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Phys. Rev. A **97**, 023401 — Published 1 February 2018

DOI: [10.1103/PhysRevA.97.023401](https://doi.org/10.1103/PhysRevA.97.023401)

Excited state vibronic wavepacket dynamics in H₂ probed by XUV transient four-wave mixing

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The complex behavior of a molecular wavepacket initiated by an extreme ultraviolet (XUV)pulse is investigated with noncollinear wave mixing spectroscopy. A broadband XUV pulse spanning 12eV to 16eV launches a wavepacket in H₂comprising a coherent superposition of multiple electronic and vibrational levels. The molecular wavepacket evolves freely until a delayed few-cycle optical laser pulse arrives to induce nonlinear signals in the XUV via four wave mixing (FWM). The angularly resolved FWM signals encode rich energy exchange processes between the optical laser field and the XUV excited molecule. The non-collinear geometry enables spatial separation of ladder and vee/lambda-type transitions induced by the optical field. Ladder transitions, in which the energy exchange with the optical field is around 3 eV, appear off-axis from the incident XUV beam. Each vibrationally resolved FWM line probes a different part of the wavepacket in energy, serving as a promising tool for energetic tomography of molecular wavepackets. Vee/lambda-type transitions, in which the energy exchange is well under 1 eV, result in on-axis nonlinear signals. The first order versus third order interference of the on-axis signal serves as a mapping tool of the energy flow pathways. Intra and inter electronic potential energy curve (PEC) transitions are decisively identified. The current study opens possibilities for accessing complete dynamic information in XUV excited complex systems.

PACS numbers: 32.80.-t, 42.65.-k, 42.79.Nv

1 Introduction

When a molecule is exposed to an external extreme ultraviolet (XUV)field, dynamics with multiple degrees of freedom can be activated, leading to a complex wavepacket including electronic, vibrational and rotational motion. Studying the dynamics of such a wavepacket is of great significance. First, if many electronic states excited by the coherent XUV pulse are closely spaced in energy, the associated electronic motion has a characteristic time scale comparable to that of the nuclear motion. Under such circumstances, the electronic and nuclear motion can be strongly coupled, and the Born-Oppenheimer(B-O) approximation starts to break down. Consequently, dynamical phenomena such as autoionization, predissociation, curve crossings, and conical intersections emerge [1-6]. Secondly, when an additional optical pulse is used to interrogate the evolution of the wavepacket in a pump-probe geometry, the energy of the electromagnetic field imparted into the molecule will be redistributed to the nuclear and electronic degrees of freedom. This laser driven electronic-nuclear correlation has attracted much attention recently [7-12]; it is a unique feature in molecular systems

compared to atomic species, offering a promising tool for manipulating photochemical reactions. In this paper, the dynamics of an XUV-excited vibronic wavepacket in a prototypical molecular system, H₂, is explored. The recently developed method of XUV/near-infrared (NIR) four wave mixing spectroscopy [13-14]is applied to characterize the many pathways from the interaction of the NIR field with the XUV-excited state, probing such effects as laser-driven electronic-nuclear correlation and quantum coherence of the molecular wavepacket.

There are many examples in which time-resolved photoion and photoelectron spectroscopies using high-order-harmonic-based XUV sources have been used to study highly excited wavepackets in molecules [1-5,15-18]. The more recently developed technique of attosecond transient absorption spectroscopy (ATAS) offers complementary capabilities, as it is an all-optical technique that requires neither photoelectron nor photoion detection, and it can thus be applied to bound states lying below the ionization continuum. For example, ATAS using coaxial XUV and NIR laser pulses has revealed rich dynamic fingerprints in the transient absorption spectrum of

molecules[19-25]. The measured result in ATAS is time-resolved and energy-resolved, a two-dimensional spectrogram[26]. Although this method holds the promise of completely characterizing the excited wavepacket exposed to an optical laser pulse, the very congested energy levels and the multitude of quantum pathways pose great challenges for interpretation of the spectra. Multidimensional spectroscopies employing one or more XUV pulses have the potential to unravel this spectral complexity[27].

Recently, it has been shown that by crossing an XUV attosecond pulse with a NIR laser pulse at a small angle, nonlinear XUV-NIR four wave mixing (FWM) from anatomic gas medium is observed at different emitting angles determined by the phase matching conditions [13]. Under such a non-collinear geometry, ultrafast XUV spectroscopy gains an additional dimension that is angle-resolved. This extra dimension can be utilized to successfully disentangle different transition pathways that appear at the same energy, offering a means to gain deeper insight into the associated physical processes. In this paper, we apply this non-collinear transient wave mixing approach to study the response of electronically/vibrationally excited molecular hydrogen to an ultrafast NIR laser pulse and uncover the detailed energy exchange pathways between the NIR pulse and the vibronic wavepacket initiated by the XUV pulse.

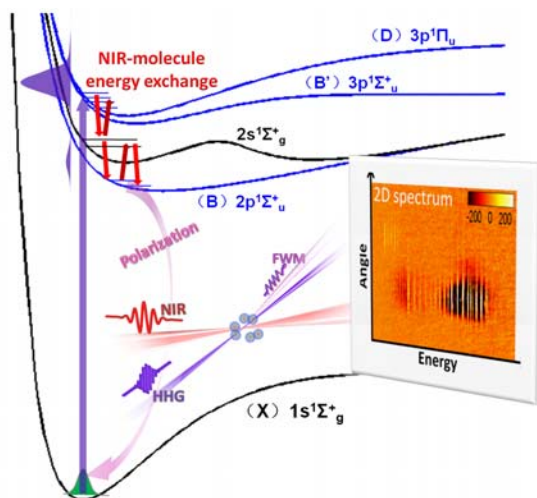


Figure 1. Schematic of non-collinear transient wave mixing spectroscopy in H_2 . The high order harmonics pulse (violet vertical arrow) promotes the molecule into a coherent superposition of multiple vibronic states in the np manifold. A delayed NIR pulse intersects with the HHG pulse at a crossing angle and drives transitions that are responsible for different energy flow pathways in the excited molecules. The laser-matter interaction induces a polarization dipole (purple arched arrow) that is detectable by a CCD camera (inset). The energy flow pathway between the NIR pulse and molecules determines the direction of the transmitted XUV signal to conserve the momentum.

Figure 1 summarizes the principle of the experiment. The XUV pulse from high harmonic generation (HHG) populates multiple potential energy curves (PECs), primarily the B' and D states, in H_2 , from which a complex vibronic wavepacket is formed that evolves freely. The coherence between the ground and excited electronic states forms a polarization dipole that can radiate XUV light. When the NIR pulse arrives first, the polarization in the XUV region is only a linear response induced by the harmonics. When the moderately intense NIR pulse arrives at or after the XUV pulse, it drives transitions between vibrational levels created by the XUV excitation. This action effectively builds up a nonlinear term in the polarization. This nonlinear term is predominantly a FWM process. By taking the difference between spectra with the NIR arriving first and NIR coinciding temporally with HHG, the laser-induced nonlinear response is captured as shown in the insets of figure 1. The molecules can either gain or lose energy during their interaction with the NIR pulse, and the energy flow direction depends on the sign of the net photon energy resulting from the two NIR photon transition. Due to phase matching, the non-collinear configuration between the two mixing pulses spreads the nonlinear XUV signals associated with different NIR induced transitions at nonzero angles with respect to the XUV beam. Laser driven vee/lambda-type transitions lead to a FWM signal emitting almost along the incident HHG propagation direction, while ladder-type transitions give rise to the background free FWM signal at larger emission angles. By examining the individual transition pathways in a time-resolved manner, energy exchange dynamics between the optical laser field and the XUV excited molecules can be extracted in great detail.

2 Results

The experimental method is similar to that reported previously [13]. In brief, HHG is carried out in xenon gas using a sub-7 femtosecond NIR pulse centered around 780 nm. The generated HHG spectrum is shaped by an indium filter to mainly contain the 9th harmonic (~15 eV) and a much weaker 7th harmonic (~12 eV). The shaped HHG field is thus an attosecond pulse train and its estimated duration is 2 fs. A replica of the few-cycle NIR pulse is picked off from the original pulse and intersects with the HHG pulse at an angle $\alpha \approx 12 \text{ mrad}$, the value of the angle is calibrated based on the interference pattern of two NIR pulses as shown in [13]. In the interaction region, the NIR pulse has a beam size of about 250 μm and the peak intensity of the NIR pulse is estimated to be $1 \times 10^{12} \text{ W/cm}^2$. The combined NIR and HHG pulse induce nonlinear wave mixing in the gas medium over a path length of about 1.5 mm, and the transmitted and emitted XUV spectrum after the medium is recorded by a high-resolution spectrometer with angular resolution.

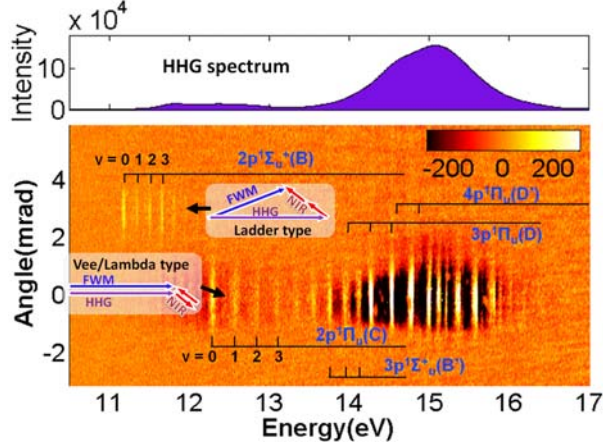


Figure 2. 2D image of the differential XUV spectrum versus angle after the nonlinear wave mixing in H_2 gas. The NIR pulse and the high harmonic pulse overlap in time at a non-collinear angle. The differential spectrum is obtained by subtracting the spectrum with the negative time delay spectrum (NIR arrives first). The zero angle indicates the propagation direction of harmonics. The color scale indicates emission or absorption in arbitrary units. Phase matching diagrams for ladder type and lambda/vee type transitions are also shown.

Figure 2 shows the 2D XUV differential spectrum when the NIR and XUV pulse are temporally overlapped. Extensive structure is seen both on and off-axis, from lambda/vee transitions and ladder transitions, respectively. The many vibronic levels activated by the XUV pulse overlap spectrally in the on-axis signal and thus can be only assigned partially.

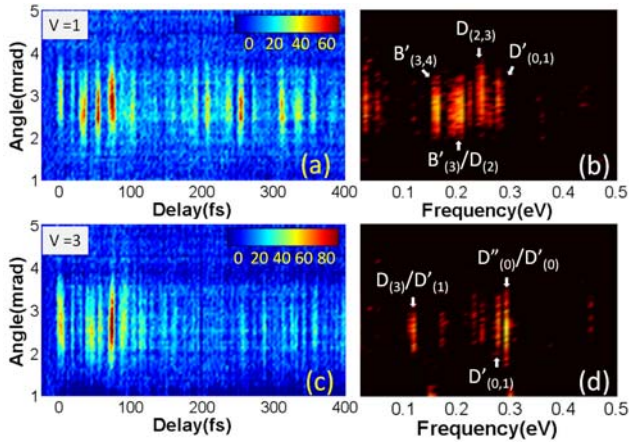


Figure 3. Angle-resolved and time-resolved off-axis FWM signal for $v=1$ (a) and $v=3$ (c) on the B electronic state, the integration window for each vibrationally resolved FWM signal is about 0.05 eV. The delay step size is 1 femtosecond. (b) and (d) are the Fourier transformations along the delay axis for $v=1$ and $v=3$, respectively.

The off-axis emission around +3 mrad in Figure 2 is background free nonlinear signal from ladder-type transitions. The time-resolved and angle-resolved intensity

of two off-axis emission lines corresponding to $v=1$ (11.34eV) and $v=3$ (11.66eV) of the B state are shown in Figures 3a and 3c. Some of these features are vertically displaced relative to others, an aspect that is discussed below. The corresponding Fourier spectra as functions of frequency (in eV) are shown in Figures 3b and 3d, respectively. The Fourier analysis provides two-dimensional information from which one can determine the states responsible for the various beat frequencies.

Figure 4 shows the delay-dependent absorption spectrum of the on-axis signals integrated over 1 mrad. This is similar to an attosecond transient absorption measurement except that ladder transitions are directed off-axis by the phase matching condition. The 7th and 9th harmonics induce polarizations associated with the B and Rydberg states, respectively. Common fingerprints in ATAS such as the energy shift/splitting at early delays due to the dynamic Stark effect as well as the periodic modulations on various transition lines are clearly observed.

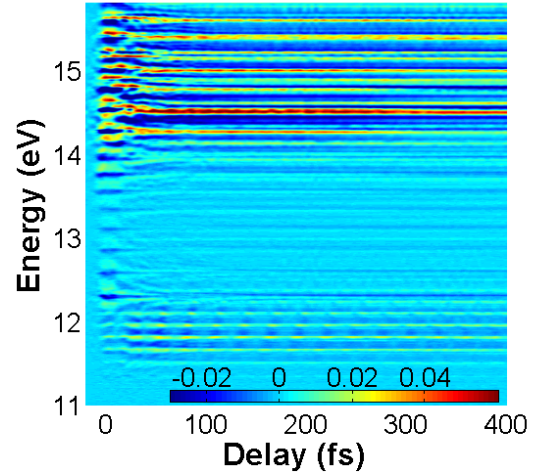


Figure 4. Absorption spectrum (optical density) of the on-axis signal as a function of time delay, positive delay means NIR arrives later.

3 Discussion

3.1 Off-axis FWM

According to the phase matching diagram in Figure 2, the emission angle θ of the nonlinear signals shown in Figure 2 is proportional to the net energy exchanged Δ between the molecule and the NIR field, $\theta = \alpha \times \Delta / E$, where E is the energy of the state where the laser driven transition ends [13]. The non-collinear wave mixing therefore projects the energy flow of laser-molecule interaction onto the emission angle, effectively separating the otherwise entangled transition pathways. The isolated signal appearing around 3 mrad is due to a 3.1 eV downward ladder type energy exchange. It results from a transition from the vibrational

levels at around 15 eV to the vibrational levels on B state by stimulated emission of two NIR photons.

The time-resolved off-axis signal shown in Figure 3 encodes the quantum coherence of the wavepacket created by the XUV pulse onto the $v=1$ and $v=3$ levels of the B state. Because there are many pathways feeding into the same final state coherently, the intensity of the nonlinear signal shows delay-dependent modulations due to interference, which can be used to trace the quantum coherence of the molecular wavepacket.

The limited bandwidth (~ 0.5 eV) of the NIR pulse sets constraints on the initial states (prepared by the XUV only) that can contribute to the FWM, i.e. the initial states must lie roughly 3.1 eV above the final state. For the $v=1$ emission line (11.34 eV) the probed states lie around 14.45 eV, where the B', D and D' states overlap (see Figure 5d). Thus, this emission line is probing quantum coherence of a complex wavepacket consisting of B', D and D' states. The beat frequency alone is not always sufficient to unambiguously determine the involved states because of the congested energy levels in this region. The emission angle of the beat frequency is closely related to the mean energy E_m of the two states contributing to be beat signal by: $\theta = \alpha \times (E_m - E_i) / E_m$, where E_i is the energy of the B state vibrational level. Hence, larger values of E_m lead to emission at larger θ , leading to the variations in the vertical displacements seen in Figs. 3a and 3c.

We can pinpoint the sources for each beat frequency in Figure 3b by combining both the observed angle and beat frequency. The two lower frequency components (0.165 eV and 0.202 eV) with angle $\theta = 2.7$ mrad are from states around 14.4 eV. From the known energy levels, we can assign them as the vibrational coherence on B' ($v=3$ and $v=4$) and vibronic coherence between B' ($v=3$) and D ($v=2$), respectively. The two higher frequency components (0.248 eV and 0.278 eV) with a slightly larger emission angle $\theta = 2.9$ mrad are from states at 14.7 eV, and they are attributed to vibrational coherences on D ($v=2$ and $v=3$) and D' ($v=0$ and $v=1$) states.

For the $v=3$ emission line (11.66 eV), the probed initial states lie around 14.76 eV, where the wavepacket consists of D, D' and D'' states. Following a similar analysis as for the $v=1$ emission line, we can assign the quantum beats in Figure 3d, and they are indeed from vibrational levels belonging to D, D' and D''. The angles for D(3)/D'(1) and D''(0)/D'(0) beating components are predicted to be 2.57 mrad and 2.52 mrad, respectively. These values are consistent with the experimental observations in Figure 3d, confirming our assignments. Therefore, the vibrationally-resolved homodyne FWM is effectively an energetic tomography for probing dynamics by sectioning the wavepacket along the energy axis, analogous to conventional geometric tomography.

3.2 On-axis FWM

Based on previous work on ATAS of Ar [30] and N₂ [20], the periodic modulations of various transition lines in Figure 4 are attributed to first order versus third order quantum path interferences. The inverse of the modulation period is equal to the beat frequency of two states coupled by two NIR photons [19-21, 30-33]. The absorption lines around 12 eV are mainly attributed to the B state. Each absorption line is oscillating along the delay axis with the period progressively increasing with the energy, and accordingly the energy difference of the adjacent vibrational levels coupled by two NIR photons decreases with energy. This regular oscillatory pattern is closely related to the anharmonic shape of a single PEC. In contrast, the absorption profile above 14 eV stems from many PECs that participate in the nonlinear process. The laser pulse can drive transitions either within the same or between different PECs, leading to a much more complex delay-dependent oscillation pattern.

Figure 5 is the Fourier transformation of Figure 4. It shows the detailed beat frequency distribution of vibrational levels involved in the laser-driven transitions. The vibrationally-resolved frequency distribution between 11 eV and 13 eV (see Figure 5a) shows clear signatures of transitions on the B electronic state. Within its bandwidth (~ 0.5 eV), the few-cycle laser pulse can induce Raman type transitions with Δv equal to 1, 2, and 3, corresponding to an energy exchange from 0.15 eV up to 0.45 eV. Each energy exchange group (i.e. $\Delta v = 1, 2, 3$) is bifurcated into two branches. In one branch, the final state lies above the initial state, corresponding to a positive energy flow where the molecule is gaining energy from the laser field, while in the other branch the energy flow direction is reversed. The cyan (white) pentagons are the predicted values for positive (negative) energy flow from the known vibrational energy levels, in good agreement with the experimental results. In this region, the energy exchange results solely from vibrational transitions.

The frequency distribution above 14 eV (Figure 5c,e,f) has a rather irregular pattern and encodes much more complicated dynamic information. The Franck-Condon factors from the ground state to the final states determine the possible involved PECs. The candidates include the $np\Sigma_u$ and $np\Pi_u$ molecular Rydberg states with $n \geq 3$. By examining the beat frequencies of these PECs carefully and comparing with the measurement, we can break up the overall distribution into multiple distinct groups and assign them to different transition pathways. The pure vibrational transitions on the lowest Rydberg states $3p\sigma_u(B')$ and $3p\pi_u(D)$ can be recognized from their characteristic beat frequencies that line up with negative slopes (Figure 5c), which is similar to Figure 5a. There is a second type of energy exchange pathway in which only the electron exchanges energy with the laser field. Such a process is

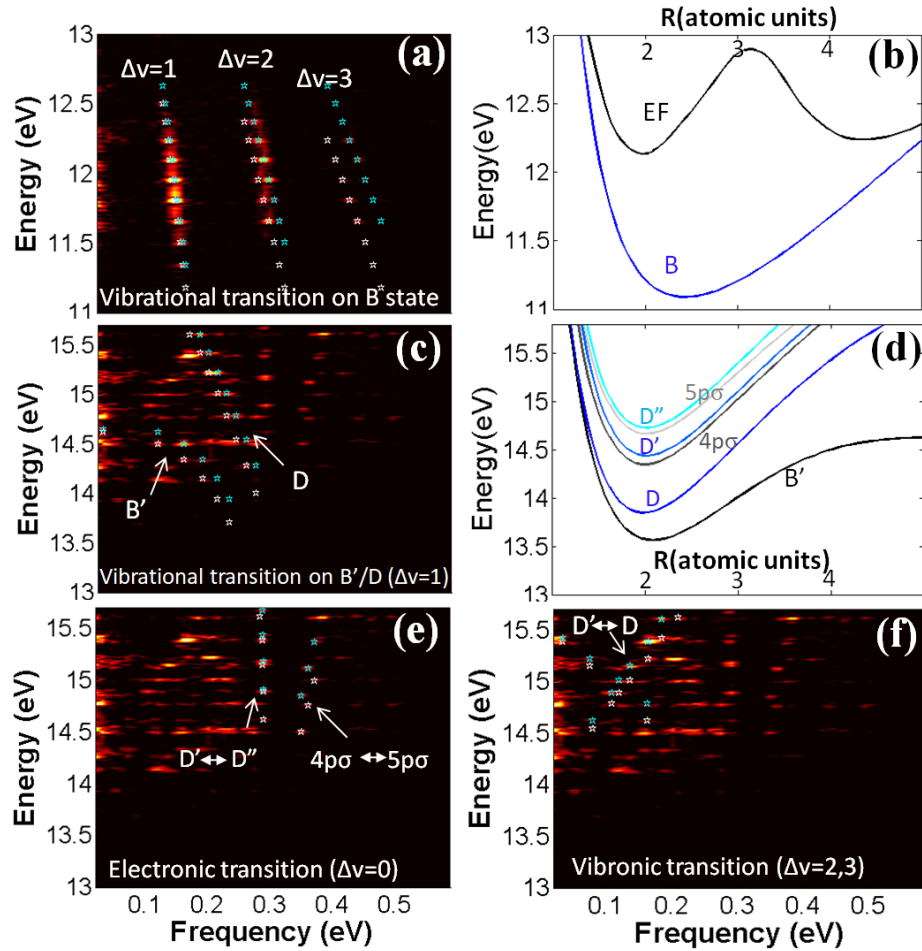


Figure 5. Fourier analysis along the delay axis in the absorption spectrogram of Figure 4, separated into low energy (a) and higher energy transitions (c,e,f). The coherences in panel (a) are from energy exchange between vibrational transitions of the B state. The energy exchange pathways in panels (c,e,f) involve the higher lying Rydberg states and are more complex. They can involve only vibrational (c) or electronic transitions, (e), or combinations of the two (f). The cyan (white) stars are the predicted values corresponding to the positive (negative) energy flow from the molecule to the laser field, respectively. The relevant PECs are shown in (b) and (d). The vibrational energy levels are adopted from Ref[28-29, 34].

indicated in Figure 5e. The beat frequencies at 0.29 eV are due to the laser driven quantum transition between $4p\pi_u(D')$ and $5p\pi_u(D'')$ with $\Delta v=0$ as predicted by the theoretical values. The similar shapes of D' and D'' states indicate a negligible change of the nuclear position after the transition, and the molecules gain or lose energy by a pure electronic transition. This value (0.29 eV) is consistent with the asymptotic energy difference between D' and D'' . From the experiment, we can also identify the signature of electronic transitions between $4p\sigma_u$ and $5p\sigma_u$ with beat frequencies around 0.35 eV. The diabatic $4p\sigma_u$ curve is strongly perturbed by the $(2s\sigma_u, 2p\sigma_u)$ doubly excited state and the ion-pair $H^+ + H^-$ ($1s\sigma^2$) state [35]. The perturbation deforms the shape of the diabatic $4p\sigma_u$ state. The slightly different shape between the $4p\sigma_u$ and $5p\sigma_u$ states leads to a larger value than 0.29 eV for transitions with $\Delta v=0$.

A third type of transition pathway is shown in Figure

5f. The profound beat frequencies forming a crossing pattern are fingerprints of transitions between Rydberg states $3p\pi_u(D)$ and $4p\pi_u(D')$ with $\Delta v=2$. They indicate vibronic transitions where both the electronic and vibrational levels change after the NIR laser-molecule interaction. The most pronounced beat frequency (~ 0.165 eV) is located at 15.388 eV ($v=3$ state on D') in energy. It results from laser induced population transfer from $D(v=5)$ to $D'(v=3)$. The D and D' states, with similar potential wells, are associated with the 3p and 4p electrons, respectively. The electron gains an energy of 0.6 eV (estimated from the asymptotic energy difference between D and D'), while the nuclei lose 0.44 eV (the energy difference between $v=5$ and $v=3$ vibrational levels on D' or D) during the interaction. This laser-driven energy correlation between the nuclei and electron leads to a net energy flow of ~ 0.16 eV from the laser field to the molecule.

Each type of energy exchange pathway identified in Figure 5 consists of two branches that represent the two opposite energy flow directions (blue stars - positive and white stars - negative). In the current non-collinear beam experiment, the nonlinear signals associated with positive energy flow for which the molecule absorbs energy from the laser field is at a slightly negative emission angle, while that responsible for negative energy flow has a small positive emission angle. Although we select the on-axis signals centered at zero angle to reveal both processes simultaneously as shown in Figure 5, the angle-resolved capability of the current spectroscopy allows us to spatially separate these two energy flows if the angular signals are isolated carefully. This indicates the possibility for accessing complete dynamic information of an excited molecular wavepacket exposed to a laser field.

4. Conclusions

The response of excited molecular hydrogen to an optical laser pulse is experimentally investigated using attosecond transient four wave mixing spectroscopy. The vibronic wavepacket prepared by attosecond pulses interacts with a time delayed laser pulse and energy exchange occurs between the optical field and the excited molecule. In the non-collinear experimental configuration, ladder transitions with energy exchanges of several electronvolts lead to off-axis nonlinear signals that are background free, and these signals are vibrationally resolved and encode quantum coherences of the molecular wavepacket. Each vibrationally resolved FWM line probes a different part of the wavepacket in energy, serving as a promising tool for energetic tomography of molecular wavepackets. Vee and lambda transitions with energy exchanges of a fraction of an electronvolt lead to nearly on-axis nonlinear signals. The first order versus third order interference of the on-axis signal serves as a mapping tool of the energy flow pathways. Intra and inter PEC transitions are conclusively identified, revealing the complicated nature of the molecular wavepackets. Such time-resolved, energy-resolved and angularly-resolved XUV nonlinear spectroscopy reveals the possibility of accessing complete dynamical information of the laser-molecule interaction.

Acknowledgements

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences through the Atomic, Molecular, and Optical Sciences Program of the Division of Chemical Sciences, Geosciences, and Biosciences of the US Department of Energy at LBNL under contract nos. DE-AC02-05CH11231. AF acknowledges funding from the National Science Foundation Graduate Research Fellowship Program.

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