

Non-linear optical properties of molecular systems under high static pressures

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Abstract.

Applied static pressure can largely modify the structure and dynamics of molecular systems, with consequences on their optical properties and chemical stability. When photochemical effects are exploited in conjunction with the structural and dynamical conditions attained at high density, chemical reactivity may become highly selective and efficient, yielding technologically attractive products. Non-linear optical spectroscopies are a powerful tool to investigate molecular energetics and dynamics, and thus unveil key aspects of the chemical reactivity at a molecular level. Their application to high-pressure samples is experimentally challenging, mainly because of the small sample dimensions and the non-linear effects generated in the anvil materials. In this paper we review the main results on the behavior of electronic states at high pressure, obtained by non-linear optical techniques, discussing the relationship between pressure-induced structural modifications and chemical reactivity, and the state of the art of ongoing research.

1. Introduction

A static pressure in the 10s of gigapascal range applied to a molecular system induces large modifications in the pattern of intermolecular forces, affecting to varying degrees both intra and inter-molecular properties such as geometries, electronic distributions and chemical behavior [1]. A novel chemical reactivity can be obtained just by compression in pure molecular systems or very simple mixtures of reactants, in liquid or solid phases, yielding products that are stable or metastable at room conditions. In several instances it has been shown that photoactivation with light matching an electronic transition is able to lower the reaction threshold pressure, improve yield and selectivity by opening specific reaction channels [1], or activate reactivity in otherwise highly stable systems [2–4].

In the last decade considerable steps forward have been made in understanding the reaction mechanisms in condensed phases at a molecular level, by using spectroscopic and diffraction techniques to investigate samples in diamond anvil cells. In this paper, we will focus on the results obtained in this field by using non-linear optical techniques.

The need for establishing fundamentals of high-pressure chemistry forces us to study simple model molecules, in order to outline some basic principles that can be applied to any other



system. Very simple organic compounds containing unsaturated bonds are quite suitable as they may give rise to appealing products by static compression in the 10 - 50 GPa range, and their lowest excited electronic states are easily accessible, laying in the near UV. Standard optical spectroscopies such as infrared absorption and Raman scattering are excellent tools to identify *in situ* the reaction products, the IR being particularly useful to determine the reaction threshold pressures, as it does not require laser light possibly inducing reactivity, and to measure reaction kinetics on a minutes timescale by using integrated areas of isolated reactant or product infrared bands. However, non-linear techniques become necessary to investigate the excited electronic states in diamond anvil cells, as we shall discuss in the next section, to observe dynamic processes at the molecular timescales, and to identify any transient intermediate species in reactive processes, which are fundamental steps in the prospect of exploiting chemistry and photochemistry in condensed phases.

Investigation of the lowest-energy optical electronic transitions, which are directly involved in photochemical processes, as a function of density, allows us to sketch a picture of the energy landscape of the molecular system. In fact, for the simple molecular liquids and solids under study, at least in the range of chemical stability, the scheme of the energy levels at a given density can be expressed in terms of the molecular energy levels, increasingly perturbed by the environment as the pressure is increased. A density increase corresponds to moving in the energy landscape along coordinates that describe the intra- and intermolecular structural changes obtained by compression, thus exploring regions where the potential energy surfaces may be quite different from the room pressure pattern: for instance, the energy ordering of excited states may be changed, and new equilibrium geometries or dissociating regions in the ground or excited electronic states may be encountered. Some results, obtained by direct or indirect evidence, will be described in this paper. On the other hand, the studies of dynamical processes involved in the reaction mechanisms (femto- or pico-second timescales) are still at a preliminary stage, mostly due to experimental complexities found in applying the well-established techniques to diamond anvil cells.

2. Multi-photon absorption in diamond anvil cells

The use of multi-photon absorption, and in particular two-photon (TP) absorption, has been proved to be much more convenient than one-photon absorption both for the photoactivation of chemical reactions and for the characterization of excited electronic states in high-pressure cells. Multi-photon absorption is the simultaneous absorption of n photons to attain a transition with an energy which is a n -multiple of the photon energy. The involved cross sections are extremely small with respect to one-photon absorption, and the probability is non-linear with the photon flux (the dependence is quadratic for TP absorption, cubic for three-photon absorption, and so on). Each of these properties implies some important advantages for use in high-pressure studies.

The use of photons of lower energy than the observed transition is the first important point. In fact, for the small organic molecules that are object of our study, even the lowest-energy electronic transitions fall in the UV or near UV region, overlapping the diamond absorption (the diamond absorption edge is around 250 nm). TP absorption requires the use of visible light, easily obtained with laboratory sources and out of the diamond linear absorption. At the same time, the non-linear dependence of multi-photon absorption probability provides an increasingly strong spatial resolution growing with the order of the non-linear process, which is essential for studies in diamond anvil cells. For a typical optical setup designed for the DAC, the depth of focus in the near UV is in the 100s microns range, largely exceeding the sample thickness (around 50 μm), so that through a linear optical process even an unlikely event in diamond may dominate the observed spectrum. TP absorption is proportional to the square of the incident light intensity, so that in the same setup absorption effectively occurs only in a 10s

of microns depth around the focal point.

The small multi-photon cross sections are responsible for important advantages both in its use for inducing photochemistry and in spectroscopy, namely avoiding sample damage and spectral saturation. With TP absorption only a ppm amount of excited molecules is present in the sample, which is enough for the optical initiation or optical catalysis of chemical reactions still avoiding heating and uncontrolled or too fast processes. Spectral saturation is very common in linear optical absorption of pure solids and liquids in the DAC, because the sample thickness is approximately fixed, whereas dilution changes the physical and chemical properties under investigation. For the molecules of interest a direct measurement of TP or higher order absorptions is not possible due to the small difference between incident and transmitted light. The most used indirect method of detection of TP absorption is the measurement of the induced fluorescence, which has been successfully applied to the DAC, with very interesting results that we shall see in the following.

Our setup for the measurement of TP excited fluorescence in the DAC is described in [5, 6]. The source is a 20 ps mode-locked Nd:YAG laser (Ekspla PL2143A), 10 Hz repetition rate, whose third harmonic (355 nm) pumps an optical parametric generator (Ekspla PG401), which gives tunable light ($\Delta\lambda \sim 0.1$ nm) in the visible (420-680 nm) and near infrared (740-2300 nm) range. After attenuation to less than 1 $\mu\text{J}/\text{pulse}$ to avoid non-linear responses from diamond, the light reaches the sample focused by an achromatic doublet, and the fluorescence is collected backwards by a pierced parabolic mirror and focused into a 1/4m monochromator, and detected by a photomultiplier tube (ET-9235QB or Hamamatsu R943-02). A reference signal is measured by a fast photodiode for normalization, and also to check the quadratic dependence of fluorescence on the beam intensity. We can measure fluorescence spectra by keeping the TP excitation wavelength fixed, or we can measure the TP excitation profile by keeping the monochromator position fixed at the fluorescence maximum and scanning the TP excitation wavelength, reporting the fluorescence intensity as a function of the excitation wavelength. Since the fluorescence intensity is proportional to the absorbed intensity through the fluorescence quantum yield Φ , in the ranges where Φ is independent of excitation wavelength the excitation profile retraces the absorption spectrum. In these measurements we do not use time-resolution and we have always observed a relaxed fluorescence, i.e. all the decay processes to the lowest vibrational level of the lowest excited singlet state (S_1) occur in shorter timescales than the observed fluorescence. This is proved by the fact that for each sample in any given pressure condition, the fluorescence spectrum is the same for any excitation wavelength and the same excitation profile is observed at any detection wavelength.

3. High-pressure fluorescence of aromatic crystals

Simple aromatic crystals are a very good benchmark for the study of pressure-induced reactivity and photochemistry. In fact, some of them can give rise to reactions yielding amorphous products which are potentially appealing, while others are quite stable with pressure. Their HOMO-LUMO transitions are located in the range 200-350 nm so that they can be excited by TP absorption in the visible range, far from the one-photon absorption edge of diamond. Several of them have a sufficient fluorescence quantum yield to be easily studied through TP excitation, and fluorescence is usually observed around 300-400 nm. The simplest aromatics can be studied with relative ease from a theoretical point of view and are ubiquitous constituent parts of more complex systems with important applicative implications.

3.1. Benzene: reactivity triggered by formation of dimers

Benzene, the simplest aromatic, reacts irreversibly as a response to the applied pressure to quantitatively give an amorphous hydrogenated carbon (a-C:H) [7]. When the reaction is performed starting from the pure, thermally annealed monoclinic phase II, the reaction threshold

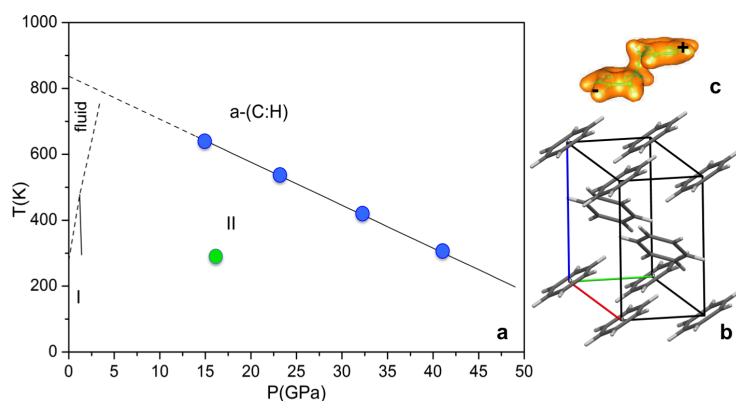


Figure 1. (a) Phase diagram of benzene [8]. Blue dots indicate the experimental threshold point for spontaneous transformation into amorphous hydrogenated carbon, the green dot indicates the threshold pressure at room temperature at which the same transformation can be induced by photoactivation with light at $\lambda \leq 514$ nm [9]. (b) unit cell of the $P2_1/c$ crystal structure of benzene (phase II). (c) Structure of the calculated dimer precursor of the pressure induced reaction [8].

pressure at any given temperature is highly reproducible, and a reproducible chemical stability line has been identified by measuring the IR spectrum with increasing pressure along different isotherms [8]. Combining the data from X-ray diffraction at room temperature as a function of pressure, and an estimate of the amplitude of thermal motion as a function of temperature, it has been shown that all the points on the stability line correspond to the same instantaneous minimum distance between nearest neighbors along the a axis, which is also the calculated critical distance for the formation of a dimer, as shown in figure 1 which is the seed for the reaction initiation [8]. The most interesting aspect, in view of understanding and exploiting photochemistry, is that irradiation with light at $\lambda \leq 514$ nm induces the same reaction at 16 GPa, very far from the critical structural and dynamical conditions to achieve the reactive approach of two neighbor molecules [9].

TP excitation profiles in the region 550–450 nm were measured up to 12 GPa. In this wavelength range we observe the symmetry forbidden TP transition from the ground state to S_1 ($^1B_{2u}$), weakly allowed by vibronic coupling, and the red edge of higher energy transitions [10]. The main insight on the reaction mechanism comes from the fluorescence spectra. At 2 GPa the fluorescence spectrum is due to benzene emission (figure 2). With increasing pressure a lower-frequency band grows in relative intensity, becoming almost 100% of the signal above 10 GPa. This band, unstructured and red-shifted by about 5000 cm^{-1} with respect to the benzene fluorescence maximum, is typical of aromatic molecules in the liquid phase, including benzene at room conditions, or in concentrated solutions and is due to the formation of excimers, i.e. dimers in which one molecule is in the S_1 electronic state, and decay dissociating back to the ground state monomers. The interaction between molecules forming an excimer occurs preferentially in a sandwich-like geometry through their π electrons. Excimer emission has also been observed in aromatic crystals under pressure, when the crystal structure allows a stacking of the π electron distributions [11, 12]. In the monoclinic phase of benzene the crystal structure allows this interaction along the a or b axes, in the same parallel-shifted geometry as the ground state dimer that is predicted to initiate the high-pressure reaction [8].

This suggests a common picture for the reaction mechanisms of the photoinduced reaction at 16 GPa and of the purely pressure-induced reactions. In crystal phase II of benzene a moderate pressure is needed to have molecules close enough to form excimers upon electronic excitation. This becomes the prevalent excited state structure above 10 GPa and by interaction with neighbor molecules can decay on the electronic ground state of a reaction product. The

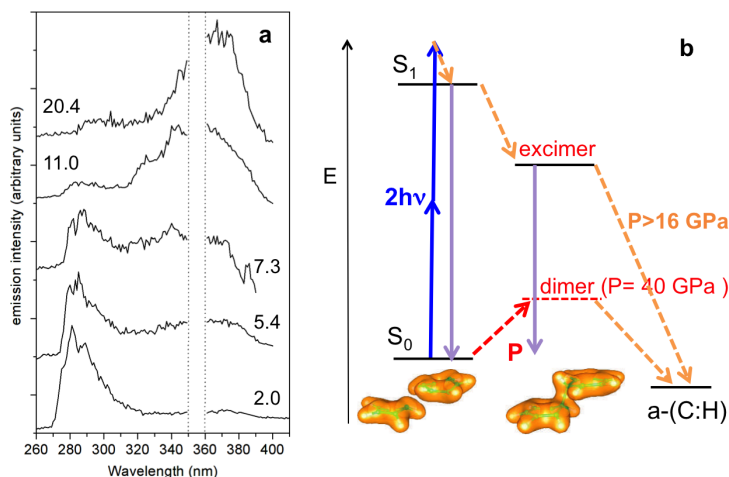


Figure 2. (a) TP excited fluorescence spectra measured upon compression of benzene in phase II [10]. Pressure values are reported above each spectrum in GPa units. The masked region correspond to scattered 355 nm light from the laser used as pump of the optical parametric generator, entering the monochromator. (b) Sketch of the mechanism of high-pressure reactivity of benzene. The a-(C:H) product is obtained through the formation of a ground state dimer at very high pressure, or of an excimer after photo-excitation above 16 GPa.

purely pressure induced reaction, in the absence of excitation, occurs through the formation of dimers with a similar geometry as the excimers, but their formation in the ground state requires a closer distance, provided by higher pressure or temperature.

3.2. Pyridine: energy inversion of electronic states

Pyridine is a liquid at room conditions and its fluorescence quantum yield is extremely small. In fact, the highest occupied molecular orbital is a n non-bonding orbital localized on the nitrogen atom, so that the lowest-energy singlet excited state S_1 is a $n\pi^*$ state [13]. Transitions between the ground and $n\pi^*$ states have cross sections typically two orders of magnitude smaller than transitions to $\pi\pi^*$ states, so the emission rate is slower and non radiative decays become dominant. Two-photon excited fluorescence of liquid pyridine [5] was not observed in the DAC for any excitation wavelength. It could be observed, near to our instrumental sensitivity limit, only in a 1 mm cuvette using a beam intensity of 30 mJ/pulse. By compressing liquid pyridine in the DAC, the $P2_12_12_1$ crystal phase II is obtained at around 1.2 GPa [14]. Upon compression we started to detect a weak fluorescence signal around 330 nm, at 3.1 GPa, blue shifted (about 400 cm^{-1} for the highest frequency peak) with respect to the liquid, being more similar to the gas phase fluorescence spectrum [13]. Given the setup characteristics and by comparison with the measurement in the cuvette, the fluorescence quantum yield is estimated to be 10^5 times larger in this compressed crystal than in the liquid. The fluorescence intensity further increases with compression up to 10 GPa.

It is known that pyridine derivatives where the nitrogen lone pair is involved in a covalent bond (pyridinium species), exhibit a weak fluorescence originated by emission from a $\pi\pi^*$ state, which is the lowest excited state [15, 16]. Indeed, we found that the emission of a mixture of pyridine and acetic acid in a 5:1 ratio, where pyridinium ions are present, is enhanced with respect to the pure liquid pyridine, particularly in the blue region of the emission spectrum [5].

The intensification of emission in the crystal, increasing with pressure, is due to the crystal structure and its pressure-induced modifications, and their effects on the electronic structure. In phase II each N atom is available for two different H bonds [17]. The involvement of the N atoms in H bonds, similarly to the effect of acidity, likely lowers the energy of the n orbital, determining a blue shift of the $n\pi^*$ state, as expected for the pyridinium species [16]. The blue shift of the

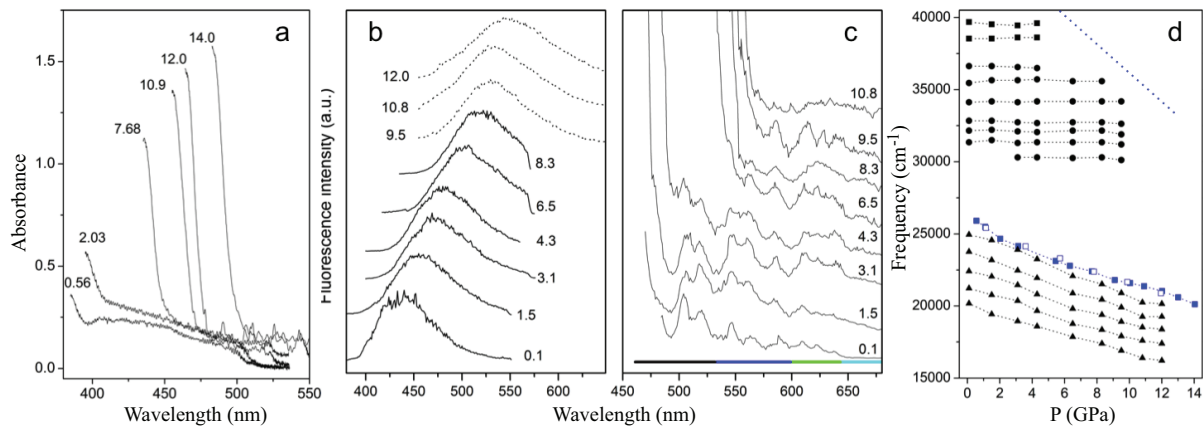


Figure 3. (a) OP absorption spectra of picene upon compression [6]. Pressure values are reported above each spectrum in GPa units. (b) Fluorescence spectra of picene upon compression. Full lines: TP excited (excitation range: 620-670 nm). Dotted lines: OP excited at 440 nm [6]. (c) TP excitation profiles of picene powder upon compression. Color lines indicate the excited states reached as a function of TP excitation wavelength; cyan: S₁, green: S₂, blue: S₃, black: S₄. At short wavelengths we observe the OP absorption edge, identified by linear dependence of the fluorescence signal on the beam intensity. (d) Full squares and circles: peak frequencies of vibronic transitions from TP excitation profiles (S₀ → S₂, S₃, and S₄ transitions). Blue dotted line: estimate of the OP absorption edge observed in the TP excitation profiles. Full triangles: peak frequencies of vibronic transitions from fluorescence spectra (S₁ → S₀ transition). Blue squares: estimate of the optical band gap from OP absorption spectra (full: compression, open: decompression).

crystal emission with respect to the liquid may thus be ascribed to the frequency difference between the electronic origin of the S₁ ($\pi\pi^*$) state in the solid and of the S₁ ($n\pi^*$) state in the liquid phase. This picture is confirmed by the observation that in the glassy form, where the ordered network of H-bonded molecules is lacking, the fluorescence intensity is strongly reduced, particularly in the blue (monomer) region [5]. We can thus state that the H bonds that are built up in the crystal, and increasing with pressure, cause an energy inversion of the $n\pi^*$ and $\pi\pi^*$ states. The red part of the emission band, on the other hand, has been ascribed to excimer emission and is the main responsible for the weak emission of the liquid and of the glassy form. It is present in the crystal phases only depending on the amount of defects, being larger in more defect-containing samples and not reversible with pressure [5].

3.3. Picene: different compressibilities of electronic states

Picene is a condensed polycyclic aromatic hydrocarbon which has been extensively studied in the last few years since the discovery of superconductivity in doped K₃-picene. The role of pressure in achieving superconductivity or increasing the T_c is a major subject in high-pressure physics [18, 19], and K₃-picene itself has a large positive pressure dependence of T_c [20]. Pressure itself induces important modifications on the electronic structure of molecular crystals, as testified by the examples above, and in this framework an investigation on pristine picene was undertaken [6]. As shown in figure 3, picene absorbs in the visible range so that the absorption edge can be measured in the DAC by one-photon (OP) visible absorption. However, the spectra are immediately saturated above the S₀ → S₁ edge, so that the optical band gap evolution can only be roughly estimated from these spectra. In fact, band broadening may affect the observed red shift of the absorption edge. Two-photon excited fluorescence spectra measured as a function

of pressure show that the optical band gap remarkably decreases by $\sim 400 \text{ cm}^{-1}/\text{GPa}$ (figure 3). This results, by comparison with several other aromatic systems, suggests that the S_1 state in the crystal is of different character than in the isolated molecule, where it is calculated to be 1L_b [6, 21]. Two-photon excitation profiles measured in the 680 - 420 nm range allow us to see the higher energy HOMO-LUMO transitions (S_0 to S_2 , S_3 , and S_4), which are inaccessible by OP absorption due to the diamond absorption. We could thus have the remarkable insight that these higher energy states do not move in energy with pressure with respect to the ground state, although S_1 has a large pressure shift, which is a unique feature with respect to all the other systems investigated. This very different pressure-response of the different states is likely due to the strong anisotropy of the crystal.

3.4. High-pressure reactivity and excimer formation

The role of the crystal structure and of defects in the formation of excimers upon excitation in aromatic crystals under pressure has been studied in detail [22, 23]. Excimers can form in crystals structures where molecules may approach in a parallel orientation allowing the complete or partial stacking of their π distributions, as in the monoclinic phase II of benzene. In crystals preventing this stacking, as for indole [24], pyridine and picene, excimer formation may only be possible at crystal defects, whereas in the bulk different kinds of intermolecular interactions (e.g. H-bonds in both indole and pyridine) build up and intensify with pressure.

In both types of crystals static pressure causes an increase of excimer emission, both providing the necessary intermolecular approach, and inducing the formation of crystal defects. However, if excimer emission is only possible at defects, its intensity is weaker and not reproducible in different experiments and mostly not reversible with pressure. In benzene, the relative intensities of monomer and excimer emission is reversible, except for a small hysteresis, if the experiment is made avoiding the irreversible chemical reaction [10], which is an evidence that the excimers are mainly formed in the bulk crystal.

We have observed that crystals with a structure preventing excimer formation are chemically quite stable and reactivity occurs at crystal defects. In fact it is of limited extent and both the threshold pressure and the amount of product formed are highly variable in different samples and depend on the crystal quality. These observations give strong support to the idea that both the purely pressure-induced and the photoactivated formation of amorphous hydrogenated carbons from aromatic crystals proceed through a similar dimeric structure, in the ground or in an excited state, which is allowed in the bulk crystal or at defects depending on the crystal structure.

4. Transient absorption in the DAC: perspectives

Fluorescence has two important limitations: only a few molecules are fluorescent, and a trade off between time resolution and sensitivity is required. Using TP excitation in the DAC we are limited to the use of photomultipliers, which have an instrumental function of several nanoseconds. Differently from fluorescence, for nearly any system it is possible to find a measurable transient absorption. By creating some population in an excited state we measure a spectrum with a delayed UV-visible-NIR or mid-IR probe to observe the evolution of the systems in the first picoseconds after excitation. Several non-fluorescent systems should be investigated to gain an insight into photochemistry at high pressure. An example is nitromethane, a prototype of explosive and fluorescence quencher. Its high-pressure reactivity in the ground state is believed to proceed through the formation of aci-ions containing a double $C=N$ bond, whereas high-pressure photochemistry suggests the breaking of the $C-N$ bond [25]. Another example is the investigation of the pressure-evolution of the lowest singlet excited states of simple alcohols. In ethanol, it has been suggested by indirect evidence, provided by the pressure-induced change in

reactivity and isotopic substitution, that S_1 , which is dissociative at room conditions, achieves a bonding character with increasing pressure [26].

However, the need of using TP excitation, in order to avoid diamond absorption and to have spatial selection, still holds and the pump beam intensity needed to have a detectable transient signal with TP excitation induces strong non linear responses in the diamond. If the experimental difficulties inherent with these spectroscopic techniques were overcome we would be able to gain an incomparable insight into the molecular reaction dynamics.

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References

- [1] Schettino V, Bini R, Ceppatelli M, Ciabini L and Citroni M 2005 *Adv. Chem. Phys.* **131** 105
- [2] Ceppatelli M, Bini R and Schettino V 2009 *Proc. Natl. Acad. Sci.* **106** 11454
- [3] Ceppatelli M, Fanetti S, Citroni M and Bini R 2010 *J. Phys. Chem. B* **114** 15437
- [4] Fanetti S, Ceppatelli M, Citroni M and Bini R 2012 *J. Phys. Chem. C* **112** 2108
- [5] Fanetti S, Citroni M and Bini R 2011 *J. Phys. Chem. B* **115** 12051
- [6] Fanetti S, Citroni M, Malavasi L, Artioli G A, Postorino P and Bini R 2013 *J. Phys. Chem. C* **117** 5343
- [7] Ciabini L, Santoro M, Bini R and Schettino V 2002 *J. Chem. Phys.* **116** 2928
- [8] Ciabini L, Santoro M, Gorelli F A, Bini R, Schettino V and Raugei S 2007 *Nat. Mater.* **6** 39
- [9] Ciabini L, Santoro M, Bini R and Schettino V 2002 *Phys. Rev. Lett.* **88** 085505
- [10] Citroni M, Bini R, Foggi P and Schettino V 2008 *Proc. Natl. Acad. Sci.* **105** 7658
- [11] Jones P F and Nicol M 1968 *J. Chem. Phys.* **48** 5440
- [12] Offen H W 1966 *J. Chem. Phys.* **44** 699
- [13] Cai Z and Reimers J R 2000 *J. Phys. Chem. A* **104** 8389
- [14] Fanetti S, Citroni M and Bini R 2011 *J. Chem. Phys.* **134** 204504
- [15] Handa T, Utena Y, Yajima H, Ishii T and Morita H 1986 *J. Phys. Chem.* **90** 2589
- [16] Yoshida Z and Kobayashi T 1971 *Theoret. Chim. Acta* **20** 216
- [17] Crawford S *et al* 2009 *Angew. Chem. Intl. Ed.* **48** 755
- [18] Kim J S, Boeri L, Kremer R K and Razavi F S 2006 *Phys. Rev. B* **74** 214513
- [19] Takabayashi Y *et al* 2009 *Science* **323** 1585
- [20] Kambe T *et al* 2012 *arXiv:1210.1632 [cond-mat.supr-con]*
- [21] Fanetti S, Citroni M, Bini R, Malavasi L, Artioli G A, Postorino P 2012 *J. Chem. Phys.* **137** 224506
- [22] Stevens B 1966 *Spectrochim. Acta* **18** 439
- [23] Dreger Z A, Lucas H and Gupta Y M 2003 *J. Phys. Chem. B* **107** 9268
- [24] Citroni M, Costantini B, Bini R and Schettino V 2009 *J. Phys. Chem. B* **113** 13526
- [25] Citroni M, Bini R, Pagliai M, Cardini G and Schettino V 2010 *J. Phys. Chem. B* **114** 9420
- [26] Fanetti S, Ceppatelli M, Citroni M and Bini R 2011 *J. Phys. Chem. B* **115** 15236