Optical harmonic generation in atomic and molecular hydrogen

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We compare calculated optical harmonic spectra for the hydrogen molecule and the hydrogen atom in an intense, linearly polarized laser field. The hydrogen atom calculations use an exact, time-dependent method and the hydrogen molecule calculations are performed in a time-dependent Hartree-Fock approximation. In both cases, the laser-matter interaction is treated completely non-perturbatively. We show that if the H2 bond length is stretched so that H2 has the same ionization potential as H, both systems produce remarkably similar harmonic spectra when irradiated with a 1064 nm laser at $1 \times 10^{14}$ or $2 \times 10^{13}$ W/cm$^2$.

1. Introduction

In a very intense laser field, an atom or molecule can radiate at multiples, or harmonics, of the laser frequency. This process, known as optical harmonic generation (OHG), has now been observed experimentally to very high order [1] (33rd in Ar, at the Nd:YAG fundamental of 1064 nm), and to very high photon energy [2] (85 eV in Ne, the 17th harmonic of KrF). OHG is observed only under proper phase matching conditions, so the emitted photons are coherent [3]. The harmonics are also surprisingly bright [4], raising the possibility of using OHG as a laboratory source of coherent vacuum ultraviolet to X-ray photons. Generation of high-order harmonics has only recently become possible, due to the development of very intense, subpicosecond lasers. Potential applications for such a light source range from surface physics to X-ray holography of biological materials.

To date, theory and experiments on intense field OHG have concentrated on atomic systems [1,2,4] #1. In this paper, we extend these investigations to the study of molecules. Molecules possess degrees of freedom, such as rotation and dissociation, not present in atoms. These additional channels increase the complexity of both calculations and experiments. However, the diversity of molecular systems enables greater control over such experimentally important parameters as the ionization potential, and density and distribution of excited states. Such considerations may make molecules the medium of choice for optimizing harmonic production at a photon frequency desired for a particular application.

In addition to the possible experimental interest, the study of harmonic generation in molecules offers a way to increase our understanding of the dynamics of OHG. We focus, in this work, on a comparison of harmonic spectra from the hydrogen atom and the hydrogen molecule, both for the number of harmonics and the conversion efficiency. The potentials in these two systems are, of course, quite different. Qualitatively, since high-order harmonics result from exceedingly non-linear interaction of light with matter, it is the steep, non-harmonic portion of the potential which should be important for OHG. For example, a strong effect of the potential on harmonic generation has been seen in calculations on the xenon atom [5]. It was observed that when the 5p$_0$ orbital was aligned with the polarization axis of the laser, it was driven strongly by the field against the steep parts of the potential, and produced much more intense harmonics than the 5p$_{\pm 1}$ orbital, which oscillated perpendicular to the regions of the potential.
having the largest gradients. Therefore, the hydrogen molecule, with its double anharmonic well, might be expected to be more efficient at generating high-order harmonics than the hydrogen atom. By comparing a simple atom to a simple molecule, our purpose is to attempt to isolate the factors important to the dynamics of OHG, and hence to aid in the design and interpretation of future experiments.

2. Theory

A laser field induces a time-dependent dipole moment in an atom or molecule. For a laser linearly polarized along the \( z \) axis, the induced dipole moment is simply the time-dependent expectation value of \( z \) [6]

\[
\langle d(t) \rangle = \int dr \psi^*(r, t)z\psi(r, t).
\]

In a weak field, \( \langle d(t) \rangle \) oscillates at the laser frequency, with a magnitude proportional to the dipole polarizability of the material. As the laser field increases, \( \langle d(t) \rangle \) develops frequency components at odd harmonics of the laser frequency (the even harmonics are forbidden by parity in a system with an inversion center), and the spectrum of harmonic frequencies can be obtained from the square of the Fourier transform of \( \langle d(t) \rangle \).

The electronic wavefunction \( \psi(r, t) \) can be calculated in a number of ways. One common method is to use perturbation theory, and to treat the matter-field interaction in a series of non-linear susceptibilities. However at the intensities of interest for high-order OHG, the laser field can be comparable to, or exceed, the Coulomb field. At such intensities the susceptibilities become intensity dependent, and conventional perturbation theory cannot be used.

In this paper, we solve for \( \psi(r, t) \) using completely non-perturbative methods. For the hydrogen atom, we solve the time-dependent Schrödinger equation,

\[
i(\partial/\partial t)\psi(r, t) = H(r, t)\psi(r, t),
\]

where \( H \) is the usual atomic Hamiltonian (in atomic units, \( \hbar = e = m = 1 \)) with a time-dependent matter-radiation interaction \( V_1(r, t) \),

\[
H(r, t) = -\frac{1}{2}\nabla^2 - \frac{1}{r} + V_1(r, t).
\]

Here, we assume a classical laser, polarized along the \( z \) axis, so

\[
V_1(r, t) = -e_0E(t)z\sin(\omega t),
\]

where \( E(t) \) is an envelope function. We solve eq. (2) with a method described previously, by expanding \( \psi(r, t) \) in spherical harmonics on a radial grid, and integrating the resulting coupled equations with a Peaceman-Rachford propagator [7]. This method is exact, in the limit of zero grid spacing.

For the hydrogen molecule, we use the time-dependent Hartree-Fock method (TDHF). For a single, doubly occupied orbital, \( \phi(r, t) \), the equations can be written as [8]

\[
i(\partial/\partial t)\phi(r, t) = \{h(r, t) + V_1(r, t)\}\phi(r, t),
\]

where \( h \) is the Fock operator, and is given by

\[
h(r, t) = -\frac{1}{2}\nabla^2 - \frac{1}{|r-r_1|} - \frac{1}{|r-r_2|} + \int dr' \left| \phi(r', t) \right|^2\frac{1}{|r-r'|}.
\]

We solve eq. (5) in a single active electron approximation by assuming, in eq. (6), that \( \phi(r', t) = \phi(r', t=0) \) for all \( t \). That is, one electron remains fixed in its ground state orbital, while the second electron interacts with the laser field, the nuclei, and the mean Coulomb field of the first electron. Calculations of the multiphoton ionization of He have shown this approximation to be reliable up to \( 10^{15} \) W/cm\(^2\) at wavelengths of 1064 and 532 nm [8]. The approximation breaks down at higher intensity, in the regime in which double excitations become important.

We also assume, in this work, that \( H_2 \) has a fixed bond length, with the bond oriented along the \( z \) axis. This preserves the cylindrical symmetry of the problem, and allows the calculations to be performed on a two-(spatial) dimensional, rather than three-dimensional, grid. For \( H_2 \), we expand the wavefunction in cylindrical coordinates, and calculate the kinetic energy with a three-point second difference formula. As in the H calculations, the equations are propagated in time by the Peaceman–Rachford method. We will discuss below how the approximations made for \( H_2 \) influence our results.
3. Results

Fig. 1 shows the time-dependent dipole induced in H$_2$, at its equilibrium bond length, by a 1064 nm laser. The field was ramped linearly over 5 optical cycles to a maximum intensity of $1 \times 10^{14}$ W/cm$^2$, and then held constant for 15 additional cycles. The calculation was performed on a grid of 200 by 100 $\alpha_0$, with a grid spacing 0.25 $\alpha_0$. The time step was 1/800 of an optical cycle. An absorbing boundary prevented, to a large degree, spurious reflection of the wavefunction from the edges of the grid [9]. To calculate the harmonic spectrum (fig. 2), we Fourier transformed the last 5 optical cycles of the time-dependent dipole moment in fig. 1. This procedure minimizes the effects of transients caused by the turn-on of the laser field, and is appropriate when the laser pulse length is long compared to the decay time of the states excited during the pulse ramp [6]. If we were modeling an ultra short-pulse experiment, we would include the entire laser envelope in the Fourier transform.

Fig. 2 reveals a series of peaks at odd multiples of the laser frequency, extending to at least the 47th harmonic, or an energy of 55 eV. The field-free ionization potential in H$_2$ is 15.4 eV, so the high-order harmonics visible in fig. 2 correspond to absorption of many photons above the field-free ionization threshold. The spectrum shows an initial sharp drop-off in intensity, followed by a rather broad plateau, and then a fairly sudden cut-off. These features are characteristic of atomic optical harmonic spectra, both theoretical [5,6,9-11] and experimental [1,2,4]. The presence of the plateau in the experimental spectra was unexpected, but has recently been explained theoretically by a careful consideration of the effects of phase matching in the experiments [12]. The peak widths are determined by the ionization rate or the bandwidth of the laser pulse, whichever is greater [6].

Visible also in fig. 2 is a broad continuous background. We have indicated previously that the background in the theoretical spectra depends on the existence of a set of low-lying excited states and, presumably, to Raman-like transitions among them [9]. A background is also observed experimentally, which may, however, derive from a different mechanism. For example, the time integrated spectrum obtained in experiments certainly has contributions from plasma processes occurring well after the pulse, while the spectrum we calculate occurs only during the pulse. In addition, we find the calculated background to be incoherent, and therefore expect this emission to be orders of magnitude weaker than the coherent harmonic peaks when the effects of phase matching are included [12].

To understand the role of the potential in OHG, we wish to compare the optical harmonic spectra of the hydrogen atom and molecule. To do this, we first eliminate the dependence of the harmonic intensities on the ionization potential (IP), which, from experiments and theory, is known to be strong. This is easily accomplished by stretching the H$_2$ bond length.
Fig. 3 shows harmonic intensities for $\text{H}_2$ at its equilibrium bond length ($1.4 \alpha_0$), and at the bond length ($2.04 \alpha_0$) at which the IP of $\text{H}_2$, in the Hartree–Fock approximation, nearly equals the IP of $\text{H}$ ($13.6$ eV). The peaks in the stretched $\text{H}_2$ spectrum are, at a given laser intensity, more intense than those for $\text{H}_2$ at its equilibrium bond length by several orders of magnitude. A similar trend is observed in the rare gases [4], where as the IP increases, the harmonic intensities decrease, though the plateau extends to higher harmonic order. Evidently, the less tightly bound the electron, the more strongly perturbed it is by the electric field. The presence of the very high harmonics can be explained by noting that once the electron reaches the quasi-continuum, any states present have become so highly broadened by the field that the electron can readily absorb additional photons. Ionization, of course, stops harmonic production, so an upper limit to the harmonic spectrum is eventually reached.

Fig. 4 shows a comparison of harmonic intensities at $1 \times 10^{14}$ W/cm$^2$ in the stretched hydrogen molecule and the hydrogen atom. Qualitatively, the spectra are very similar, though individual harmonics, such as the 11th, are quite different. The higher harmonics in the $\text{H}_2$ spectrum appear to be considerably more intense than the corresponding H harmonics. As mentioned previously, though, it is very difficult to completely prevent reflection from the grid boundaries at high laser intensity [9], so variations of intensity of up to an order of magnitude may not be significant, especially for the high-order harmonics.

Fig. 5 compares the stretched $\text{H}_2$ harmonics to the H harmonics at an intensity of $2 \times 10^{13}$ W/cm$^2$. At this intensity, boundary reflection is not a problem [9]. Once again, the spectra are very similar. In this case, it is the 7th harmonic, rather than the 11th, which shows the greatest variation in the low-order harmonics. This may be the result of resonant interference. The resonance energies vary with laser in-
4. Discussion

We presented, in this paper, the first calculations, to our knowledge, of high harmonic generation by a molecule in an intense laser field. We found that, when the difference in the ionization potential was considered, $H_2$ produces harmonics of comparable intensity to $H$. This result was contrary to our expectation that since the absorption and emission of photons occurs primarily near the nucleus, the differences in the short range potentials of $H$ and $H_2$ might be strongly reflected in the harmonic spectrum. We also found, at the wavelength and intensities considered in this paper, no strong contribution from resonances to the harmonic spectra. Some possible indications of resonant behavior are evident, primarily in the sensitivity of specific peaks to the laser intensity, but in general, the $H$ and $H_2$ spectra show the same qualitative intensity dependence. Resonances would be much more important had we chosen to study 2 or 3 photon ionization, for example, rather than the 11, 12 photon ionization case examined in this paper [13]. These results suggest that the factors most important to OHG are those relating to the polarizability of the atom or molecule, and hence to the structure of the continuum, rather than the details of the short range potentials, and the bound electronic structure.

Our calculations of harmonic generation in $H_2$ involved a number of approximations. First, they were performed in a TDHF single active electron model. As mentioned above, we expect this to be a very good approximation until very high intensities are reached. More seriously, we did not include the motion of the nuclei in the calculations. Rotation is slow on the time scale of ionization, and can probably be neglected. In addition, experiments measuring angular distributions of protons from multiphoton ionization of $H_2$ found that the protons are rather tightly focused along the polarization axis of the laser [14], indicating that the molecule absorbs photons most efficiently when it is aligned with the laser. Recent experimental and theoretical evidence suggests [15], in fact, that the molecules may actually become strongly aligned in intense laser fields, so the approximation that the bond is oriented along the polarization axis, which we made for numerical convenience, may accurately reflect the experimental situation. As we mentioned above, calculations on Xe also show that alignment with the laser field produces the most intense harmonics [5]. The effects of changing the $H_2$ bond length, as seen in the comparison of stretched versus the unstretched hydrogen in fig. 3, can be quite large. However, the zero point vibration of $H_2$ is fairly small, so the harmonic spectra may not be too sensitive to this motion, and should not differ significantly from the spectra calculated at the equilibrium bond length. This point must be tested by more elaborate calculations. Finally, we have not included dissociation in these calculations. Experiments indicate that ionization is the dominant channel [14], and hence, as long as the bond length does not change significantly during the length of the pulse this approximation should be reasonable.

We would also like to emphasize that the spectra presented in this paper represent the response of a single atom or molecule interacting with a laser field. OHG is only observed experimentally under proper phase matching conditions, indicating that such factors as pressure, geometry of the gas jet, and the shape and size of the laser spot are important [12]. There is no guarantee that $H_2$ will behave similarly to $H$ when the effects of these contributions are included. However, the fact that above threshold ionization is readily observed in molecular hydrogen [16] increases the chance that harmonic generation can be observed as well.

We are considering a number of possible extensions to these calculations. One way to include the effects of nuclear motions is to run classical trajectories for the hydrogen nuclei, and then calculate the response of nuclei due to electronic motion with the Hellman–Feynman theorem [17].

References