

Selective excitation of vibrational modes of polyatomic molecule

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Abstract. Mode-selective dynamics of triatomic molecule in the electronic ground state under continuous wave laser pulse is investigated for the discrete vibrational bound states. A non-perturbative approach has been used to analyse the vibrational couplings and dynamics of the molecule.

Keywords. Polyatomic molecule; quasienergy; vibrational coupling.

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1. Introduction

Selective excitation and dissociation of molecules by laser radiation is a subject of considerable interest in recent years [1,2]. It may be useful for subsequent selective chemical reactions, laser-induced dissociation, control of molecular collisions, investigation of energy redistribution in inter and intramolecular processes and spectroscopic studies [3–5]. Selective steering of a molecule to a specified target may result in various types of intramolecular selectivity including isotope selectivity [1], mode selectivity [6], state selectivity [7], laser-controlled isomerisation [8] and related isotope separation.

In the present work, we have extended the study from the simpler linear ABA model system to the somewhat more realistic non-linear, non-bending, non-rotating HOD system. As there are a number of efficient numerical schemes [9,10] with varying degrees of freedom to solve the equations of motion for the simulation of various physical processes, we have used non-perturbative approach for laser-molecule interaction. Here we have investigated the mode-selective excitation and dissociation of selected bonds in HOD molecule using continuous wave laser. Although, there have been some theoretical results on multiphoton excitation of polyatomic molecules [11], all these studies are limited to a few modes whereas in our model

one can generalise it to any number of levels. An important point is that the study of excitations of vibrational mode from any level of interest to a selected level is possible.

In the next section, we have described briefly the computational approach and the formalism used in the solution of time-dependent Schrödinger equation which proved to offer many interesting results discussed in §3 and has given a good insight into the complex multistage excitation process in polyatomic molecules. Finally in §4, the mode-selective vibrational dynamics of the triatomic molecule has been analysed.

2. Theory

We consider the vibrational motion of a triatomic molecule in the presence of a single-mode laser beam defined by

$$\vec{E}(t) = \vec{E}_0 \cos \omega t,$$

where E_0 and ω are respectively the amplitude and frequency of the laser beam. Here we have taken the example of HOD molecule. The molecular vibrations of the HOD system are defined in coordinates such that r_{OH} is the OH bond length, r_{OD} is the OD bond length and θ is the bond angle between the two bonds OH and OD (figure 1).

The Hamiltonian of a molecule interacting with a coherent, x -polarised monochromatic laser field can be written as

$$H(t) = H_{\text{mol}} + H_{\text{int}}, \quad (1)$$

where H_{mol} is the triatomic vibrational Hamiltonian. The coupled vibrational stretches of the molecule are represented by molecular Hamiltonian

$$H_{\text{mol}} = H_{\text{OH}} + H_{\text{OD}} + H_{\text{OH,OD}} + D_0, \quad (2)$$

where H_{OH} and H_{OD} are Hamiltonians of isolated OH and OD bonds respectively. $H_{\text{OH,OD}}$ is the coupled Hamiltonian of both OH and OD bonds defined as

$$H_{\text{OH,OD}} = \frac{P_{\text{OH}} P_{\text{OD}} \cos \theta}{M_0}, \quad (3)$$

with $P_{\text{OH}}, P_{\text{OD}}$ are the associated conjugate moments, M_0 is the mass of O atom and D_0 is the potential depth for the molecule (here taken as 0.1994 Hartree).

The Schrödinger equation for the vibrational motion of the considered system in the absence of any perturbation can be written as

$$H_{\text{mol}}|\psi_v\rangle = E_v|\psi_v\rangle. \quad (4)$$

Equation (4) yields eigenenergies E_n and the corresponding wavefunctions ψ of the vibrational stretch modes. The $v (= m, n)$ corresponds to m quanta of OH and n quanta of OD vibrational modes [12]. For the local OH mode $m > 0, n = 0$ and for local OD mode $m = 0, n > 0$ but $m = n$ for symmetric modes.

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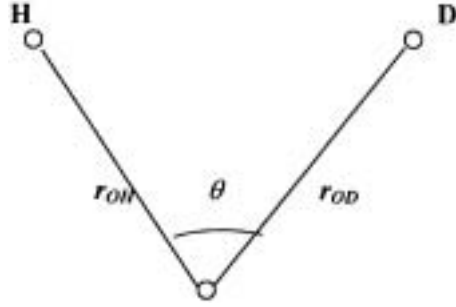


Figure 1. Model of HOD molecule.

The wave function ψ_v can be expanded as

$$|\psi_v\rangle = \sum_{k_{\text{OH}}l_{\text{OD}}} C_{k_{\text{OH}}l_{\text{OD}}} |k_{\text{OH}}\rangle |l_{\text{OD}}\rangle \quad (5)$$

with k_{OH} and l_{OD} satisfying the basic Schrödinger equation

$$H_{\text{OH}}|k_{\text{OH}}\rangle = E_{k_{\text{OH}}}|k_{\text{OH}}\rangle, \quad H_{\text{OD}}|l_{\text{OD}}\rangle = E_{l_{\text{OD}}}|l_{\text{OD}}\rangle. \quad (6)$$

Substituting eqs (2), (3) and (5) in eq. (4) and on multiplying the resulting equation by $\langle l'_{\text{OD}}| \langle k'_{\text{OH}}|$ and using equation (6), we get

$$\begin{aligned} & [C_{k_{\text{OH}}l_{\text{OD}}} E_{k_{\text{OH}}} + C_{k_{\text{OH}}l_{\text{OD}}} E_{l_{\text{OD}}} + D_0 C_{k_{\text{OH}}l_{\text{OD}}}] \delta_{k_{\text{OH}}k'_{\text{OH}}} \delta_{l_{\text{OD}}l'_{\text{OD}}} \\ & + \frac{\cos \theta}{M_0} \sum_{k_{\text{OH}}l_{\text{OD}}} C_{k_{\text{OH}}l_{\text{OD}}} \langle k'_{\text{OH}}| P_{\text{OH}} |k_{\text{OH}}\rangle \langle l'_{\text{OD}}| P_{\text{OD}} |l_{\text{OD}}\rangle \\ & = \sum_{k_{\text{OH}}l_{\text{OD}}} \langle l'_{\text{OD}}| \langle k'_{\text{OH}}| E_v |k_{\text{OH}}\rangle |l_{\text{OD}}\rangle C_{k_{\text{OH}}l_{\text{OD}}}. \end{aligned} \quad (7)$$

Using the Morse oscillator wavefunctions we have evaluated the coupling matrix. The diagonalisation of the molecular Hamiltonian yields eigenenergies for various modes of the triatomic molecule.

Now, consider the case of interaction of the molecule with continuous wave (CW) laser field having angular frequency ω , linearly polarised with real polarisation vector $\vec{\varepsilon}_0$ and that the dipole approximation is valid. In this case, the time-dependent Schrödinger equation can be written as

$$i \frac{\partial \psi(t)}{\partial t} = H(t) \psi(t), \quad (8)$$

where $H(t)$ is defined by eq. (1), H_{mol} is defined by eq. (2) and H_{int} is the interaction of laser beam with the molecule defined as

$$\begin{aligned} H_{\text{int}} &= -\vec{\mu}(r_{\text{OH}}, r_{\text{OD}}) \cdot \vec{\varepsilon}_0 E(t), \\ H_{\text{int}} &= -\mu(r_{\text{OH}}, r_{\text{OD}}) E(t) \cos \omega t \cos \phi, \\ E(t) &= E_0 \cos \omega t, \end{aligned} \quad (9)$$

with

$$\mu(r_{\text{OH}}, r_{\text{OD}}) = r_{\text{OH}}\mu_{\text{OH}}^*e^{-r_{\text{OH}}/r^*} + r_{\text{OH}}\mu_{\text{OD}}^*e^{-r_{\text{OD}}/r^*}. \quad (10)$$

μ_{OH}^* , μ_{OD}^* are permanent dipole moments per unit distance of OH and OD bond respectively, r^* is the parameter constant for a given molecule [13], E_0 is the electric field strength amplitude of explicitly laser field and ϕ is the angle between the bonds and direction of the x -polarised electric field, perpendicular to molecular axis. It is a well-established fact that a molecule situated in the radiation field is characterised by a set of quasi-energy states. The solution of eq. (8) can be written in quasi-energy formalism as [14]

$$\phi_m = e^{-i\lambda_m t} \sum_{kl} a_{kl}^m |k\rangle |l\rangle e^{-i[E_{kl} - (k+l)\omega]t}, \quad (11)$$

where a_{kl}^m 's are eigenvectors and λ_m 's are defined as quasi-energies. $|k\rangle$ and $|l\rangle$ are molecular eigenfunctions in the absence of laser fields. Substituting eq. (11) in (8) and using orthogonality conditions along with rotating wave approximation ((RWA), i.e., neglecting highly oscillating terms and we have made use of the fact that energy levels with nearly the same energies are considered degenerate), we get a set of coupled differential equations [15]. These coupled differential equations give rise to quasi-energy matrix defined as

$$\begin{bmatrix} E_{00} & V_{0001} & V_{0010} & V_{0101} & \cdots \\ V_{0100} & E_{01} - E_{00} - \omega & V_{0110} & V_{0111} & \cdots \\ V_{1000} & V_{1001} & E_{10} - E_{00} - \omega & V_{1011} & \cdots \\ V_{1100} & V_{1101} & V_{1110} & E_{11} - E_{00} - 2\omega & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix} = 0. \quad (12)$$

In this equation we have

$$V_{mnkl} = -\frac{E_0}{2} \cos \phi \langle m | \langle n | \mu | k \rangle | l \rangle \quad (13)$$

is the off-diagonal vibrational dipole coupling.

The quasi-energies ψ_m and corresponding eigenvectors a_{kl}^m are calculated by diagonalising the quasienergy matrix (12) by using a standard diagonalisation method.

Most experimental interest relates to studies at or below room temperature where molecules are populated only among the lowest symmetric mode (here $m = 0, n = 0$) and studies of the dynamics of the transitions evolved from ground symmetric state are essential to much spectroscopic information. The transition probability from initial state $I(|m = 0\rangle |n = 0\rangle)$ to final state $f(kl)$ can be computed from the eigenvectors of quasi-energy matrix as

$$P_{mn \rightarrow kl} = \sum_i |a_{mn}(\lambda_i) a_{kl}(\lambda_i)|^2. \quad (14)$$

In the next section we discuss the results of spectra of the molecule.

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Table 1. Constants for OH and OD bonds (in electronic ground state).

Bonds	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	D_e (cm ⁻¹)
OH	1.8597	3735.21	82.81	18.871	4.35
OD	1.8584	2720.9	44.2	10.09	4.39

3. Results and discussion

The purpose of this paper is to investigate multiphoton excitation of symmetric, local modes as well as other modes of a HOD molecule. The quasi-energies and the corresponding eigenvectors are calculated as described in §2. In constructing the quasi-energy matrix we require the vibrational dipole matrix elements between different modes of the molecule. These have been calculated numerically. The spectroscopic constants for OH and OD bonds are listed in table 1. For all calculations the atomic masses taken are $M_H = 1.008$ a.m.u., $M_O = 16.00$ a.m.u., $M_D = 2.014$ a.m.u.

In this paper we have studied the excitation to different modes from ground symmetric mode (i.e. $m = 0, n = 0$) although excitations from modes other than ground symmetric mode can also be studied. As can be seen, the quasi-energy matrix is a function of laser intensity and frequency, we have studied the effect

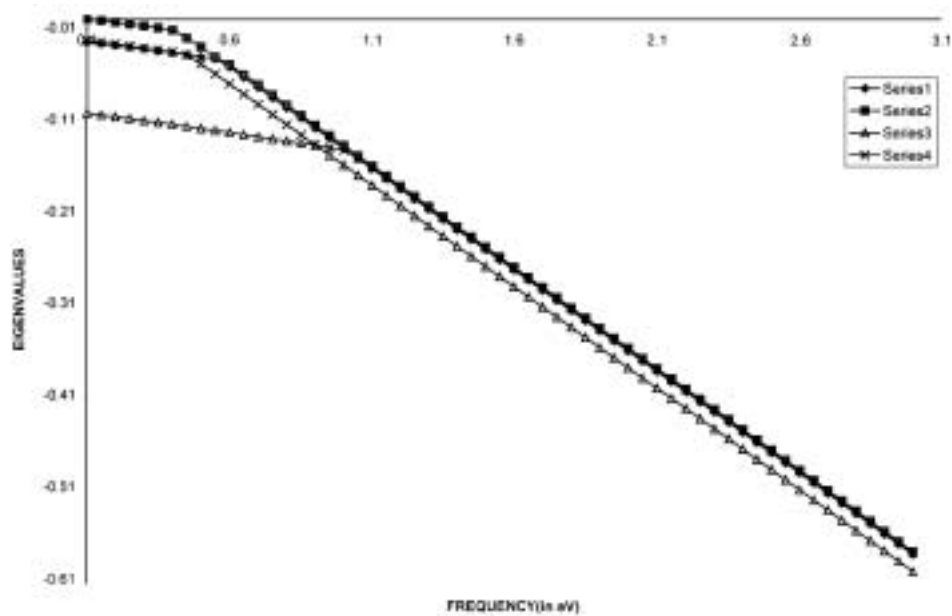


Figure 2. Variation of two eigenvalues as a function of frequency at intensity $I = 10^8$ W/cm² (Series 1, Series 2) and at intensity $I = 10^{12}$ W/cm² (Series 3, Series 4) respectively.

of these parameters on mode-selective excitation processes. In figure 2, we have presented variation of two lowest eigenvalues at intensity $I = 10^8 \text{ W/cm}^2$ (Series 1, Series 2) and at intensity $I = 10^{12} \text{ W/cm}^2$ (Series 3, Series 4) respectively as a function of laser frequency (in eV). Although we can present variation of all 23 eigenvalues, here only two eigenvalue variations are presented so that they are clearly observable. In figure 2 all eigenstates at lower frequencies are approximately separable and hence during excitation process dephasing occurs due to coupling of various vibrational modes.

As described in §2 we have used quasi-energy formulation where dressed states are a combination of eigenvectors a 's which are functions of laser parameters. As laser frequency reaches to a particular resonance frequency, the eigenvector for that particular dressed state is quite large as compared to other states (e.g. if $\omega \rightarrow E_{10} - E_{00}$, where E_{kl} 's are bare state energies, then ϕ_1 (first dressed state) contains more of second bare state as compared to first bare state). So, near resonance frequency the levels change their characters as observed in figure 2 at a frequency of 0.5 eV [16]. At lower intensity, coupling is not very strong and hence the separation of eigenvalues is not more at higher frequencies. But at higher intensity, the coupling is more and separation of eigenvalues is also clearly observable.

In figure 3, we have presented the variation of transition probabilities for various transitions with laser frequency at intensity $I = 10^8 \text{ W/cm}^2$ of the molecule. In this figure, the laser pulse amplitude is fixed to the optimal value while the laser frequency is varied in a certain domain so as to obtain the maximum final population

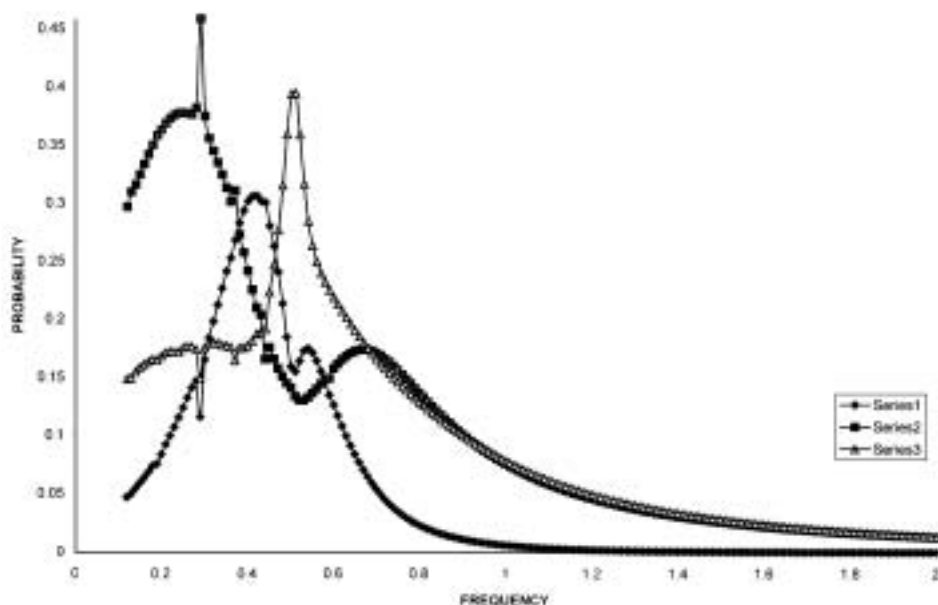


Figure 3. Variation of transition probabilities of first symmetric (i.e. $m = 1, n = 1$) (Series 1), first local OH (i.e. $m = 1, n = 0$) (Series 2), and first local OD (i.e. $m = 0, n = 1$) (Series 3) mode of the molecule as a function of laser frequency at intensity $I = 10^8 \text{ W/cm}^2$.

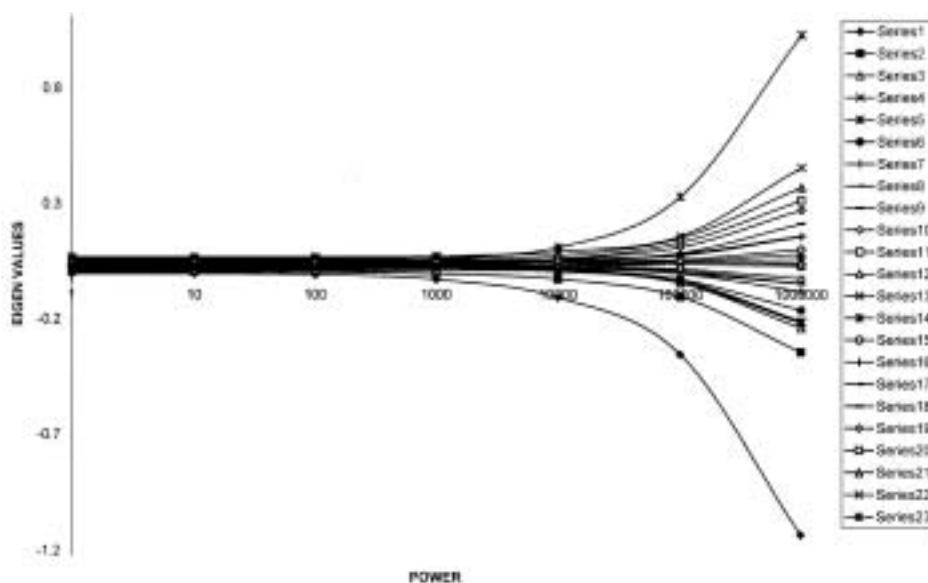


Figure 4. Variation of lowest 23 eigenvalues of the molecule as a function of intensity at frequency $\omega = 0.117$ eV.

P of target levels of different modes. Here, Series 1 represents symmetric modes ($m = 0, n = 0$), Series 2 local OH modes ($m > 0, n = 0$) and Series 3 local OD modes ($m = 0, n > 0$). It is clear that excitation of local OH mode during the pulse dominates the excitation of all other modes. This indicates the dominant role of $m > 0, n = 0$ mode excitation and very weak competition of any side transitions. The probability of every mode is maximum near the resonance frequency of each corresponding mode. From the plot it can be seen that at 0.3 eV frequency there is a fall in the probability of symmetric mode and local OD mode due to the maximum population transfer to local OH mode. Similarly probability of local OD mode increases with increase in frequency and have the maximum value at 0.5 eV, but at this frequency the probability of symmetric and local OH modes are minimum due to the maximum coupling of local OD modes of vibrational levels. Thus multiphoton excitation is almost completely mode-selective as specified local mode acquire substantial population during the excitation process at the expense of decreasing population of other modes.

Figure 4 illustrates the variation of 23 calculated eigenvalues (in a.u.) as a function of field strength (W/cm^2) at frequency $\omega = 0.117$ eV of HOD molecule. We have presented all 23 eigenvalues in figure 4 (Series 1–23). At lower intensity most of the series are overlapping but with increase in intensity, eigenvalues get non-degenerate and are clearly observable. This is due to the change in couplings between different vibrational levels with increase in intensity.

In figure 5, we have presented the population of symmetric (Series 1), local OH (Series 2), local OD (Series 3) and ground (Series 4) modes as a function of laser beam intensity at frequency $\omega = 0.117$ eV. At very low intensities, most of the population remains in the ground state (Series 4) of the molecule. With increase

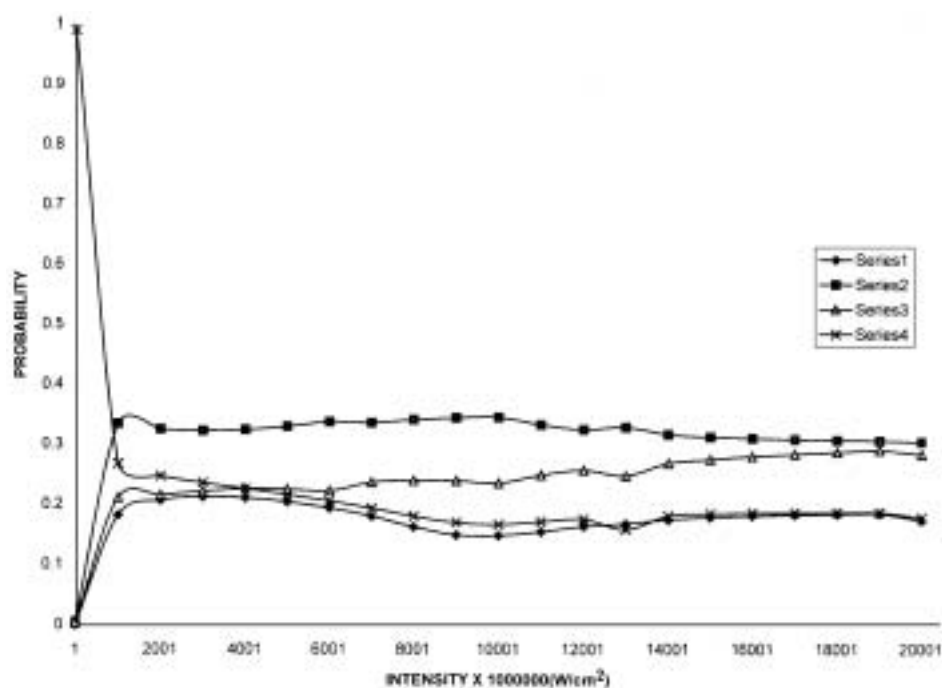


Figure 5. Variation of transition probabilities of first symmetric (Series 1), first local OH (Series 2), first local OD (Series 3) and ground state (Series 4) of the molecule as a function of laser intensity at frequency $\omega = 0.117$ eV.

in intensity, population transfer of local OH, local OD and symmetric modes also increases gradually because of the different order of couplings between different vibrational levels. This shows that laser field is also one of the parameter to control the mode-selective excitation of vibrational levels of triatomic molecule.

4. Conclusion

We have discussed here the dynamics of vibrational excitation of a model triatomic molecule from ground symmetric state in the presence of a CW laser beam. We have used the recently developed non-perturbative quasi-energy technique to describe the laser-molecule interaction. This 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.

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References

- [1] D W Lupo and M Quack, *Chem. Rev.* **87**, 181 (1987)
- [2] P Brumer and M Shapiro, *Ann. Rev. Phys. Chem.* **43**, 257 (1992)
- [3] Y Ohtsuki, K Nakagami, Y Fujimura, W Zhu and H Rabitz, *J. Chem. Phys.* **114**, 8867 (2001)
- [4] A Abrashkevich, M Shapiro and P Brumer, *Phys. Rev. Lett.* **81**, 3789 (1998); Erratum: *Phys. Rev. Lett.* **82**, 3002 (1999)
- [5] R A Smith, J W G Tisch, T Ditmire, E Springate, N Hay, M B Mason, E T Gumbrell, A J Cornley, L C Mountford, J P Marangos and M H R Hutchinson, *Phys. Scr.* **80**, 35 (1999)
- [6] C D Schwieters and H Rabitz, *Phys. Rev.* **A44**, 5224 (1991)
- [7] B W Shore, K Bergmann, A Kuhn, S Schiemann, J Oreg and J H Eberly, *Phys. Rev.* **A45**, 5297 (1992)
- [8] J Combariza, B Just, J Manz and G K Paramonov, *J. Phys. Chem.* **95**, 10351 (1991)
- [9] A Vijay, R E Wyatt and G D Billing, *J. Chem. Phys.* **111**, 10794 (1999)
- [10] G Barinova, N Markovic and G Nyman, *J. Chem. Phys.* **111**, 6705 (1999)
- [11] J R Bochinski, C C Yu, T Rofthus and T W Honbeg, *Phys. Rev.* **A63**, 051402-1 (2001)
- [12] G Hose and H S Taylor, *Phys. Rev. Lett.* **51**, 947 (1983)
- [13] R T Lawton and M S Child, *Mol. Phys.* **40**, 773 (1980)
- [14] J H Shirley, *Phys. Rev.* **B138**, 979 (1965)
- [15] N Singhal, V Prasad and M Mohan, *Euro. Phys. J.* **D21**, 293 (2002)
- [16] D I Duncan, J G Story and T F Gallagher, *Phys. Rev.* **A52**, 2209 (1995)