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# Pressure-Induced Reverse Reaction of the Photochemical Decomposition of Germanium Tetraiodide Molecular Crystal

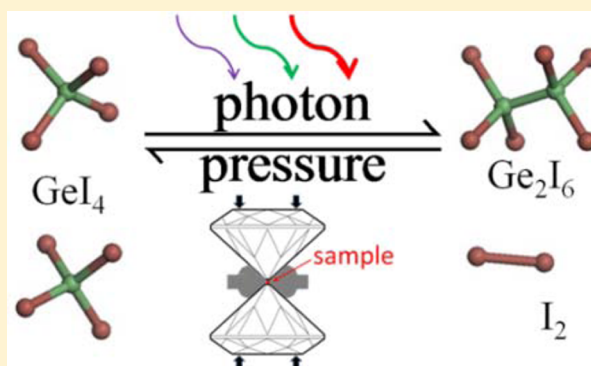
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## S Supporting Information

**ABSTRACT:**  $\text{GeI}_4$  molecular crystal and its solution in cyclohexane were irradiated by lasers of different wavelengths to investigate the critical wavelength for photochemical decomposition of  $\text{GeI}_4$ . We have observed that 633 nm laser can photochemically decompose  $\text{GeI}_4$ , exceeding the previously reported wavelength limit of 514 nm. XPS spectra indicate that  $\text{GeI}_4$  is photochemically decomposed into  $\text{Ge}_2\text{I}_6$  and  $\text{I}_2$ ; unlike  $\text{GeBr}_4$ ,  $\text{Ge}^{2+}$  ( $\text{GeI}_2$ ) cannot be found in the photochemical reaction products. Raman spectra measurement of  $\text{GeI}_4$  under high pressure up to 24 GPa show that Raman signals of  $\text{Ge}_2\text{I}_6$  and  $\text{I}_2$  vanish at 0.5 to 1.7 GPa. This finding clearly shows that high pressure can effectively reverse the photochemical decomposition of  $\text{GeI}_4$  and influence the direction of the solid-state reaction, which is usually found on gas-phase reactions.



## 1. INTRODUCTION

Because of the weak bonding nature of van der Waals force, molecular crystals have relatively lower melting points than those of ionic or covalent crystals and are much easier to compress. As a result, relatively lower pressure can give rise to a drastic shortening of intermolecular distance and modifications of various physical and chemical properties of molecular crystals. Recently, the properties of molecular crystals have become the subject of extensive researches because of the novel physical phenomena under high pressure.<sup>1–6</sup> For example, pressure-induced insulator–metal transition in solid Xe has been found at 150 GPa.<sup>1</sup> Because of the bond breaking induced by pressure, the diatomic molecular crystals  $\text{I}_2$  and  $\text{Br}_2$  transform to stabilized monatomic crystal at 21 and 80 GPa, respectively.<sup>2,3</sup> Besides these, amorphization, polyamorphism, and superconduction of molecular crystals under high pressure have been studied.<sup>4–6</sup> Under high pressure the intermolecular distance is extremely shortened, which results in the thermodynamic instability because at such distance the intermolecular and intramolecular forces are comparable in magnitude. Thus, the system tends to minimize the free energy through a reorganization of chemical bond connectivity.<sup>7</sup> For instance, crystalline benzene under high pressure of 23 GPa experiences a chemical transformation in which the ring is deformed and the electronic charge is no longer distributed on the molecular ring uniformly. In this case, laser irradiation can reduce the threshold pressure for such a chemical trans-

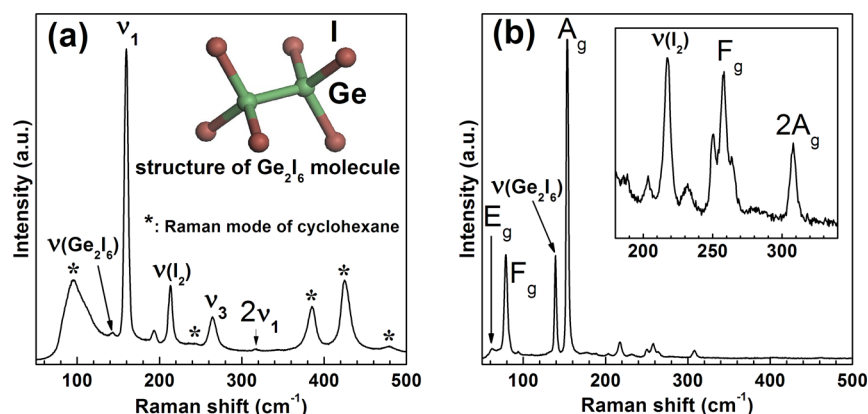
formation, representing the united effect of light irradiation and pressure on chemical reactions.<sup>8</sup>

Tin tetraiodide ( $\text{SnI}_4$ ), crystallizing as a bright-orange solid in the cubic structure with space group  $T_h^6\text{-Pa}3$  at ambient pressure,<sup>9</sup> undergoes both amorphization and metallization almost simultaneously under high pressure. To explain this phenomenon, Pasternak and Taylor proposed that  $\text{SnI}_4$  molecules are linked to each other to form randomly oriented conducting chains due to the pressure-induced bridging iodines.<sup>10</sup> These bridging atoms construct the charge delocalization path and contribute to the formation of amorphous-metallic phase. Sugai considered the pressure-induced dimerization of  $\text{SnI}_4$  to happen in the amorphization process.<sup>11</sup> As the isostructural compound of  $\text{SnI}_4$ , germanium tetraiodide ( $\text{GeI}_4$ ) shows similar properties under high pressure, such as pressure-induced metallization and amorphization.<sup>12,13</sup> In the meantime, as a member of group IV tetraiodide,  $\text{GeI}_4$  tends to be photochemically decomposed, like carbon tetraiodide ( $\text{CI}_4$ ) and silicon tetraiodide ( $\text{SiI}_4$ ).<sup>14</sup> It has been found that  $\text{CI}_4$  is rapidly decomposed to  $\text{I}_2$  and other products even at a long wavelength of 667.82 nm.<sup>14</sup> As for  $\text{SiI}_4$ , the decomposition could be triggered by light with wavelength shorter than 514.5 nm due to the higher bond energy.

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**Figure 1.** Raman spectra of (a)  $\text{GeI}_4$  in cyclohexane solution and (b)  $\text{GeI}_4$  molecular crystal at ambient pressure. The bands at 96, 245, 385, 428, and  $478\text{ cm}^{-1}$  in panel a are Raman modes of cyclohexane.

However, the critical wavelength for photochemical decomposition and the reaction product are still unclear for  $\text{GeI}_4$ .

Although high-pressure XRD, Mossbauer spectroscopy, extended X-ray absorption fine-structure (EXAFS) and electrical measurement studies have been employed to study  $\text{GeI}_4$ , there are few reports on lattice vibrations of  $\text{GeI}_4$  molecular crystal. High-pressure Raman spectra research of  $\text{GeI}_4$  is presented. The time evolution of Raman spectra of  $\text{GeI}_4$  is investigated with different exciting wavelengths. It is found that  $\text{GeI}_4$  molecular crystal experienced structural modification with the increasing pressure. After the pressure was released, the Raman spectrum of  $\text{GeI}_4$  was recovered to the initial status. We also found that laser with wavelength 514.5 nm or shorter could induce the decomposition of  $\text{GeI}_4$  into  $\text{Ge}_2\text{I}_6$  and  $\text{I}_2$ , which is contrary to the previous report<sup>14</sup> that 514.5 nm laser cannot lead to decomposition reaction. The present results demonstrated that pressure higher than 0.5 GPa exerted on  $\text{GeI}_4$  is able to reverse the photochemical decomposition, an uncommon phenomenon for solid-state reactions. This finding may open a new approach to control the direction of chemical reactions of molecular crystals by using high pressure.

## 2. EXPERIMENTAL SECTION

A diamond anvil cell (DAC) was used to produce high pressure. Without further purification, the  $\text{GeI}_4$  sample (99.99% purity, Sigma-Aldrich Company) was packed into a hole in diameter of  $150\text{ }\mu\text{m}$  in a stainless-steel gasket. The pressure calibration was achieved by applying the well-known pressure shift of Ruby luminescence R1 line.<sup>15</sup> To avoid the reaction with the sample, we did not load pressure-transmitting media. Moreover,  $\text{GeI}_4$  molecular crystal is soft enough to transmit pressure through itself. A confocal microscope Raman spectrometer system (equipped with Princeton Instruments Acton SP2750 monochromator and Princeton Instruments Pixis 100-BR multichannel CCD) was used to collect signals in situ. 514.5 nm  $\text{Ar}^+$  laser was utilized to excite the sample, and the Raman spectra were detected in the reflection geometry.

In photochemical decomposition experiments,  $\text{GeI}_4$  dissolving in cyclohexane (concentration:  $10^{-2}\text{ M}$ ) was first sealed in capillaries and then irradiated by lasers in wavelength of 325, 514.5, 632.8, and 785 nm. LabRAM HR800 Raman spectrometer (HORIBA Jobin Yvon) was used to collect Raman signal. The time evolution of  $\text{GeI}_4$  Raman spectrum was also performed with this instrument.

An X-ray photoelectron spectroscopy (PHI 5000 VersaProbe) was employed to analyze the chemical shift of elements in the sample.  $\text{GeI}_4$  molecular crystal was first compressed into a disk and irradiated by 514.5 nm laser for several hours. Then Al  $K\alpha$  source was applied to excite the X-ray photoelectron spectrum of the disk.

## 3. RESULTS AND DISCUSSION

$\text{GeI}_4$  molecular crystal belongs to the  $T_h-Pa3$  space group at ambient pressure and has 49 normal modes:<sup>16</sup>  $5A_g + 5E_g + 15F_g + 5A_u + 5E_u + 14F_u$  in the optical branches, among which all 25 gerade modes ( $5A_g, 5E_g, 15F_g$ ) are Raman-active and the  $14F_u$  modes are infrared-active. Because of the weak van der Waals bond between adjacent molecules in crystals, the similar Raman modes between  $\text{GeI}_4$  molecular crystal and  $\text{GeI}_4$  molecules dissolved in organic solvents cyclohexane are observed. Figure 1 demonstrates Raman spectra of  $\text{GeI}_4$  in cyclohexane solution and  $\text{GeI}_4$  molecular crystal. The corresponding positions of Raman bands are listed in Table 1; most of them agree with

**Table 1.** Raman Bands of  $\text{GeI}_4$  in Cyclohexane and  $\text{GeI}_4$  Molecular Crystal<sup>a</sup>

mode	$\text{GeI}_4$ molecular crystal ( $\text{cm}^{-1}$ ) <sup>b</sup>	$\text{GeI}_4$ in cyclohexane solution ( $\text{cm}^{-1}$ ) <sup>b</sup>	$\text{GeI}_4$ in cyclohexane solution ( $\text{cm}^{-1}$ ) <sup>c</sup>
$A_g$	153	160	159
$E_g$	62	—	60
$F_g$	250, 258, 264	264	264
$F_g$	79	—	81
$2A_g$	308	316	318
$3A_g$	463	—	475
$\text{Ge}_2\text{I}_6$	139	143	143
$\text{I}_2$	218	213	213
other	94, 204, 232	194	—

<sup>a</sup>— means the mode does not exist or is too weak to detect. <sup>b</sup>Our experiment. <sup>c</sup>Values taken from literature.<sup>14,18</sup>

reported data.<sup>14,17,18</sup>  $\nu_4$  mode of  $\text{GeI}_4$  molecules in cyclohexane could not be seen because it overlaps with a strong Raman band of cyclohexane. For the  $\text{GeI}_4$  molecular crystal, the 264 band is split into 250, 258, and  $264\text{ cm}^{-1}$ , perhaps owing to the lift of triply degenerated  $F_g$  modes caused by the crystallization of the  $\text{GeI}_4$  molecules. The similar splits of  $F_g$  mode were also observed in the Raman spectra of  $\text{SnI}_4$  as the isostructural material of  $\text{GeI}_4$ .<sup>11</sup>

As for Raman bands around 213 and 143  $\text{cm}^{-1}$ , they are assigned to the vibrational mode of I–I bonding and Ge–I stretching mode of  $\text{Ge}_2\text{I}_6$  molecule, a digermanium iodide, respectively.<sup>14</sup>  $\text{I}_2$  and  $\text{Ge}_2\text{I}_6$  were considered to be generated photochemically by the reaction



which was triggered by the exposure of the sample to UV laser. The class of digermanium halides includes  $\text{Ge}_2\text{F}_6$ ,<sup>19</sup>  $\text{Ge}_2\text{Cl}_6$ ,<sup>20</sup> and  $\text{Ge}_2\text{Br}_6$ .<sup>21</sup>

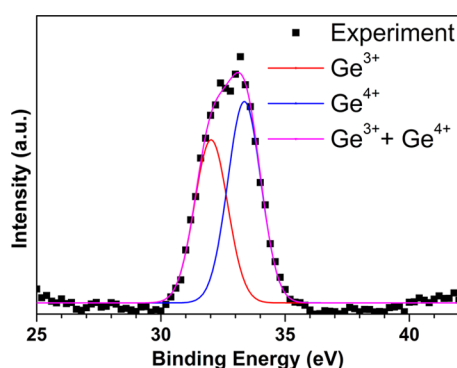
For many group IV-A element tetraiodides compounds, photochemical decomposition is a common phenomenon. For example, carbon tetraiodide can be rapidly decomposed to  $\text{I}_2$  under the irradiation of 667.82 nm light.<sup>22</sup> With the excitation of 514.5 nm laser, the considerable photochemical decomposition of silicon tetraiodide and the generation of  $\text{I}_2$  were also observed.<sup>14</sup>

According to the depolarization ratio measured by Clark and Dines,<sup>14</sup>  $\text{Ge}_2\text{I}_6$  has  $D_{3d}$  symmetry, which coincides with  $\text{Ge}_2\text{Br}_6$  molecule. Considering the similarity on the structural and component between these two kinds of molecules, we may understand the photochemical decomposition of  $\text{Ge}_2\text{I}_6$  by referencing following reactions of  $\text{Ge}_2\text{Br}_6$ .<sup>21,23</sup>



It is then likely that UV laser or visible laser can decompose part of  $\text{GeI}_4$  into  $\text{GeI}_2$  and  $\text{I}_2$ ,<sup>24</sup> the generated  $\text{GeI}_2$  molecules combine immediately with  $\text{GeI}_4$  to produce  $\text{Ge}_2\text{I}_6$ . This conclusion is supported by the XPS results presented below.

Besides the reasons mentioned in ref 14, we have excluded the possibility that other reaction products were generated due to laser irradiation, such as  $\text{GeI}_2$ , Ge, and  $\text{GeO}_2$ , by comparing their respective Raman spectra<sup>25–27</sup> with the present Raman spectrum of  $\text{GeI}_4$  in cyclohexane solution and that of  $\text{GeI}_4$  molecular crystal. XPS results of  $\text{GeI}_4$  molecular crystal also strongly support the laser-inducing decomposition of  $\text{GeI}_4$ . Figure 2 shows the XPS spectrum of Ge 3d in the compressed

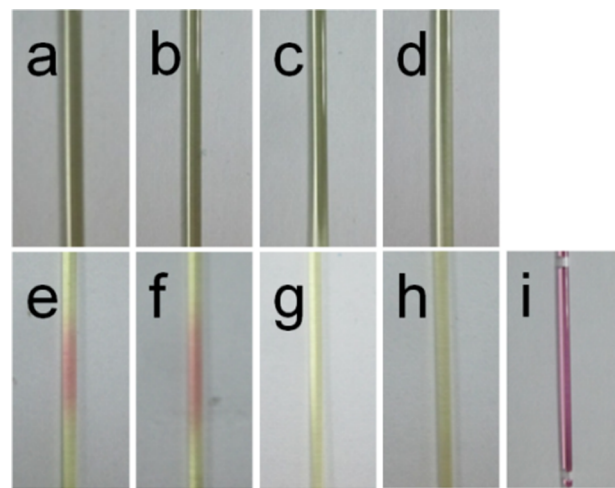


**Figure 2.** X-ray photoelectron spectrum of  $\text{GeI}_4$  molecular crystal after 514.5 nm laser irradiation.

$\text{GeI}_4$  disk irradiated by 514.5 nm laser. The Gaussian-resolved result shows that there are two components for the Ge 3d peak, centering at binding energies about 32.0 and 33.4 eV, respectively, from  $\text{Ge}^{3+}$  and  $\text{Ge}^{4+}$ . The splitting of Ge 3d peak in the present  $\text{GeI}_4$  sample proved the existence of the photochemical decomposition reaction. Additionally, the absence of 3d peak for  $\text{Ge}^{2+}$  confirms the conclusion that in

the photochemical decomposition process  $\text{GeI}_2$  is a reaction intermediate and it will react with  $\text{GeI}_4$  immediately to generate the final products.

Clark et al. pointed out that no  $\text{I}_2$  and  $\text{Ge}_2\text{I}_6$  Raman modes could be detected if 514.5 nm laser was used as the excitation source.<sup>14,18</sup> Nonetheless, according to the present study, 514.5 nm laser irradiation can lead to the photochemical reaction of  $\text{GeI}_4$  as well.  $\text{GeI}_4$  dissolved in cyclohexane was irradiated by lasers at different wavelengths, including 325 (9.5 mW), 514.5 (5.6 mW), 632.8 (9.3 mW), and 785 nm (10.0 mW). Both 325 and 514.5 nm lasers can clearly change the color of the solution from yellow to purple, as seen in Figure 3; the color indicates

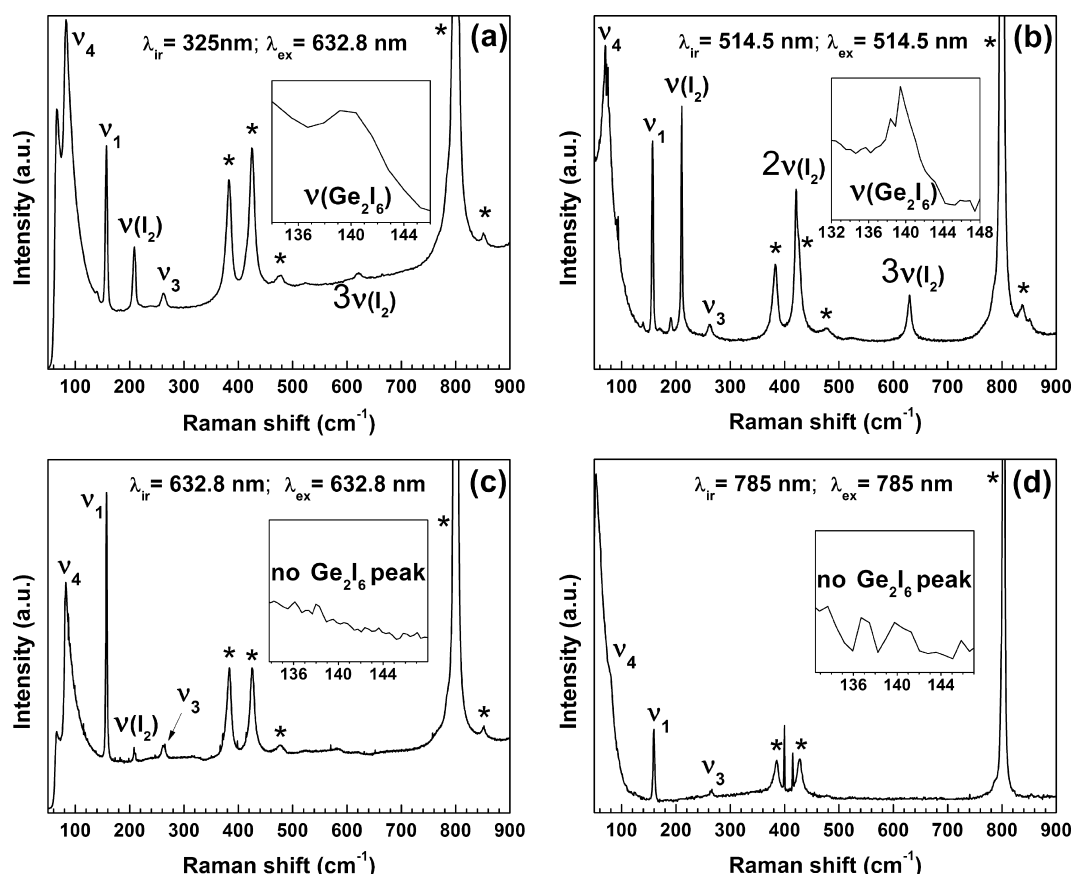


**Figure 3.** Photographs of  $\text{GeI}_4$  in cyclohexane solutions before and after laser irradiation with different wavelengths. (a–d)  $\text{GeI}_4$  solutions before 325, 514.5, 632.8, and 785 nm laser irradiation; (e–h) correspond to the situations after laser irradiation. Photograph (i) demonstrates the color of iodine in cyclohexane solution ( $10^{-2}$  M).

the existence of iodine. Figure 3 shows that the 632.8 nm laser also changes the color of the solution. The reason is that a small amount of  $\text{I}_2$  dispersed in cyclohexane and mixed with  $\text{GeI}_4$  molecules to present the color of the ends region of purple, as seen in Figure 3c,g. This indicates that the 632.8 nm laser can also drive the decomposition reaction, although the reaction rate is very slow. However, 785 nm laser could not induce this obvious color change, even if the sample had been exposed to the irradiation for several hours.

Besides these obvious color changes in Figure 3, evidence can also be found from the Raman spectra of the four samples recorded after laser irradiation in Figure 4. Raman band around 210  $\text{cm}^{-1}$ , corresponding to the vibrational mode of I–I bonding in  $\text{I}_2$  molecule, can be discerned in the Raman spectra irradiated by 325, 514.5, and 632.8 nm lasers. A weak Raman band around 140  $\text{cm}^{-1}$ , which is attributed to Ge–I stretching mode of  $\text{Ge}_2\text{I}_6$  molecule, is present in the spectra irradiated by 325 and 514.5 nm lasers. The intensity of the vibrational mode of I–I bonding at 210  $\text{cm}^{-1}$  is much stronger than that of the Ge–I stretching mode, and the 140  $\text{cm}^{-1}$  mode is hardly observed for 632.8 nm irradiation. Therefore, we conclude that not only UV lasers, such as 325 and 363.8 nm,<sup>14</sup> but also the 514.5 and 632.8 nm visible lasers can also lead to the photochemical reaction 1. The reason why we have detected 140 and 210  $\text{cm}^{-1}$  bands after 514.5 nm laser irradiation whereas they had not been found in literature<sup>14</sup> is due to the high sensitivity of the state of the art Raman measurement

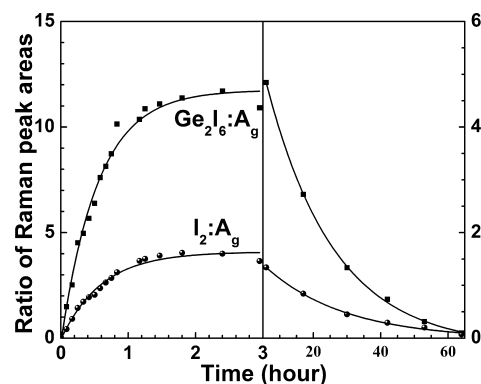




**Figure 4.** Raman spectra of  $\text{GeI}_4$  in cyclohexane solutions after irradiation of different lasers: (a) 325, (b) 514.5, (c) 632.8, and (d) 785 nm. The insets in panels a and b show the Raman peak for  $\text{Ge}_2\text{I}_6$ . The excitation wavelengths for Raman signals are 632.8 nm for (a,c), 514.5 nm for (b), and 785 nm for (d). Instead of the excitation wavelengths of 325 nm, 632.8 nm laser cannot induce the serious decomposition of  $\text{GeI}_4$  in the case of panel a during the spectrum measurement.

system. Only when molecules are provided the necessary activation energy in the form of light, heat, and so on can chemical reactions occur. It can be expected that 785 nm laser, which has smaller photon energy than the 325, 514.5, and 632.8 nm lasers, cannot provide enough energy to activate  $\text{GeI}_4$  into an excited state.

It has been pointed out that  $\text{GeI}_4$  is recoverable after experiencing photochemical decomposition.<sup>14</sup> In the present work, the  $\text{GeI}_4$  crystal was irradiated by 514.5 nm laser for a long time up to over 64 h to observe the time evolution of Raman spectra. (See Figure 5.) To obtain the relative contents of  $\text{Ge}_2\text{I}_6$  and  $\text{I}_2$  to  $\text{GeI}_4$  after laser irradiation, we have integrated Raman peak area for dominating  $A_g$  mode of  $\text{GeI}_4$ ,  $143\text{ cm}^{-1}$  mode of  $\text{Ge}_2\text{I}_6$  and  $213\text{ cm}^{-1}$  mode of  $\text{I}_2$ ; calculated intensity ratios between areas can then be used to estimate the relative content as described in some works.<sup>28–30</sup> We have found that ratios of Raman peak areas,  $\text{Ge}_2\text{I}_6:A_g$  and  $\text{I}_2:A_g$ , increase with time until saturation is achieved after 3 h under continuous laser irradiation; this means an equilibrium state has been attained in the decomposition reaction. Then, the laser is switched off and it is on only for collecting Raman signal; the two ratios decrease with increasing time and vanish after 64 h. This fact shows that  $\text{GeI}_4$  is indeed recoverable and agrees with previous observation.<sup>14</sup> The dependence of the Raman intensity of  $\text{I}_2$  mode and  $\text{Ge}_2\text{I}_6$  mode on the laser irradiation time reveals the great influence of 514.5 nm laser on  $\text{GeI}_4$ 's decomposition and also substantiates the existence of the reaction 1.



**Figure 5.** Time evolution of intensity ratio of Raman spectrum of  $\text{GeI}_4$  crystal irradiated by 514.5 nm laser. Exponential functions (curves) are used to fit the experimental data (symbols). Left is for the continuous laser irradiation case; right is for the case that laser irradiates only when collecting Raman signal.

Figure 6a shows the Raman spectra of  $\text{GeI}_4$  under high pressure up to 24.0 GPa. By the two sides of the  $F_g$  mode at  $80\text{ cm}^{-1}$ , new broad bands around 69 and  $92\text{ cm}^{-1}$  emerged at 1.4 and 3.3 GPa, respectively. The appearance of new Raman modes often indicates a change of crystal structure. The two new bands are blue-shifted with increasing pressure; the peaks are flattened gradually into humps and disappear eventually beyond 12.4 GPa. The  $A_g$  mode at  $153\text{ cm}^{-1}$ , the breathing mode of  $\text{GeI}_4$  molecule, remains up to 20.4 GPa and disappears

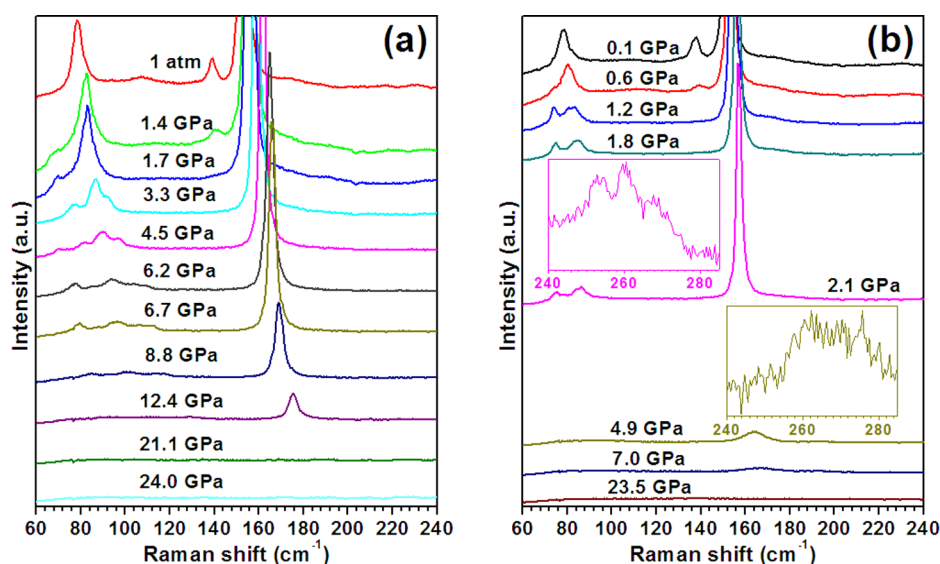


Figure 6. Raman spectra of  $\text{GeI}_4$  under (a) increasing pressure and (b) releasing pressure.

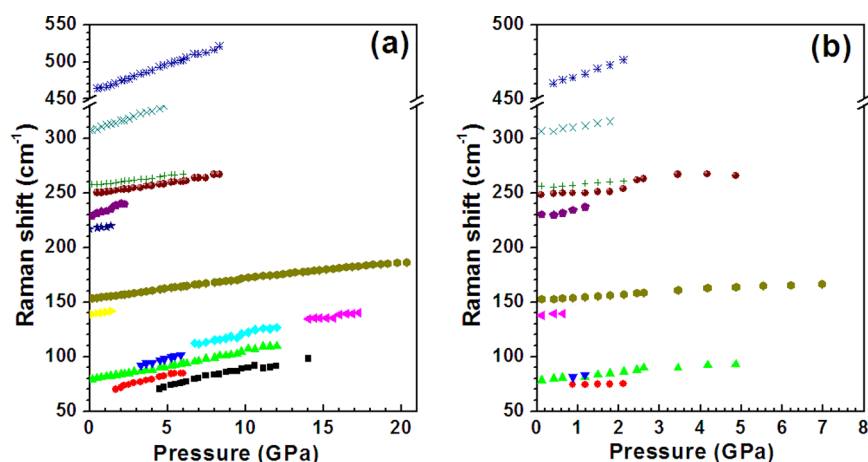


Figure 7. Dependence of Raman shifts on pressure at room temperature in (a) pressure-increasing process and (b) pressure-releasing process.

at 21.1 GPa. Pressure-induced vanishing of Raman modes is a common phenomenon for molecular crystals because high pressure affects Raman intensities via changes in bond polarizabilities.<sup>31</sup> Raman spectra in the decompressing process are shown in Figure 6b. The breathing mode around  $160\text{ cm}^{-1}$  reappears at  $\sim 7.0\text{ GPa}$ ; then, the intensity increased sharply with decreasing pressure. Around  $4.9\text{ GPa}$ , two  $\text{F}_g$  modes at  $93$  and  $266\text{ cm}^{-1}$  are recovered, and both modes split at  $2.1\text{ GPa}$ . The two broad bands by the two sides of the  $\text{F}_g$  mode around  $80\text{ cm}^{-1}$  are vanished at  $0.6\text{ GPa}$ . When pressure is released completely, the residual pressure in the sample was  $0.1\text{ GPa}$  because of compressed sample chamber, where we observed the recovery of nearly all modes as the virgin sample, including the mode of  $\text{Ge}_2\text{I}_6$ . Phonon energies as functions of pressure are plotted in Figure 7, in which we observed that all Raman modes shifted almost linearly to higher frequency during compression, indicating the pressure-induced shortening of chemical bonds.

Figure 7a shows that Raman bands of impurities  $\text{I}_2$  and  $\text{Ge}_2\text{I}_6$  at  $218$  and  $139\text{ cm}^{-1}$ , respectively, gradually become weak with increasing pressure and finally disappear at  $1.7\text{ GPa}$ . This fact clearly indicates that the photochemical decomposition process of  $\text{GeI}_4$  has been reversed by pressure. When releasing pressure, these Raman peaks may reappear at similar pressure. To

confirm this reverse effect of pressure on the photochemical decomposition reaction of  $\text{GeI}_4$ , we have repeated experiments for several times. As observed in Figure 8, the intensity of Ge–I stretching mode of  $\text{Ge}_2\text{I}_6$  at  $139\text{ cm}^{-1}$  is weakened gradually

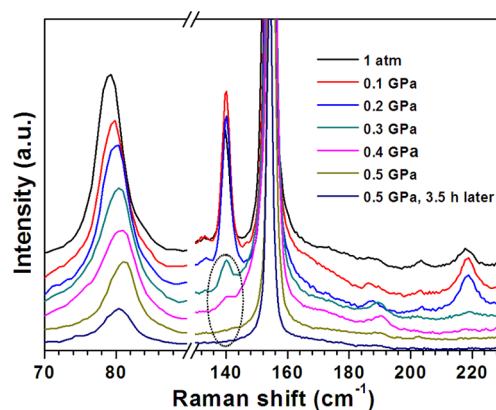
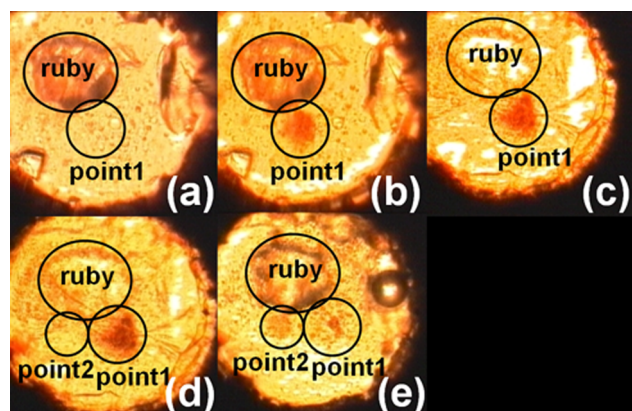


Figure 8. Raman spectra of  $\text{GeI}_4$  molecular crystal under pressure up to  $0.5\text{ GPa}$ . The dashed circle represents the region where pressure is shown to reverse the photochemical decomposition reaction of  $\text{GeI}_4$ .

with increasing pressure, and it disappears completely at 0.5 GPa. Reducing critical pressure may be due to smaller laser power used. Keeping sample at this pressure, this band could not be observed, even by long time ( $\sim 3.5$  h) laser irradiation, any more. Therefore, the photochemical decomposition of  $\text{GeI}_4$  is mostly favored at atmospheric pressure and the high pressure is helpful to prevent  $\text{GeI}_4$  from being decomposed by 514.5 nm laser. The possible reason is that with increasing pressure the distance between reaction products,  $\text{I}_2$  and  $\text{Ge}_2\text{I}_6$  molecules, is effectively shortened, which makes their combination reaction, as the reversed reaction 1, possible.



Color change of  $\text{GeI}_4$  in cyclohexane solution after 514.5 nm laser irradiation also supports this point. Figure 9 gives



**Figure 9.** Photographs of  $\text{GeI}_4$  solution in the gasket hole, the irradiation wavelength is 514.5 nm. (a) Point 1 before irradiation and at atmospheric pressure. (b) Point 1 after irradiation and at atmospheric pressure. (c) Point 1 at 4.4 GPa. (d) Point 2 after irradiation at 4.4 GPa. (e) Point 2 after irradiation, atmospheric pressure.

transmission photographs of the solution under different conditions. At ambient pressure, laser irradiation can decompose  $\text{GeI}_4$  into  $\text{I}_2$ , changing the color of the solution from yellow to red, as seen in Figures 9a,b. When pressure was increased to 4.4 GPa, the red color did not return to yellow in Figure 9c, but when the position of laser irradiation is changed from point 1 to point 2, unlike the situation at ambient pressure the laser cannot induce the color change, as displayed in Figure 9d, indicating the reverse effect of pressure on the decomposition reaction of  $\text{GeI}_4$ . In point 1, the diffusion of decomposition products  $\text{Ge}_2\text{I}_6$  and  $\text{I}_2$  molecules in cyclohexane makes pressure hard to reduce the distance between  $\text{Ge}_2\text{I}_6$  and  $\text{I}_2$  to the same extent as the case in molecular solid. So pressure-induced combination reaction 4 cannot occur and the color cannot return to yellow. In point 2, pressure can prevent  $\text{GeI}_4$  from decomposing because there is not enough time for decomposition products to diffuse too far before they are recombined, so pressure can reverse the decomposition immediately. When pressure was released, the laser irradiation decomposed  $\text{GeI}_4$  again, as seen in Figure 9e.

The competition between the photochemical decomposition and high-pressure-induced combination determines the direction of the photochemical reaction. Laser irradiation promotes reaction 1, while high pressure tends to reverse it. There are many examples also demonstrating the joint function of high pressure and photoexcitation. Irradiation on the mixture of red

phosphorus and water at pressure 0.6 GPa can produce  $\text{H}_2$  and phosphorus compounds.<sup>32</sup> In another case, pressure-induced dimerization of butadiene above 0.7 GPa can be inhibited by 488 nm laser irradiation.<sup>33</sup> For molecular crystals, the weak van der Waals bonding makes the compression on these materials able to induce pressure–volume work, which is sometimes big enough to cause chemical reactions, just like the role played by heat or light. As a result, both high pressure and light irradiation should be taken into account when considering chemical reactions of molecular crystals.

Pressure is a very important thermodynamic parameter influencing chemical reaction equilibrium and chemical kinetics. Young's moduli of molecular crystals are so small that pressure can induce large volume compression. The free-energy change (pressure–volume work) associated with this volume compression is big enough to cause changes in the chemistry of molecular systems.<sup>34</sup> Several pressure-induced chemical reactions in mixture of simple molecular systems, such as methane–hydrogen mixture<sup>35</sup> and oxygen–hydrogen mixture,<sup>36</sup> have been found. The present finding of pressure reversion effect on the photochemical decomposition of  $\text{GeI}_4$  expands the field of pressure-induced chemical reactions and provides new insight into controlling chemical reactions by application of pressure other by adding catalysts.

## 4. CONCLUSIONS

Raman and XPS spectra indicated that the laser irradiation with wavelength shorter than 632.8 nm can induce the photochemical decomposition of  $\text{GeI}_4$  either in molecular crystal or dissolved in cyclohexane solution; the reaction products are iodine and  $\text{Ge}_2\text{I}_6$ , and the reaction is suggested as  $2\text{GeI}_4 \rightarrow \text{Ge}_2\text{I}_6 + \text{I}_2$ . High-pressure Raman spectra measurement of  $\text{GeI}_4$  molecular crystal exhibits a new phenomenon on reverse effect of the photochemical decomposition: Raman signals of  $\text{Ge}_2\text{I}_6$  and  $\text{I}_2$  vanish at 0.5 to 1.7 GPa; by releasing pressure, these signals reappear. We propose that the combination reaction  $\text{Ge}_2\text{I}_6 + \text{I}_2 \rightarrow 2\text{GeI}_4$  as the reversed reaction could diminish Raman intensities of decomposition products. The competition between the photochemical decomposition and high-pressure-induced combination determines the direction of the photochemical reaction of  $\text{GeI}_4$ .

## ■ ASSOCIATED CONTENT

### Supporting Information

Information about the high-pressure apparatus and the method to seal  $\text{GeI}_4$  in cyclohexane solution in the capillary. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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