In situ Raman spectroscopy of shock-compressed benzene and its derivatives

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Real-time Raman spectra of shock compressed benzene and its monosubstitutes, iodobenzene, and nitrobenzene, have been measured in the pressure range up to 7.5 GPa. Spectral peaks show almost linear blueshifts against shock pressure. However, nitrobenzene, compared to the other two compounds, shows smaller shifts. Especially the increase in Raman frequency of the NO_2 stretching mode (1346 cm^{-1}) is extremely small. An intermolecular interaction between nitrobenzene molecules seems responsible for this behavior.

In order to understand shock-induced phenomena, it is essential to obtain real-time information of materials under shock compression. The dynamic nature of shock compression, i.e., fast rise, short duration, and fast release of shock loading, often generates nonequilibrium states or unstable intermediates in the process of shock compression and usually they are not quenchable. In situ laser spectroscopy is a good tool to investigate those transient states or species. It can provide real-time information on shock-induced structural and chemical changes. Some sophisticated applications of laser spectroscopy to in situ observation of shock-induced phenomena have been reported over the last couple of decades.[1–6] In this paper we report shock-induced changes in vibrational spectra of benzene, iodobenzene, and nitrobenzene measured by a single-pulse laser Raman spectrometer in conjunction with a plate impact technique. It was found that shock-induced changes in Raman spectra of nitrobenzene are quite different from those of benzene and iodobenzene. Spectral peak shifts (blue shifts) against shock pressure were found smaller for nitrobenzene compared to those of benzene and iodobenze, especially the NO_2 stretching mode of nitrobenzene showed very small shifts. The relatively strong intermolecular interaction existing between nitrobenzene molecules seems to play an essential role. In this study we determined Raman frequency changes against shock pressures for three very common organic solvents. This kind of data can also be used as pressure calibration standards for certain shock experiments. For example, unlike shock experiments by plate impact, in some laser shock experiments pressure determination is difficult and may involve large uncertainties. In such cases, shock pressures can be easily determined by measuring the spectral shift for a standard sample whose spectral peak shift vs shock pressure data are available.

In general vibrational frequencies of stretching modes increase with pressure because bond lengths are reduced[7] under pressure and effective force constants at the new equilibrium positions are usually larger than those at the original equilibrium position. This simplified description is qualitatively valid at relatively low pressures where the compression energy is small compared to the electronic energies.[8] However, in the case where a strong intermolecular interaction such as hydrogen bonding exists, the situation can become quite different. In static high-pressure experiments of some hydrogen-bonded solids, softening of vibrational

modes with pressure has been observed,[9–11] where certain vibrational mode frequencies decrease with pressure. An example is softening of the O-H stretching vibration in H_2O ice in which this mode decreases in frequency with pressure until it disappears at ~60 GPa.[11] Above this pressure it is reported that the nonmolecular, symmetric hydrogen-bonded state is formed, where the proton is delocalized along O-O directions.[9]

Figure 1 shows a schematic diagram of the experimental setup. Projectiles with an aluminum impactor (8 mm thick) were accelerated by a propellant gun (30 mm bore diameter) up to the maximum velocity 2.0 km/s. Two shorting pins fixed on the aluminum driver plate (1 mm thick) were used to give an electric trigger pulse for the YAG laser (532 nm, 8 ns, and 10–20 mJ). The laser pulse was collimated down to about 1 mm in diameter and irradiated from 45° direction into the central part of the sample just before the shock wave reached the exit surface of the sample. In this configuration only the scattered light from the central region of the sample was detected. This should have ensured that detected scattered light came mostly from the shock-compressed region of the sample and the contribution of scattered light from uncompressed region of the sample is very small. The scattered light was collected and focused into an optical fiber
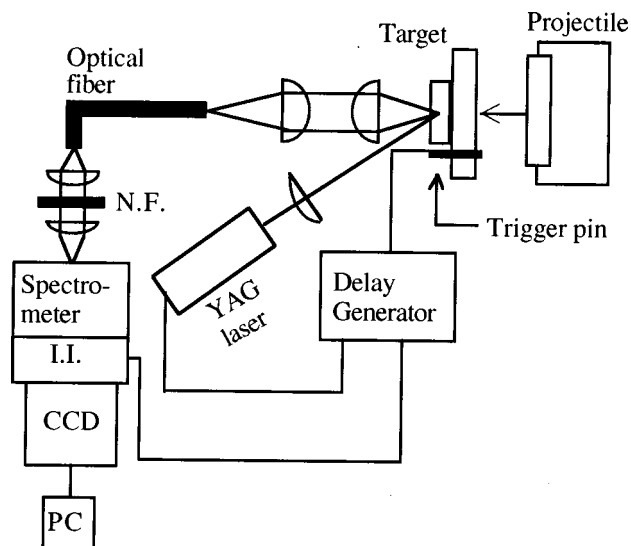

FIG. 1. Schematic diagram of single-pulse laser Raman system for shock compression experiment.

through a couple of lenses and then introduced into a spectrometer. The dispersed light was amplified by an image intensifier (II) and recorded on a CCD camera. For each shot the II was open for a few hundred ns which was long enough for Raman measurements of samples used in this study. Vibrational peak positions were determined as the Raman frequency at the center of each peak. Uncertainties in peak positions were ± 5 cm^{-1}.

Samples used in this study were in liquid state at room temperature and confined in a sample cell which consists of a 0.15 mm thick glass window and a 4–5 mm thick stainless steel tube placed on the driver plate. At room temperature all three samples solidify at relatively low pressures but under shock conditions with increased temperatures all samples were supposed to remain in the liquid state.[12] Shock pressures were determined using the impedance match method with measured projectile velocities and initial sample densities (benzene: 0.875 g/cm^3, iodobenzene: 1.832 g/cm^3, nitrobenzene: 1.204 g/cm^3). The Hugoniots used were $U_s = 5.35 + 1.34 U_p$ for Al,[13] $U_s = 1.50 + 1.67 U_p$ for benzene,[13] and $U_s = 2.52 + 1.23 U_p$ for nitrobenzene.[14] Since the Hugoniot of iodobenzene are not known, we determined approximate shock velocities of iodobenzene by estimating the time intervals for shock waves to propagate through samples. It was found that the shock velocity of iodobenzene is very small and roughly half of that of benzene or nitrobenzene under the same impact conditions.

Representative Raman spectra of three samples under ambient and shock pressures are shown in Fig. 2. All spectra were measured with a single excitation laser pulse and their S/N ratios are relatively low. Because of this it is hard to identify weaker vibrational bands clearly in the spectra but there are two strong Raman peaks clearly seen in each spectrum. They are the C-C stretching mode (992 cm^{-1}) and the C-H stretching mode (3080 cm^{-1}) of benzene, the C-C stretching mode (1002 cm^{-1}) and the C-H stretching mode (3065 cm^{-1}) of iodobenzene, and the NO$_2$ stretching mode (1346 cm^{-1}) and the C-H stretching mode (3082 cm^{-1}) of nitrobenzene. These six Raman peaks were chosen and examined in detail on how they change under shock compression. It is seen in the figure that all the peaks are shifted towards blue under compression. Although this result was well expected, it was found that the magnitude of peak shift strongly depends upon the vibrational mode and the molecule. Except for the blueshifts of spectral peaks Raman spectra of the three samples under shock compression indicated no other changes due to chemical reactions, phase transitions, etc., in the pressure range covered in this study. It is reported that decomposition of benzene under shock compression was observed at near 13 GPa (Ref. 15) and C$_6$H$_6$ molecular structure is retained up to this shock pressure.[16]

Raman frequency shifts under shock compression at various shock pressures were measured and the results are summarized in Fig. 3. It is seen that shock-pressure dependence of peak shifts are roughly linear in this pressure range for all the investigated Raman modes. Iodobenzene is heavier in density than benzene by over a factor of 2 but the peak shift behavior is about the same as that of benzene. Raman frequency shifts of benzene under very weak shock compression (up to 1.3 GPa) and static compression have been reported[12] and agree with our present results within the ex-
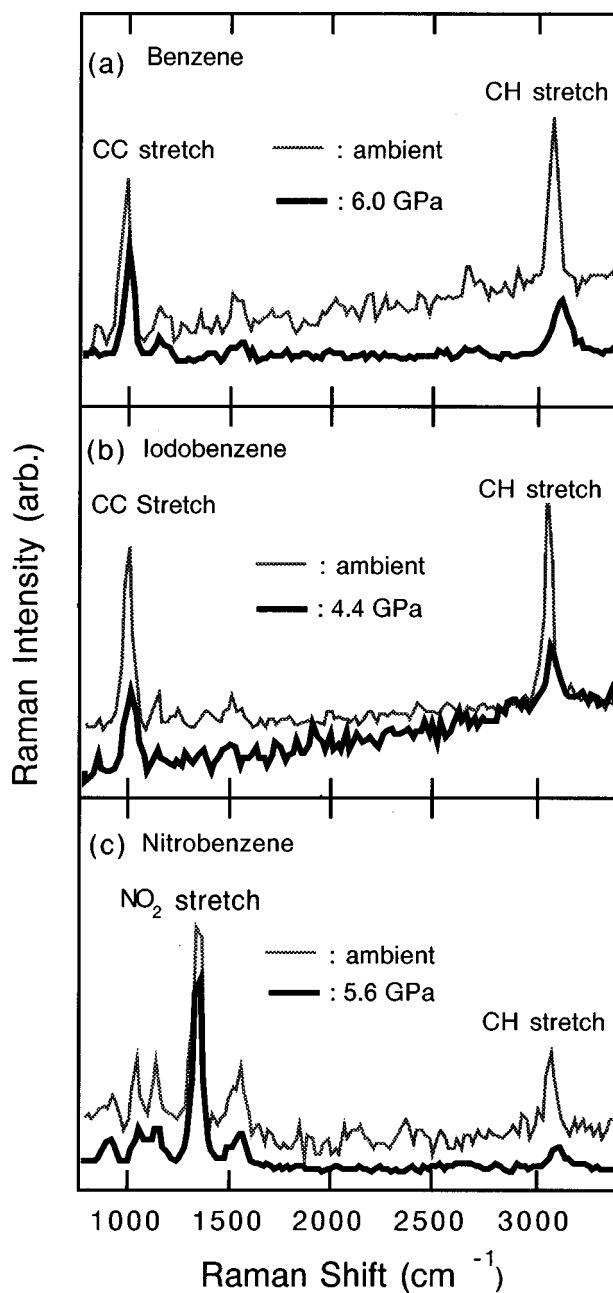

FIG. 2. Raman spectra of (a) benzene, (b) iodobenzene, and (c) nitrobenzene at ambient pressure and under shock compression. All spectra were measured with a single laser pulse (532 nm, 8 ns, 10–20 mJ).

perimental errors. It is noted here that, in general, Raman peaks become broader and shift towards red with temperature, and hence the increase of Raman frequency under shock compression is smaller than that under static isothermal compression because the temperature is significantly increased owing to the adiabatic nature of shock compression.[17] Raman frequency shifts of iodobenzene and nitrobenzene under shock compression have not been known so far. Most notable is the very small peak shifts of the NO$_2$ symmetric stretching mode. Peak shifts of the C-H stretching mode of nitrobenzene also seem somewhat smaller than those of benzene and iodobenze. It is reported that pressure-dependent Raman frequency shifts are well correlated with the ambient Raman frequencies,[18] although there exists some mode de-
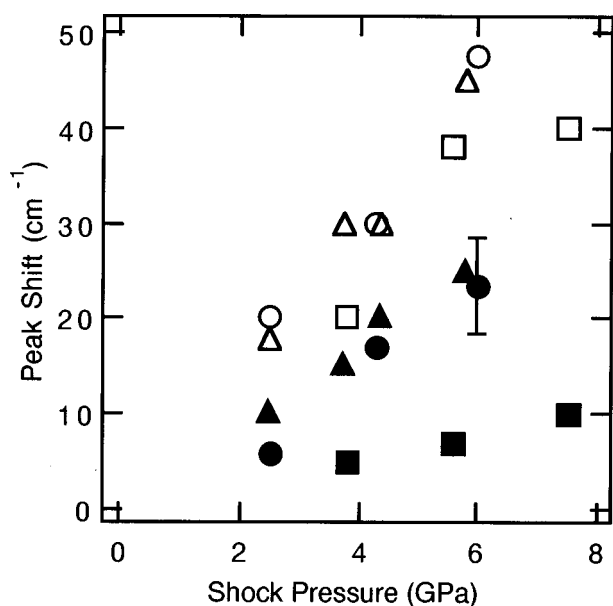
FIG. 3. Raman vibrational frequency shift vs shock pressure. ○: benzene C-H stretching mode (3080 cm^{-1}), ●: benzene C-C stretching mode (992 cm^{-1}), △: iodobenzene C-H stretching mode (3065 cm^{-1}), ▲: iodobenzene C-C stretching mode (1002 cm^{-1}), □: nitrobenzene C-H stretching mode (3082 cm^{-1}), ■: nitrobenzene NO$_2$ stretching mode (1346 cm^{-1}). Wave numbers in the parentheses are ambient Raman frequencies. The uncertainties in the peak shifts are about ±5 cm^{-1} and it is indicated on only one data point in the figure.

pendence. The ambient NO$_2$ stretching mode frequency of nitrobenzene (1346 cm^{-1}) is larger by over 30% than the C-C stretching mode frequencies of benzene and iodobenzene (~1000 cm^{-1}) but the pressure-dependent frequency shifts of the NO$_2$ stretching mode is 60–70% smaller than those of the C-H stretching mode of benzene and iodobenzene. There must exist some kind of softening mechanism in the NO$_2$ stretching vibrational mode under compression.

Nitrobenzene has relatively large dipole moment (1.4 $\times 10^{-29}$ C m) caused mainly by negative charges on oxygen atoms. Hydrogen bonds are formed between nitrobenzene molecules through negatively charged oxygen atoms and slightly positively charged hydrogen atoms. If the situation is similar to that of H$_2$O ice mentioned earlier, softening of the NO$_2$ stretching mode may take place under shock compression while the O—H bonds between nitrobenzene molecules become stronger. However, the softening of the NO$_2$ stretching mode of nitrobenzene would not be as significant as that of the O-H stretching mode of H$_2$O ice because hydrogen bonds in nitrobenzene are not as strong as those in H$_2$O ice. The small Raman frequency shifts under pressure observed for the NO$_2$ stretching mode of nitrobenzene may be explained as a result of two factors, i.e., (1) the pressure-induced softening mechanism in hydrogen-bonded materials which decreases the vibrational frequency and (2) the general pressure-induced hardening mechanism which increases vibrational frequencies of stretching modes. The cancellation of these two effects seems responsible for the small frequency shifts of the NO$_2$ stretching mode. When the pressure-induced softening of the NO$_2$ stretching mode occurs, some charge would flow from the nitro group into the hydrogen bond and then this would result in drawing some electron density from the aromatic ring into the nitro group. This might explain the fact that the peak shifts of the C-H stretching mode of nitrobenzene appear somewhat smaller than those of benzene and iodobenzene. Much further experimental work is necessary to better understand intermolecular interactions under pressure. At higher temperatures contributions of hot bands become significant and they should be taken into account when vibrational frequency shifts are discussed.[19]

In plate impact experiments shock pressure determination is simple and precise but in other shock experiments it may not be so easy and may involve large uncertainties. In such cases vibrational frequency shift data for common organic compounds such as presented in this paper can be used to determine shock pressures or to check the results of shock pressure calculations. For example, in certain laser shock experiments where shock velocities are difficult to measure but spectroscopic measurements are possible, shock pressures of a sample with known Hugoniot can be determined by the impedance match method if the sample is replaced by a standard material and its peak shifts are measured under exactly the same experimental conditions used for the sample.

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