Pulsed laser Raman spectroscopy in the laser-heated diamond anvil cell

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We describe the design and operation of a spatially-filtered Raman/fluorescence spectrometer that incorporates a pulsed 532 nm laser excitation source and a synchronized and electronically gated CCD detector. This system permits the suppression of undesired continuous radiation from various sources by a factor of up to 50,000 providing the possibility of acquiring Raman signals at temperatures exceeding 5,000 K. We present performance comparisons of this system with that of a state-of-the-art conventional CW system using a 458 nm excitation source. We also demonstrate that the pulsed system is capable of suppressing an impurity-induced (single nitrogen defects) fluorescence in diamond, and further suggest that this capability can be used to suppress the stress-induced fluorescence in diamond that may appear at pressures near or above 150 GPa.

Raman spectroscopy in combination with the DAC is an extremely versatile experimental tool. It is used to investigate the behavior under extreme pressure of many different material properties including vibrational, structural, electronic and elastic [1-7]. The results of these studies find application in various diverse disciplines including the geo- and planetary sciences [1,2,4,5], fundamental physics and chemistry [2,6], and material science [7,8]. Under simultaneous conditions of extreme temperature further information concerning phase changes, chemical kinetics, superconductivity etc. may be obtained. While sample temperatures of up to several thousand degrees can be obtained with the laser heated DAC (LHDAC), routine Raman studies above approximately 2000 K are difficult because of the intense incandescent radiation that is emitted over a wide and continuous spectral range. Background signal due to fluorescence in one or both of the diamonds of the DAC may also be sufficient to completely preclude various types of experiment. Diamond fluorescence may vary strongly from one stone to another depending on the concentration of impurities. Chemically pure diamonds have very low fluorescence [9], but are also expensive. A separate issue is the stress–induced fluorescence [10] that may be generated in the vicinity of the diamond tip (even in chemically pure diamond [11]) at very high pressures. This greatly hampers Raman (and even ruby fluorescence) measurements, although the use of red and near IR excitation wavelengths can partly remedy the situation [12].

Since the processes described above have very different characteristic time-scales, there is the possibility to separate them using various gated techniques. A technique that has previously been used includes the use of a pair of rotating chopper wheels synchronized to occlude short-lived radiation including the excitation laser light and

short-lived fluorescence. This approach has been used to suppress diamond fluorescence in order to permit measurements of ruby fluorescence (the basis of the common pressure scale) above 100 GPa [13-15]. The latter process can be separated from the stress-induced diamond fluorescence because it is longer lived (5-20 ms). In another technique the detector is gated to collect the desired signal only when the excitation is present. It has been used for high-temperature Raman measurements at ambient pressure to suppress unwanted thermal radiation. Different types of apparatus have been used including mechanical choppers [16], pulsed lasers and a single-channel gated detector [17]. More recently, pulsed-laser excitation and gated CCD array detectors have been used for in situ Raman monitoring of diamond film growth [18]. Very recently, a pulsed-laser Raman system, which employs either a gated CCD detector or a Pockels switch has been developed, and Raman spectra in the 2000 K range have been reported [19]. However, in the case of the LHDAC even CW Raman measurements are very rare [20-22], while none at all in the time-resolved regime have, to our knowledge, been reported. We present here our pulsed Raman system and compare its performance with the CW confocal system that is described in Ref. [22]. Pulsed mode operation permits suppression of the unwanted radiation by more than 4 orders of magnitude, and also allows the determination of lifetimes of processes in the nanosecond range.

A schematic representation of the time-resolved process is shown in Fig. 1 (see also Refs. [13,19]). The detector is triggered by the laser repetition and is appropriately gated; continuous radiation is thus suppressed by a factor that is proportional to the ratio of the pulse interval to the gate width. A similar principle applies in the case of long-lived fluorescence processes. For a Raman measurement, in order for fluorescence

suppression to be effective, both the Raman process and the minimum gate width must of course be significantly shorter than the fluorescence lifetime (τ). In practice it is the minimum gate width that is the limiting parameter.

In our system the laser radiation (532 nm, 100 ps pulse length, 4 KHz repetition rate) from a pulsed source (a Time-Bandwidth Jaguar) is delivered to the DAC via an optical fiber for reasons of convenience. In the experiments described below the average laser power delivered to the DAC was approximately 5 mW. Unfortunately, optical aberration in the 30 ft fiber resulted in a distorted focal spot at the sample position of approximate dimensions 15 x 5 μm (which may be compared with the regular 3 μm diameter spot of our CW system). It was thus necessary to reduce the degree of spatial filtering accordingly. The collected signal from the DAC may be directed to either an HR-460 Jobin Yvon spectrograph equipped with a Roper Scientific back illuminated deep-depleted CCD detector in CW mode, or, in pulsed operation, to an Andor Technology Inc. Shamrock 303i spectrograph equipped with an i-Star intensified CCD detector. The minimum gate width for this device is 2.5 ns, while repetition rates in the range of tens of kHz are achievable. Further details of our combined laser-heating/Raman system may be found in Ref. [22].

Fig. 2 displays a Raman spectrum acquired from the bulk of a millimeter-sized diamond sample using the pulsed system. Total acquisition time was one second. The sample was bright-field illuminated with white light that was delivered by optical fiber from a 100 W halogen lamp operating at full power. Two different gate widths were used: 100 and 10 ns. The results show that the rejection factor corresponds respectively to the theoretical values of 2,500 and 25,000 (Fig. 2a). The signal-to-noise ratio (Fig. 2b)

clearly deteriorates when the sample is illuminated by white light, but is tolerable in the case of the 10 ns gate.

Fig. 3 demonstrates the effectiveness of the pulsed Raman system to suppress the thermal radiation that is emitted by a hot sample..A bare tungsten wire has been heated in air by direct current to a visible glow (well above 1000 K). A tungsten oxide (WO_3) forms on the surface very quickly when temperature exceeds several hundred centigrade. The presented high-temperature spectrum corresponds to the moment just preceding that at which the wire broke. The reference 300 K spectrum was acquired after this event, under otherwise the same conditions. The 300 K spectrum corresponds to that reported in the literature [23] for WO_3. In a previous attempt to measure Raman spectra at high temperature using a conventional CW system, the authors observed an overwhelmingly strong thermal radiation above 973 K that prevented them from observing the orthorhombic-to-tetragonal transition at 1013 K [24]. By contrast, the thermal radiation is almost totally suppressed in our high-temperature spectrum (in spite the substantial emissivity of the sample), while the sample temperature was substantially higher than in Ref. [23]. We find that the Raman spectrum at high temperature contains three broad peaks. This observation is consistent with group-theory calculations [23], which predict 4 Raman bands of $2A_{1g}+2E_g$ symmetry for the high-temperature tetragonal WO_3. As opposed to Ref. [23], we did not see the disappearance of the band centered at 710 cm^{-1}at the orthorhombic-to-tetragonal transition: instead we saw a very pronounced broadening and softening. It is likely that this mode was simply overwhelmed by the thermal background in the spectra of Ref. [23].

Before continuing we make some general remarks concerning the LHDAC Raman technique. In practice an optical thermal coupler is typically used to absorb laser radiation and to consequently heat the sample (that is to say in the case of sample materials that do not adequately couple to the heating radiation); this usually takes the form of a suitably-sized metal square having a central hole [21,22,25]. That part of the sample material that resides in the hole is then uniformly heated (at least in the plane normal to the DAC axis) and comprises the region of interest. Since the material under study often has a low emissivity (e.g. transparent nitrogen), it is expedient to use spatial filtering to suppress the thermal radiation from the coupler, which typically has a much larger emissivity. Additional suppression of the thermal radiation can be obtained by using blue or even ultraviolet radiation as the Raman excitation source [19,22]. By combining these two methods we have, for example, obtained CW Raman spectra of cubic boron nitride at 2300 K [22,26] at pressures of up to 26 GPa.

Fig. 4 shows the results of two sets of measurements of nitrogen in the LHDAC. The sample and heat absorber arrangement were virtually identical for these experiments. The iridium heat exchanger had a central hole of diameter of approximately 5 μm. As noted above, in the case of the pulsed experiment the probed area was larger, so intense thermal radiation from the absorber was collected along with the Raman signal. In the CW experiment this radiation was efficiently reduced using spatial filtering, while the laser beam (200 mW on the sample, 458 nm) was tightly focused to probe only that part of the sample residing in the hole in the optical coupler. We determined temperature by fitting the spectrum of the incandescent radiation to the Planck law and verified this determination by analyzing the relative intensities of the Raman bands corresponding to

the transitions from different excited vibrational levels of nitrogen. Vibrational spectra, which show these "hot" bands, were observed previously in CARS shock wave [27] and DAC [28] experiments. The intensities of these bands are determined by the populations of excited states, which critically depend on temperature and are governed by Boltzmann-type statistics, i.e. $I_{\upsilon, \upsilon+1} \propto (\upsilon+1)\exp(-\upsilon\hbar\nu_{\upsilon}/kT)$, where υ is a vibrational quantum number, ν_{υ} is the corresponding transition frequency. Energies associated with transitions from the excited states are smaller compared with those associated with transitions from the ground state because of anharmonicity. The results of these two temperature determinations are consistent within the experimental precision. As can be seen from Fig. 4, the results of the pulsed and continuous excitation experiments are very similar. As temperature increases above the melting line, the ν_1 and ν_2 vibron bands of the solid ε phase [29] broaden and shift in frequency towards each other. A new band corresponding to a liquid state appears at a frequency slightly lower than that of the ν_2 vibron band. The transitions from the excited states change their intensities continuously with temperature.

For the systems in the present state, the Raman spectra acquired in CW operation have better signal-to-noise ratio compared with those acquired in pulsed operation. Three factors account for this. One is related to the different detectors. The gated detector has an intensifier stage (not cooled), which is a source of additional noise. Moreover, the second (CCD) stage of this detector could be only cooled to –25 C (compared to –105 C for the other detector). A second factor is the respective wavelengths of the excitation sources (excitation in the blue spectral range effectively reduces the thermal radiation compared with the green excitation because the Raman signal is being collected in the spectral range where the thermal radiation is much smaller), while a third is, of course,

the different degree of spatial filtering. It is interesting to note however, that as result of overwhelmingly strong thermal radiation no Raman spectra could be obtained above approximately 1100 K when using the spectrograph and detector from the continuous system with the pulsed laser. Apart from the efficacy of the gated system, this fact clearly shows the importance of spatial filtering for *in situ* LHDAC experiments. It is also apparent that the temperature of 1273-1573 K, quoted in Ref. [19] as the limit at which thermal radiation becomes noticeable in Raman spectra, is highly uncertain. It depends on at least the experimental factors described above and also on the sample arrangement and the Raman scattering efficiency. Since DAC samples are by necessity very small, *in situ* observation of the Raman spectra in the LHDAC poses additional experimental difficulties compared with the macroscopic case.

The present system is far from optimized for this application; if we were to use a pulsed laser focal spot of comparable dimensions to that of our CW system, for example, we may reasonably expect to obtain LHDAC Raman spectra in excess of 5000 K. Indeed, the thermal radiation in the range of Raman shifts between 100 to 3000 cm^{-1} (458 nm excitation line) changes by a factor of $2.7*10^4$ to $0.45*10^4$ (respectively) when heating from 1900 K to 5000 K, so it can be adequately dealt with using the pulsed technique described here.. This estimation does not take into account the difference in detector noise level (see above). Another important factor, which has not been tested in this work is the possibility of pulsed-laser induced diamond damage (or sample). The damage threshold of diamond is about 0.1-0.3 TW/cm^2 for ps range lasers [30]. In our experiment we were below the damage threshold by at least 2 orders of magnitude, so the averaged power comparable to that used in CW experiments (200 mW*)* may be used in future

pulsed experiments. Since there is significant uncertainty in the 5000 K projection it should of course be verified experimentally. Also we have only discussed here case of materials that are near-transparent at the excitation wavelength and that have high Raman scattering efficiencies, such as molecular solids with strongly polarizable covalent bonds.

The remaining part of the paper is devoted to the suppression of diamond fluorescence. Fig. 5 shows Raman spectra of diamond acquired with the CW and pulsed systems using the 532 nm pulsed source. The chosen diamond was a typical natural type Ia anvil (specifically not a low-fluorescence stone). We have tested two more anvils of the same kind and have obtained very similar results for all of three. The Raman spectrum measured with the conventional CCD system shows a strong fluorescence in the yellow spectral range; the second order Raman peak at 2450 cm^{-1} is in fact masked by this fluorescence (Fig. 5). Contrary to this, spectra acquired using the pulsed system with a gate width of 90 ns clearly show this peak while fine structure becomes visible with a 2.5 ns gate width. The intensity of the fluorescence at 585 nm (1700 cm^{-1}) measured with different gate widths, is shown in Fig. 6. This dependence is very abrupt at short gate times, and it flattens out above 30 ns. From these data we have determined the fluorescence lifetime τ_D=10.4(7) ns. Single defect centers (individual nitrogen-vacancy) are characterized by a fluorescence lifetime of about 10 ns (see Ref. [31] and references therein), while blue fluorescence has a longer lifetime of about 20 ns [32]. We also speculate that the technique described in this paper can be used to suppress stress-induced fluorescence and thus improve the quality of Raman spectra measured in the DAC under ultrahigh pressures [10,12].

In conclusion, we describe the first time-resolved system for Raman measurements in the diamond anvil cell. By synchronizing the laser pulses with the operation of a gated detector, we have achieved a suppression of continuous undesired radiation by a factor of $5*10^4$. This work suggests that Raman spectroscopy under conditions of very high temperatures (to 5000 K) and/or ultrahigh pressures (to 300 GPa) is entirely viable.

Bibliography.

[1] R. J. Hemley, R. F. Porter, Scr. Metall. **22**, 139 (1988).

[2] P. Gillet, R. J. Hemley, P. McMillan, Rev. Mineral **37**, 525 (1998).

[3] A. F. Goncharov and V. V. Struzhkin, J. Raman Spectrosc. **34**, 532 (2003).

[4] S. Merkel, A. F. Goncharov, H.-K. Mao, P. Gillet, and R. J. Hemley, Science, **288**, 1626 (2000).

[5] H. Olijnyk, A. P. Jephcoat, K. Refson, Europhys. Lett. **53**, 504 (2001).

[6] F. Occelli, P. Loubeyre, R. Letoullec, Nature Materials **2,** (2003).

[7] E. Gregoryanz, C. Sanloup, M. Somayazulu, J. Badro, G. Fiquet, H-K Mao, R. J. Hemley, Nature Materials **3**, 294 (2004).

[8] H. W. Hubble, I. Kudryashov, V. L. Solozhenko, P. V. Zinin, S. K. Sharma and L. C. Ming, J. Raman Spectrosc. **35**, 822 (2004).

[9] J. Liu, Y. K. Vohra, Appl. Phys. Lett, **68**, 2049 (1996).

[10] H. K. Mao, R. J. Hemley, Nature **351**, 721 (1991).

[11] J. Liu, Y. K. Vohra, Appl. Phys. Lett. **68**, 2049 (1996).

[12] A. F. Goncharov, V. V. Struzhkin, R. J. Hemley, H-K. Mao, Z. Liu, in *Science and Technology of High Pressure*, edited by M. H. Manghnani, W. J. Nellis, and M. F. Nicol (Universities Press, Hyderabad, India, 2000), p. 95.

[13] J. H. Eggert, K. A. Goethel, I. F. Silvera, Appl. Phys. Lett. 5**3**, 2487 (1988).

[14] N. H. Chen and I. F. Silvera, Rev. Sci. Instrum. **67**, 4275 (1996).

[15] M. I. Eremets, J. Raman Spectrosc. **34**, 515 (2003).

[16] R. J. Nemanich, D. K. Biegelsen, R. A. Street, and L. E. Fennell, Phys. Rev. B 29, 6005 (1984).

[17] H. Herchen and M. A. Capelli, Phys. Rev. B **47**, 14193 (1993).

[18] N. Rosman, L. Abello, J. P. Chabert, G. Verven, G. Lucazeau, J. Appl. Phys. **78**, 519 (1995).

[19] P. Simon, B. Moulin, E. Buixaderas *et al*., J. Raman Spectrosc. **34**, 497 (2003).

[20] P. Gillet, Physics and Chemistry of Minerals (Historical Archive) **23**, 263 (1996).

[21] J. F. Lin, M. Santoro, V. V. Struzhkin, H-K Mao, R. J. Hemley, Rev. Sci. Instrum. **75**, 3302 (2004).

[22] A. F. Goncharov and J. C. Crowhurst, Low Temp. Phys., in press.

[23] E. Cazzanelli, C. Vinegoni, G. Mariotto, A. Kuzmin, J. Purans, Solid State Ionics **123**, 67 (1999).

[24] K.L. Kehl, R.G. Hay, D.Wahl, J. Appl. Phys. **23**, 212 (1952).

[25] A. F. Goncharov et al., Phys. Rev. Lett., in press.

[26] A. F. Goncharov, J. C. Crowhurst, J. K. Dewhurst, S. Sharma, submitted.

[27] S. C. Schmidt, D. S. Moore, M. S. Shaw, Phys. Rev. B **35**, 493 (1987).

[28] B. J. Baer and C.-S. Yoo, Rev. Sci. Instrum. **76**, 013907 (2005).

[29] R. LeSar, S. A. Ekberg, L. H. Jones, R. L. Mills, L. A. Schwalbe, D. Schiferl, Solid Stale Commun. **32,** 131 (1979).

[30] C. A. Klein, R. DeSalvo, Appl. Phys. Lett., **63**, 1895 (1993).

[31] A. Dräbenstedt, L. Fleury, C. Tietz, F. Jelezko, S. Kilin, A. Nikovtzev, J. Wratchrup, Phys. Rev. B **60**, 11503 (1999).

[32] M. F. Thomaz, Marilia F. Thomaz and C L Braga, J. Phys. C: Solid State Phys. **5,** L1 (1972).

Figures.
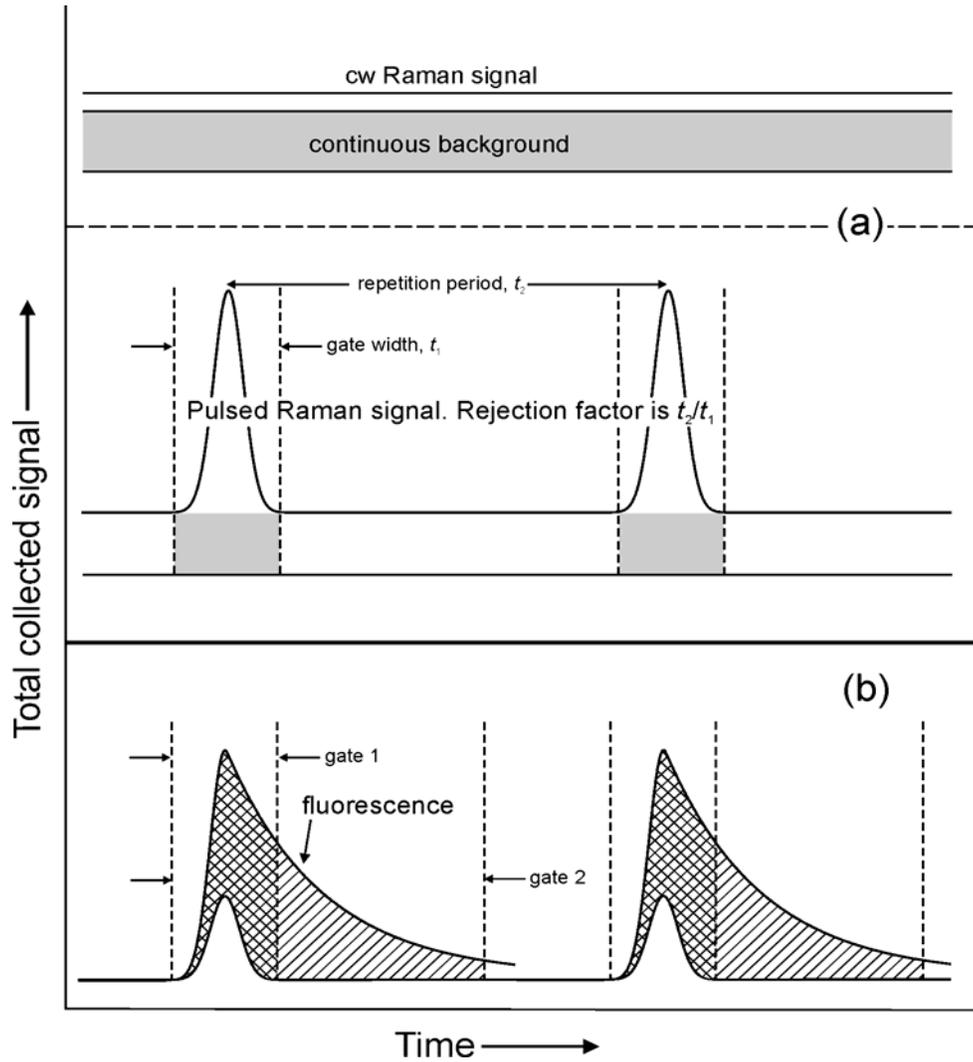
Fig. 1. Schematic comparing CW and pulsed gated Raman operation in the presence of a continuous background, (a), and the gate-width sequence for determining fluorescence lifetimes, (b). In (a) above the Raman signal is small compared with the background signal. In (a) below pulsed gated operation is seen to yield a "rejection factor" equal to the laser repetition period divided by the gate width. This factor is equal to the improvement in Raman signal-to-background ratio assuming CW and average Raman-scattered pulsed powers are equal. Fig.1 (b) is a graphic representation of the method for rejecting (and determining) fluorescence lifetimes. Gate widths are successively

increased; correspondingly measured intensities as a function of gate width are then used to derive the exponential decay constant.
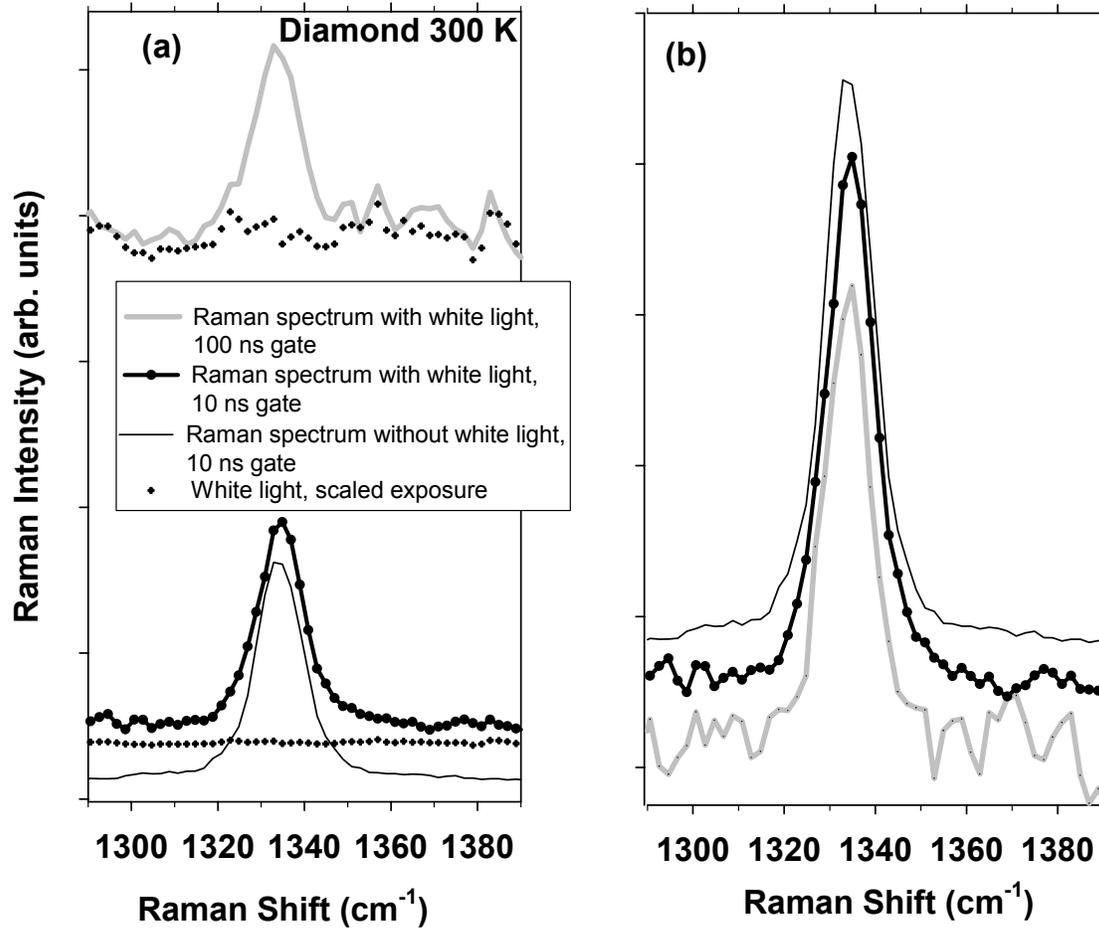

Fig. 2. Raman spectra of diamond in the presence of a strong white-light illumination measured using the pulsed gated Raman system. The exposure time of the CCD detector was one second. (a) Raman spectra measured together with the white light. Also shown are separate scaled white light acquisitions for acquisition times of $4*10^{-5}$ and $4*10^{-6}$ s for the 100 ns and 10 ns gates, respectively, which correspond to the total acquisition times of the Raman spectra. (b) Raman spectra after subtraction of the white-light background.
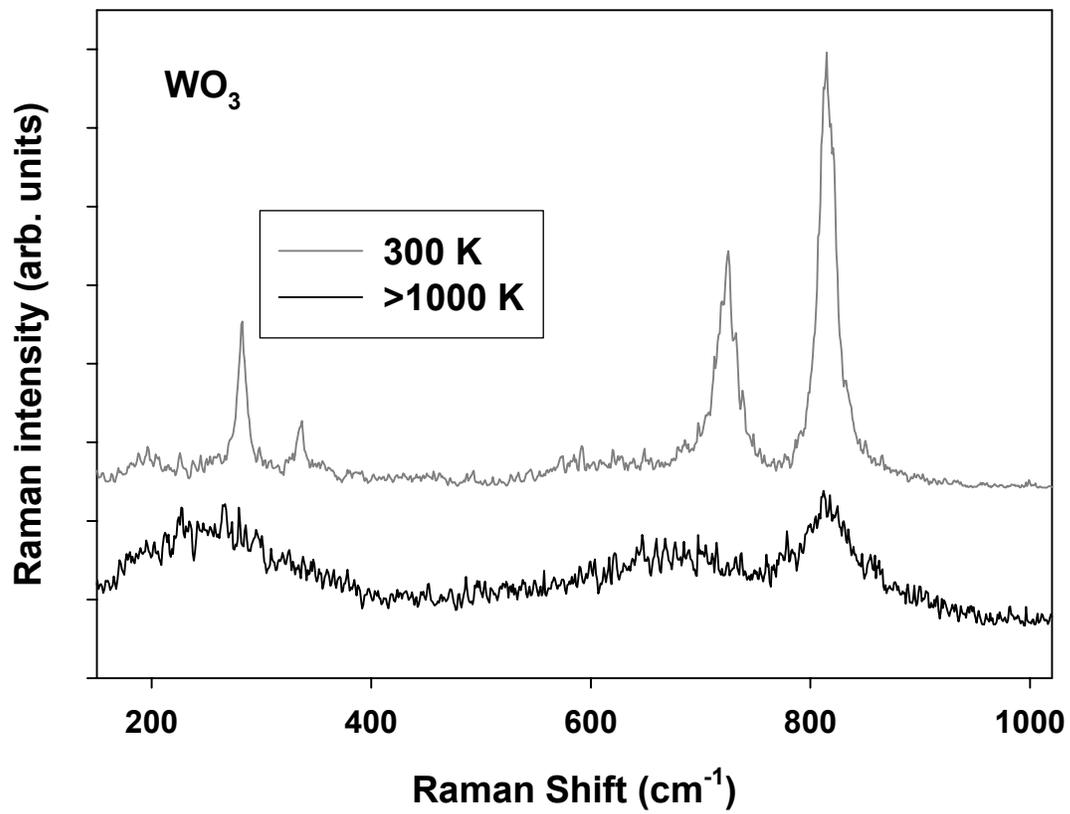
Fig. 3. Raman spectra of WO$_3$ measured using the pulsed gated system.
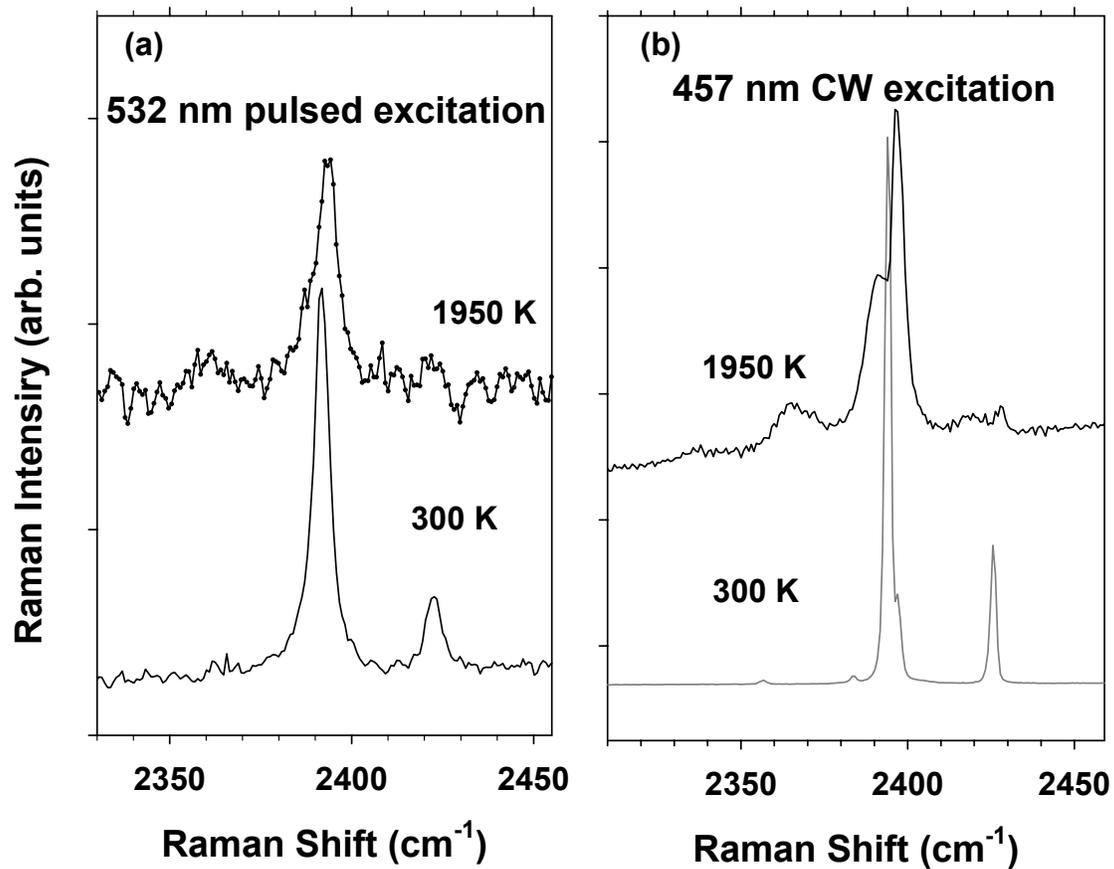
Fig. 4. Raman spectra of hot compressed liquid nitrogen at 1950 K compared with 300 K spectra. Nominal pressure was 35 GPa. The exposure time of the CCD detector was 5 s. (a) Data obtained with the pulsed gated Raman system. (b) Data obtained using the conventional CW system [22].
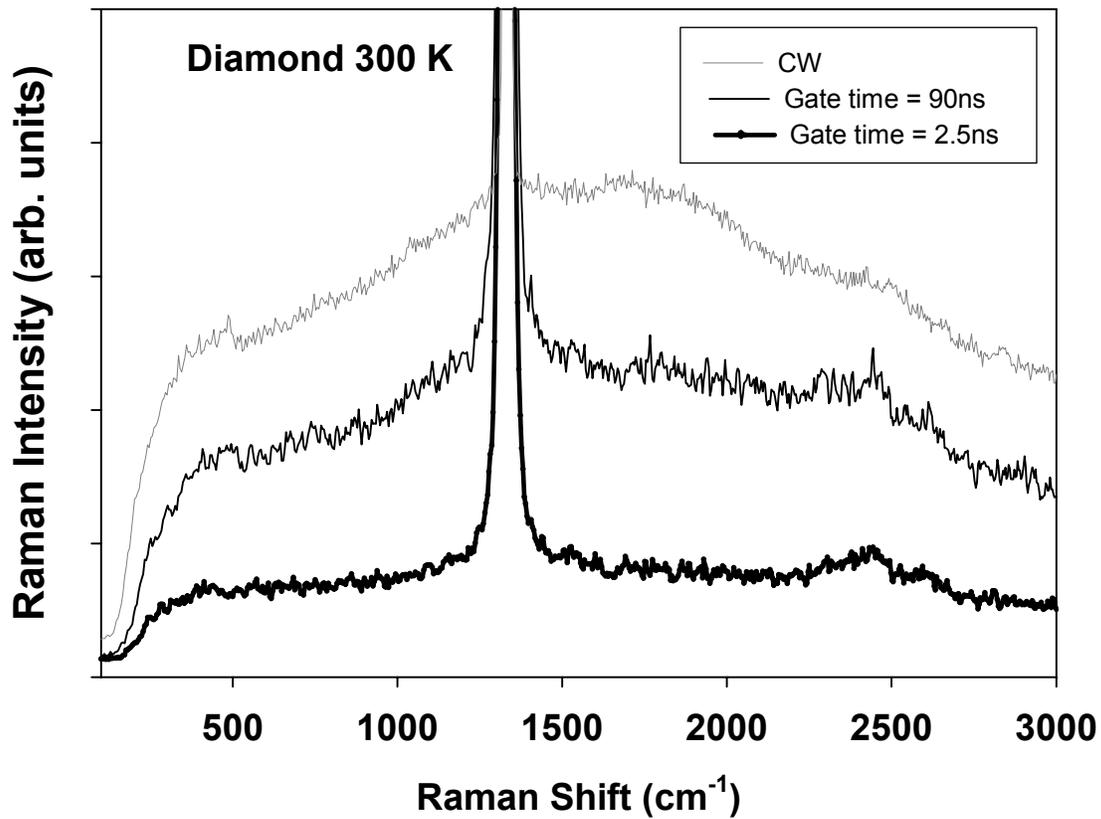
Fig. 5. Raman spectra of a diamond anvil in the presence of impurity-induced fluorescence and excited by the same (pulsed 532 nm) laser. The detection system was a conventional CCD detector for the "CW" spectrum and an intensified CCD detector for the time resolved spectra. The exposure time of the CCD detector was 5 s in both cases.
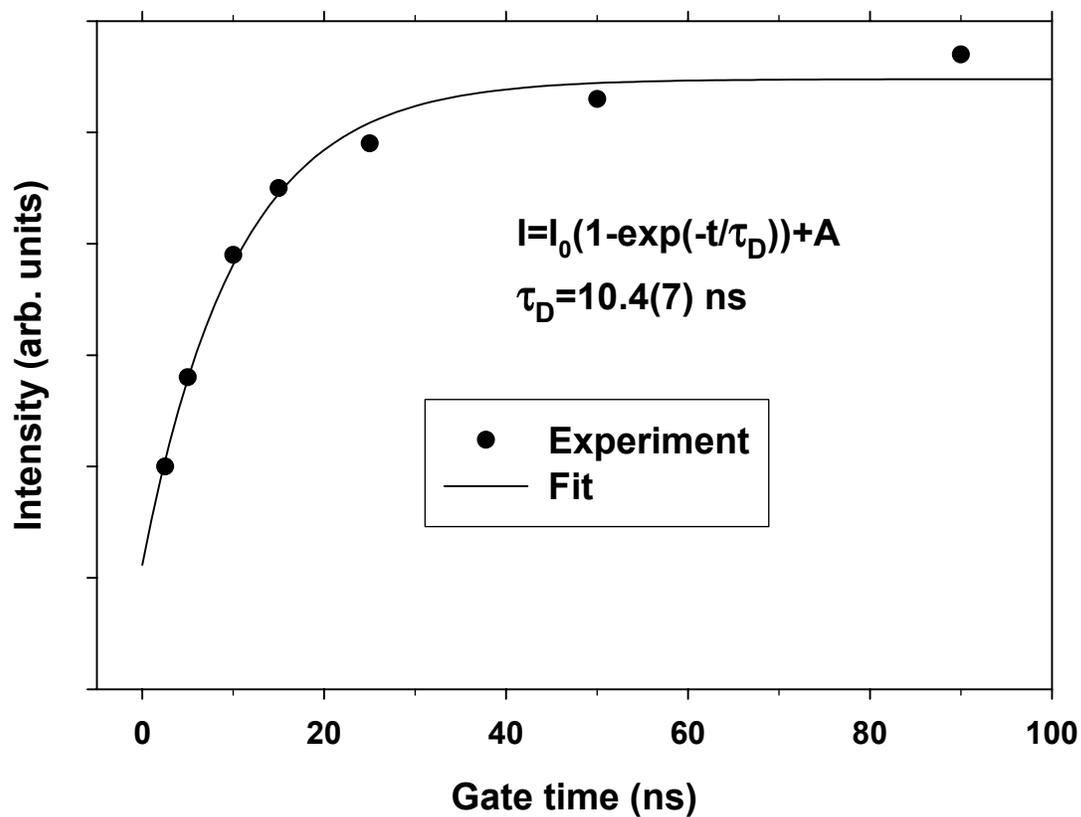
Fig. 6. The intensity of the fluorescence at 585 nm (1700 cm^{-1}) observed in the Raman spectra of Fig. 5. The solid line is the fit to the experimental data. Further details are given in the text and in Fig.1b.