# High-Order Harmonic Generation in Aligned Molecules

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We demonstrate alignment control in high density vapors of $CS_2$, hexane, and $N_2$ ($\sim 10^{17}$ molecules $cm^{-3}$) using the electric field of a 300 ps duration laser pulse. This was sufficient to study for the first time the molecular orientation dependence of high-order harmonic generation using a second, 70 fs duration laser pulse of intensity $\sim 5 \times 10^{14}$ $W\,cm^{-2}$. We were able to modulate and significantly enhance the harmonic intensity in aligned molecules compared to the randomly oriented case. Our results are consistent with the existence of an anisotropic dipole phase.

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High-order harmonic generation (HHG) resulting from the interaction of intense laser light with atoms has been extensively studied in recent years as a unique source of coherent extreme ultraviolet radiation [1]. An intuitive and durable theoretical picture based on the classical electron trajectory in the laser field [2] has helped to elucidate this process. Several workers have observed the similarity of HHG in atoms and small molecules [3,4], and recently it was shown that if sufficiently short pulses are used (<100 fs) then even larger (organic) molecules exhibit atomlike behavior [5]. However, unlike atoms, molecules are not isotropic systems, and it is known that processes such as multiphoton ionization can be strongly influenced by the angle between the laser electric field vector and the molecular axis [6]. It is therefore natural to ask if there is any orientation dependence of the closely related process of HHG. This question is addressed in a recent theoretical paper [7] in which it was shown that the single-molecule HHG response in a $H_2{}^+$ ion is enhanced if the laser field is polarized perpendicular to the molecular axis.

To study experimentally how HHG depends upon molecular orientation, it is first necessary to align a dense ($>10^{17}$ $cm^{-3}$) ensemble of molecules. Alignment has been demonstrated at low densities ($\sim 10^{10}$ $cm^{-3}$) for molecules having no permanent dipole moment [8,9] where the electric field of a laser pulse induces a molecular dipole moment and simultaneously exerts a torque upon it [10]. Under the conditions discussed below, this torque leads to an ensemble of molecules having an angular distribution of molecular axes that is peaked about the direction of the electric field. From the quantum mechanical point of view, the eigenstates of aligned molecules in the adiabatic limit correspond to the so-called pendular states and can be labeled by the quantum numbers $\tilde{J}$ and $M$ of the field-free rotational state [11]. The degree of alignment is quantified by the expectation value of $\cos^2\theta$, $\langle \cos^2\theta \rangle$, where $\theta$ is the polar angle between the molecular axis and the electric field vector. It ranges from 0.33, corresponding to an isotropic distribution, to 1 when the molecule is in a perfectly aligned state along the electric field vector. For an ensemble of molecules in thermal equilibrium, the average of the Boltzmann distribution of the rotational states has also to be considered [8,11]. In earlier work [8,12–14], a $\approx 3.5$ ns duration laser pulse was used to align several species of neutral molecules in samples of density $<10^{10}$ $cm^{-3}$, and a degree of alignment as high as $\langle \cos^2\theta \rangle = 0.9$ was realized.

In this Letter, we present results from the first study of HHG in dense vapors of spatially aligned molecules. To our knowledge, this is also the first time that controlled alignment has been demonstrated at densities as high as $10^{17}$ $cm^{-3}$.

Our experimental arrangement is shown in Fig. 1. A Ti:sapphire, chirped pulse amplified laser system with center wavelength 798 nm and repetition rate 10 Hz was used to simultaneously produce 300 ps duration laser pulses for molecular alignment and 70 fs laser pulses to pump HHG in the aligned molecules. A beam splitter immediately before the grating pulse compressor divided the linearly polarized laser pulse into two parts. The reflected fraction propagated through a beam expanding telescope into the pulse compressor to produce 70 fs full width at half maximum (FWHM) duration, 40 mJ pump pulses. The transmitted fraction remained uncompressed to

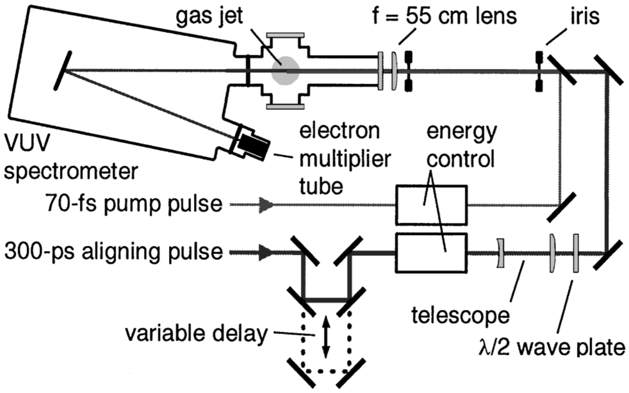

FIG. 1. Experimental setup showing 300 ps duration alignment laser pulses and 70 fs duration high-order harmonic generation pump pulses focused collinearly into a dense molecular gas jet.

provide laser pulses for control of molecular alignment with 300 ps FWHM duration and energy up to 60 mJ.

A variable optical delay controlled the relative timing between the two pulses with <100 fs resolution over a range of 700 ps. The energy of the pump pulses was varied by rotation of a $\lambda/2$ wave plate placed before the pulse compressor which had a very strong polarization dependence in its transmission efficiency. A wave plate and a polarizing beam splitter were used to vary the aligning pulse energy. Control of the molecular alignment plane was achieved by rotating the electric field vector of the aligning beam to be either parallel with or perpendicular to the electric field vector of the pump beam. The aligning beam was modulated at 5 Hz by a mechanical chopper wheel phase-locked to the laser pulses to optimize the signal to noise ratio of measurements comparing the harmonic intensity with and without the aligning pulse. The pump and aligning beams were recombined with a 50:50 beam splitter and focused into a small vacuum chamber with a 55 cm focal length lens. The beams were sampled by an optical wedge inserted after the focusing lens and the focal volume was then imaged onto a charge-coupled device camera and sampled by a personal computer (PC) equipped with a frame grabber. The focused intensities in the interaction region could be varied in the range $5 \times 10^{13}$–$5 \times 10^{14}$ W cm$^{-2}$ for the 70-fs HHG pump pulses and $1 \times 10^{11}$–$2 \times 10^{12}$ W cm$^{-2}$ for the 300-ps aligning pulses (below the threshold for HHG).

A pulsed molecular jet was introduced into the interaction region via a solenoid valve. The valve was modified to allow helium buffer gas to be mixed with the molecular vapor prior to the pulsed valve opening, thus enhancing the rotational cooling experienced by the molecular vapor during its supersonic expansion into vacuum. The laser beam was focused 3 mm below the 500 $\mu$m diameter nozzle to give an interaction region ~6 mm long with density ~$10^{17}$ molecules cm$^{-3}$. These conditions optimized rotational cooling while retaining an acceptable signal to noise ratio. We estimate the rotational temperature of molecules in the jet [15] to be ≈10 K for $CS_2$ (350 Torr $CS_2$ with 1400 Torr He) and ≈25 K for $N_2$ and $H_2$.

High-order harmonics generated in the interaction were spectrally resolved using a vacuum ultraviolet monochromator and detected using an electron multiplier tube (EMT). The signal from the EMT (harmonic intensity) and a signal defining the aligning beam state (blocked or unblocked) were sampled by a digital oscilloscope and transferred to a PC. The ratio $R$ of the harmonic intensity with the aligning beam (molecules aligned) to the harmonic intensity without the aligning beam (molecules randomly distributed) was determined. For each datum, the average and the standard error of $R$ were calculated over 400 laser pulses.

Figure 2 shows the measurement of $R$ as a function of the delay between the aligning and harmonic pump pulses $\Delta t$ for 9th order harmonics in $CS_2$, $H_2$, and $N_2$. Positive values of $\Delta t$ correspond to the pump pulse arriving after the aligning pulse. For each of the molecular species, alignment directions parallel with and perpendicular to the pump pulse electric field vector are compared. Measurements were also made of 11th, 13th, and 15th order harmonics which showed evidence of the same magnitude of alignment effect. We present here only the 9th harmonic as it coincides with the peak response of our detection system, resulting in the optimum signal to noise ratio.

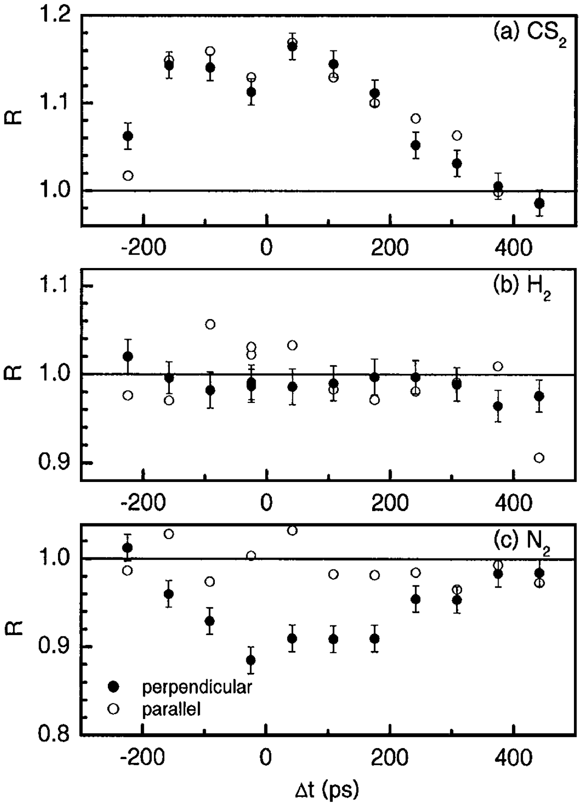

FIG. 2. Ratio $R$ of harmonic intensity with aligning pulse to harmonic intensity without aligning pulse as a function of delay $\Delta t$ between aligning and harmonic pump pulses for the 9th harmonic using perpendicular (●) and parallel (○) laser polarizations in (a) $CS_2$, (b) $H_2$, and (c) $N_2$.

HHG in $CS_2$ is enhanced in the presence of an aligning laser pulse [Fig. 2(a)]. The aligning pulse intensity is $2 \times 10^{12}$ W cm$^{-2}$ and the intensity of the pump pulse is $5 \times 10^{14}$ W cm$^{-2}$. The enhancement of $R$ follows the aligning pulse temporal history, although the aligning pulse FWHM duration is 300 ps, whereas for $R$ we have a FWHM of approximately 400 ps. The broadening can be attributed to the nonlinear behavior of $R$ as a function of aligning pulse intensity (see Fig. 3). There is no significant difference between the parallel and the perpendicular polarizations, suggesting that the observed enhancement of HHG is related to the increased order in the aligned molecules and is independent of the alignment direction. The aligning pulse has no effect ($R = 1$) when it precedes the pump pulse, implying that the aligning pulse induces no significant ionization or dissociation. We observed similar results in hexane, although this molecule was less extensively investigated than $CS_2$.

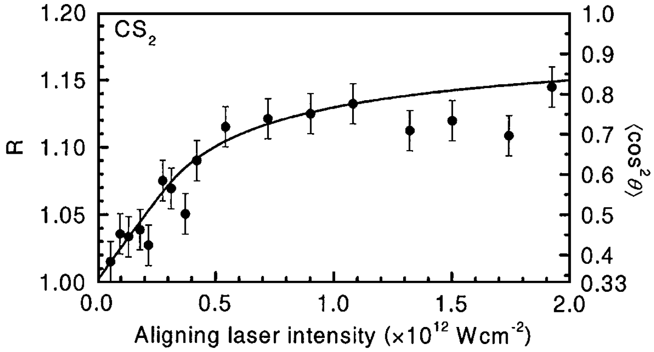

FIG. 3. Ratio $R$ as a function of aligning laser intensity for the 9th harmonic in CS$_2$ using parallel aligning and pump laser polarizations.

No effect is observed in H$_2$ for either aligning pulse polarization [Fig. 2(b)]. This allows us also to rule out any significant direct influence of the aligning pulse on the harmonic generation process, e.g., through electric field addition or modified ionization dynamics. In N$_2$ [Fig. 2(c)], prealignment of the molecules perpendicular to the pump pulse causes harmonic emission to be suppressed ($R < 1$), whereas prealignment parallel to the pump pulse has no observable effect.

The alignment dependence of HHG in CS$_2$ is studied as a function of aligning pulse intensity (Fig. 3). The intensity of the harmonic pump pulse is $5 \times 10^{14}$ W cm$^{-2}$ and its polarization is parallel to that of the aligning pulse. The temporal delay between the two pulses is chosen to maximize $R$. As the aligning pulse intensity increases from $<1 \times 10^{11}$ W cm$^{-2}$ to $\sim 5 \times 10^{11}$ W cm$^{-2}$, the harmonic intensity is progressively enhanced ($R > 1$). The effect then saturates and $R$ increases only gradually up to the maximum aligning pulse intensity of $2 \times 10^{12}$ W cm$^{-2}$. In the same figure, we also show the predicted degree of molecular alignment $\langle \cos^2\theta \rangle$ calculated using the formula reported in [11]. The measured variation of HHG and the calculated degree of alignment are strongly correlated. Further evidence for alignment was obtained when we observed that the effect of the aligning pulse was optimized when we decreased the rotational temperature by either maximizing the buffer gas pressure or moving the nozzle throat as far as possible from the laser focus.

To explain these observations, we must consider a number of factors: the degree of steady-state alignment caused by the aligning field, realignment of the molecules by the stronger but shorter HHG pump pulse, and the effect of alignment on the HHG process itself.

The alignment dynamics will be in the adiabatic limit if the laser pulse duration exceeds the rotational time, $T_R$. In our experiment, this condition is always satisfied by the 300 ps duration aligning pulse, as the highest $T_R$, corresponding to the lowest rotational energy, is $\approx 100$ ps for CS$_2$ ($B = 0.109$ cm$^{-1}$), 5 ps for N$_2$ ($B = 2.0$ cm$^{-1}$), and 0.2 ps for H$_2$ ($B = 61$ cm$^{-1}$). We evaluated $\langle \cos^2\theta \rangle$ [11] using our predicted rotational temperatures to estimate the degree of alignment induced by an aligning pulse with intensity $2 \times 10^{12}$ W cm$^{-2}$. We find $\langle \cos^2\theta \rangle \approx 0.82$ for CS$_2$, 0.38 for N$_2$, and 0.33 for H$_2$. Thus, the aligning pulse produces strong alignment in CS$_2$ and poor alignment in N$_2$. In H$_2$ there is no alignment at all, and so this molecule represents the null case (no prealignment).

The subsequent high intensity, ultrashort pump pulse can also influence the alignment of molecules. It has been shown experimentally that the molecular moment of inertia plays a crucial role in alignment with short pulses. In particular, H$_2$ and N$_2$ are forced into alignment by sub-100-fs laser pulses ($I \sim 2 \times 10^{14}$ W cm$^{-2}$), whereas in the same conditions I$_2$ shows no signs of reorientation [16]. The same conclusion for I$_2$ is reached by [17] with higher intensity ($10^{15}$ W cm$^{-2}$), shorter duration (80 fs) pulses. We can assume that no significant reorientation of CS$_2$ occurs during the pump pulse. The CS$_2$ rotational constant is only 3 times that of I$_2$, whereas this factor is $\approx 54$ for N$_2$ and $\approx 1600$ for H$_2$. In CS$_2$, we have observed no dependence of $R$ on the pump pulse intensity, which would be expected if aligning effects of the pump pulse were significant.

H$_2$ is not oriented by the aligning pulse and so, though it may be subsequently aligned by the pump pulse [16], it remains independent of the aligning pulse [Fig. 2(b)]. For N$_2$, we have a system that is initially slightly aligned ($\langle \cos^2\theta \rangle \approx 0.38$) and subsequently realigned by the ultrashort harmonic pump pulse. To gain insight into why this situation leads to different behavior for the two polarization directions [Fig. 2(c)], we have modeled the interaction of N$_2$ with an ultrashort pulse using a classical approach [18,19]. The dynamics of the molecule in the potential well generated by the ultrashort laser pulse and the induced electric dipole are strongly nonlinear [18]. In particular, the dynamics of the angle $\theta(t)$ between the molecular axis and the laser electric field vector strongly depend upon the initial angle, $\theta_0$ [18,19]. This means that a small difference in the initial distribution of $\theta_0$ can lead to a very different distribution of $\theta(t = 0)$, at the peak of harmonic emission. The behavior observed with N$_2$ is explained by considering that reorientation induced by the pump pulse is assisted when the aligning pulse is polarized parallel to the pump pulse; whereas, for perpendicular polarization, reorientation is impeded and so the harmonic intensity is reduced.

As stated above, our measurements for CS$_2$ are consistent with HHG efficiency depending on the degree of alignment but not on the direction of alignment. In earlier theoretical work [7], the direction of alignment was important, but in these calculations the effects of phase matching on the process were not considered. To explain the behavior, we invoke a dependence of the phase of the emitted harmonic wave upon the molecular orientation. In the semiclassical picture of HHG, this corresponds to the anisotropy of the molecule leading to slightly different classical trajectories depending upon the direction along which the electron is emitted.

A harmonic wave generated by an atom in the presence of a laser field is shifted in phase with respect to the fundamental wave. This phase shift is equal to the phase of the atomic dipole moment induced by an electromagnetic field. The dependence of such a phase on the laser intensity has been discussed in a number of papers (e.g., [20,21]). In particular, it has been shown that in the semiclassical approach, apart from a small correction, the dipole phase is given by [20]

$$\varphi_{\mathrm{dip}} = \frac{S}{\hbar} \approx \frac{(U_p + I_p)\tau_s}{\hbar}. \qquad (1)$$

In Eq. (1), $U_p$ is the ponderomotive potential, $S$ is the quasiclassical action describing the motion of the electron, $I_p$ is the ionization potential, and $\tau_s$ is the so-called return time, i.e., the time for the electron to recollide with the nucleus after it tunnels out. In the plateau region, $\tau_s$ is approximately one period of the fundamental wavelength [20]. Assuming $\lambda = 800$ nm, $U_p = 30$ eV ($I = 5 \times 10^{14}$ W cm$^{-2}$), and $I_p = 10$ eV, we get $\varphi_{\mathrm{dip}} \approx$ 120 rad.

In an anisotropic system, such as a linear molecule, we expect $\varphi_{\mathrm{dip}}$ to depend upon the relative orientation of the molecular axis and the electric field vector of the fundamental beam. In the semiclassical approach, the action depends upon the details of the binding potential through $I_p$ [21]; in a molecule, this factor is orientation dependent. On the other hand, the return time as well as the tunneling time depend upon the atomic binding potential. Thus, it is reasonable to expect that in an anisotropic system the numerator of Eq. (1) will show a dependence upon the direction considered. In our conditions, $\varphi_{\mathrm{dip}} \approx 120$ rad and we see that a change as small as 1% in the numerator of Eq. (1) leads to a change of 1 rad in $\varphi_{\mathrm{dip}}$.

Once we assume an orientation dependence of the phase of the emitted harmonic [i.e., $\varphi \equiv \varphi(\theta)$], the intensity of the given harmonic will include the contributions coming from all the possible orientations of the molecules. This means that the measured intensity depends on the spatial distribution of the molecular axes. In particular, the maximum intensity is obtained when all the molecules are aligned along a certain direction (whatever it is), because in this case $\varphi$ is constant for all emitters. Any other distribution (e.g., isotropic) will lead to a suppression of HHG. Thus, we suggest the increase of $R$ we have observed with $CS_2$ can be ascribed to a reduced angular distribution of the molecular axes.

These effects should be common to all molecules, such as $CS_2$ and hexane, for which controllable alignment can be produced with adiabatic pulses of intensity $\sim 10^{12}$ W cm$^{-2}$. Investigation of these effects in other species is now underway. In the meantime, we hope these results stimulate further theoretical work. Modulation of the harmonic yield by controlled molecular alignment may also permit exploitation in a scheme for enhanced HHG using quasiphase matching [22].

In conclusion, we have made the first experimental observation of an alignment dependence of HHG in molecules. This required us to demonstrate, for the first time to our knowledge, molecular alignment in a dense vapor ($\sim 10^{17}$ cm$^{-3}$) corresponding to $\sim 10^{13}$ molecules in the laser focus. We propose an explanation for the alignment dependence in terms of an anisotropic intensity-dependent dipole phase. Enhanced HHG is found in aligned molecular systems and this may have implications for future developments of this unique light source. Moreover, studies of the harmonic response of aligned molecules provides a powerful new tool for the understanding of anisotropic molecular electron dynamics in intense fields.

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