PHYSICAL REVIEW B, VOLUME 65, 174116

Time-resolved Raman spectroscopy of benzene and cyclohexane under laser-driven shock compression

Akitaka Matsuda, Kazutaka G. Nakamura,* and Ken-ichi Kondo
Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama, Kanagawa 226-8503, Japan

(Received 18 October 2001; revised manuscript received 1 March 2002; published 2 May 2002)

Nanosecond time-resolved Raman spectroscopy has been performed on cyclic hydrocarbons, benzene, and cyclohexane under laser-driven shock compression at about 1.3 GPa. The spectral peak attributed to the ring-breathing mode of both benzene and cyclohexane showed a blue shift of about 10 cm^{-1}. Intensity increase of the shifted peak due to the propagation of the shock wave was observed. The decreasing rate of the intensity ratio suggests a decrease in the Raman cross section of compressed matters.

DOI: 10.1103/PhysRevB.65.174116 PACS number(s): 62.50.+p, 78.30.−j, 78.47.+p

It is necessary to obtain real-time information of matter under shock compression in order to understand shock-induced phenomena. Vibrational spectroscopy is a well-suited tool to investigate molecular dynamics, since direct observation of molecular structural and chemical changes is possible. Recently, Raman spectroscopic study of benzene under shock compression has been performed using impact guns.[1,2] Kobayashi and Sekine[1] have studied Raman spectra of shock-compressed benzene and benzene derivatives above 2 GPa and found that the magnitude of the frequency shift strongly depends on the vibrational modes and the molecule. Schmidt *et al.*[2] have measured Raman spectra of benzene under shock compression up to 1.2 GPa and frequency shift of the vibrational ring-breathing mode was observed. However, considering the frequency shift of vibrational ring-breathing mode of benzene, the extrapolated lines from Kobayashi and Schmidt's data do not match each other. Vibrational features of benzene under shock compression have not yet been fully understood. Laser-driven shock wave is reproducible at a high repetition rate, and using pump-probe technique, the signal can be accumulated and low noise Raman spectra can be obtained.[3] In this work, we performed nanosecond time-resolved Raman spectroscopy of benzene and cyclohexane both bearing a hexagonal C-C ring structure, using a pump-probe technique.

A *Q*-switched Nd:YAG (yttrium aluminum garnet) laser (Continuum Corp., Powerlite Plus) is used. The 10-ns-duration fundamental light is used for shock generation and the 8-ns-duration second-harmonic light was used for excitation of Raman scattering after passing an optical delay line. The shock generating fundamental light is focused on the target through a multilens array coupled with a normal lens to improve the Gaussian laser profile to a flat top profile. The diameter of the focused light is 1.25 mm. The target assembly was fabricated with a back-up float glass substrate ($100\times100\times3\ \mathrm{mm}^3$), an aluminum foil (25-$\mu$m thick), a 130-$\mu$m teflon spacer, and a cover float glass substrate ($100\times100\times3\ \mathrm{mm}^3$). Liquid sample was confined in a space ($100\times100\ \mathrm{mm}^2\times130\ \mu\mathrm{m}$) surrounded by the teflon and the glasses. Benzene (99.8%) and cyclohexane (99.8%) were obtained from Wako Pure Chemical Industries, Ltd. The target assembly was mounted on a motorized X–Z stage. When the laser is pulsing, the target assembly is moved by the motorized stage. Each laser shot was focused on a fresh sample. By focusing the laser beam onto the aluminum foil with a spot, confined plasma is generated near the aluminum-glass interface, which drives a shock wave though the aluminum foil into the liquid sample. The irradiated laser energy was 512 mJ. The peak pressure driven by laser irradiation is determined using the impedance-matching method[4] with measured particle velocity of benzene-aluminum interface using optically recording velocity interferometer system (ORVIS) method[5,6] and initial sample densities (aluminum: 2.69 $\mathrm{g/cm}^3$, benzene: 0.879 $\mathrm{g/cm}^3$, cyclohexane: 0.780 $\mathrm{g/cm}^3$). The Hugoniots used were $U_S=5.15+1.37u_p$ for Al,[7] $U_S=1.31+2.328u_p-0.3188u_p^2$ for benzene,[8] $U_S=1.26+2.720u_p-0.8260u_p^2$ for cyclohexane,[8] where U_S is shock wave velocity and u_p is particle velocity. Interface velocity was measured to be 0.60 ± 0.02 km/s and the peak pressure in the samples in the present experimental conditions was calculated to be 1.38 ± 0.05 GPa for benzene and 1.25 ± 0.05 GPa for cyclohexane. Optically delayed Raman probe laser light passes through a glan laser prism and is focused on the rear side of the sample with S polarization and a diameter of 500 μm at the center of the spot focused on the pump beam. The probe-laser energy was 5 mJ for benzene and 36 mJ for cyclohexane. Raman-scattered light was collected and focused into a 400-μm-core optical fiber through camera lenses and introduced into a spectrometer. The dispersed light was detected with an intensified charge-coupled device camera (Andor Technology Ltd.). Each Raman spectrum was obtained by accumulating data of 60 laser shots at 1.25 Hz. The resolution of the spectrometer is about 3 cm^{-1}. Details of the experimental setup are described elsewhere.[9]

Figure 1(a) shows a Raman spectrum of benzene at ambient pressure. The observed lines at 607 and 995 cm^{-1} are assigned to the C-C stretching mode and the ring-breathing mode, respectively. The C-H wag mode, the C-C stretching mode, and the combination band are found at 1180, 1586, and 1605 cm^{-1}. The time-resolved Raman spectrum of the ring-breathing mode, which appeared to have the most prominent shift, is shown in Fig. 2(a). The spectrum at a delay time of 13 ns after the pump irradiation showed a slight change in the high-frequency part of the line. At 18 ns, the generation of a new blue shifted peak became obvious. The intensity of this new peak increased as the delay time

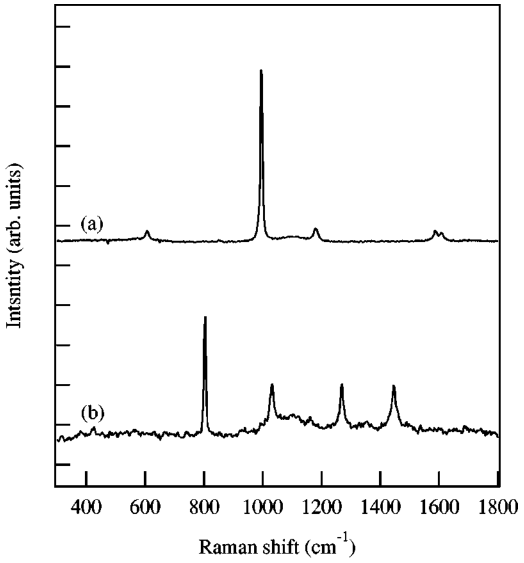

FIG. 1. Raman spectra of (a) benzene and (b) cyclohexane at ambient pressure.

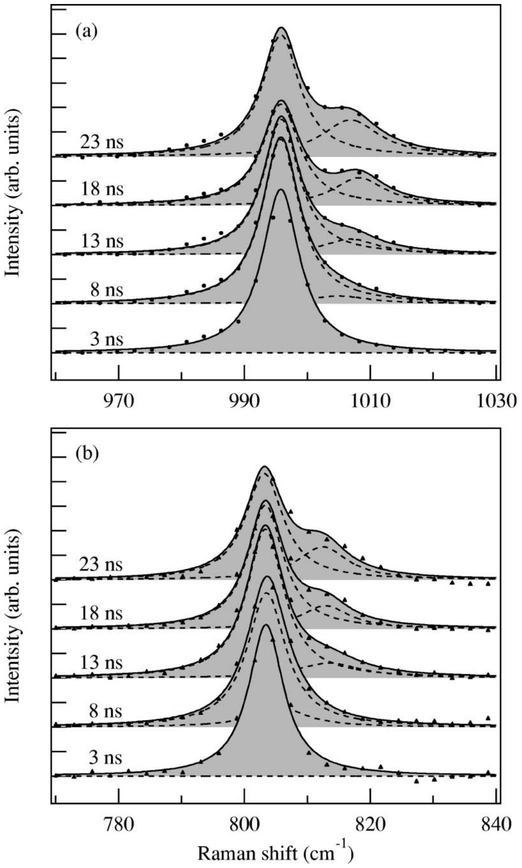

FIG. 2. Time-resolved Raman spectra of ring-breathing mode of (a) benzene and (b) cyclohexane under shock compression. The solid lines and dashed lines show the fitted Lorentzian function and the separated peaks, respectively.

increased. The magnitude of the shift was obtained by fitting this peak with a sum of two Lorentzian line shape functions. In case of fitting the data, the Raman shift and full width at half maximum of the peak due to the unshocked area of the sample were fixed to that of the ambient. Because the zero point of the delay time was determined by detecting the light scattered at the surface of the aluminum, there lies a time lag of a few nanoseconds for the shock wave to reach the liquid sample. This time lag is due to the propagation of the shock wave through the 25-μm thick aluminum. Calculating the shock wave velocity inside aluminum from the measured particle velocity results in an estimated time lag of 4 ns. Open circles in Fig. 3 show the magnitude of the blue shift of shock-compressed benzene as a function of the delay time. The line is shown to guide the eye. Rise of the blue shift is observed. After the rise time of about 10 ns, the magnitude of the shift reaches a stable value of about 10 cm^{-1}. This result agrees with the extrapolated line of the reported data of Schmidt *et al.*[2] within the experimental errors, while does not agree with the extrapolated line of Kobayashi.[1] Compared with the static compression data,[2,10] our result agrees with the extrapolated line of liquid.

Figure 1(b) shows a Raman spectrum of cyclohexane at ambient pressure. The observed lines at 805 and 1033 cm^{-1} are assigned to ring-breathing mode and stretching mode of C-C. The C-H twist mode and the C-H scissors mode are found at 1270 and 1446 cm^{-1}. The broad line at 1100 cm^{-1} is due to the glass substrate. The time-resolved Raman spectrum of the ring-breathing mode, which appeared to have the most prominent shift, is shown in Fig. 2(b). The spectrum at 13 ns after the pump irradiation shows a slight change in the high-frequency part of the line. At 18 ns, the generation of a new blue shifted peak becomes obvious. The intensity of this new peak increased with delay. Open triangles of Fig. 3 show the magnitude of the blue shift of shock-compressed cyclohexane as a function of the delay time. The line is shown to guide the eye. Rise of the blue shift is observed. After the rise time of about 10 ns, the magnitude of the shift reaches a stable value of about 10 cm^{-1}. This result agrees with the reported data of static compression of cyclohexane.[11] However, no other spectral

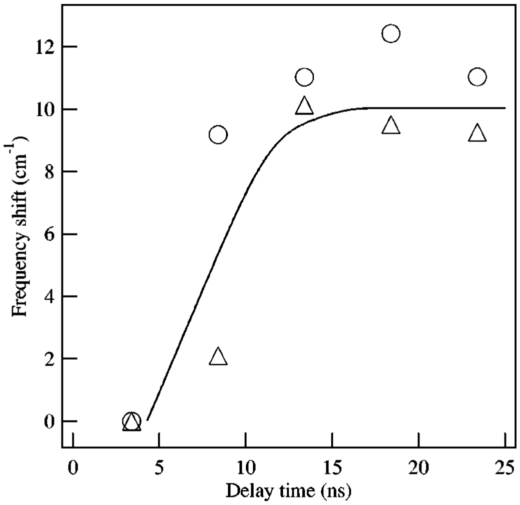

FIG. 3. Ring-breathing mode frequency shift vs delay time. Open circle and triangle represent benzene and cyclohexane, respectively. The solid line is guide to the eye.

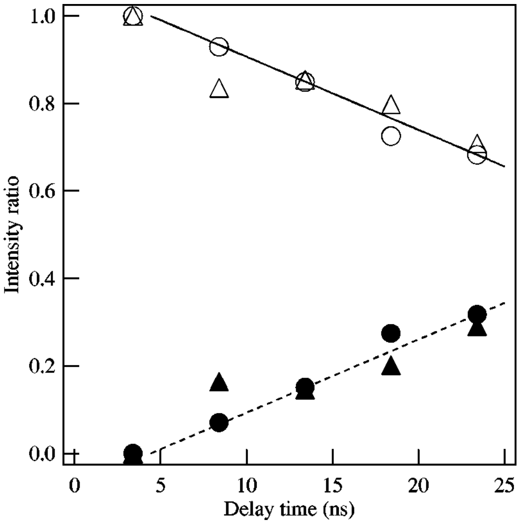

FIG. 4. Intensity ratio vs delay time. Open and solid symbols represent intensity ratio belonging to the unshocked and shocked areas. Circle and triangle represent benzene and cyclohexane, respectively. Solid and dashed lines are the fitted lines of the intensity ratio of the unshocked and shocked areas, respectively.

shift was observed. Therefore, the compressed cyclohexane is supposed to be in the liquid state and no phase transition is expected.

The intensity ratio of the peak to the total intensity is plotted in Fig. 4 as a function of delay time. Here the total intensity is the sum of the peak intensity of the unshocked and the shocked region at that delay time. The ratio belonging to the unshocked area decreases as the delay time increase. This is due to the propagation of the shock wave, resulting in the volume decrease and increase of the unshocked and shocked areas. It is expected that the shock-wave velocity is determined by the decreasing ratio of the unshocked region according to the following equation:

$$U_S = s_u d, \tag{1}$$

where U_S is the shock wave velocity, s_u is the decreasing rate of the intensity ratio belonging to the unshocked area, d is the thickness of the sample. The shock-wave velocity obtained from this equation is 2.29 ± 0.10 km/s for benzene and 2.06 ± 0.31 for cyclohexane. Since the shock-wave velocity obtained from impedance-matching method based on ORVIS data is 2.60 ± 0.03 km/s for benzene and 2.62 ± 0.03 km/s for cyclohexane, the calculated velocities are smaller by 12% and 21%, respectively. There are three possible reasons for this mismatch. The decrease of the Raman cross section,[12] the reflection of the probe laser and scattered light at the shock front,[13] and the decrease in the population of the ground state due to temperature increase induced by shock compression. Considering these effects, the intensity ratio (R) is calculated by the following equations:

$$R = \frac{I_u}{I_u + I_s}, \tag{2}$$

$$I_u = \sigma_R N \left[1 - \frac{U_S(t - t_0)}{d} \right] (2 - r^2 + r^3) I_L \sum F_u(\nu), \tag{3}$$

$$I_s = (1 - \delta) \sigma_R N \frac{U_S(t - t_0)}{d} (2 - 2r^2) I_L \sum F_s(\nu), \tag{4}$$

where I_u is the integrated intensity of unshocked area, I_s is that of shocked area, σ_R is the Raman cross section, δ is the decreasing ratio of Raman cross section, t is the delay time, t_0 is the arrival time of the shock front, r is the reflectivity, I_L is the intensity of the Raman stimulating laser, $F_u(\nu)$ is the population of vibrational state (ν) in the unshocked region, and $F_s(\nu)$ is that of the shocked region. Decrease of the Raman cross section in shocked state is reported by Venkateswaran *et al.*[12] Although the decreasing ratio of the Raman cross section cannot be estimated, the reflectivity and the decrease in population can be estimated as follows. The reflectivity is calculated using the Fresnel's equation and the refractive index of the compressed and uncompressed liquids. The density of the compressed liquids are derived from the shock wave velocity and the particle velocity, which is about 1.3 times larger than the initial density for both benzene and cyclohexane. The refractive index is calculated from the density ratio,[14] which was 1.65 for benzene and 1.43 for cyclohexane. The reflectivity is obtained to be about 0.2%, and the contribution to the intensity ratio is little. The shock temperature for benzene is reported to be about 600 K at 1.5 GPa, and the population of vibrational ground state decreases by about 8%. The Raman cross section is independent of temperature, which is obtained by harmonic approximation on molecular vibrations and phonons.[15] The intensity ratio of anti-Stokes line to Stokes line increases with temperature.[16] However, the intensity of the Stokes line is independent of the depopulation of vibrational states, because Raman scattering from all vibrational states is summed up. Therefore, the change of Raman cross section, which is due to a change of polarizability[17] or orientation in compressed state, is considered to be the main reason.

In summary, nanosecond time-resolved Raman spectroscopy was performed to study cyclic hydrocarbons, benzene, and cyclohexane under laser-driven shock compression at about 1.3 GPa. A blue shift of the vibrational ring-breathing mode was observed under shock compression, while no change was observed in other modes. The magnitude of the frequency shift reached a stable value of about 10 cm^{-1} after a rise time of about 10 ns. The intensity of the shifted peak increases along the propagation of the shock wave, although, the decreasing rate of the intensity ratio belonging to the unshocked area did not match the shock wave velocity obtained from impedance-matching method. The results suggest that the decrease of the Raman cross section due to a change of polarizability or orientation of molecules in compressed state are responsible for this mismatch.

We thank K. Wakabayashi, N. Miyake, and A. Akiyoshi for their help in the early stage of experiments.

[*] Author to whom correspondence should be addressed.

[1] T. Kobayashi and T. Sekine, Phys. Rev. B **62**, 5281 (2000).

[2] S.C. Schmidt, D.S. Moore, D. Schiferl, and J.W. Shaner, Phys. Rev. Lett. **50**, 661 (1983).

[3] I.-Y.S. Lee, J.R. Hill, H. Suzuki, B.J. Baer, E.L. Chronister, and D.D. Dlott, J. Chem. Phys. **103**, 8313 (1995).

[4] *High-Pressure Shock Compression of Solids*, edited by J.R. Asay and M. Shahinpoor (Springer, New York, 1992).

[5] L.M. Barker and K.W. Schuler, J. Appl. Phys. **45**, 3692 (1974).

[6] D.D. Bloomquist and S.A. Sheffield, J. Appl. Phys. **54**, 1717 (1983).

[7] *LASL Shock Hugoniot Data*, edited by S.P. Marsh (University of California Press, Berkeley, 1980).

[8] P.C. Lysne, J. Chem. Phys. **57**, 492 (1972).

[9] K. Wakabayashi, K.G. Nakamura, M. Yoshida, and K. Kondo, Appl. Phys. Lett. **75**, 947 (1999).

[10] M.M. Thiery and J.M. Leger, J. Chem. Phys. **89**, 4255 (1988).

[11] J. Haines and D. F. R.Gilson, J. Phys. Chem. **93**, 7920 (1989).

[12] U.D. Venkateswaran, A.M. Rao, E. Richter, M. Menon, A. Rinzler, R.E. Smalley, and P.C. Eklund, Phys. Rev. B **59**, 10 928 (1999).

[13] P. Harris and H.N. Presles, J. Chem. Phys. **74**, 6864 (1981).

[14] S.B. Kormer, Usp. Fiz. Nauk **94**, 641 (1968) [Sov. Phys. Usp. **11**, 229 (1968)].

[15] *Raman Scattering in Materials Science*, edited by W.H. Weber and R. Merlin (Springer, New York, 2000).

[16] T.R. Hart, R.L. Aggarwal, and B. Lax, Phys. Rev. B **1**, 638 (1970).

[17] E. Kuss and H.H. Heydemann, Z. Phys. Chem. (Frankfurt) **43**, 97 (1964).