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Mechanisms of Shock-Induced Reactions in High Explosives

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Abstract. Understanding the mechanisms by which shock waves initiate chemical reactions in explosives is key to understanding their unique and defining property: the ability to undergo rapid explosive decomposition in response to mechanical stimulus. Although shock-induced reactions in explosives have been studied experimentally and computationally for decades, the nature of even the first chemical reactions that occur in response to shock remain elusive. To predictively understand how explosives respond to shock, the detailed sequence of events that occurs – mechanical deformation, energy transfer, bond breakage, and first chemical reactions – must be understood at the quantum-mechanical level. This paper reviews recent work in this field and ongoing experimental and theoretical work at Sandia National Laboratories in this important area of explosive science.

INTRODUCTION

Despite much research into the mechanisms by which shock waves initiate chemical reactions in explosive materials, the reaction processes that take place in response to shock, the physical processes that drive them, and the material properties that enable reactions are not fully understood at the molecular level. Questions surround many important elements of the reaction process: which chemical bonds are the first to break, the physical processes that cause these bonds to break, the microscopic and macroscopic variables that control the initial reaction steps, the timescales of reaction, the influence of crystal structure, and the mechanisms of energy localization by crystal defects. The practical results of these shortcomings are that explosive sensitivity is not well understood, initiation of detonation is difficult to model predictively, and the design of new and less sensitive materials is challenging.

A recent review by Politzer and Murray [1] describes many of the challenges involved in understanding shock sensitivity. In that work, the authors summarize the many empirical correlations that have been drawn between shock sensitivity and various molecular properties in attempts to understand the chemical origins of shock sensitivity in explosives. Bond energies, bond lengths, bond polarities, band gaps, rates of vibrational energy transfer, thermochemical quantities, and other properties have been found to correlate with shock sensitivity of explosive compounds. Correlations of this type, however, have only been found within limited sets of similar materials; few (if any) correlations have been found between shock sensitivity and molecular properties that apply broadly to explosives in general. In the words of Politzer and Murray, these correlations "reflect causation but do not directly reveal it"; that is, these limited correlations appear to provide glimpses of underlying mechanisms that are not yet fully understood. Ultimately, the mechanisms that we need to understand are the detailed quantum-mechanical mechanisms that govern the reaction processes.

The work described in this paper aims to develop a better understanding of the chemical physics of shock-induced reactions in explosive materials, particularly at the quantum-mechanical level. A major goal of this paper is to highlight potential gaps in our understanding of shock-induced reactions and outline experimental and computational strategies to probe these areas. A survey of recent work in this area is first presented. This is followed by a comprehensive discussion of chemical and physical phenomena that may be important to shock-induced reactions, with particular attention focused on aspects of the problem where significant knowledge gaps exist. Finally, strategies for probing these phenomena and closing these knowledge gaps are presented in a discussion of recent and ongoing work at Sandia National Laboratories.

SURVEY OF PREVIOUS WORK

A brief survey of previous work on the quantum mechanisms of shock-induced reactions is presented below. This survey is not meant to be comprehensive, but to provide an overview of some major results in the area and provide a basis for comprehensive discussion of physical phenomena that may be relevant to shock-induced reactions.

Previous Work: Theory

Theoretical work on quantum-mechanical processes involved in shock-induced reactions has primarily been focused along two directions: thermal reactions produced by shock heating [2-4], and prompt reactions caused by shock-induced electronic excitations [6-11]. Previous work on thermal reactions is primarily focused on the effects of weak shock waves near or below the threshold required to produce observable reaction [2, 3]. Work on electronically-induced reactions, by contrast, is expected to be more relevant to stronger shocks and near detonation conditions [7].

Shock heating and thermal reactions of explosive crystals have been described within the framework of vibrational up-pumping by Dlott and Fayer [2] and Tokmakoff, Fayer, and Dlott [3]. In vibrational up-pumping, the passage of a shock wave excites phonons (low-frequency crystal lattice vibrations), which rapidly equilibrate. This vibrational energy within the lattice is then transferred to molecular vibrations *via* anharmonic coupling. Particularly rapid lattice-to-molecule vibrational energy transfer occurs *via* excitation of low-frequency "doorway" modes in the molecule, which are low enough in frequency to be excited by low-order anharmonic coupling processes (such as two-phonon absorption). Vibrational energy within the molecules then quickly equilibrates by intramolecular vibrational redistribution (IVR). Reaction occurs upon accumulation of sufficient vibrational energy to break chemical bonds. This mechanism provides a means for localization of thermal energy and reaction at defect sites, which are known to be important in shock-induced reactions, as local increases in anharmonic coupling can occur in the vicinity of crystal defects. Predictions of the vibrational up-pumping model have been confirmed experimentally as described below, and Fried and Ruggiero [4, 5] have shown that energy transfer rates predicted by the up-pumping model strongly correlate with impact sensitivity for a variety of explosive compounds.

Electronically-induced reactions have been predicted by Gilman [6], Kuklja, Stefanovich and Kunz [7], and Kuklja *et al.* [8, 9]. A framework has been developed that predicts large changes in the electronic structure of molecules and the lattice in response to strain and lattice compression. In the isolated molecule, strain leads to large-amplitude bending, which generally decreases the difference in energy between the ground and excited states of the molecule (i.e. reduces the HOMO-LUMO gap). Similarly, in solids, compression of the lattice decreases the difference in energy between the valence and conduction bands (i.e. reduces the band gap). Kuklja *et al*. predict a significant effect to occur under hydrostatic compression and during shock compression, and to be enhanced by the presence of dislocations and other crystal defects. As of this writing, these effects do not appear to have been quantified experimentally, although Kulkja [9] describes numerous experimental observations that are consistent with and suggest the participation of electronic effects in shock-induced reactions.

Previous Work: Experiment

Experimental work on probing the quantum-mechanical mechanisms of shock-induced reactions have primarily been centered around spectroscopic investigations of vibrational dynamics and observation of reaction products. Dlott *et al*. [12, 13] have conducted a series of experimental investigations to demonstrate the vibrational up-pumping model. McGrane *et al*. [14, 15] have used temperature-dependent Raman spectroscopy to analyze the anharmonic couplings that are key to rapid vibrational energy transfer. A variety of Raman spectroscopy measurements have been performed to examine changes in molecular and crystal structure under static and shock compression [16-20]. Davidson *et al*. [20] performed static compression experiments on TATB, and using Raman spectroscopy noted apparently reversible changes in crystal structure and electronic structure up to 150 GPa, with no evidence of chemical decomposition.

Experimental investigations by Dick *et al*. [21], Dreger *et al.* [22], and Dang *et al.* [23] have examined emitted light from single crystals of PETN and RDX subject to varying shock conditions. The earlier experiments of Dick *et al*. [21] established that the sensitivity of single crystals of PETN depends on the orientation of the shock wave with respect to the crystal axes, and hypothesized that the orientation dependence was caused by variations in mobility of

dislocations along different orientations. A steric hindrance model was developed to explain the observations, which shows that motion of dislocations along the sensitive directions is hindered by steric interactions between adjacent molecules on either side of the slip plane, and the motion of dislocations along the insensitive directions is not. They hypothesized that these steric interactions result in sensitivity along certain directions because dislocation motion along sensitive directions result in either vibrational excitation of molecules, or possibly even bond rupture by collisions. The later experiments of Dreger *et al*. [22] showed time-varying emission from shocked PETN single crystals, which the authors attributed to emission from NO_2^+, and devised a four-step initiation mechanism outlining the initial steps of reaction.

CHEMICAL PHYSICS OF SHOCK-INDUCED REACTIONS

The results described above illustrate the complexity of shock-induced reactions, the importance of a broad variety of material properties, and the participation of various phenomena in shock-induced reactions. Here we describe many of those important processes and properties, with particular attention to those areas in need of further measurements and modeling.

Influence of Material Properties

Material properties at all scales (macroscopic to molecular) are known to affect shock-induced reactions. At the molecular level, the geometry of molecules and their functional groups dictate their properties and reactivity. The vibrational structure of molecules and anharmonic couplings between modes dictate rates of vibrational energy transfer as shown by Dlott and Fayer [2] and Tokmakoff, Dlott, and Fayer [3]. The electronic structure of molecules, which depends strongly on the functionality of the molecule and its geometry, determine the electronic band structure of the solid, which is key to the electronically-induced reaction mechanism of Kuklja *et al*. [7-9]. At the crystal lattice level, the geometric arrangement of the molecules in the lattice is key to all known and proposed reaction mechanisms – the relative geometry of molecules affects vibrational coupling in the solid, affects the electronic band structure, and influences relative motion of defects and collisions between molecules as Dick *et al*. [21] describe. Crystal defects are well-known to affect nearly all properties of solids [24], from bulk mechanical properties (such as hardness and elasticity) to quantum mechanical properties (such as electronic band structure [9] and vibrational energy transfer [3]). Crystal defects often have a greater impact on the behavior of solids than the lattice istelf [24]. Point defects (such as vacancies), line defects (such as dislocations), and volume defects (surfaces, voids) all introduce local variations in the vibrational and electronic structure with potentially lower barriers to reaction.

Dynamic Variables

While the dynamic behavior of explosive materials at the continuum level are typically parameterized in terms of temperature and pressure, connecting the concepts of bulk temperature and pressure to dynamic events at the molecular level is not straightforward. At the macroscopic level, temperature is a measure of random equilibrium thermal motion in a material; shock compression, by contrast, initially sets up highly nonequilibrium conditions in the crystal lattice that require time to thermalize [2, 3]. Two central questions surrounding shock-induced reactions are how much time is required for the shocked material to undergo vibrational redistribution and achieve thermal equilibrium, and whether reactions occur before equilibrium is established [2, 3, 10, 11, 25]; i.e. whether particular reactions are thermal or athermal. In the electronic excitation reaction mechanisms of Kuklja *et al*. [7-9], for example, reactions are expected to occur immediately behind the shock front well before temperature is well defined. Pressure, at the macroscopic level, is defined as force per unit area. At the microscopic level, shock compression causes compression of the crystal lattice, mechanical distortion of molecules [6], and acceleration of molecules into one another [21]. Some reactions at the molecular level could be caused by changes in electronic properties [7-9], by large-amplitude distortion [6], or by collision [21], all of which are the result of instantaneous mechanical changes rather than random thermal motion in the lattice. A characteristic difference between thermal and athermal reactions is time; truly thermal reactions occur once the shocked system to relaxes to an equilibrium environment; athermal reactions do not require establishment of equilibrium.

Dynamic Processes

Consideration of the above results in a variety of dynamic processes that occur at the molecular level whose results must be understood. At the molecular level, compression results in (*i*) mechanical deformation, (*ii*) changes in electronic structure, and (*iii*) vibrational energy transfer. At the lattice level, shock compression results in (*i*) mechanical deformation of the lattice, (*ii*) interactions and collisions between molecules, (*iii*) changes in electronic structure, (*iv*) vibrational energy transfer, and (*v*) thermalization and establishment of equilibration. Additionally, the presence of crystal defects enable (*i*) relative motion of portions of the lattice, (*ii*) interactions between molecules, (*iii*) localization of vibrational energy, and (*iv*) local variations in electronic structure. These are the dynamic processes that must be quantified experimentally and computationally in order to fully understand shock-induced chemical reactivity.

PROBING DYNAMIC PROCESSES IN SHOCK-INDUCED REACTIONS

Sandia National Laboratories has begun a large-scale effort to understand many of the dynamic processes relevant to shock conditions. These efforts include a variety of spectroscopic measurements and quantum chemical modeling, as well as molecular dynamics and grain scale modeling of effects at larger scales. Some recent and ongoing investigations aimed at understanding quantum mechanisms at the individual molecule and lattice levels are summarized here.

Modeling Dynamic Processes Using Quantum Chemistry

A central question, raised by Gilman [6], is what effect mechanical deformation has on the electronic structure of molecules in a crystal lattice and what types of reactions this might enable. Gilman's results imply that large-amplitude bending (of a form more severe than would be found in ordinary gas-phase and liquid phase thermal environments) could enable spontaneous bond breakage. A series of calculations were undertaken to understand how secondary explosive molecules respond to large amplitude bending, and whether unimolecular dissociation could be directly induced by bending [26]. DFT calculations were undertaken on nitromethane, trinitrotoluene (TNT), and 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) using the B3LYP functional and the 6-311++G(2d,2p) basis set. The potential energy surfaces of the ground singlet and triplet states were calculated as the nitro moieties of the molecules were bent along the angles shown in Figure 1. Figure 2 shows representative results for nitromethane and TATB; simple bending does not appear to induce dissociation, as evidenced by the lack of a perceptible dissociation asymptote and lack of degeneracy between the singlet and triplet states. Motivated by these results, a series of calculations were performed for other large-amplitude motions, including the "shearing" motion shown in Figure 3. Results of these calculations are shown in Figure 4, along with similar results for simple C-NO_2 stretching motion. The calculations show that transverse displacement of the NO_2 moiety does induce dissociation, with an energetic landscape similar to C-NO_2 stretching motion. This result is interesting as it supports the notion put forth by Dick [21] that collisions between molecules during relative motion of the lattice could potentially cause direct mechanical rupture of bonds, and also connects Dick's results with Gilman's notion [6] that chemical reactions could be directly triggered by mechanical forces in solids because (unlike gases or liquids) solids support shear strains.

Probing Reaction Chemistry Using Spectroscopic Techniques

One experimental approach to interrogating chemical reaction mechanisms involves identifying intermediate and product species and their rotational-vibrational-electronic quantum state distributions, which can be used to infer details about the potential energy surfaces that govern reaction processes. This approach has been used extensively in chemical physics, particularly in areas such as photochemistry [27]. In energetic materials, Dick *et al*. [21] and Dreger *et al.* [22] have used emission spectroscopy to characterize intermediate species and the first reaction steps in pentaerythritol tetranitrate (PETN) crystals. At Sandia we have begun a campaign [28, 29] to identify reaction products using streaked emission spectroscopy, in which light emitted from a reacting sample is passed through a spectrometer and then a streak camera, generating a two-dimensional record (wavelength vs. time) of the emitted light. Figure 5 shows results from experiments conducted on detonating thin films of hexanitrostilbene (HNS, thickness ~200 μm). The streak spectrum shows emission from the detonating explosive, as well as artifacts due to

the impurities in and transmission of light through a fused silica sample fixture. The most prominent emission features are from the $B^2\Sigma^+ - X^2\Sigma^+$ system of the CN radical; broadband emission from 300 – 650 nm is also observed. Figure 5b compares the time-integrated spectrum with a simulation of CN emission, in which the rotational and vibrational temperatures of CN are set to 10,000 K. Given that the detonation temperature of HNS is approximately 3,600 K [30], it is clear that the CN observed in this spectrum is created with a much higher degree of rotational and vibrational excitation than would be expected in an equilibrium thermal environment. The late broadband emission is compared with several blackbody curves in Figure 5c; no blackbody curve of reasonable temperature fits the emission spectrum, and blackbody emission with the same peak wavelength (~400 – 450 nm) would corresponds to a temperature of 6,000 – 7,000 K. The broadband emitted light is therefore assigned as electronic emission from one or more unknown intermediate species. Controlled impact experiments, in which emission from the film is monitored following controlled impact of a thin flyer, are ongoing and may help identify the intermediate species by isolating the early stages of reaction.

Probing Electronic Structure Changes Using Ultrafast Spectroscopy

An aspect of shock-induced reactions that remains not well quantified is the degree to which electronic structure of explosive materials change under shock. The electronic excitation mechanism of Kuklja *et al*. [7-9] predicts the energy difference between the valence and conduction bands to significantly decrease under shock and allow instantaneous reactions to occur (in the case of complete closure) or to allow thermal reactions to occur (in the case of incomplete closure). The band gap for RDX, for example, is expected to decrease from 5 eV in the uncompressed crystal to as little 1-1.5 eV or less under compression in the presence of crystal defects. At the time of this writing, there appear to be no measurements available that quantify changes in band gap of explosive materials under shock. At Sandia, we are developing an experimental platform that uses transient absorption spectroscopy [31] to examine dynamic changes in electronic structure of shocked explosive materials. A schematic of the experiment is shown in Figure 6. An ultrafast laser pulse is used to generate ultrafast broadband continuum pulses, which are used to acquire a frequency-resolved spectrum of the shocked material. Measurements of the electronic spectrum of the shocked explosive material would help resolve the question of whether or not electronic excitations participate in shock-induced reactions.

Probing Effects of Crystalline Defects Using Nonlinear Ultrafast Spectroscopy

Defects are widely known to localize energy and initiate reactions in explosive materials, but few measurements have quantified the associated dynamics at the molecular level. Kuklja *et al*. [9] have predicted strong changes in the electronic structure of explosive materials in the vicinity of a variety of crystal defects, including vacancies, cracks, and dislocations. One suite of experimental techniques that is potentially capable of probing dynamics at defects is ultrafast nonlinear sum frequency spectroscopy [32]. These techniques can be sensitive to crystal defects, because at defect sites, the symmetry of the crystal can be broken, leading to a nonzero $\chi^{(2)}$ susceptibility that can be probed optically. Two laser pulses are combined in a sample, and the $\chi^{(2)}$ susceptibility leads to production of a signal whose frequency is the sum of the two input pulses. The signal is greatly enhanced when the sum frequency spectrum is resonant with a transition in the material, and therefore directly reports the spectrum of the material in the vicinity of the defect with no contribution from the bulk. This strategy is being used at Sandia to probe the electronic structure of crystal defects in explosive materials. A schematic of an experiment designed to acquire the electronic spectrum of a crystal surface (the simplest type of crystal defect) is shown in Figure 7. In this experiment, two pulses, a nonresonant 800 nm pulse and a visible continuum pulse, are combined at a sample surface, where inversion symmetry is broken and a $\chi^{(2)}$ susceptibility exists. The nonzero $\chi^{(2)}$ susceptibility produces a signal at the sum frequency, which is resolved by a spectrometer. The sum frequency spectrum directly reflects the electronic spectrum of the surface of the crystal. As an interior crystal void is, at its simplest, a crystal surface folded onto itself, this measurement may suggest whether the electronic structure at crystal defects (such as voids) is locally distorted enough to enable shock-induced reactions below their ordinary thresholds.

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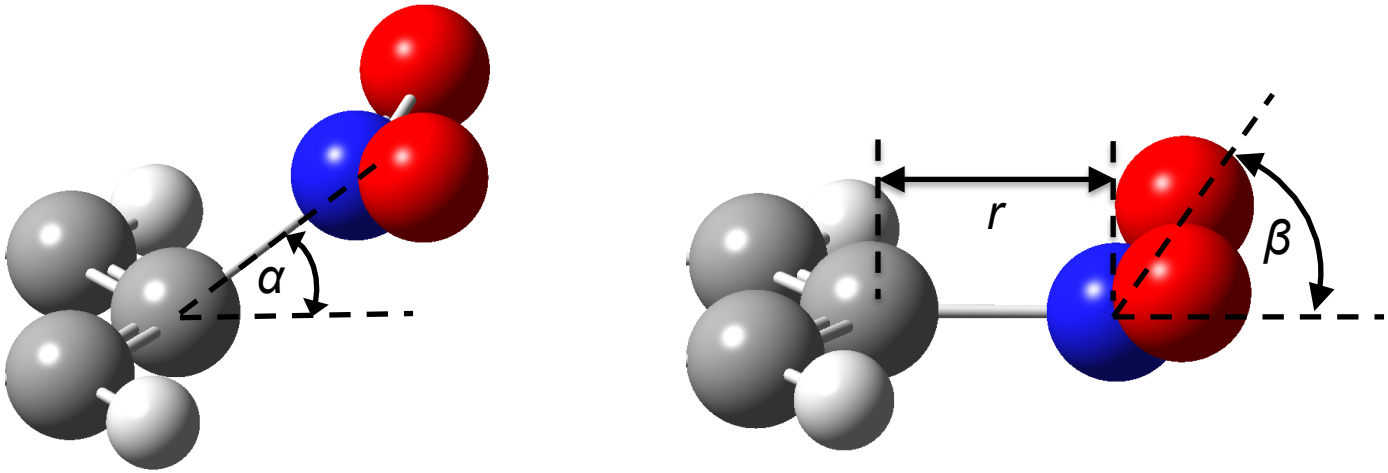
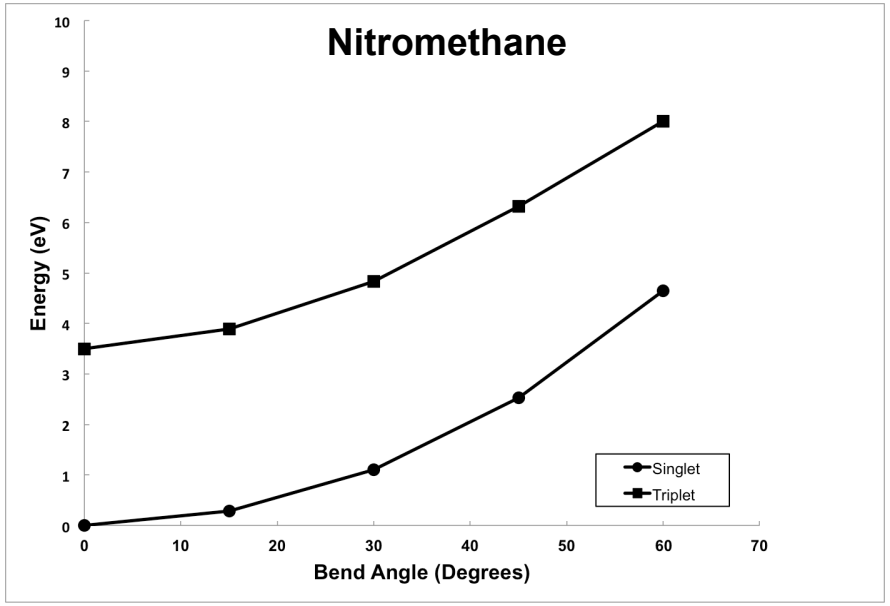


Figure 1. Bending angles considered in DFT study of large-amplitude deformation.



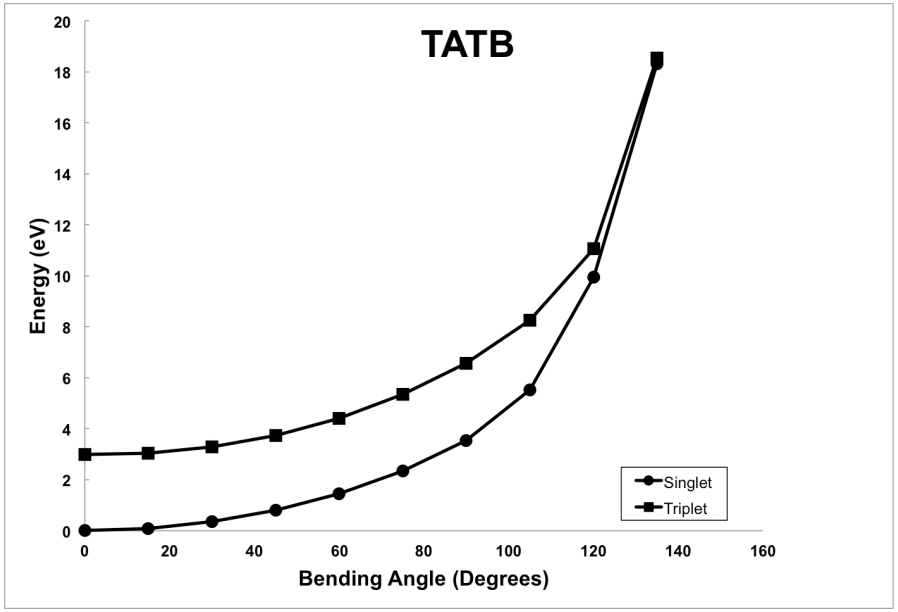


Figure 2. Potential energy curves corresponding to bending along angle *α* in nitromethane and TATB. Bending along angle *β* (results not shown here) produces qualitatively similar results. Neither type of large-amplitude bend leads to unimolecular dissociation.

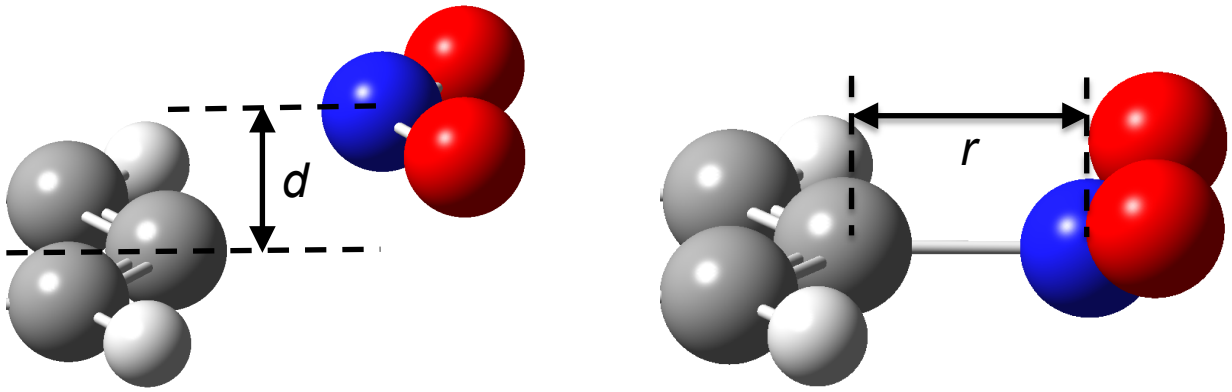


Figure 3. Diagram showing transverse displacement of NO_2 moiety (coordinate *d*) and C-NO_2 stretching motion (coordinate *r*).

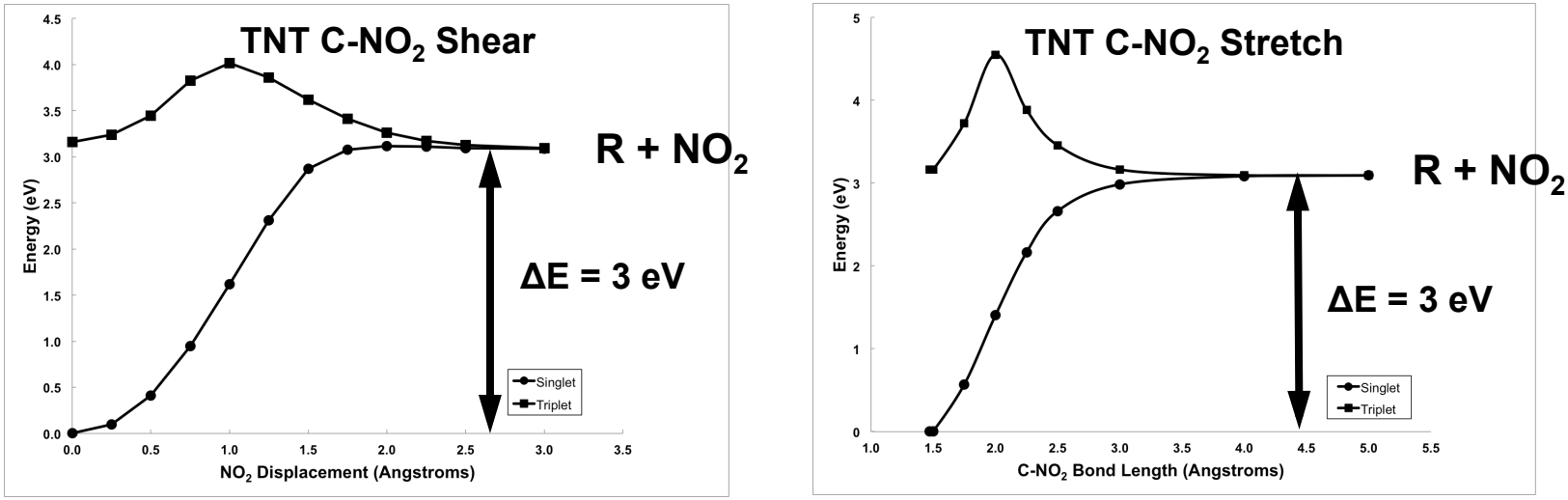


Figure 4. Potential energy curves corresponding to transverse displacement along coordinate *d* in TNT, compared with C-NO_2 stretching motion. Transverse displacement along *d* leads to direct dissociation of the NO_2 group.

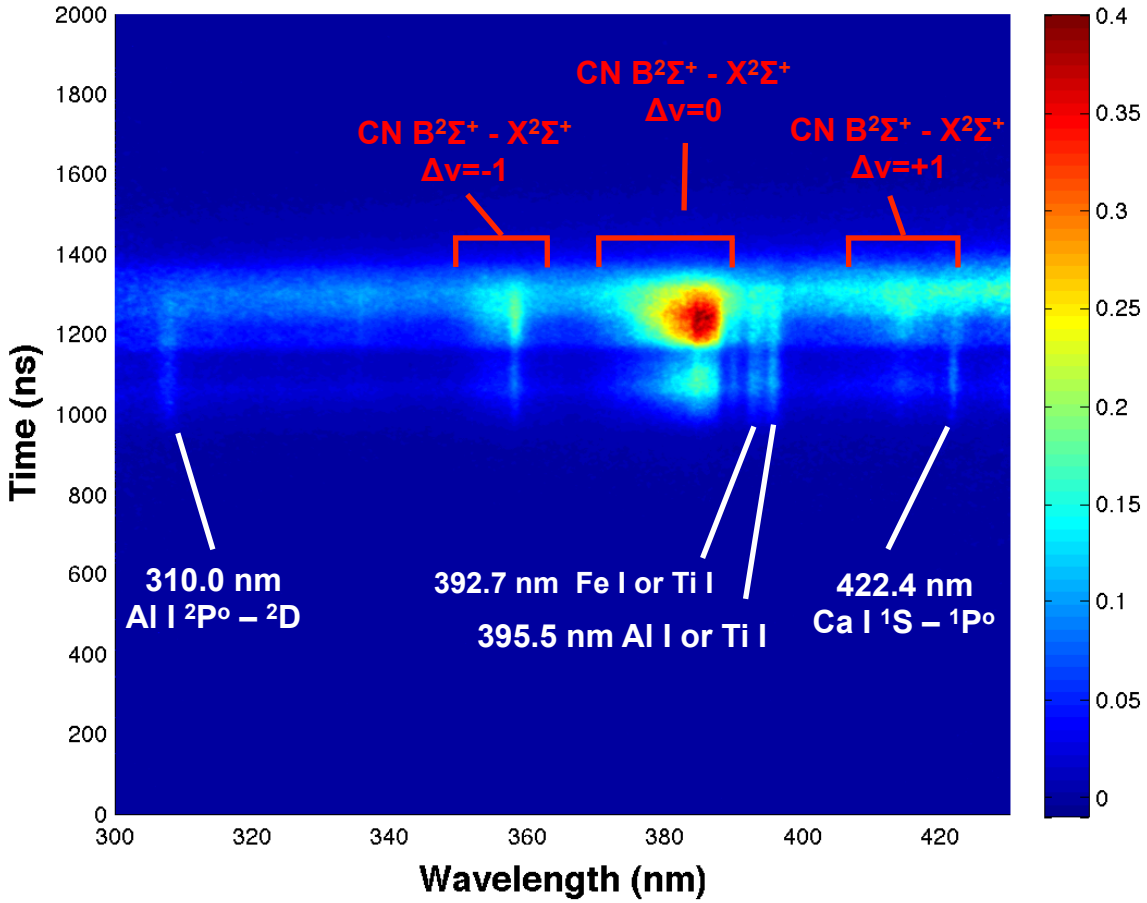


Figure 5. (a) Streaked emission spectrum showing emission from detonating HNS thin film. The spectrum shows vibrationally-resolved emission from CN, broadband emission from unknown species, and atomic emission lines due to impurities in the sample fixture.

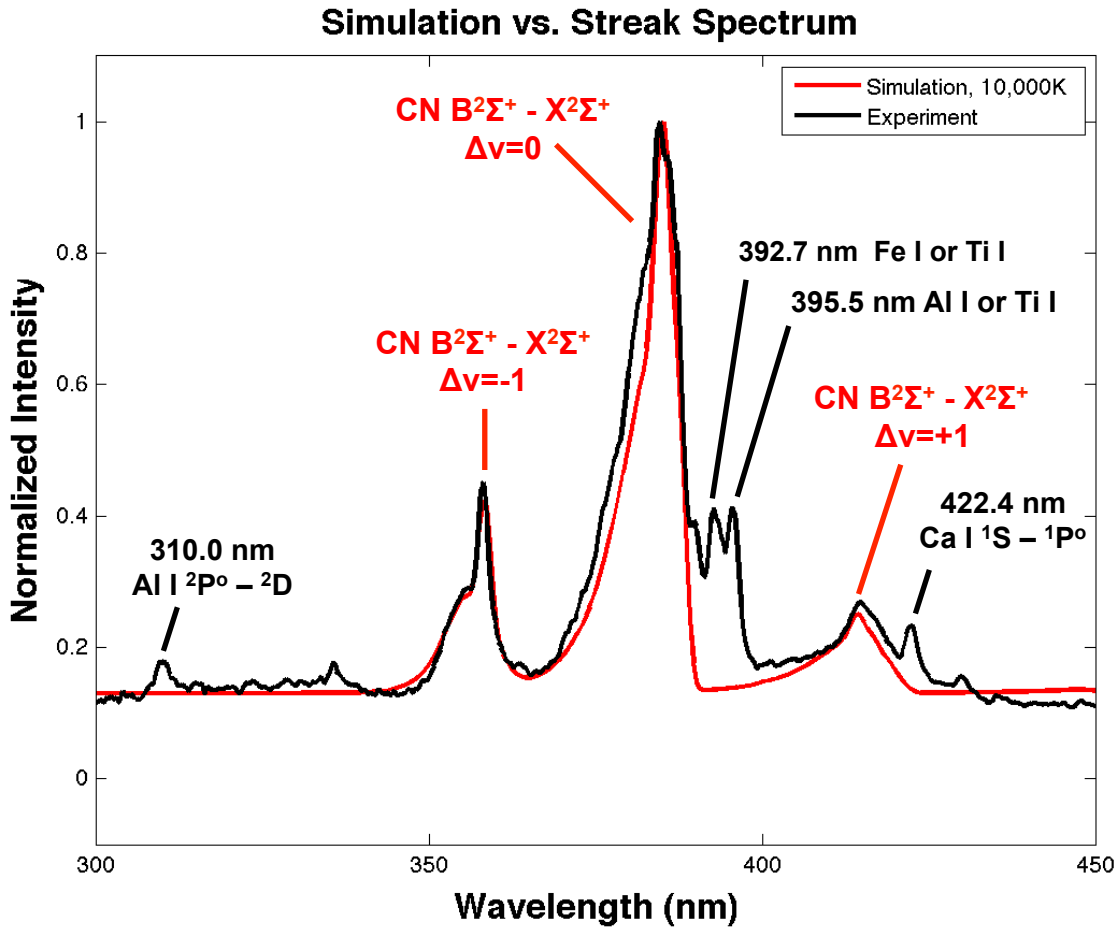


Figure 5. (b) Experimental time-integrated spectrum compared with simulated emission spectrum of CN with rotational and vibrational temperatures set to 10,000 K.

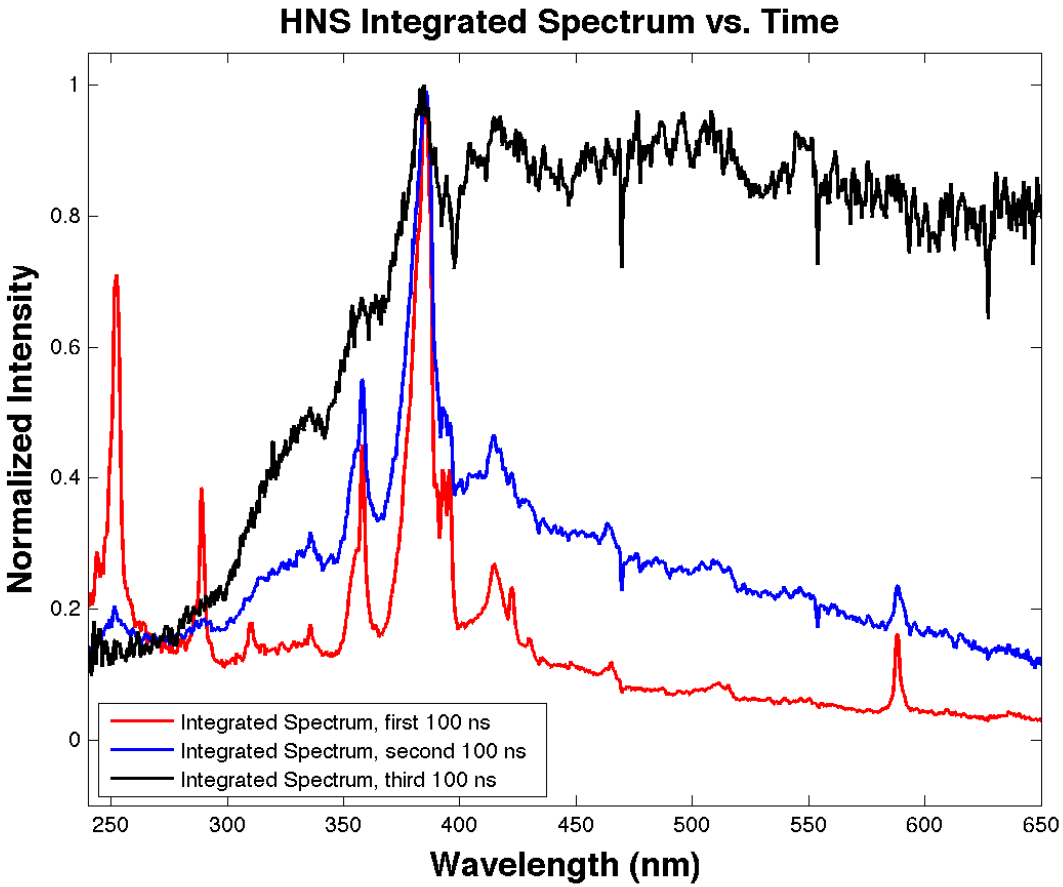


Figure 5. (c) Time-integrated emission spectra of detonating HNS. Red: 0-100 ns, Blue: 100-200 ns, Black: 200-300 ns.

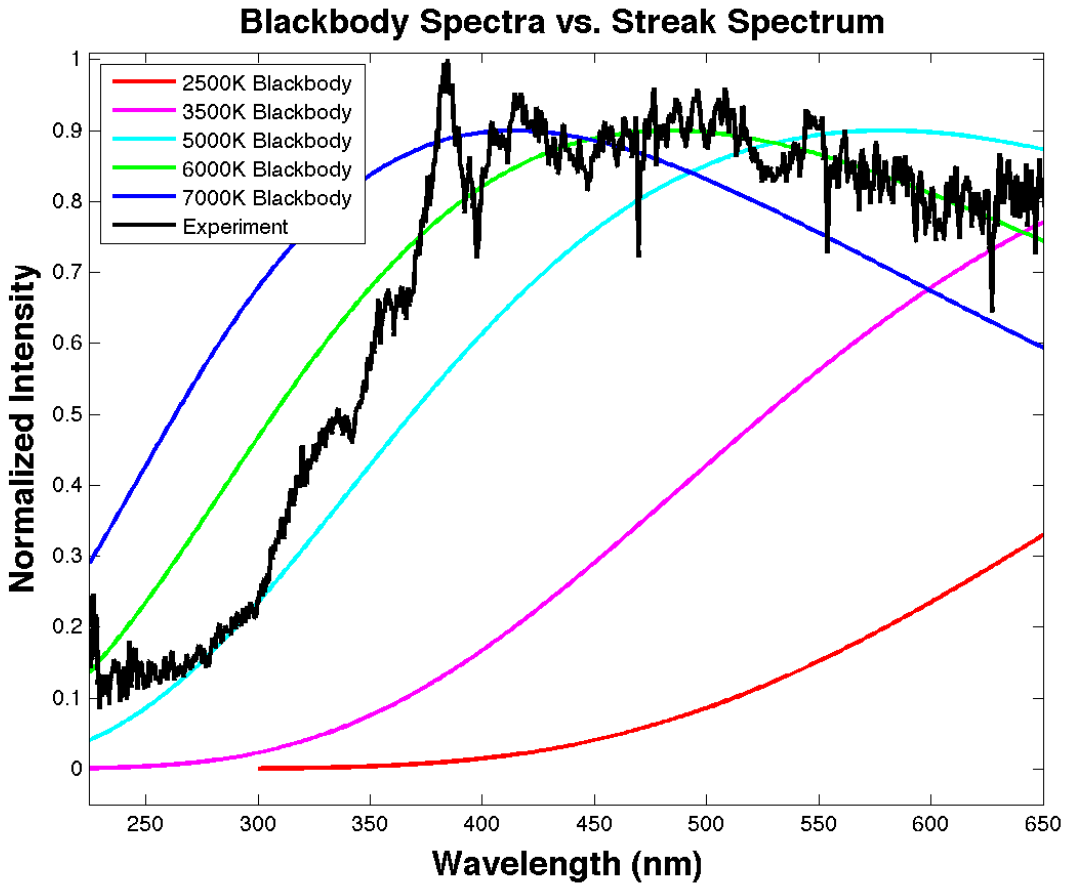


Figure 5. (d) Comparison of late-time emission with blackbody spectra.

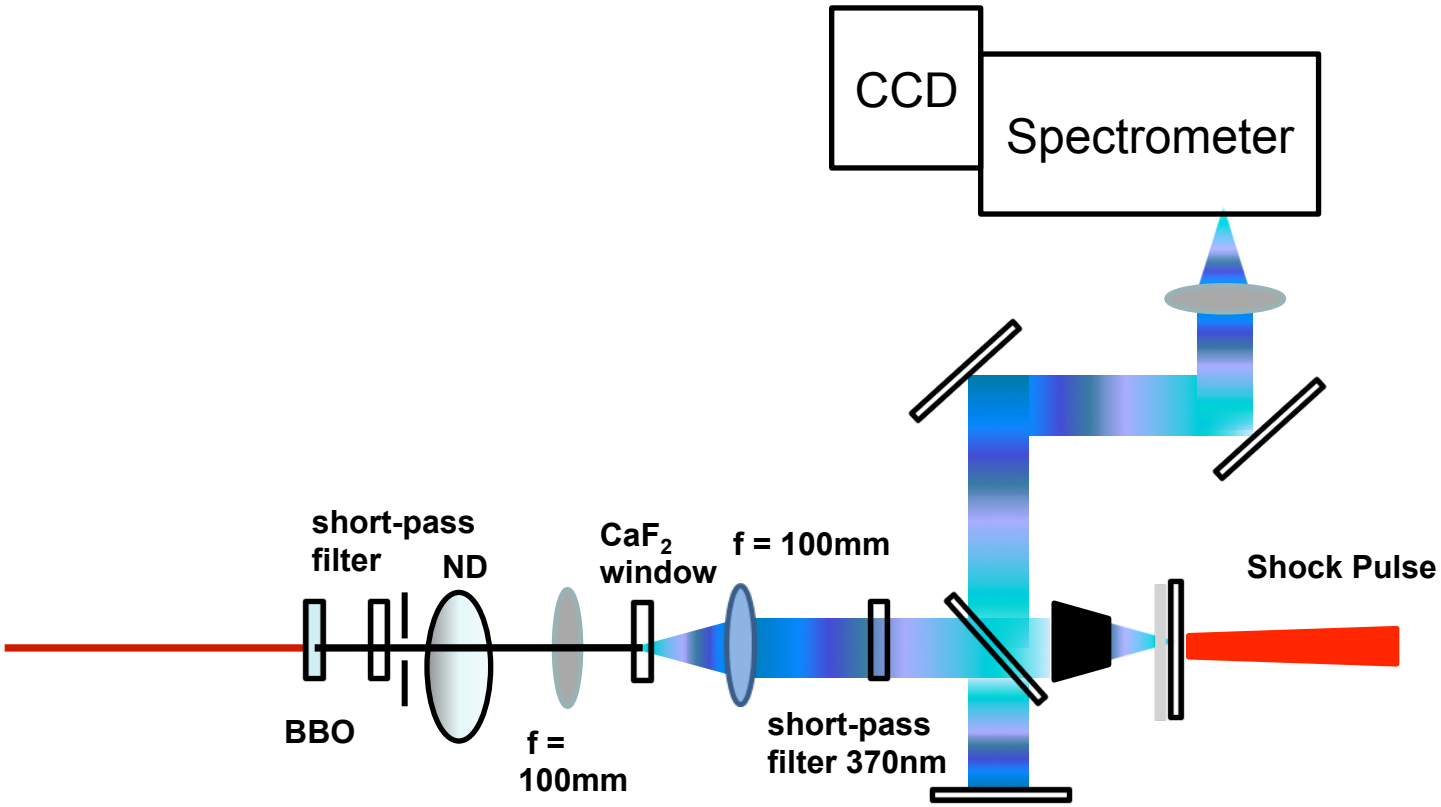
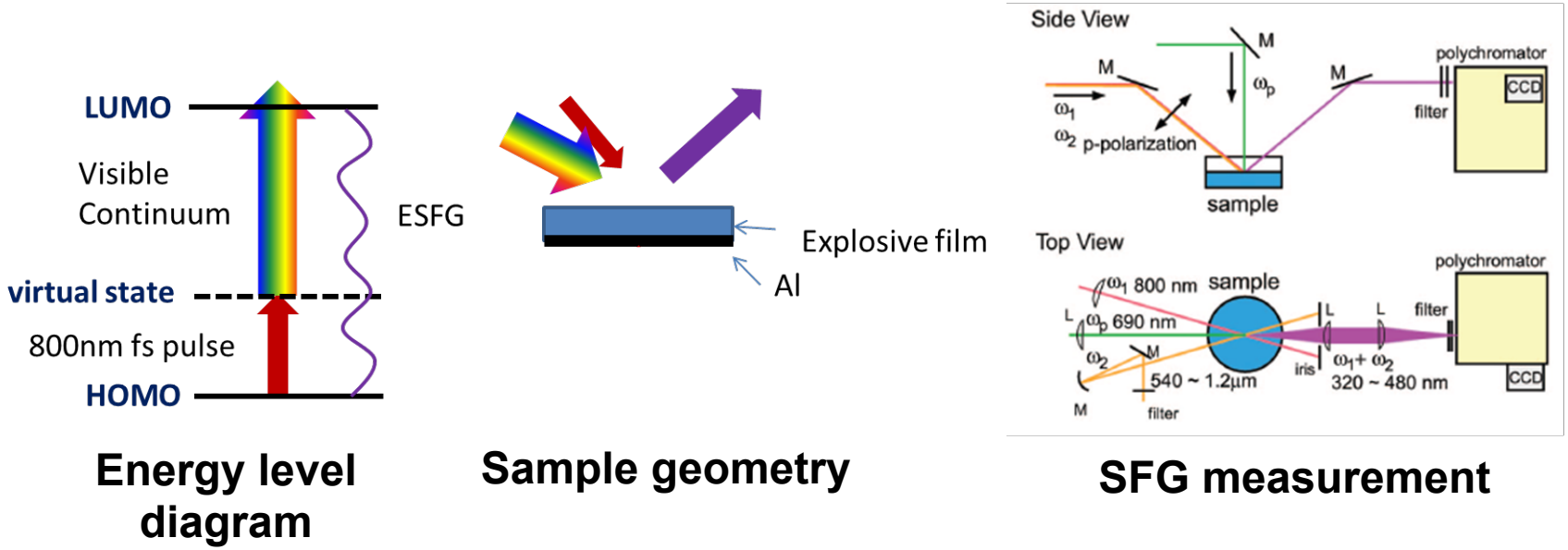


Figure 6. Schematic of transient absorption experiment for monitoring changes in electronic structure under shock compression.



Energy level diagram

Sample geometry

SFG measurement

Figure 7. Schematic of electronic sum frequency generation experiment for measuring electronic spectrum of crystal surface.