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Harmonic generation in molecular systems: Application to H_2^+ in intense laser fields

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Abstract. A combination of Floquet theory and the complex coordinate method is used to establish a compact time independent expression for the generation of harmonics by a diatomic molecule. Only the nuclear motion is considered as a source for the spectra. In the assumption that a single Floquet state describes the system, only odd harmonics are obtained. An application to H_2^+ is presented. Correlation between the multiphoton nature of the absorption process and the appearance of higher harmonics is observed.

1. Introduction

The possibility of creating coherent ultra-high frequency radiation without enormous technical equipment has been the subject of a decades-long quest. Production and investigation of fusion plasmas, biological structures and solid surface characterizations are only several examples of the use of high frequency lasers [1]. The efficient generation of very high harmonics has been proposed as one possible orientation of current and near future research, aiming at the activation of mechanisms leading to coherent light of very high frequency (reaching even the x-ray band of the spectrum) [2].

In recent experiments on atomic gases, harmonic generation (HG) spectra with high harmonics have been registered [3, 4]. This feature, revealed in the presence of intense laser fields only, is accompanied by a plateau in the HG spectra, followed by a cutoff at a harmonic of high order [4]. An explanation for the occurrence of these effects in ionizing systems has recently been proposed by Kulander and coworkers in terms of one-electron processes [5]. These processes are closely correlated to the heavy mixing of the multitude of photon continua into which the system ionizes, and which takes place at high laser intensities. At such intensities, other non-standard effects are also observed, such as the so-called above-threshold ionization (ATI) [6, 7]. Numerical experiments and computer simulations on model systems confirm the experimental findings [8–12]. In all those cases, only odd harmonics were observed [13], however, as a consequence of the symmetry properties of the potential only [14], to remain invariant under reflection of the coordinate followed by translation in time by half a period of the field [15].

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Contrary to the harmonic generation in atomic systems, not much experimental research has up to date been invested on molecules able to uncover analogous properties. Since the atomic high harmonic generation spectrum is accomplished through the ATI phenomenon, one may expect that for molecules for which ATD (above-threshold dissociation) [16–19] is obtained, an efficient generation of high molecular harmonics would be obtained as well. Theoretical investigations on the harmonic spectra of molecules up to high order have recently been carried out by Bandrauk and coworkers, implemented by full time-dependent propagation and including also the rotational coupling. Effects analogous to those of the atomic spectra were observed there, while, in addition, the existence of two plateaux was observed [20, 21]. Parity selection in harmonic spectra has been first obtained theoretically in molecules by Hammerich, Kosloff and Ratner [22].

In this paper the probability for the system to spontaneously emit a certain frequency is given by a time-dependent analytic expression developed in section 2, whose application requires only matrix elements of the dipole moment operator with the diabatic photon channel components of the quasi-energy (QE) resonance wavefunction. Its derivation is based on Fourier transform of the expectation value of the dipole operator by means of a single quasi-energy resonance wavefunction. This way to extract harmonic spectra is an approximation, based on a decorrelation in the formally correct (but more complicated) expression where the dipole autocorrelation function is explicitly treated [23]. Although this approximation has been extensively used in the literature, its justification was attempted only lately [24].

Our strategy is as follows. In section 2 we prove that only odd harmonics are obtained provided that:

(1) The time periodic field is monochromatic. It implies that the envelope of the laser pulse is broad enough to support several tens of optical cycles.

(2) The initial bound state (i.e. eigenfunction of the field free Hamiltonian for the ground-electronic state) is associated with a single resonance QE state. This is the case when the laser is turned on sufficiently slowly or after a time long enough to ensure that the only surviving QE state will be the longest living resonance state. The observation of even harmonics would imply the violation of at least one of these two conditions.

The key point in our derivation is the combination of complex scaling and Floquet theory which allows for a derivation of the HG spectrum from a single square-integrable complex-scaled quasi-energy solution. The proof that only odd harmonics are obtained is similar to that given in the one-potential surface model Hamiltonian [15]. It is based on the properties of the wavefunction under inversion of all coordinates (electronic and nuclear), i.e. parity.

In section 3 as an illustrative numerical example we study the HG spectrum of H_2^+ using the formula derived in section 2. As the field intensity increases a clear relative enhancement of the higher harmonics is obtained.

2. Theory

Let us consider a photodissociating diatomic system described by two electronic states of Σ symmetry, $\langle r, R|\psi_i^{\text{elec}}\rangle = \psi_i^{\text{elec}}(r, R)(i=1, 2)$, coupled via the dipole moment operator μ, where R and r stand for the nuclear and electronic degrees of freedom,

respectively. The dipole moment operator is given by

$$\hat{\boldsymbol{\mu}} = \boldsymbol{\mu}_{11}(R)\,|\psi_1^{\text{elec}}\rangle\langle\psi_1^{\text{elec}}| + \boldsymbol{\mu}_{12}(R)\,|\psi_1^{\text{elec}}\rangle\langle\psi_2^{\text{elec}}| + \boldsymbol{\mu}_{12}^*(R)\,|\psi_2^{\text{elec}}\rangle\langle\psi_1^{\text{elec}}| + \boldsymbol{\mu}_{22}(R)\,|\psi_2^{\text{elec}}\rangle\langle\psi_2^{\text{elec}}| \tag{1}$$

where

$$\boldsymbol{\mu}_{ij}(R) = \langle\psi_i^{\text{elec}}|\,e\boldsymbol{r}\,|\psi_j^{\text{elec}}\rangle_{\boldsymbol{r}} \qquad i,j = 1,2 \tag{2}$$

where $\boldsymbol{r}$ is the position vector of the optical electron in a molecular system of axes. The subscript $\boldsymbol{r}$ denotes integration over the electronic degrees of freedom. All vectors $\boldsymbol{\mu}_{ij}(R)$ are aligned with the internuclear axis. $|\psi_i^{\text{elec}}\rangle$ are the eigenvectors of the electronic Hamiltonian operator;

$$\hat{H}^{\text{elec}}(\boldsymbol{r}, R)\,|\psi_i^{\text{elec}}\rangle = U_i(R)\,|\psi_i^{\text{elec}}\rangle, \qquad i = 1, 2. \tag{3}$$

The electromagnetic field is assumed to be linearly polarized along the laboratory z-axis. The molecule-plus-field time-dependent Hamiltonian matrix is given by:

$$H(\boldsymbol{R}, t) = H_0(\boldsymbol{R}) - \mu(R)\cos\theta E_0(t)\cos\omega t \tag{4}$$

θ is the angle between the internuclear axis and the laboratory z-axis, $E_0(t)$ an envelope function for the pulse and ω the laser carrier wave frequency. H_0 is the free molecule nuclear Hamiltonian

$$H_0(\boldsymbol{R}) = T(\boldsymbol{R}) + V(R) \tag{5}$$

with

$$V(R) = \begin{pmatrix} U_1(R) & 0 \\ 0 & U_2(R) \end{pmatrix} \tag{6}$$

$\mu(R)$ is the matrix of the norms of the vectors defined in equation (2).

$$\mu(R) = \begin{pmatrix} \mu_{11}(R) & \mu_{12}(R) \\ \mu_{12}^*(12) & \mu_{22}(R) \end{pmatrix}. \tag{7}$$

For a homonuclear diatomic ion such as H_2^+ the matrix $\mu(R)$ has only off-diagonal elements with $\mu_{12}(R)$ a real function which diverges with increasing R [17]. The state vector of the system evolves in time as:

$$|\psi(t)\rangle = \Phi_1(\boldsymbol{R}, t)\,|\psi_1^{\text{elec}}\rangle + \Phi_2(\boldsymbol{R}, t)\,|\psi_2^{\text{elec}}\rangle. \tag{8}$$

We assume that the free molecular state which correlates with the molecule-plus-field state of interest (see below for the conditions for such a correlation) is the ground state of electronic wavefunction ψ_1^{elec} and rovibrational quantum numbers $J=0$, $v=0$. The selection rule for an electronic $\Sigma_u \leftarrow \Sigma_g$ transition being $\Delta J = \pm 1$, only the electronically excited state of wavefunction $|\psi_2^{\text{elec}}\rangle$ and $J=1$ is radiatively coupled with the ground state. There is no selection rule for vibrational motion. We assume that the electronically excited state is dissociative. We restrict our treatment to these two rotational quantum numbers. The conclusion to be given below that only odd harmonics are to be found in the HG spectra is not affected by the inclusion of channels with higher rotational quantum numbers. This is the consequence of the matrix elements of the electron-dipole

operator: they are non-zero only when the two molecular wavefunctions are of opposite parity.

The vector $\mathbf{\Phi}(\boldsymbol{R}, t)$ is thus:

$$\mathbf{\Phi}(\boldsymbol{R}, t)=\begin{pmatrix} \Psi_1(R, t)\, Y_{00}(\hat{R}) \\ \Psi_2(R, t)\, Y_{10}(\hat{R}) \end{pmatrix}. \tag{9}$$

$\hat{R}$ denotes the two angles θ and φ fixing the orientation of the internuclear axis in the laboratory frame. The vector $\mathbf{\Phi}(\boldsymbol{R}, t)$ satisfies the time-dependent Schrödinger equation in matrix form:

$$H(\boldsymbol{R}, t)\mathbf{\Phi}(\boldsymbol{R}, t)=\mathrm{i}\hbar\frac{\partial\mathbf{\Phi}(\boldsymbol{R}, t)}{\partial t}. \tag{10}$$

The time-dependent dipole moment amplitude is defined as

$$d(t)=\langle\mathbf{\Phi}(\boldsymbol{R}, t)\,|\,\mu(R)\cos\theta\,|\,\mathbf{\Phi}(\boldsymbol{R}, t)\rangle_{\boldsymbol{R}}. \tag{11}$$

The subscript $\boldsymbol{R}$ signifies integration over the nuclear coordinates.

For laser pulses slowly varying in time (i.e. pulses whose envelope supports more than 100 optical cycles [25]), $E_0(t)$ can be thought of as being constant at any small time interval. This idea, directly related to the so-called adiabatic theorem [26], is an old one and a good set of references appear in the paper by Reinhardt and Dana [27] (see also references in [28]). In this case, as is also discussed elsewhere [29], although the Hamiltonian is no longer periodic the Floquet theorem still applies. Then $\mathbf{\Phi}(\boldsymbol{R}, t)$ can be expressed as an infinite expansion over the so-called quasi-energy solutions of the time-dependent Schrödinger equation [30]:

$$\mathbf{\Phi}(\boldsymbol{R}, t)=\sum_{\alpha} C_\alpha\, \mathrm{e}^{-\mathrm{i}\varepsilon_\alpha t/\hbar}\,\phi_\alpha(\boldsymbol{R}, t) \tag{12}$$

where $\phi_\alpha(\boldsymbol{R}, t)$ are the column vector eigenfunctions of the Floquet Hamiltonian matrix, $\boldsymbol{H}_F$, which are periodic in time, and ε_α are the corresponding eigenvalues

$$H_F(\boldsymbol{R}, t)\phi_\alpha(\boldsymbol{R}, t)=\varepsilon_\alpha\,\phi_\alpha(\boldsymbol{R}, t) \tag{13}$$

where

$$H_F(\boldsymbol{R}, t)\equiv-\mathrm{i}\hbar\frac{\partial}{\partial t}+H(\boldsymbol{R}, t). \tag{14}$$

Complex rotation of the coordinate R, $R\to\rho$, can be performed either throughout the entire range of the coordinate (uniform scaling [31]), $\rho=\mathrm{R}\exp(\mathrm{i}\Theta)$, or beyond a certain position on the real axis [32], R_0 with

$$\rho=\begin{cases} R & \text{if } R\leqslant R_0 \\ R_0+(R-R_0)\,\mathrm{e}^{\mathrm{i}\Theta} & \text{if } R>R_0 \end{cases}. \tag{15}$$

This is the version of complex scaling which is used in the calculations to be presented in section 3.

The vector solutions $\phi_\alpha(\boldsymbol{R}, t)$ of the Floquet Hamiltonian matrix, $H_F(\boldsymbol{R}, t)$ (see equation (12)) are replaced by the corresponding complex solutions $\phi_\alpha(\boldsymbol{\rho}, t)$ of the rotated Hamiltonian matrix, $H_F(\boldsymbol{\rho}, t)$. $\boldsymbol{\rho}$ denotes the nuclear coordinates ρ, θ and φ

(no scaling of angular variables). The solutions $\Phi(\rho, t)$ of the scaled time-dependent Hamiltonian matrix are given by:

$$\Phi(\rho, t) = \sum_{\alpha} C_{\alpha}\, e^{-i\varepsilon_{\alpha} t/\hbar} \phi_{\alpha}(\rho, t) \tag{16}$$

where, for the sake of simplicity, the same symbols as in equation (12) have been retained.

Under certain conditions which are in principle fulfilled in gaseous media, the HG spectra can be directly taken from the square modulus of the Fourier transform of the time dependent dipole moment amplitude:

$$\sigma_{\mathrm{HG}}^{\Omega} \propto \left| \int_0^{\infty} e^{i\Omega t} d(t)\, dt \right|^2 \tag{17}$$

Ω denoting the spontaneously emitted frequency and $d(t)$ defined by equation (11). This expression constitutes an approximation, based on a decorrelation of the dipole autocorrelation function [23, 24]. According to the above analysis, the time-dependent amplitude of equation (11) can now be replaced by its counterpart, $d^{\mathrm{res}}(t)$, over the time-dependent vector $\phi(\rho, t)$ which corresponds to a unique complex energy resonance:

$$d^{\mathrm{res}}(t) = \langle \Phi(\rho, t) | \mu(\rho) \cos\theta | \Phi(\rho, t) \rangle_{\rho} = \langle \phi(\rho, t) | \mu(\rho) \cos\theta | \phi(\rho, t) \rangle_{\rho} \tag{18}$$

where $\Phi(\rho, t)$ and $\phi(\rho, t)$ are defined by equation (16) when the summation reduces to a single term. It should be noted that, due to the fact that the resonance energy has become complex, all expectation values involved in the derivation must be calculated using the c-inner product rather than the conventional scalar inner product, $\langle \cdot | \cdot \rangle$ [33, 34]. The meaning of the c-inner product is that no complex conjugation is performed on quantities which become complex due to the resonance considerations (i.e. complex scaled coordinates or complex wavenumber). A strong numerical support for the use of the c-product rather than of the usual scalar product has been obtained by the results presented in figure (7) in [28]. This figure shows a remarkable agreement between the HG spectra obtained by making use of the c-inner product and those from full time-dependent numerical calculations [28]. Note in passing that the scalar product is defined only for wavefunctions which are in the Hermitian domain of the Hamiltonian. The Siegert resonance wavefunctions exponentially diverge and thereby are not in the Hermitian domain of the Hamiltonian. Therefore, a new inner product should be considered. A simple representation for the most general case is given in [35] when the Hamiltonian is presented by a finite matrix using real or complex basis functions.

Given also that a monochromatic laser has been assumed and that the components of the column vector $\phi(\rho, t)$ are periodic in time, $d^{\mathrm{res}}(t)$ can be calculated over a single period of the field, T. Equation (17) then takes the form:

$$\sigma_{\mathrm{HG}}^{\Omega} \propto \left| \frac{1}{T} \int_0^{T} e^{i\Omega t} d^{\mathrm{res}}(t)\, dt \right|^2. \tag{19}$$

The fact that $d^{\mathrm{res}}(t)$ in (19) is a time-periodic function due to the periodicity of the time-dependent components $\phi^{(j)}(\rho, t)$ ($j = 1, 2$) of the vector function $\phi(\rho, t)$ (see (18)) allows for an analytic integration over electronic and nuclear coordinates in (19). They

can be expanded as

$$\phi^{(1)}(\rho, t) = \sum_{n=-\infty}^{+\infty} e^{i\omega nt}\varphi_n^{(1)}(\rho)\, Y_{00}(\theta, \varphi)$$
$$\phi^{(2)}(\rho, t) = \sum_{n=-\infty}^{+\infty} e^{i\omega nt}\varphi_n^{(2)}(\rho)\, Y_{10}(\theta, \varphi) \tag{20}$$

where the two components are associated with the eigenfunctions of the complex scaled multichannel Floquet Hamiltonian $[H_F(\rho)]_{n',n}$.

As a result of the fact that we envisage here only transitions which involve a change of electronic state, $H_F(\rho)$ can be split into two non-coupled block matrices, H_F^I, H_F^{II} where

$$[H_F^I]_{n',n} = \frac{E_0}{2\sqrt{3}}\mu(\rho)\delta_{n',n\pm1} + ([T(\rho)]_{n,n} + V_n^I(\rho))\,\delta_{n',n} \tag{21}$$

$$V_n^I(\rho) = \begin{cases} U_1(\rho) + n\hbar\omega & \text{if } n \text{ is even} \\ U_2(\rho) + n\hbar\omega & \text{if } n \text{ is odd} \end{cases} \tag{22}$$

and similarly

$$[H_F^{II}]_{n',n} = \frac{E_0}{2\sqrt{3}}\mu(\rho)\delta_{n',n\pm1} + ([T(\rho)]_{n,n} + V_n^{II}(\rho))\,\delta_{n',n} \tag{23}$$

$$V_n^{II}(\rho) = \begin{cases} U_1(\rho) + n\hbar\omega & \text{if } n \text{ is odd} \\ U_2(\rho) + n\hbar\omega & \text{if } n \text{ is even} \end{cases}. \tag{24}$$

The factors $\frac{1}{2}$ and $1/\sqrt{3}$ in equations (21) and (23) came from the decomposition of $\cos\omega t$ in the exponentials and from the integration over angular variables respectively.

Without loss of generality, let us associate the Fourier components $\varphi_n^{(1)}$ and $\varphi_n^{(2)}$ of (22) with the eigenvectors of H_F^I (a similar analysis might also be carried out in which $\varphi_n^{(1)}$, $\varphi_n^{(2)}$ are associated with H_F^{II}):

$$H_F^I(\rho)\varphi(\rho) = \varepsilon^{\text{res}}\varphi(\rho) \tag{25}$$

where ε^{res} is a complex quasi-energy and

$$\varphi(\rho) = \begin{bmatrix} \vdots \\ \varphi_3^{(2)} \\ \varphi_2^{(1)} \\ \varphi_1^{(2)} \\ \varphi_0^{(1)} \\ \varphi_{-1}^{(2)} \\ \varphi_{-2}^{(1)} \\ \varphi_{-3}^{(2)} \\ \vdots \end{bmatrix}. \tag{26}$$

From the symmetry property of φ, as shown in (26), $\varphi_n^{(1)}$ is always associated with even values of n whereas $\varphi_n^{(2)}$ with only the odd ones. Equation (18) reads:

$$d^{\text{res}}(t) = \sum_{n(\text{even})} \sum_{n'(\text{odd})} e^{i(n'-n)\omega t} \langle \varphi_n^{(1)} | \mu_{12} | \varphi_{n'}^{(2)} \rangle + \text{c.c.} \tag{27}$$

c.c. accounting for complex conjugation only of quantities which have *not* become complex due to complex scaling of the coordinate or to eventual use of outgoing-wave boundary conditions.

By substituting (27) into (19) a time-independent expression for the harmonic generation spectra is obtained

$$\sigma_{\text{HG}}^{\Omega=m\omega} = \left| \sum_{n(\text{even})} [\langle \varphi_n^{(1)} | \mu_{12} | \varphi_{n+m}^{(2)} \rangle + \langle \varphi_{n-m}^{(2)} | \mu_{12} | \varphi_n^{(1)} \rangle] \right|^2 \tag{28}$$

$$m = 1, 3, 5, \ldots$$

When numerical techniques implemented within real basis sets or grid methods are used, (28) takes the more compact form:

$$\sigma_{\text{HG}}^{\Omega=m\omega} = \left| \sum_{n(\text{even})} \langle \varphi_n^{(1)} | \mu_{12} | (\varphi_{n+m}^{(2)} + \varphi_{n-m}^{(2)}) \rangle \right|^2 \tag{29}$$

where m gets odd values only.

Only odd harmonics are present even if we allow for higher rotational quantum numbers, or even if we introduce the transitions within each of the two electronic manifolds (in the assumption that $\mu(R)$ has diagonal matrix elements), that is when we deal with a heteronuclear diatomic molecule. Of course the frequencies needed to achieve a multiphoton excitation within one electronic state are generally very different from those needed to produce a change of electronic state. However we give a brief account of the proof when the two types of transitions are taken into account. The channel function of a Floquet state is written as:

$$| k, n, J \rangle$$

where k stands for the electronic state ($k = 1, 2$). n and J are the photon and rotational quantum numbers. The operator responsible for the coupling between those channels has a $\cos\theta \cos\omega t$ dependence. If both electronic states are of Σ character, the factor $\cos\theta$ results in a $\Delta J = \pm 1$ selection rule, irrespective of the fact that we describe an intra- or inter-electronic transition. The factor $\cos\omega t$ results in a $\Delta n = \pm 1$ selection rule. Suppose we look for a Floquet state correlating with the channel $|1, 0, 0\rangle$. We can only reach the following classes of channels:

$$| k, n(\text{odd}), J(\text{odd}); \rangle \qquad | k, n(\text{even}), J(\text{even}); \rangle \qquad k = 1, 2.$$

The component at $\Omega = m\omega$ of the HG spectrum is

$$\sigma_{\text{HG}}^{\Omega=m\omega} \propto \left| \sum_{k=1}^{2} \sum_{k'=1}^{2} \sum_{n=-2}^{n=+2} (\langle \varphi_{nJ}^{(k)} | \mu_{k,k'} | \varphi_{n+m,J+1}^{(k')} \rangle + \langle \varphi_{nJ}^{(k)} | \mu_{k,k'} | \varphi_{n+m,J-1}^{(k')} \rangle) \right|^2. \tag{30}$$

If n and J are odd, $J+1$ and therefore $n+m$ are even, so that m is odd. If n and J are even, $J-1$ is odd and therefore $n+m$ is odd, so that m is odd again. In the case where only interelectronic transitions are considered, electronic index $k = 1$ goes always with n and J even, while $k = 2$ goes with n and J odd. Diagonal elements of $\mu(R)$ cannot be encountered, since they imply $k = k'$ and J of opposite parity.

The formula for the odd harmonics given in equation (30) requires the determination of a single square-integrable QE solution. Procedures which calculate one eigenvalue and the corresponding vector of the Floquet Hamiltonian matrix are to be preferred in this case to methods which calculate all eigenvalues and eigenfunctions. This is the case of the inverse-iteration procedure or of the matching method used in the following section.

3. Illustrative numerical example

To illustrate the use of the expression derived here (equation (29)) for the harmonic generation spectra in homonuclear diatomics when two electronic states interact with an intense monochromatic laser, we study the case of H_2^+, as an example. The harmonic generation spectra of H_2^+ have been studied by Bandrauk and coworkers in a full time-dependent calculation, by taking also into account the coupling between the vibrational and the rotational motion of the diatomic [20]. In the present paper, the vibration-to-rotation coupling is limited to a subset of channels with either $J=0$ or $J=1$, although it may become important for higher values of the laser intensity. Such study is out of the scope of the present paper, which is centred mainly on qualitative trends.

We use the model Hamiltonian previously studied by Chu [36]. The matching method is described in [19] and [37]. For the molecular parameters, see [38] or table 1 in [36].

In order to favour the efficient generation of high harmonics, a relatively long wavelength is considered, namely $\lambda = 730$ nm, for which the single photon absorption channel converges to a threshold above the '$v=0$' resonance position. In strong laser fields, the behaviour of the width with respect to the intensity becomes highly nonlinear, while, in addition there is no single dominant term in the Born expansion of the transition operator. This is a clear indication of the heavy mixing of the adjacent continua which is also accompanied by a multitude of stimulated photon absorptions and emissions in the course of the process. It is exactly in this region of intensities that the spontaneous emission of photons of frequencies higher than the principal one are expected to be favoured. The results, presented in panels (*a*), (*c*), (*e*) and (*g*) of figure 1, show a clear relative enhancement of the higher harmonics with increasing intensity. This tendency is shown for four representative values of intensity corresponding to different regimes, from moderate up to strong laser field amplitudes. A rich absorption spectrum which strongly depends on the laser field amplitude is graphically shown in panels (*b*), (*d*), (*f*) and (*h*) of figure 1. We note in passing that when the branching ratios are converged (absorption spectra) HG spectra are converged too, and vice versa. This is due to the fact that in both cases the information is extracted from the same calculated Fourier components of the resonance QE solution. In all of them there are four physically relevant channels sharing the total dissociation rate, i.e. those corresponding to two-three- and four-net-photon absorption. As it has been thoroughly discussed in reference [19], this spectral structure can be understood in terms of R-dependent partial fluxes along the diabatic and adiabatic photon pathways which are always formed in curve-crossing situations (see equation (19) in reference [19]). The main cause of the transfer of flux among different channels is the strong non-adiabatic couplings around avoided crossing positions. Given the topology of the curves which changes as the intensity varies, the total flux is partitioned in a different way, leading to fragments with a very different kinetic energy distribution [19]. At high laser intensities, all photon peaks are

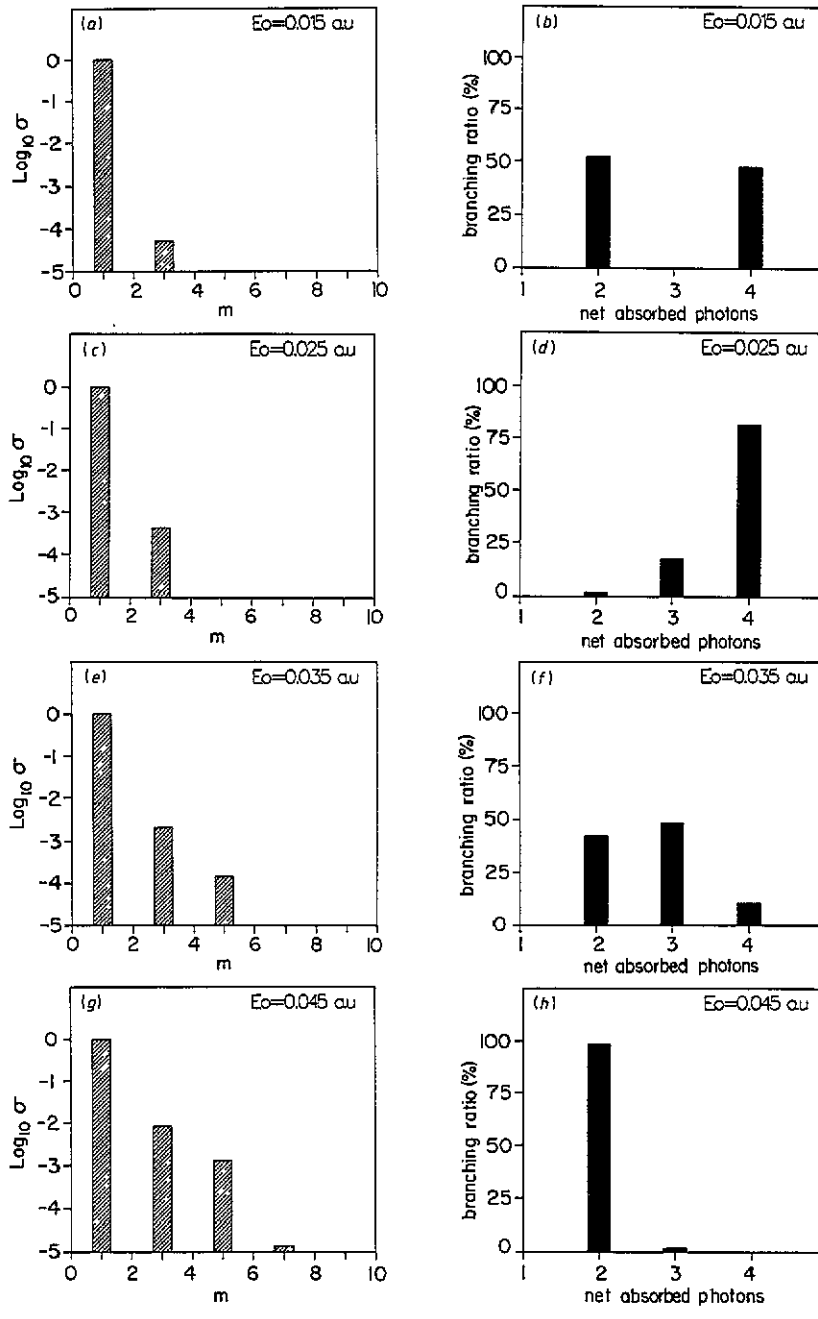

Figure 1. (*a*) Harmonic generation spectrum by means of equation (29). Vertical axis measures cross sections (arbitrary units) in logarithmic scale. (*b*) Absorption spectrum (by means of equation (19) of [19]). Horizontal and vertical axes measure number of net absorbed photons and percentage branching ratios respectively. Radiative coupling $\bar{E}_0 = E_0/2\sqrt{3} = 0.015$ au, i.e. laser intensity 9.45 10^{13} W cm^{-2}. (*c*), (*d*) Same as in panels (*a*) and (*b*), respectively, but for $\bar{E}_0 = 0.025$ au, i.e. laser intensity 2.63 10^{14} W cm^{-2}. (*e*), (*f*) Same as in (*a*) and (*b*), respectively, but for $\bar{E}_0 = 0.035$ au, i.e. laser intensity 5.15 10^{14} W cm^{-2}. (*g*), (*h*) Same as in (*a*), (*b*) respectively but for $\bar{E}_0 = 0.045$ au, i.e laser intensity 8.51 10^{14} W cm^{-2}.

supressed except one, i.e. the peak corresponding to two absorbed photons. The origin of the suppression of all but a single peak, namely of that corresponding to dissociation toward the first energetically allowed photon channel (in our case that of two net absorbed photons), has been evidenced both theoretically [16–19] and experimentally [39]. A possible explanation for this effect is associated to the deformation of certain barriers (bond softening), up to their complete flattening which takes place at high intensities. Although a single peak appears in the absorption spectrum (see figure 1(*h*)), this process is certainly of a multiphotonic origin. There are several evidences in support of this argument. Most of those are discussed in [18, 19, 40, 41]. One additional evidence is given graphically in figures 1(*a*), (*c*), (*e*) and (*g*) where the gradual and constant enhancement of harmonics of higher order manifests the collective, many-photon nature of the phenomenon.

Resonances issued from vibrational levels other than $v=0$ might eventually exhibit much richer harmonic spectra. As is borne out from our calculations, for relatively high laser intensities, high order harmonic peaks of such resonances may become even comparable to the principal one, while inversion of harmonics of high order may also

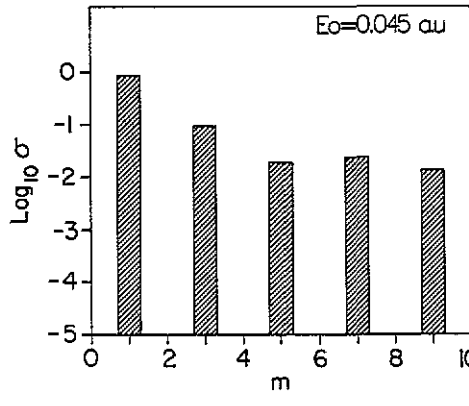

Figure 2. Harmonic generation spectrum of a short living resonance for radiative coupling $\bar{E}_0 = E_0/2\sqrt{3} = 0.045$ au, i.e. laser intensity 8.51×10^{14} W cm^{-2}. Its harmonic spectrum is exceptionally rich. The corresponding absorption spectrum exhibits structure similar to that of figure 1(*h*). The multiphotonic nature of the photodissociation mechanism for this intensity is shown more pronouncedly.

be observed. This situation is graphically illustrated in figure 2 for the highest examined intensity and a short lived resonance associated to it. For the same intensity the absorption spectrum of this resonance turns out to contain a single photon peak, in a way similar to that of figure 1(*h*). This fact constitutes an even more striking manifestation of the multiphotonic nature of the mechanisms which are responsible for the occurrence of single absorption peaks in strong laser fields. It should be stressed here that the results presented in figure 2 were obtained for high field intensity for which there is no single dominant diabatic state (to be labelled by $v=1, 2, \ldots$) in the expansion of the complex scaled QE solution. Therefore, in such a case one cannot associate the resonance QE solution with a specific v diabatic state without carrying out calculations where the field is adiabatically turned on. The shift of the resonance that we associated with $v=0$, nevertheless shows a smooth behaviour (presented in figure 3). The corresponding widths (and lifetimes which are proportional to the inverse widths) of the resonance

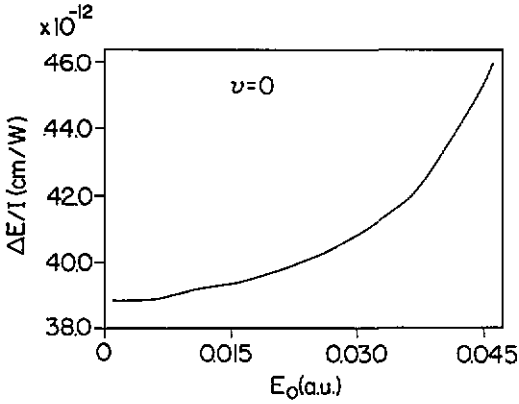

Figure 3. Field-induced energy shift per unit of intensity ($\Delta E/I$) for the $v=0$ resonance (in cm W^{-1}) as a function of the radiative coupling $\bar{E}_0$ (in au). $-\Delta E/I$ acquires a gradually enforced nonlinear behaviour with increasing field amplitude. However it varies smoothly, serving thus as a good criterion of resonance identification.

$v=0$ as function of the field intensity are summarized in table 1. As one can see even for the maximum field amplitude the lifetime of the resonance state is larger than 100 optical cycles ($T \equiv \lambda/c = 0.2435 \times 10^{-14}$ s). Therefore, the Floquet analysis used here is valid.

All computational steps are implemented as it is described in [19]. They can be briefly summarized as follows.

(i) The electronic coordinates of the system are removed by integration, giving rise to a system of 12 close-coupled differential equations corresponding to 12 physical channels, or to 6 Floquet blocks (2 channels in one Floquet block). This size turned out to be adequate for all examined intensities. In this system of equations, all photon channel wavefunctions, $\varphi_n^{(1)}$, $\varphi_n^{(2)}$, correspond to the diabatic representation, given that all analytic derivation implemented in section 2 refers to both diabatic Born–Oppenheimer (BO) potential curves and diabatic molecular Hamiltonians. Note that BO is in the context of field-free Hamiltonian. Diabatic-adiabatic is defined here in the context of the coupling of molecular states dressed by the field.

(ii) The system is solved by making use of the Fox–Goodwin propagative method on a partially complex grid. The rotation of the coordinate is held in the asymptotic region, beyond the position 12 Bohr. Regularity at the origin is imposed for the Fox–Goodwin ratio of the solution matrix which is propagated outward, while outgoing wave asymptotic conditions are imposed for the matrix which is propagated

Table 1. $\bar{E}_0$ is the radiative coupling $E_0/2\sqrt{3}$ where E_0 is the maximum electric field amplitude (of equations (21) and 23)). $\Gamma/2$ is the halfwidth of the QE state correlating with the state $v=0$, $J=0$ of the field-free molecule. τ is the corresponding lifetime. The period of the electric field is 0.2435×10^{-14} s.

$\bar{E}_0$ (au)	$\Gamma/2$ (cm^{-1})	τ (s)
0.015	0.2462 (−4)	6.77 (−7)
0.025	0.2125 (−2)	7.85 (−9)
0.035	0.1417	1.18 (−10)
0.045	0.5740 (+2)	2.91 (−13)

inward. When complex scaling is applied, it has been proved that these conditions are equivalent to initializing the latter matrix by zero [42]. The scaling angle is chosen as $\Theta = 0.5$ rad. However, well defined plateaux of stability are formed for a large range of values (as well as of exterior scaling positions).

(iii) The resonance issued from $v = 0$ is carefully followed at each intensity, using as trial complex energy that of the previous converged calculation. In order to ensure that the same resonance, i.e. the $v = 0$, is followed for all examined intensities, the response of the energy shift of the resonance as a function of the laser intensity turns out to be a good criterion. For weak intensities this dependence is expected to be linear, being smoothly deformed as the intensity increases. This is graphically illustrated in figure 3.

(iv) The criterion for resonance quantization emerges from a determinantal matching condition, which has to be obeyed by the two Fox–Goodwin matrices at a joint position. In our calculations this position is chosen at the equilibrium of the attractive potential curve. The matching gives rise to discrete complex energies, whose imaginary part is interpreted as the half width of the resonance.

(v) Once convergence on the resonance is achieved, the diabatic channel functions, $\varphi_n^{(1)}$, $\varphi_n^{(2)}$, are obtained by inverse propagations from the joint point toward the two extremities of the potential. As regards HG spectra, the information obtained in steps (i)–(v) is sufficient for the application of equation (29).

(vi) Concerning stimulated absorption spectra, asymptotic transformation of the diabatic channel functions to the adiabatic representation must be carried out. This transformation is able to provide physical photon channels. These channels provide the information on the partial widths by means of a non-perturbative partial flux analysis. This analysis is described in a detailed way in [19, 42].

As a word of conclusion, for the conditions inherent in our model of homonuclear diatomic ions subjected to continuous wave radiation, only odd harmonics can be generated. The formulae that we derived for the HG spectra enable one to avoid time-dependent calculations and to obtain the HG spectra from a single square-integrable complex-scaled QE eigenfunction of the Floquet Hamiltonian. We performed calculations on H_2^+ up to high laser intensities for an incident frequency corresponding to a non-resonant situation. As the laser intensity increases, the higher harmonics exhibit substantial amplitudes. These numerical findings were obtained by making use of the expectation value of the dipole operator, rather than the dipole correlation function.

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