

# HIGH-ORDER HARMONIC GENERATION (HHG) AS A PROBE OF ROTATIONAL DYNAMICS

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## INTRODUCTION

HHG is a coherent, highly nonlinear optical process whereby the frequency of the incident laser is converted to its integer multiples due to interaction with a suitable medium (1). The HHG spectrum usually spans the extreme UV and since part of the emitted radiation consists of a train of very short bursts it forms the basis for the generation of attosecond pulses (1). During the past three years, there has been intense interest in HHG from aligned molecules, largely inspired by the proposal of Ref. (2) that HHG can be applied to image the electronic orbitals of molecules provided that the molecules are aligned with respect to the ionization pulse. The method of nonadiabatic alignment by short moderately intense laser pulses was found useful as it offered field-free alignment (3). The HHG signal from such aligned molecules strongly correlated with alignment dynamics (3) and in a recent letter we developed a theory that establishes the basis for the observed correlation between revival structures of rotational wave packets and the harmonic intensities (4). The theory is extended to include HHG from gas mixtures containing molecules and atoms by reformulating the theory in a more general density matrix formulation and by studying the imprints of dissipation, due to collisions of the aligned molecule with the bath atoms, on the HHG signal (5).

## THEORY AND RESULTS

The HHG signal is related to the Fourier transform of the expectation value of the time-dependent dipole operator. Defining this expectation value in terms of the density operator which obeys the quantum Liouville equation, the signal is shown to depend on vibrational and rotational coherences prior to the arrival of the ionizing pulse which is responsible for HHG. Obtaining a complete expression involves proper modeling of the electron dynamics incorporating the tunnel ionization of the electron from the ground state, its acceleration in the continuum states, initially away from the core and subsequently toward the core following the phase of the electric field, and finally recombination of the high energy electron leading to the HHG signal. The electron dynamics is treated coherently whereas rotational dynamics initiated by the aligning pump pulse and probed by the ionizing pulse includes dissipative effects. The expression for the HHG signal is cast in terms of a series of rotational expectation values that are determined by the geometry of the experiment and the symmetry of the ground electronic state. The electron dynamics is subsumed in the coefficients accompanying the rotational expectation value series. In addition to useful insight (4) the expressions also provide a convenient computational framework. Evaluation of the rotational expectation values requires the solution of the quantum Liouville equation for the elements of the rotational density matrix. A multi-level Bloch model obtained within the Markov and the secular

approximation is used (6).

The signal can be partitioned into two components of which one corresponds solely to rotational population relaxation and the other follows the time evolution of the rotational coherences. Based on this partitioning one can decompose the signal into a baseline and an oscillatory part (5,7). The baseline part of the signal shown as a red line in Fig. 1 depends only on the timescales of relaxation of the excited rotational population towards thermal equilibrium. The oscillatory part contains information on both the timescales of population relaxation as well as decoherence. From an analysis of the signal one can estimate the rates of population relaxation and decoherence from the experimental signals. The usefulness of the decomposition in unraveling the interplay between different dipole moment components that make up the signal is also delineated (5). Finally we show that the phase of the harmonic signal contains unique information regarding the phases of the electronic dipole matrix elements and hence the underlying electronic continuum (5).

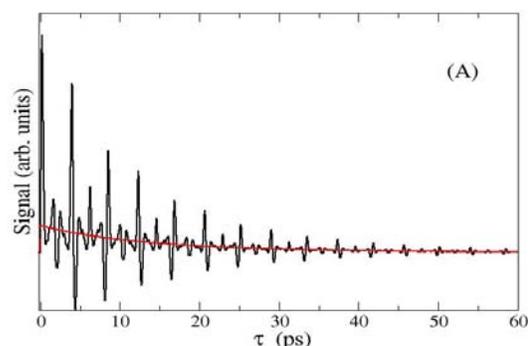


Fig. 1(A). The 23<sup>rd</sup> harmonic versus time delay between alignment and ionization pulses from N<sub>2</sub> molecules subject to an atomic bath of Ar atoms at a pressure of 200 Torr and a temperature of 30 K. The solid black curve shows full signal whereas the red curve traces only the baseline.

## REFERENCES

1. T. Brabec and F. Krausz, *Rev. Mod. Phys.* **72**, 545 (2000).
2. J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pepin, J. C. Kieffer, P. B. Corkum, and D. M. Villeneuve, *Nature (London)* **432**, 867 (2004).
3. T. Kanai, S. Minemoto, and H. Sakai, *Nature (London)* **435**, 470 (2005).
4. S. Ramakrishna and T. Seideman, *Phys. Rev. Lett.* **99**, 113901 (2007).
5. S. Ramakrishna and T. Seideman, *Phys. Rev. A* **77**, 053411 (2008).
6. S. Ramakrishna and T. Seideman, *J. Chem. Phys.* **124**, 034101 (2006).
7. S. Ramakrishna and T. Seideman, *Phys. Rev. Lett.* **95**, 113001 (2005).

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