

Measurement of transient Raman spectrum on gas-gun loading platform and its application in liquid silane*

Yi-Gao Wang(汪贻高)^{1,2}, Fu-Sheng Liu(刘福生)^{1,2,†}, Qi-Jun Liu(刘其军)^{1,2}, Wen-Peng Wang(王文鹏)^{1,2}, Ming-Jian Zhang(张明建)^{1,2}, Feng Xi(习锋)³, Ling-Cang Cai(蔡灵仓)³, and Ning-Chao Zhang(张宁超)⁴

¹Key Laboratory of Advanced Technologies of Materials, Ministry of Education of China, School of Physical Science and Technology, Southwest Jiaotong University, Chengdu 610031, China

²Sichuan Provincial Key Laboratory (for Universities) of High Pressure Science and Technology, Southwest Jiaotong University, Chengdu 610031, China

³Institute of Fluid Physics, China Academy of Engineering Physics, Mianyang 621900, China

⁴College of Electronics and Information Engineering, Xi'an Technological University, Xi'an 710032, China

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Combining a low temperature liquidizing system with a transient Raman spectroscopy, a new experimental technique is established for the first time on a two-stage light-gas gun, and it is employed to study shock-compressed fluid silane. With this experimental technique, we first obtain a Raman peak shift relating to the Si-H stretching vibration mode of molecular liquid silane under shock loading conditions. The Raman peak of 2184 cm^{-1} at an initial state of 0 GPa and 85 K moves to 2223.4 cm^{-1} at a shocked state of 10.5 GPa and 950 K, and its full width of half maximum broadens from 33 cm^{-1} to 118 cm^{-1} . The shocked temperature, calculated by the thermodynamic equation of state, is well consistent with that estimated by the Doppler broadening function.

Keywords: fluid silane, Raman spectra, shock compression, equation of state

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1. Introduction

The transformation of molecular hydrogen to metallic hydrogen has been studied intensely.^[1-4] However, the conditions for preparing metallic hydrogen are too harsh. It has recently been suggested that silane is expected to be metalized at much lower pressures due to the fact that the electron density of hydrogen atoms in silane is equivalent to pure hydrogen atoms under mega-bar pressures.^[5-10] Thus, the behavior of silane under high pressure and high temperature has been a hot research topic due to its special status. However, little information is available about the high-pressure behavior of silane. Especially, the experimental data of silane under high pressure are scarce.^[11-13] Accordingly, there is a great deal of interest in exploring the unique properties under high pressures and high temperatures.

The shock wave propagating in material can cause pressure, strain and temperature to abruptly change. Unlike static pressure, such a dynamic loading technology can quickly reach a thermodynamic state of high temperature and high pressure on a time scale of nanoseconds. So it becomes one of the effective ways to study the dynamic behaviors of materials. Moreover, the sample size of the shock loading

experiment is much larger than that of static compression, thus it is conducive to observe the characteristics of samples under high temperature and high pressure. The micro dynamic behavior of material is also an important issue in the field of chemistry and materials science. In the process of dynamic loading, the real-time detection of microstructure change is very important, and it can provide abundant micro dynamic information for researchers. Now several main real-time measurement techniques have been used in dynamic loading experiments, including a light reflection method,^[14] light transmission method,^[15,16] VISAR method,^[17] and spectrum method.^[18,19]

The Raman spectroscopy is a useful tool to determine molecular changes, so, the time-resolved Raman spectrum measurements in shock experiments have attracted a great deal of attention. Accordingly, it is necessary to develop a portable transient Raman spectroscopy system on a two-stage light-gas gun to study the Raman peak shifts of silane under shock compression, and it will offer better understanding of the dynamic behavior of the sample. In the present work a new experimental system is described for performing real-time Raman measurements.

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†Corresponding author. E-mail: fusheng_l@163.com

2. Experimental approach

High purity samples were prepared through using a low-temperature liquidizing technology. The shock wave experiment was conducted using a two-stage light-gas gun. A flyer plate of copper was used, which was 3.0 mm in thickness and 24 mm in diameter, and stuck on the surface of the projectile. Then, the samples were shocked by the impact velocity of 3 km/s. Finally, the shocked samples were characterized by Raman scattering technique.

The shock pressure and temperature of fluid silane were calculated by using the measured velocity of the flyer and the Hugoniot equations of state (EOSs) of the copper impactor, aluminum base plate, quartz window and fluid silane (85 K). The EOS of fluid silane was described by the perturbation theory of molecular fluid. The shock adiabat was described through a relation between the initial and final internal energy, pressure and volume, i.e., (E_0, P_0, V_0) and (E_1, P_1, V_1) , respectively, according to the Rankine–Hugoniot equation: $(E_1 - E_0) = 1/2(V_1 - V_0)(P_0 + P_1)$. The specific calculation method is given in Subsection 3.2.

2.1. Preparation of sample

An effective way to prepare liquid silane with high purity gas is a low-temperature liquidizing technology as shown in Fig. 1. The facility is composed of the low temperature target, the sample pool, the cooling circulation channel, and the liquid nitrogen storage chamber. The temperature of the sample can

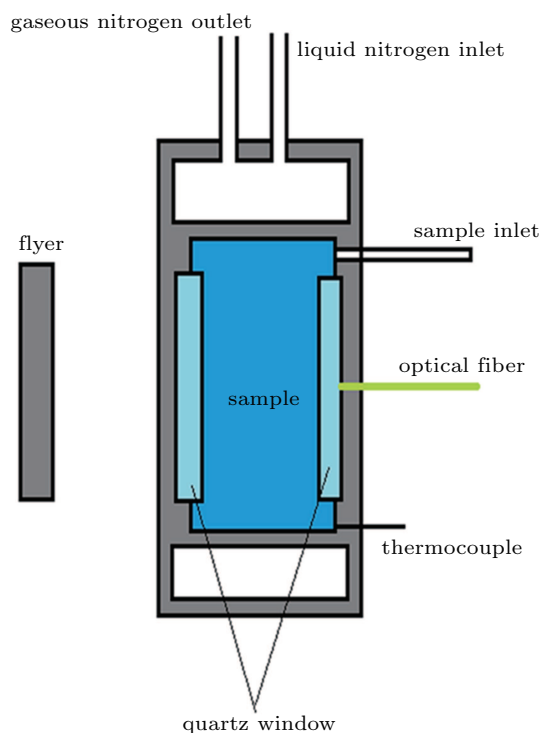


Fig. 1. (color online) Low temperature molecular liquid preparation system composed of low temperature target, sample pool, cooling circulation channel, and liquid-nitrogen storage chamber.

be adjusted in a range of 77 K–300 K. Firstly, liquid nitrogen was stored in the dewar, which was used as a coolant. The liquid nitrogen was driven into the cooling chamber by the liquid nitrogen vaporization, until the temperature reached the expected value. Secondly, the sample pool was evacuated, and then the sample gas was continually pressed into it until the liquefaction was completed. The advantage of the approach is that it can avoid the leaking of silane, which may cause a fire or possibly explosion in air.

2.2. Measurement system

As depicted in Fig. 2, the transient Raman spectrum detection system is composed of four main components, namely, the sample target, the time delay control units, the laser source and the spectrum detection system. The system was placed on a movable platform and docked with the observation window in the target room. Raman excitation was provided by a YAG laser system with a pulse duration of 10 ns. The incident laser of 532 nm was extracted from the laser system and transmitted to the sample through optical fibers, and then focused at the rear of the target. The Raman scattered light was collected along an angle of 45° to the excitation source with optical fibers. To increase the intensity of the Raman signal, the fiber optic bundles were used. The signal from these fibers was delivered to a spectrometer using a pair of lenses to match the optical fibers and the spectrometer. In the end, the output was delivered to a spectrometer and recorded using a gated intensified charge-coupled device (ICCD).^[20]

In general, the entire shock compression process maintains only a few hundreds of nanoseconds in this experiment. In order to increase the experimental precision, the lamp trigger signal and Q trigger signal were used to solve the synchronization problem caused by the random emission of gas gun loading and influence of precision laser mechanism and spectrum system. The lamp trigger signal was generated by the magnetic speed measuring unit and transferred to the digital oscilloscope via a cable. After a period of delay, the signal was used to trigger the laser flash; the delay time depended on the forecast length between the flyer and the target. The Q trigger signal was generated from the hitting of the shock wave on the interface between a metal substrate and the substrate. The photoelectric multiplier tube converted the light signal into an electrical pulse signal, which then was input to the delay time controller. It arrived at the detection system with a controlled time delay to synchronize the time window of the gated intensifier with the laser pulse. The delay time depended on the thickness values of quartz glass substrate and compressed layer of the sample. The signal always triggered the ICCD detection system at the same time.

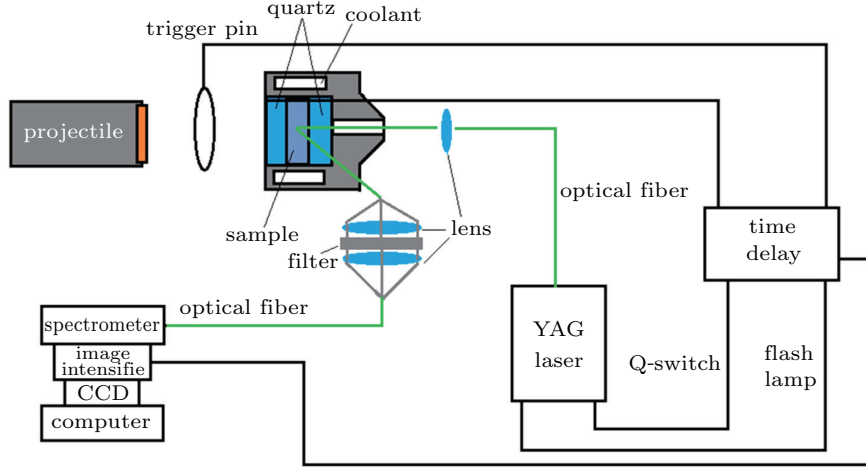


Fig. 2. (color online) Measurement system of transient Raman spectrum.

2.3. Thermodynamic equation of state

To calculate the state of the liquid sample during shock compression, the perturbation theory of molecular fluid was used to describe the EOS of fluid silane.^[21] The values of parameters (ϵ , r^* , α) of molecular interaction potential in exp-6 formula

$$\phi(r) = \epsilon \left[\frac{6}{\alpha - 6} \exp \left[\alpha \left(1 - \frac{r}{r^*} \right) \right] - \frac{\alpha}{\alpha - 6} \left(\frac{r^*}{r} \right)^6 \right]$$

were 2719 K, 4.653 Å, and 13.0, which are determined according to its critical state based on the corresponding principle.^[22] The silane molecule has 9 vibration modes, and their corresponding frequencies are 2187.1 K(1), 975 K(2), 2191 K(3), and 914 K(3). All of these vibration modes were used to estimate their contributions to the Heilmholtz function. The initial state of liquid silane was at its solid/liquid equilibrium line (85 K) in our experiments, its initial density was 0.711 g/cm³ at this state.^[23] Heilmholtz free energy was calculated by taking into account its translational and rotational freedoms. The initial internal energy was 46.44 kJ/mol, and its specific volume was 45.18 cm³/mol.^[23] All thermodynamic calculations were completed by a computation program written by ourselves.

The following formulas were used in the program.

Heilmholtz free energy is given by the free energy of ideal gas and interaction terms

$$F(V, T) = F_{\text{id}}(V, T) + A_P(V, T). \quad (1)$$

The ideal term includes the molecular vibration and rotation:

$$F_{\text{id}}(V, T) = F_{\text{trans}}(V, T) + F_{\text{int}}(T), \quad (2)$$

$$F_{\text{trans}}(V, T) = \sum_i NkT \left[\ln \left(\frac{N\lambda^3}{V} \right) - 1 \right], \quad (3)$$

$$F_{\text{int}}(T) = - \sum_i NkT \ln(j(T)), \quad (4)$$

$$A_P(V, T) = A_{\text{HS}}(\eta) + F_{12}(\eta) + \frac{1}{2} \rho \int_d^\infty g_{YP}(\eta, r) \Phi(r) dr, \quad (5)$$

$$F_{12} = -(\eta^4/2 + \eta^2 + \eta/2)NkT, \quad (6)$$

$$A_{\text{HS}} = (4\eta - \eta^2)/(1 - \eta^2)NkT, \quad (7)$$

where $\lambda = (h^2/2\pi mkT)^{1/2}$ is the thermal wavelength of molecular motion, N the number of particles, k the Boltzmann constant, T the temperature, $j(T)$ the rotational partition function, $A_{\text{HS}}(\eta)$ the hard sphere excess free energy, $g_{YP}(\eta, r)$ the hard sphere radial distribution function, $F(\eta) = -(\eta^4/2 + \eta^2 + \eta/2)$ the soft-sphere correction, $\Phi(r)$ the pair potential of equation exp-6 formula, $\eta = (d^3/6)N/V$ with d being a hard-sphere diameter, ρ is the number density, V the specific volume, h the Plank constant, m the mass of molecules, and $\pi = 3.1416$.

The Hugoniot equation of state of the sample is determined by

$$E - E_0 = \frac{1}{2}(P + P_0)(V_0 - V), \quad (8)$$

where the pressure and internal energy of the system are calculated from

$$E = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right)_V, \quad P = - \left(\frac{\partial F}{\partial V} \right)_T. \quad (9)$$

3. Results and discussion

We firstly record Raman spectra of silane at 85 K and 0 GPa, then the Raman spectra of silane are measured under shock compression. The copper flyer impact velocity is 3 km/s in the shock compressed experiment, and the measurement results are shown in Fig. 3. The Raman characteristic peak (corresponding wave number is 2184 cm⁻¹) of silane is used as the standard light for calibrating the spectral system.

It is noted that the spectra measured in the shock compression experiment includes the contributions from shocked and unshocked sample as shown in Fig. 4. That is, the position of shock wave front is located at the laser focal spot. The results of the thermodynamic state equation show that the sample is

at a temperature of 950 K and a pressure of 10.5 GPa under shock compression. The 2184-cm⁻¹ peak comes from the unshocked samples (the Raman peak of the sample in front of the wave corresponds to the Si-H stretching vibration, which is in agreement with the calibration result). The newly emerged peak 2223.4 cm⁻¹ comes from the compressed part of the sample (rear of the wave front). The value of the blue shift of wave number is 39.4 cm⁻¹, which is in agreement with the previous result.^[24] On the other hand, the peak broadening is observed in the measurement. Concretely, the width of Raman peak is 33 cm⁻¹ at ambient pressure, therefore the width of Raman peak is 118 cm⁻¹ under the shock compression, with peak broadening being as large as more than twice.

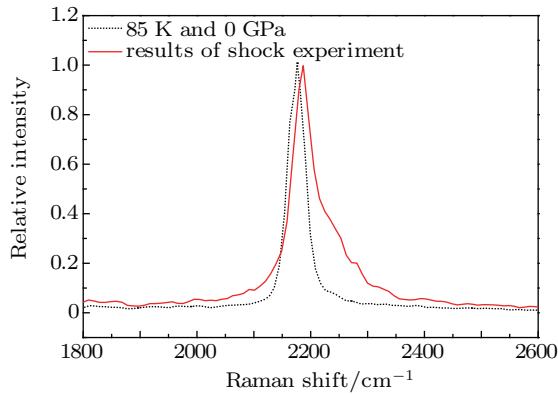


Fig. 3. (color online) Measured Raman spectra of silane. The dotted line is for the calibration results of silane under 85 K and 0 GPa, the solid line is recorded under shock compression, with the flyer impact velocities being 3 km/s.

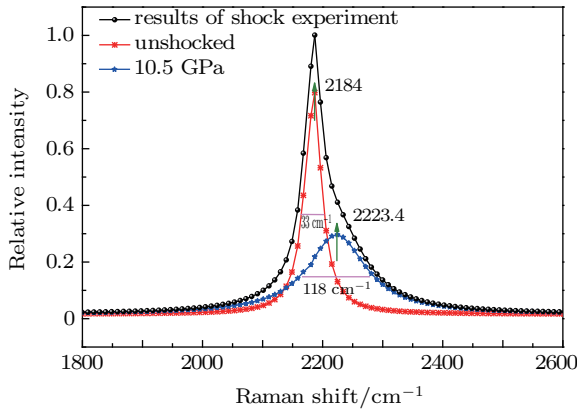


Fig. 4. (color online) Variations of relative intensity with Raman shift.

3.1. Analysis of spectral broadening

The Doppler broadening follows the velocity distribution of particles. If the observer is close to the emitter with a speed of v_x , Doppler frequency shift is given by^[25]

$$-\frac{\Delta\lambda}{\lambda} = \frac{\Delta\nu}{\nu} = \frac{v_x}{c}. \quad (10)$$

The distribution of the particles is nearly a Maxwell distribution,^[26]

$$\frac{dN(v_x)}{N} = \frac{\alpha}{\sqrt{\pi}} e^{-v_x^2/\alpha^2} dv_x, \quad (11)$$

where α is the most probable speed, $\alpha = (2kT/m_A)^{1/2} = (2RT/M)^{1/2}$, with m being the real mass of particle, M the relative molecular mass, $k = 1.38 \times 10^{-23}$, $R = 8.317742$ J/mol·K, and T the temperature. The intensity at frequency ν is proportional to $dN(\nu)$. The shape of the line can be expressed with the central strength I_0 as

$$I_\nu = I_0 \exp\left[-\frac{c^2(\nu_0 - \nu)^2}{\nu_0^2 \alpha^2}\right], \quad (12)$$

which is a Gaussian distribution, whose width is determined by α , and ν_0 is the central frequency. Half the scattering intensity is $I_{1/2} = I_0/2$. The full width at half maximum (FWHM) can be expressed by the following formula:^[26]

$$\begin{aligned} \delta\nu_D &= 2|\nu_0 - \nu_{1/2}| = 2\sqrt{\ln 2} \frac{\nu_0 \alpha}{c} \\ &= \frac{2\nu_0}{c} \sqrt{\frac{2\ln 2 \cdot RT}{M}} \end{aligned} \quad (13)$$

or

$$\delta\nu_D = 7.16 \times 10^{-7} \sqrt{\frac{T}{M}} \nu_0. \quad (14)$$

According to the characteristic peaks of Raman spectra before and after shock compression, the temperature of the sample can be estimated.

Raman scattering is used for measuring the temperature of shocked silane. The calculated temperature is 1021 K, and this result is in qualitative agreement with that calculated from the thermodynamic equation of state (950 K). The difference between the values from the two methods is 6.8%. This difference may be caused by the pressure contribution. If the pressure contribution is taken into account, the difference will be lower. So, it is hard to measure the shock temperature in the shock compression experiment. The spectral measurement of shock temperature can provide reliable results for the molecular liquid with good optical transparency.

3.2. Force constants

The blue shift of Raman peak usually rises with pressure increasing.^[27] Under the shock loading condition, the change of silane is related to the interaction between the molecules. The overlap of electron cloud can reduce the band gap of the system, and the repulsion force between the atoms increases gradually. We measure the vibrational frequency of the tetrahedral silane molecules as a function of force constant. The function is given by^[28,29]

$$m\omega_1^2 = f, \quad (15)$$

where m is the atomic mass of hydrogen. Before shock compression, the vibrational frequency is $\omega_1 = 2184$ cm⁻¹ and force constant is $f_1 = 2.82 \times 10^5$ dyn/cm (1 dyn = 10⁻⁵ N). In the process of compression, the experimental value is $\omega_2 = 2223$ cm⁻¹ and the force constant is $f_2 = 2.925 \times 10^5$ dyn/cm.

4. Summary

Transient Raman spectrum measurement is performed to characterize the high pressure and high temperature behaviors of fluid silane. The blue shift 39.4 cm^{-1} and broadening 85 cm^{-1} of Raman peak are observed. The thermodynamic equation of state is used to calculate the shocked state of the sample, and the pressure and temperature of the sample in the shock state are 10.5 GPa and 950 K. Furthermore, a similar temperature value 1031 K is obtained for the spectral measurements of the temperature. The characteristic of Si–H stretching vibration at this state is obtained.

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