probability (series 1) rises quite sharply around the frequency $\omega = 0.004$ eV and reaches an extremum value near $\omega = 0.0051$ eV as there exists one-photon resonance between $j = 0$ and $j = 1$ levels for $\omega = 0.005$ eV. At higher intensity (series 2) probability increases quite steadily from $\omega = 0.0047$ eV where it has an extremum value. However with further increase in frequency the probability $P_{0\to1}$ decreases. Shifting of resonance with increase of laser power by 10^2 W/cm^2 is clear indication of dynamic Stark shift which increases with increasing intensity of the laser beam. Further, the full width half maxima ($FWHM$) increases as intensity increases as $FWHM \propto I^{1/2}$. Which indicates that the line broadening is very pronounced for HF molecule and increases with increase in intensity.

Figure 2 demonstrates the variation of transition probability for the transition from $j = 0$ level to $j = 1$ level as a function of frequency ω (in eV). We have shown this variation at intensity $I = 10^8$ W/cm^2. Series 1 is for circularly polarised and series 2 is for linearly polarised electromagnetic fields. Both the curves have maximum value at $\omega = 0.005$ eV corresponding to one photon resonance between $j = 0$ and $j = 1$ levels. In case of circularly polarised radiation, in accordance with the selection rule discussed in Section 2 a large number of channels get open up resulting in more number of transitions as compared to linearly polarised case. This is basic reason of steadily increase in probability as frequency increases in above case. Due to more allowed transitions, the probability transfer to $j = 1$ level is less in case of circularly polarised light.

For a given geometry the onset of non-perturbative effects depends on laser intensity I. Increasing the laser intensity, the quasi-energy level splitting also increases. Figures 3 and 4 report the values of 25 quasi-energies corresponding to lowest five rotational states as a function

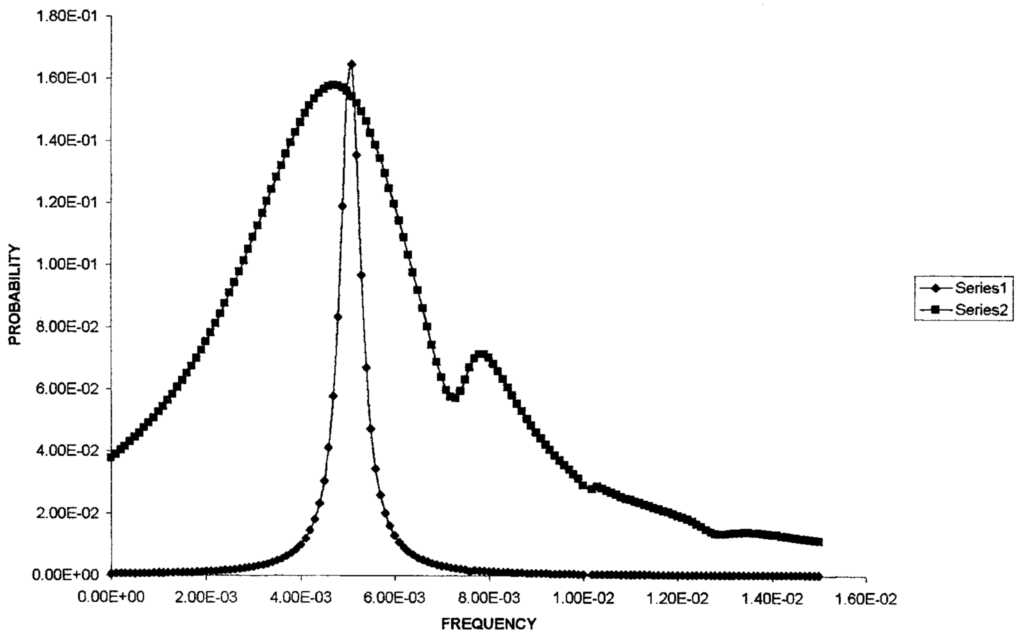

Fig. 1. Variation of transition probability $P_{0\to 1}$ as a function of laser frequency for circularly polarised field at: (a) intensity $I = 10^7$ W/cm^2 (series 1), (b) intensity $I = 10^9$ W/cm^2 (series 2).

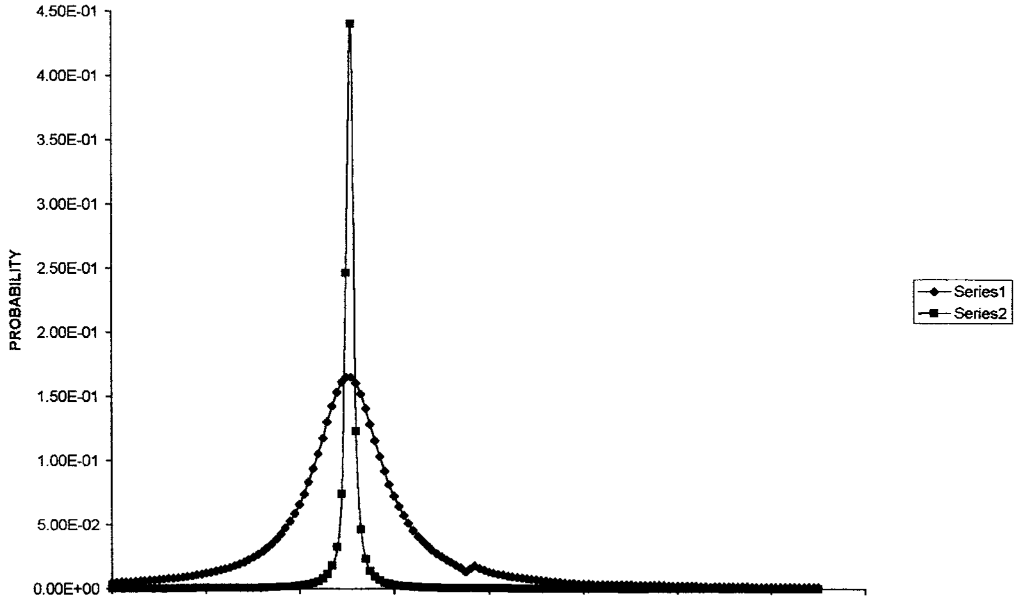

Fig. 2. Variation of transition probability $P_{0\to 1}$ as a function of laser frequency at intensity $I = 10^8$ W/cm^2, (a) for circularly polarised field (series 1), (b) for linearly polarised field (series 2).

of laser intensity at one photon near resonance frequency $\omega = 0.00507$ eV for the circularly polarised laser field and linearly polarised laser field respectively. In both the cases, splitting of levels is observed but in case of circularly polarised electromagnetic field the splitting appears to be more prominent. Thus degeneracy over projection quantum number m_j is removed in presence of both circularly and linearly polarised field but order of degeneracy removal is different.

Much information can be obtained from the plot of the eigenvalues of the Hamiltonian. The main feature of the quasi-energy plot is illustrated in Figure 5. In this figure quasi-energies λ's are plotted as a function of the frequency for the circularly polarised field. It is noticed that resonance occurs whenever the quasi-energy curves for two eigenvalues approach each other closely (or crossed). Although we have presented in figures (Figs. 3–5) 25 series

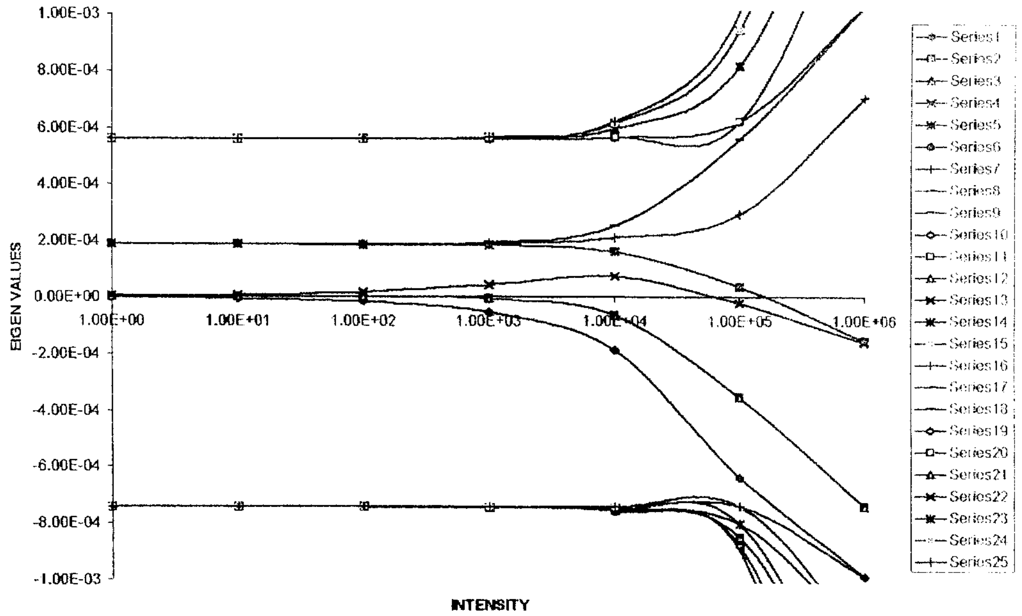

Fig. 3. Variation of eigenvalues with intensity at one-photon resonance frequency $\omega = 0.00507$ eV for circularly polarised field.

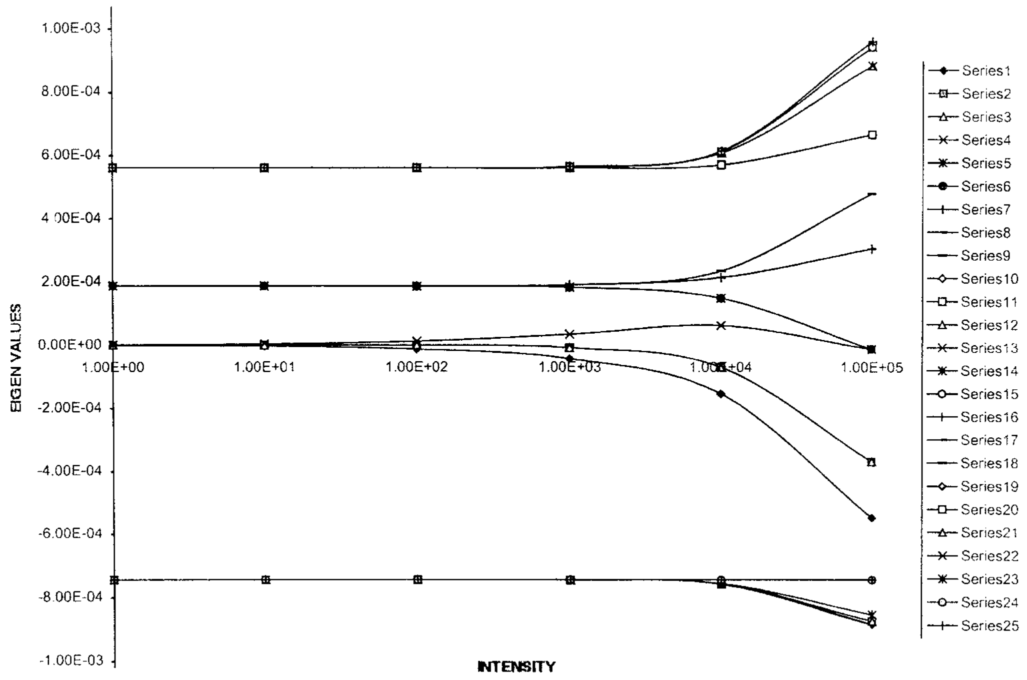

Fig. 4. Variation of eigenvalues with intensity at one-photon resonance frequency $\omega = 0.00507$ eV for linearly polarised field.

but only few noticed. Rest of the series are overlapping on the shown series.

4 Conclusion

We have discussed here the dynamics of rotational excitation of HF molecule in presence of electromagnetic radiation having linear and circular polarisation nature. We have used the recently developed non-perturbative quasi-energy technique to describe the laser-molecule interaction. The advantage of the non-perturbative treatment is that the interaction can be taken to all orders. Further the quasi-energy method saves the bulk of the computer time for the non-perturbative description of laser-molecule interaction. Further work in the area of laser-assisted collisional processes is in progress using this quasi-energy technique. The results are expected to be published soon.

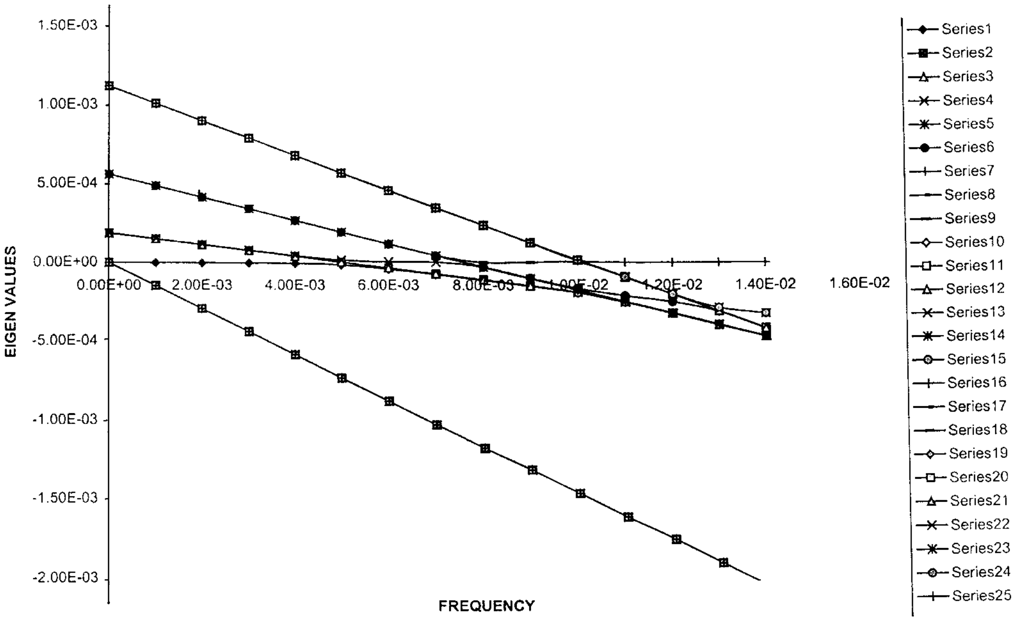

Fig. 5. Variation of eigenvalues with frequency at intensity $I = 10^8$ W/cm^2 for circularly polarised field.

One of us (NS) is thankful to Council of Scientific Industrial Research (CSIR) India, for financial support in form of a Research fellowship and MM is thankful to DST, UGC for financial help.

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