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Backward Stimulated Raman Scattering in Shock-Compressed Benzene

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Backward stimulated Raman scattering measurements have been used to measure the fre-
quency shift of the 992-cm^{-1} vibrational ring-stretching mode of benzene shock-compressed
to pressures of 0.6 to 1.2 GPa. Results of the dynamic experiment are compared to shifts
measured for benzene isothermally compressed with a diamond-anvil cell. A Grüneisen
mode γ was determined for this vibrational degree of freedom.

We report here the observation of backward
stimulated Raman scattering in a shock-com-
pressed material. Previously, Keeler, Bloom,
and Mitchell[1] and Bloom and Keeler[2] have ob-
served stimulated Brillouin scattering in shock-
compressed acetone and water, and numerous
authors[3-10] have reported emission and absorp-
tion spectroscopic measurements of shocked
materials. Direct Raman measurements have
also been used to identify transient species in
shocked explosives.[11,12] Our measurements dem-
onstrate the feasibility of using a nonlinear opti-
cal process to measure molecular vibrational
frequency shifts in shock-compressed liquids.

The experiment was carried out in liquid ben-
zene shock-compressed from a pressure of 1 atm
and a temperature of 24 °C to pressures up to
1.18 ± 0.2 GPa, compressions of $(23 \pm 5)\%$, and
temperatures of approximately 150 °C to 200 °C.
The uncertainties are dominated by the lack of
shock data for benzene below 1.5 GPa. An extrap-
olation was used for the Hugoniot in determining
the pressures for these experiments. A schema-
tic of the apparatus is shown in Fig. 1. An alum-
inum projectile of known velocity from a 51-mm-
diam, 3.3-m-long gas gun impacted an aluminum
target plate producing a shock wave which ran
forward into a 9–11-mm-thick benzene sample.
The benzene used was reagent grade (Mallinck-
rodt Inc.). Standard data reduction techniques[13]
using published shock-velocity/particle-velocity
data[14] were used to determine the state of the
shock-compressed benzene. A single 6-ns-long
frequency-doubled Nd-doped yttrium aluminum
garnet laser pulse was focused through the quartz
window to a point in the benzene 2 to 6 mm in
front of the rear sample wall. The timing se-
quence was determined by the incoming projectile.
Interruption of a HeNe laser beam, in conjunction
with an appropriate time delay, triggered the
laser flash lamp approximately 300 μs prior to
impact. A time-of-arrival pin activated just be-
fore impact and the appropriate time delay served
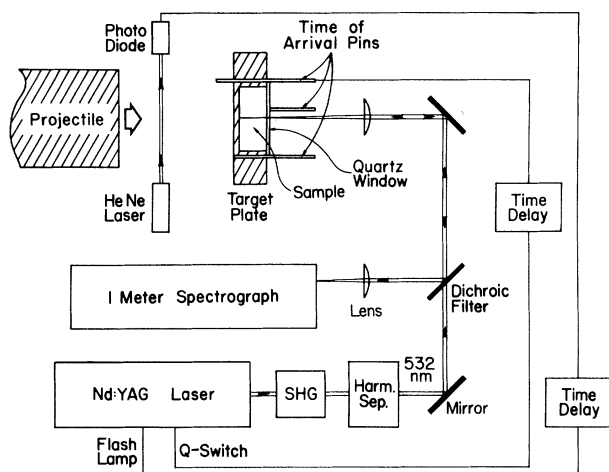to Q switch the laser just prior to the shock wave

FIG. 1. Schematic representation of backward stimulated Raman-scattering experiment. SHG, second harmonic generator; Harm. Sep., harmonic separator; Sample, liquid benzene.

FIG. 2. Scattered light spectrogram for shock-compressed benzene.

striking the quartz window and after it was well past the focal point of the incident laser light.

Stimulated Raman and Brillouin scattering occur when the incident laser intensity in a medium exceeds a threshold level.[15] This threshold level is determined by the cross section and linewidth of the transition, and by the focusing parameters of the incident beam. In liquid benzene, the ν_1 symmetric stretching mode[16] at 992 cm^{-1} has the lowest threshold for stimulated Raman scattering induced by 532-nm light, and is the transition observed in these experiments. As depicted in Fig. 1, the backward stimulated Raman beam is separated from the incident laser by means of a dichroic filter and is then focused onto the 10-μm-wide entrance slit of a 1-m Czerny-Turner spectrograph equipped with a 1200-grooves/mm grating used in first order. Figure 2 shows the resulting spectrogram for benzene shock-compressed to 0.92 GPa. The reflected incident laser line and the backward stimulated Brillouin-scattering line at 532 nm are observable, as are the backward stimulated Raman-scattering line from the shocked sample and the backward stimulated Raman-scattering line from ambient benzene. The latter feature resulted as a consequence of the shock wave having passed only about two-thirds of the way through the sample, and hence a stimulated Raman signal was also obtained from the unshocked liquid.

The frequency shift of the Raman line will have small contributions of approximately 0.1 cm^{-1} because the light crosses the moving interface
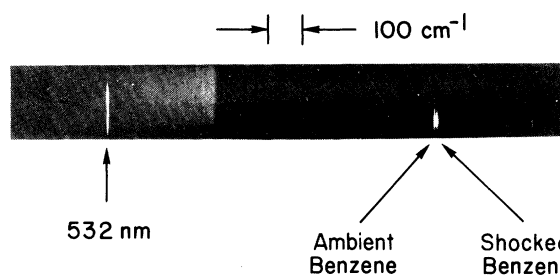
between two media of different refractive indices and because the material behind the shock wave is moving.[1] Since these errors are considerably less than the experimental uncertainty of ± 0.5 cm^{-1} for the measured frequency shifts and are a small fraction of the shift due to compression, no attempt is made to correct the data for these effects.

Figures 3 and 4, respectively, give the measured shift of the ν_1 ring-stretching mode vibrational wave number versus pressure and specific volume, V, of the shocked benzene. Observation of the ring-stretching mode at 1.18 GPa strongly suggests that benzene molecules still exist several millimeters behind the shock wave at this pressure, but does not, however, preclude some decomposition.[17] Future experiments employing a more sensitive measuring technique will be performed in an attempt to detect species with small concentrations.

Also depicted in Fig. 3 is the ring-stretching mode vibrational wave-number shift measured for benzene isothermally compressed at temperatures between 24 °C and 209 °C with a diamond-anvil cell and techniques previously described.[18] Measurements of the phonon spectrum in the region 40–200 cm^{-1} were used to distinguish between benzene I, benzene II, and liquid benzene. The vibrational frequencies obtained from spontaneous-Raman-scattering measurements at 24 °C with use of the 568.2-nm line of a krypton laser agree well with previous results for benzene.[16]

At fixed pressure, no temperature shift was observed in these static measurements. The wave-number shifts for the dynamic experiments agree well with the static data for either liquid benzene or benzene II, but differ substantially from those for benzene I. At pressures below the I-II-liquid triple point near 1.2 GPa,[19,20] the shocked benzene is therefore probably at temperatures high enough for it to be in the liquid
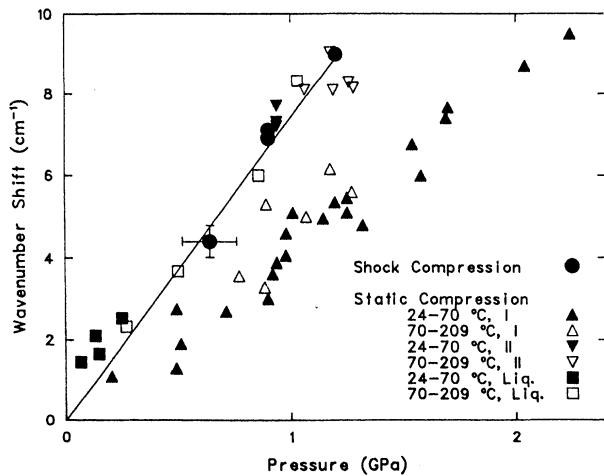
FIG. 3. Benzene ring-stretching mode vibrational frequency shifts (with respect to 992 cm^{-1}) vs pressure. The phase of the benzene during the diamond-anvil cell compression has been determined from phonon spectrum measurements. At 24 C benzene I was observed as a metastable phase above 1.2 GPa and benzene II was observed as a metastable phase below this pressure (Ref. 16). Both spectrometers were calibrated with liquid benzene at room temperature. The straight line is a fit of the shock-compressed data. Uncertainties for the shock-compressed data are given on one data point.

FIG. 4. Benzene ring-stretching mode vibrational frequency and Grüneisen mode parameter γ vs specific volume.

state. The temperatures achieved in the dynamic experiments are difficult to estimate to better than ± 40 K at 1.2 GPa. At pressures near 1.2 GPa, the shock-compressed material could be either liquid or benzene II since both phases exhibit about the same magnitude of wave-number shift for the ring-stretching mode, and the Hugoniot lies close to the phase boundary.

The measurement of vibrational frequency shifts at high pressures offers the additional opportunity of directly determining a single-mode Grüneisen parameter γ_i. The definition, $\gamma_i = -\partial \ln\nu_i/\partial \ln V$, and a curve fitted through the data points plotted in Fig. 4 were used to determine γ_{ν_1} as a function of specific volume. These results, also given in Fig. 4, show that γ_{ν_1} for the ring-stretching mode increases by a factor of 4 for a volume compression of 23%. As this mode is very insensitive to density changes at ambient conditions, this rapid increase in the mode gamma is not surprising.

This experiment is part of an effort directed toward understanding both the equation of state and the dynamic behavior of shock-compressed molecular systems. With shock-wave techniques, materials can be rapidly pulsed in a well con-
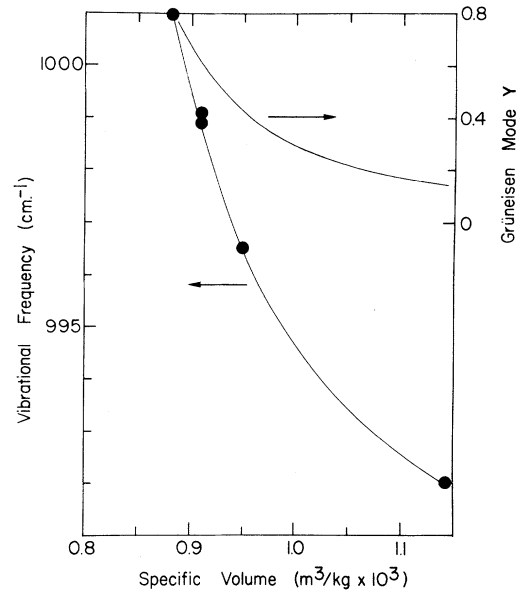
trolled laboratory environment to extreme pressures and temperatures. Under such conditions, intramolecular and intermolecular forces will have changed considerably and nonequilibrium conditions may be expected. Chemical behavior may be dramatically different from that expected on the basis of either extrapolations from ambient conditions or thermodynamic equilibrium. The experiment described represents the use of fast nonlinear optical methods to make measurements which will help us understand processes, e.g., detonation waves, governed by transient and possibly nonequilibrium phenomena. By these first measurements, we have shown that backward stimulated Raman scattering can be used to verify the existence of a particular molecular species behind a shock front, and we have determined the Grüneisen parameter γ_{ν_1} for the ring-stretching mode of benzene at Hugoniot pressures and temperatures.

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Measurement of the $1s2p2p'$ $4P^e$ Resonance in He⁻ Photodetachment

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A large resonance in the photodetachment spectrum of metastable He⁻, which was recently predicted theoretically, has been observed experimentally. Located at 1.2344 eV with a width of 7.0 meV, the detachment cross section reaches a maximum of ~70 Å². Its size results from the large oscillator strength associated with the first allowed transition in He⁻, $(1s2s2p)^4P^o \rightarrow (1s2p2p')^4P^e$.

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Although He⁻ has been known for a number of years to exist in the metastable $(1s2s2p)^4P$ state, and is the simplest negative ion next to H⁻, little attention has been given to its photodetachment properties until recently and very little theoretical work has been done on higher-lying He⁻ states in the quartet system (as compared to the doublet resonances seen in electron scattering). Recently, we made a preliminary survey[1] of the He⁻ photodetachment spectrum, using a variety of lasers to make measurements at 15 photon energies between 0.12 and 4 eV. Independently, and by a different measurement technique, Compton, Alton, and Pegg[2] obtained cross sections between 1.77 and 2.75 eV using a flash-lamp–pumped dye laser. Agreement between these

two experiments was quite good, considering their preliminary nature.

Although there were large energy gaps between some of our data, they nevertheless showed an interesting skeletal profile, and suggested[1] that the cross section increases significantly at or near the energy threshold for leaving the neutral He in the excited 2^3P state. Subsequently, Hazi and Reed[3] carried out the first photodetachment calculations on He⁻. They obtained quite good agreement with our results, and found a large peak just above the 2^3P threshold, where the cross section increased by two orders of magnitude to about 25 Å². From a separate scattering phase-shift analysis, they found the peak to be a shape resonance located at about 1.233 eV,
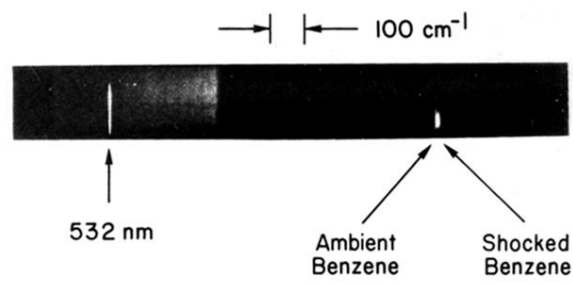
FIG. 2. Scattered light spectrogram for shock-compressed benzene.