Monitoring Molecular Dynamics using Coherent Electrons from High-Harmonic Generation

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Here we report the first observation of intramolecular dynamics using electrons rescattered during the process of high-order harmonic generation. We excite coherent vibrations in SF$_6$ using impulsive Raman scattering with a short laser pulse. A second, more-intense laser pulse generates high-order harmonics of the fundamental laser, at wavelengths of ~20-50 nm. The high-order harmonic yield is observed to oscillate, at frequencies corresponding to all the Raman-active modes of SF$_6$, with an asymmetric breathing mode most visible. This is in contrast to conventional impulsive stimulated Raman spectroscopy where only the symmetric breathing mode of the molecule is easily observed. The data also show evidence of relaxation dynamics following impulsive excitation of the molecule. Our results indicate that high harmonic generation is a sensitive probe of vibrational dynamics and may yield more information simultaneously than conventional ultrafast spectroscopic techniques. Since the de Broglie wavelength of the recolliding electron is on the order of interatomic distances, i.e. ~1.5 Å, small changes in the shape of the molecule lead to large changes in the high harmonic yield. This work therefore demonstrates a new spectroscopic technique for probing ultrafast internal dynamics in molecules that uniquely combines ultrafast time resolution with atomic-scale structural information.
INTRODUCTION

A number of recent experiments have used high-harmonic generation (HHG) as a probe of molecular structure.\textsuperscript{1-4} In high-harmonic generation, an atom or molecule is first field-ionized in an intense femtosecond laser field. Part of the electron wavepacket then propagates in the optical field, and can recollide with the parent ion after approximately 1/2 cycle of the driving optical field.\textsuperscript{5, 6} In this picture, the energy of the high-harmonic emission can be directly related to the recolliding electron energy, and therefore to its de Broglie wavelength.\textsuperscript{7, 8} For electron energies of 20-100 eV, the de Broglie wavelength of the recolliding electrons is in the range of \~1-3 Å, and is therefore well-matched to interatomic distances in molecules. Thus, high harmonic generation shows great promise as an in-situ probe of femtosecond and even attosecond\textsuperscript{9-13} nuclear and electron dynamics in molecules.

Recent experimental and theoretical studies have demonstrated that the spectral characteristics of high-harmonic emission from molecules is sensitive to the static structure of a molecule.\textsuperscript{1-3, 14} These studies rely on the fact that the orientational distribution of molecules can be readily manipulated by impulsively exciting rotational wave packets using an ultrashort pulse.\textsuperscript{15-17} A second probe pulse can then be used to generate high harmonics from the rotationally excited molecular ensemble. The symmetry, shape and relative orientation of the molecular orbital to the propagation direction of the returning electron determine the probability of recombination and high-harmonic emission. Thus, by monitoring the high harmonic yield as a function of the orientation of the molecule with respect to the propagation of the recolliding electron, one can map out a molecular orbital. Recent studies have shown promise that both simple two-center interference models\textsuperscript{2, 4, 14} and tomographic reconstruction methodologies\textsuperscript{3} can be used to relate high harmonic generation to the projection of the valence orbitals with respect to the direction of propagation of the recolliding electron.

Nevertheless, these past experiments probed only the static structure of small molecules, leaving largely unanswered the question of broader applicability of these techniques as a probe of structural dynamics in more complex systems. Since the high-order harmonic generation process inherently involves femtosecond pulses and femtosecond-to-attosecond time scales, this process should in principle be extendable to dynamics studies. This technique would thus be
complimentary to techniques such as femtosecond electron diffraction,\cite{18} or proposed experiments to use ultrashort-pulse x-rays,\cite{19} to probe of molecular dynamics.

In this work, we demonstrate that it is possible to use the modulation of high harmonic emission as probe of internal dynamics in molecules. We impulsively excite\cite{20-23} [ref keith nelson, bartels, weinacht, korn] a vibrational wave packet in SF$_6$ using a short laser pulse, and observe oscillations in the intensity of the extreme-ultraviolet high-order harmonic emission generated from these molecules using an intense probe pulse. SF$_6$ was chosen as a spherically-symmetric molecule that can be excited using the impulsive Raman interaction,\cite{22} and that is not excited rotationally. The observed vibrational spectrum contains all the Raman-active modes of SF$_6$ with an asymmetric breathing mode most visible. Furthermore, the oscillation amplitude varies with observed harmonic order, and different vibrational modes exhibit differing behavior. The data also show evidence of relaxation dynamics following impulsive excitation of the molecule.

RESULTS

A Ti:sapphire laser system producing 3 mJ energy pulses with 25 fs duration, at a repetition rate of 1 kHz and at a center wavelength of 760 nm,\cite{24,25} was used to generate the pump and probe pulses. The pump pulse was focused onto an SF$_6$ gas jet at an incident intensity of $5 \times 10^{13}$ W cm$^{-2}$. This pulse excited a vibrational wave packet in the molecular gas through impulsive stimulated Raman scattering (ISRS).\cite{22} To generate high harmonics, the second probe pulse was focused collinearly into the vibrationally-excited gas jet at an intensity of $2.4 \times 10^{14}$ W cm$^{-2}$. This pulse was polarized parallel to the pump pulse, and had a variable time delay. The intensity of harmonic orders 19 through 47 were then recorded as a function of pump-probe delay using an EUV spectrometer and an x-ray CCD camera.

Figure 1 shows the intensity of the 39$^{th}$ harmonic generated in SF$_6$ as a function of pump-probe time delay. The red curve shows the 39$^{th}$ harmonic emission as a function of time after the pump pulses, while the black curve shows the high harmonic signal when the pump pulse is blocked, to determine the baseline noise level of the data. When the pump and probe pulses are overlapped, a coherent artifact appears due to the superposition of the two pulses. At positive delay times, the harmonic intensity is periodically modulated with 17 oscillation periods recorded. The amplitude of the oscillations decays as the delay time is increased. At very small delay times, the baseline
is lowered and then recovers within ~300fs. A similar modulation is observed for all detected harmonic orders.

Figure 2a shows a discrete Fourier transform of the data shown in Figure 1, for an interval between 0.3 ps to 1.2 ps. The red curve shows the Fourier transform of the modulated high-harmonic signal after the pump pulse, while the black curve corresponds to the Fourier transform of the unmodulated high harmonic background (without the pump pulse present). The vertical axis corresponds to the peak-to-peak percent amplitude modulation of the high harmonic signal. Three peaks are visible at 775 cm\(^{-1}\), 643 cm\(^{-1}\), and 525 cm\(^{-1}\), corresponding to oscillation periods of 43 fs, 52 fs, and 63 fs, respectively. The Fourier spectrum was normalized such that the spectral amplitude is the percentage modulation of the high harmonic signal in the time domain. These peaks can be assigned to the three Raman-active vibrational modes of SF\(_6\): \(\nu_1\), \(\nu_2\), and \(\nu_5\).\(^{26,27}\) A representation of the normal vibrational modes of SF\(_6\) is shown in Figure 3. The mode \(\nu_1\) is totally symmetric, whereas \(\nu_2\) and \(\nu_5\) are asymmetric and doubly and triply degenerate, respectively.

The spectrum in Figure 2a demonstrates that electron re-scattering in high harmonic generation is sensitive to all three Raman-active vibrational modes in SF\(_6\), regardless of their symmetry or degeneracy. In contrast, when visible laser light is used as a probe of ultrafast vibrational excitation, only the symmetric breathing mode, \(\nu_1\), is observed (Figure 2b). For this experiment, the vibrational wave packet was created by the same pump pulse as in the high harmonic experiment (Fig. 2a). Thus all the Raman-active vibrational modes are excited. However, instead of probing the molecular vibrations by observing the modulation of the harmonic emission, the oscillations were probed by coherent Raman scattering to study the effect of the vibrational motion on the index of refraction of SF\(_6\), using a longer laser pulse of 400 fs in duration at a central wavelength is 400 nm. The oscillations produce sidebands in the detected spectrum of the 400 nm probe pulse, as depicted in Figure 2b. This result is also consistent with earlier measurement by Bartels and Weinacht\(^{22}\) as well as by Korn\(^{28}\).

For each of the three observed vibrational modes, Figure 4 shows the modulation of the high harmonic signal as function of harmonic order 19 through 47, which corresponds to photon energies 30 eV to 72 eV. The amplitude of both asymmetric modes (\(\nu_2\) and \(\nu_5\)) increases with
harmonic order, with the signal of the mode $v_2$ being above the noise level only for harmonic orders greater than 37. However, the signal strength of the symmetric vibration $v_1$ shows no such trend.

**DISCUSSION**

There are several interesting aspects to the data presented in Figures 1 to 4. First, it is clear that high harmonic emission is sensitive to all three Raman-active modes of SF$_6$, independent of their symmetry. Figure 3 shows the Raman- and infrared-active vibrational modes of SF$_6$, as well as illustrating representative motion of the atoms in the symmetric and asymmetric modes. In our data, we do not observe the infrared-active modes. However, it is likely that the Raman excitation scheme – and not the high harmonic probe technique – precludes us from observing the other vibrational modes of SF$_6$. In general, it is reasonable to expect that the dynamics of most of if not all vibrational modes or conformational dynamics of a molecule might be observable using high harmonic generation as a probe. This is in contrast to optical or infrared probing techniques, where only a subset of modes can be observed.

Second, high harmonic emission is sensitive to small amplitude motions of the nuclei. In the experiment, we observe modulations of up to $\sim$10% in high-harmonic yield. We estimate that this results from an oscillation amplitude of $\sim$2% in the internuclear distance. This estimate is based on calculating the time evolution of the expectation value of the S-F internuclear distance for the symmetric breathing mode $v_1$ during and after the pump laser pulse. After the laser pulse, the relative populations of the states composing the vibrational wave packet are $p(v=0) = 0.85$ and $p(v=1) = 0.14$. Higher excited states are not significantly populated in this experiment.

To explore the high sensitivity of high harmonic emission to different vibrational modes in a molecule, we considered theoretically high harmonic emission from diatomic and linear triatomic molecules. Exact modeling is very challenging because a 3-D, fully quantum model would be required to reproduce the experimental data. However, a 1-D model allows us to study the magnitude of the modulation of the high harmonic emission due to the motion of the nuclei. The model is based on numerically solving the time-dependent Schrödinger equation for H$_2^+$ and H$_3^{2+}$, where the molecule is aligned along the polarization axis of the optical field. For both the diatomic and triatomic case, a $\sim$1% change in bond length results in a $\sim$10% modulation of the
high harmonic signal, which is consistent with our estimate of the level of Raman excitation. Moreover, calculations for a 1-D triatomic molecule show that high harmonic signal is modulated by approximately equal amounts for the two vibrational modes, only one of which would be Raman-active. This agrees qualitatively with our experimental results. It is interesting to note that since the noise level in our experiment is 0.5-1%, which from our calculations corresponds to a ~0.1% modulation in bond length, the sensitivity in this experiment should be ~2 milliangstrom. Such small amplitude motions are on the order of a fraction of the de Broglie wavelength of the recolliding electron, or 0.15nm at a photon energy of 70 eV. Our numerical calculations suggest that while small amplitude motions of molecules are detectable, large amplitude motions should modulate the high harmonic signal even more strongly. High harmonic emission may thus be useful for studying floppy molecules or molecular dissociation. We note that when describing high harmonic generation in a three-step model, both the ionization rate and the recombination probability will be affected by the vibrational excitation of the molecule. However, our current experiment is not able to separate the contributions of these two processes.

Third, as discussed above, the relative intensity distribution of the high harmonic modulation signal corresponding to the three observed vibrational modes differs from that observed in spontaneous Raman as well as in impulsive stimulated Raman scattering experiments. For spontaneous Raman scattering, the symmetric mode produces a much stronger signal that the asymmetric modes - an observation which is made in many molecules. In our experiments probed by modulation of the high harmonic emission, the asymmetric mode \( \nu_5 \) is stronger than the symmetric mode. Two considerations may help to explain this observation. Since we excite SF\(_6\) by impulsive Raman scattering, the ratio of the vibrational oscillation period to the laser pulse duration will determine the strength of the impulse excitation, and this factor favors the lower-frequency asymmetric mode. However, to our knowledge, all experiments that employ coherent Raman scattering as a probe of this impulsive vibrational excitation (and the data in Figure 2b), only observe the symmetric mode \( \nu_1 \), because of lower sensitivity of the stimulated probe to the asymmetric modes. This suggests that using the modulation of high harmonic emission as a probe of vibrational dynamics in molecules might in general be more sensitive to all the vibrational modes in a molecule. This contrasts with other detection techniques that are
limited by selection rules and by lower sensitivity to distortions in the molecule. Moreover, a second significant advantage is that a much smaller number of molecules is needed to observe the vibrational signal. Comparing the relative molecular densities in the two cases studied here, we estimate that high harmonic generation requires a factor of $10^3$ lower density-length product than a comparable stimulated Raman scattering experiment.

Finally, another interesting aspect in our experiment is that we observe relaxation dynamics within the molecule because the amplitude of the modulation of the high harmonic signal in Figure 1 decays for increased delay times. Figure 2c shows the Fourier transform of the data of Figure 1 for early and late time intervals after excitation by the pump pulse. Just after excitation, the peak corresponding to the asymmetric mode $\nu_5$ is approximately twice as strong as the peak corresponding to the symmetric mode $\nu_1$. However, at larger time delays around 1 ps, the magnitude of the asymmetric mode peak decays to the same level as that due to the symmetric mode. In contrast, no decay is observed in the case of the symmetric mode. (Due to the low spectral resolution, the other asymmetric mode $\nu_2$ cannot be identified.) This observation of rapid decay of the $\nu_5$ asymmetric mode might be attributed to rotational dephasing of the excited molecular ensemble. In the impulsive Raman excitation process, the asymmetric modes will be excited in the direction of the polarization of the pump pulse. Subsequently, the molecules rotate randomly. Thus, when the probe pulse arrives, a smaller fraction of molecules will have the $\nu_5$ mode vibrating along the polarization axis of the probe pulse. The modulation of the observed high harmonic emission signal will thus be reduced. This argument does not apply to the spherically symmetric mode $\nu_1$ – which is consistent with the observation of a constant amplitude for that mode, as shown in Figure 2c. One aspect of our data in Figure 1 that is not understood as yet is the observed recovery of the high harmonic signal in the few hundred fs after the pump pulse.

It is worth noting that in Figure 1, the modulation of the high harmonic signal due to the vibrational wave packet also depends on the harmonic order. Figure 4 displays the integrated strength of each peak corresponding to the vibrational modes as a function of harmonic order. Whereas the signal of the symmetric breathing mode is constant within the noise level for all harmonic orders, the magnitude of the peaks corresponding to the asymmetric vibrations clearly increase for orders greater than 37. This indicates that it is desirable to use higher harmonic
orders as a probe of vibrational dynamics, likely due to the shorter de Broglie wavelength of the recolliding electron. Moreover, the timing of the electron recollision process varies with the electron energy. Thus, variations in harmonic signal as a function of harmonic order also potentially provide information on sub-optical-cycle, attosecond time-scale dynamics that can compliment the pump-probe data.

CONCLUSION

In summary, although, high harmonic generation in molecules is not completely understood, this work already demonstrates the potential for a new kind of vibrational spectroscopy with unique advantages. First, the high harmonic emission as a probe of internal dynamics in a molecule is more sensitive to all vibrational modes in a molecule, and is not be limited by “dark states” present in other vibrational spectroscopies. Furthermore, these data provide useful information on dynamics even without extensive analysis of the recollision physics and phase-matching issues. This technique should thus be generally useful for observing dynamics in polyatomic molecules, and could be used to investigate energy redistribution among vibrational modes in molecules, or coherences between vibrational modes. Second, this technique is useful for observing chemically-important ground state dynamics in molecules, and since the vibrations observed herein are small-amplitude motion, the utility of this technique to monitor (generally much larger) conformational changes in molecules is very likely. Third, HHG is a coherent ultrafast process that occurs on sub-cycle timescale. Thus, it may be possible to monitor ultrafast electronic redistribution within the molecule. For example, nonadiabatic processes are ubiquitous in polyatomic molecules, where nuclear and electronic motions are coupled. Since high-harmonic generation is sensitive to nuclear motion and to the symmetry of the electronic state, and has sufficient time-resolution to separate nuclear motion from non-adiabatic processes such as internal conversion, it shows promise as an in-situ probe of femtosecond and even attosecond nuclear and electron dynamics in molecules. And finally, by combining this technique with molecular alignment techniques, structural information about the molecule can retrieved as a function of time as both vibrational and rotational wave packets evolve, or as molecules are highly excited and dissociate.
REFERENCES


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FIGURE CAPTIONS

Figure 1: Intensity of 39\textsuperscript{th} harmonic generated from vibrationally excited SF\textsubscript{6} as a function of time delay between the pump pulse and the x-ray generating pulse. Red curve: high harmonic emission as a function of time after the pump pulse. Black curve: high harmonic emission without the pump pulse present.

Figure 2: \textbf{a} - Discrete Fourier Transform (DFT) of the 39\textsuperscript{th} harmonic emission from Figure 1. \textbf{b} - Stimulated Raman scattering from SF\textsubscript{6} after excitation by the pump pulse, probed by a narrow-band femtosecond laser at a wavelength of 400nm. \textbf{c} - DFT of data from Figure 1 for 0.3 ps time intervals centered at 4.5 ps, 7.5 ps and 10.5 ps.

Figure 3: Normal modes of vibrations for SF\textsubscript{6}. The wavenumber, period, degeneracy and activity of each mode is stated.\textsuperscript{26}

Figure 4: Peak to peak amplitude of the observed modulation for the three vibrational peaks shown in Figure 2a, as a function of harmonic order; \nu\textsubscript{3} (red), \nu\textsubscript{2} (green), and \nu\textsubscript{1} (blue).
Figure 1
Figure 2
$\nu_1$ 775 cm$^{-1}$
43 fs
Raman-active
very strong

$\nu_2$ 643 cm$^{-1}$
52 fs
Raman-active
Doubly Degenerate
weak

$\nu_5$ 525 cm$^{-1}$
63 fs
Raman-active
Triply Degenerate
very strong

$\nu_3$ 948 cm$^{-1}$
35 fs
Infrared-active
Triply Degenerate
very strong

$\nu_4$ 615 cm$^{-1}$
54 fs
Infrared-active
Triply Degenerate
very strong

$\nu_6$ 351 cm$^{-1}$
94 fs
Forbidden
Triply Degenerate
very weak

Figure 3
Figure 4