

# Raman spectroscopy of hot hydrogen above 200 GPa

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**It has been theorized that at high pressure the increased energy of the zero-point oscillations in hydrogen would destabilize the lattice and form a ground fluid state at 0 K (ref. 1). Theory has also suggested that this fluid state, representing a new state of matter, might have unusual properties governed by quantum effects, such as superfluidity or superconductivity<sup>2,3</sup>. Here, by combining Raman spectroscopy and *in situ* high-temperature, high-pressure techniques, we demonstrate that above 200 GPa a new phase transition occurs as temperature is increased, for example 480 K at 255 GPa. If the transformation is interpreted as melting, it would be the lowest melting temperature of any material at these high pressures. We also find a new triple point between phases I and IV and the new phase, and demonstrate that hydrogen retains its molecular character around this point. These data may require a significant revision of the phase diagram of hydrogen above 200 GPa.**

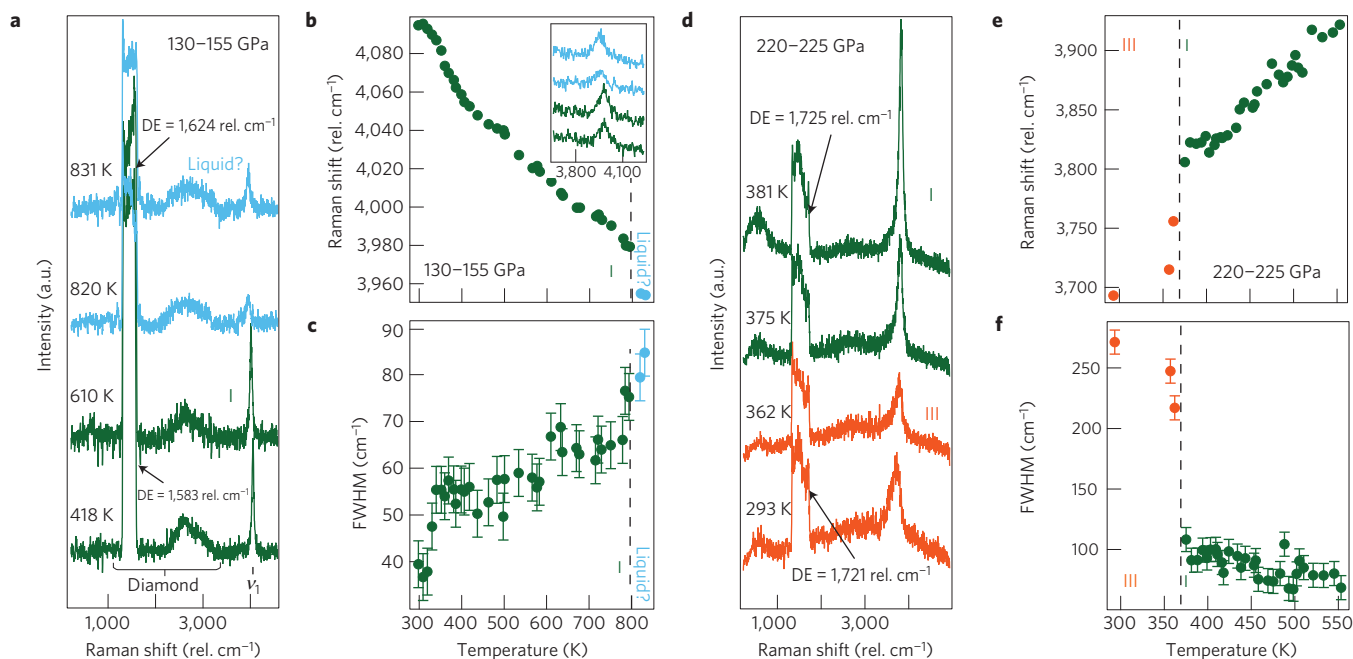
It has been argued that the ground state of hydrogen could be an (atomic) liquid under sufficient compression<sup>1</sup>. It is widely accepted that the melting curve of hydrogen features a maximum, even though there is no convincing experimental evidence to establish this. In the first experiment to gigapascal pressures, melting was visually observed between 5 and 15 GPa and then extrapolated to much higher pressures (>300 GPa; ref. 4). The authors found that the empirical Kechin law (which models the melting curve as going through a maximum<sup>5</sup>) provides the best fit to their data. That work was extended to 45 GPa, where melting was detected using Raman spectroscopy<sup>6</sup>; extrapolation to 200 GPa using the Kechin law suggested that the melting maximum would occur at around 130 GPa and 1,100 K. Subsequent laser heating experiments, combined with Raman spectroscopy, extended the pressure range to 150 GPa (refs 7,8). These two studies did not use extrapolations, but owing to issues inherent to laser heating (for example, large temperature gradients and/or chemical reactions) they did not provide a convincing indication of melting, and the data points obtained did not present conclusive proof of the melting temperature decreasing with pressure (Supplementary Fig. 1). Nevertheless, no data above 150 GPa and above 300 K exist, and the extrapolation of the existing data to higher pressures suggests that dense hydrogen might melt at room temperature above 250–300 GPa (refs 6–8). Theoretical calculations find the molecular to atomic transformation in liquid hydrogen over a wide pressure–temperature ( $P$ – $T$ ) range<sup>9–11</sup>. These calculations show that the line dividing two very dissimilar liquids joins the melting curve between 200 and 300 GPa and between 500 and 1,000 K (refs 9–11). Recently, hydrogen and deuterium were successfully compressed to above 230 GPa at 300 K, where transformations to mixed atomic and molecular structures, phases IV and IV', were observed<sup>12–15</sup>. It is fascinating that these many measured, extrapolated and predicted phenomena seem to happen in approximately the same  $P$ – $T$

area of hydrogen phase space, which represents a crossover of intramolecular, intermolecular and quantum energy scales.

Using available technology, the detection of hydrogen melting in a diamond anvil cell is a formidable task because of numerous factors. The high reactivity, mobility and diffusion of hydrogen at elevated temperatures (>250 K) lead to the destruction of the diamonds and/or rapid loss of sample, making dense hydrogen notoriously difficult to study. The number of available probing techniques is also limited: X-ray diffraction is not straightforward even in the solid state owing to hydrogen's low  $Z$  number, and to the best of our knowledge no X-ray studies of liquid hydrogen at elevated pressures have been carried out. Visual observations are impossible at higher pressures owing to the greatly diminished sample size, thus leaving Raman spectroscopy as the only viable tool to probe transformations at high pressures. The appearances of the Raman spectra above 180 GPa at 300 K in phases III and IV(IV') are very peculiar and characterized by the presence of very intense and temperature dependent librational and vibrational bands<sup>14</sup>. It could be expected that the temperature driven changes in phases III and/or IV(IV') would be accompanied by changes detectable with optical spectroscopy.

Here, we have succeeded in confining hydrogen at high temperatures in the diamond anvil cell long enough to collect high quality Raman spectra, tracking the evolution of the Raman modes in phases I, III, IV and a new phase, which we speculate could be a liquid state. The monitoring of the phase transformations is more elaborate than before, not only studying the changes of the position (and appearance/disappearance) of the mode(s), but also their full-width at half-maximum (FWHM). The data presented provide points below 200 GPa up to 800 K, between 200 and 275 GPa up to 500 K, and at 325 GPa at 300 K. Our measurements provide constraints on the phase diagram, demonstrating the existence of a third triple point, which suggests a melting minimum.

We find that the behaviour of hydrogen at elevated temperatures and pressures above 130 GPa is very unusual. In the heating run between 132 and 155 GPa (phase I) we clearly observe the transformation, which could be interpreted as melting above 800 K (Fig. 1a–c and inset to 1b). Both the frequency of the vibron,  $\nu$ , and its FWHM change discontinuously (for examples and explanations of the experimentally observed discontinuous changes in the position and FWHM of the vibrational band through the phase transitions at lower pressures and further experimental details the reader is referred to Methods, Supplementary Methods and references therein). The FWHM broadens as expected through the solid–liquid transition and the frequency of the vibron significantly downshifts ( $\sim 30$  cm<sup>-1</sup>). This softening is opposite to what is observed on melting at lower pressures (Supplementary Figs 3 and 4) and could be explained, as suggested by the negative slope of the melting curve, by the liquid being denser than phase I, thus



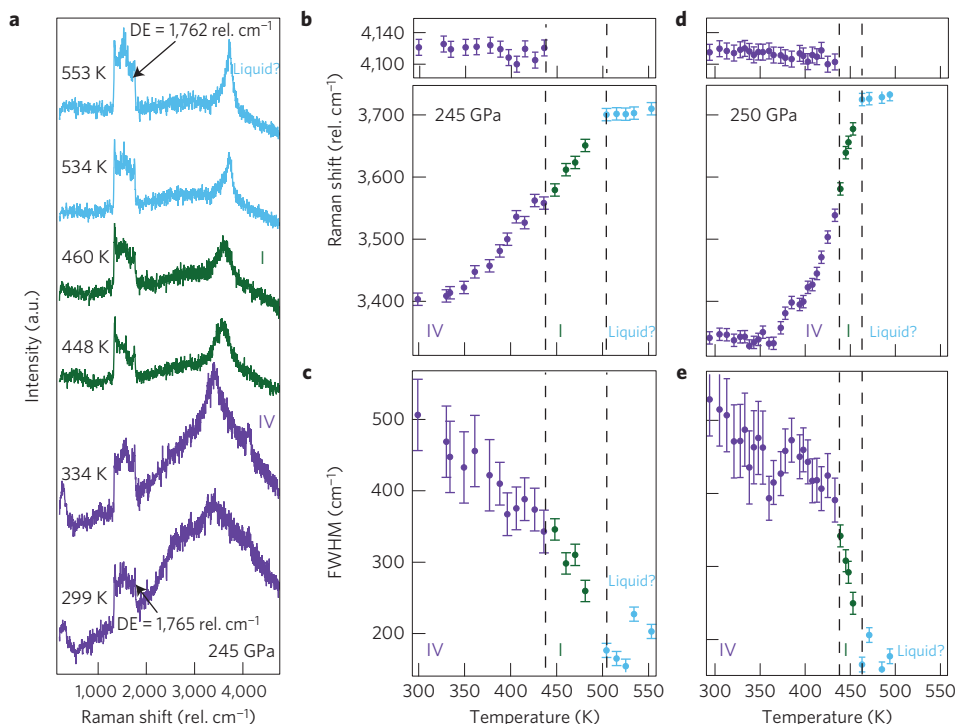
**Figure 1 | Representative Raman spectra, position and FWHM of the vibrational band in hydrogen.** **a**, Raman spectra on heating in phase I (dark green) and the HPHT phase (light blue) at pressures between 130 and 155 GPa. **b,c**, Position (**b**) and FWHM (**c**) of the vibrational mode  $\nu_1$  at 130–155 GPa as a function of temperature through the phase I  $\leftrightarrow$  HPHT phase transformation, which is marked by the vertical dashed line. The inset to **b** shows a magnified view of the vibrational mode through the transformation. **d**, Representative Raman spectra of hydrogen on heating in phases III (orange) and I (dark green) at pressures between 220 and 225 GPa. **e,f**, Position (**e**) and FWHM (**f**) of the vibrational mode  $\nu_1$  at 220–225 GPa as a function of temperature through the phase I  $\leftrightarrow$  phase III transformation, which is marked by the vertical dashed line. The broad peak between 1,333 and  $\sim$ 1,700  $\text{cm}^{-1}$  in **a** and **d** is due to the stressed diamond. The observed DE frequency is indicated.

driving the frequency down through melting. Qualitatively similar behaviour is observed up to  $\sim$ 190–200 GPa, which is in agreement with our previous study<sup>6</sup>. However, in the heating runs above 200 GPa, the  $(d\nu/dT)_P$  term changes sign, leading to an increase of the vibron frequencies with temperature while the FWHM is very slowly decreasing (Figs 1d–f and 2). For example, in the 225 GPa run, we observe the phase III  $\leftrightarrow$  I transformation and hardening of the vibron frequencies as temperature is increased in phase I. The effect becomes more pronounced as hydrogen is compressed to above 230 GPa, leading to values of  $(d\nu/dT)_P$  of the order of  $2\text{--}3 \text{ cm}^{-1} \text{ K}^{-1}$  (Fig. 2b,d), whereas at 190–200 GPa  $(d\nu/dT)_P$  is around  $-0.1 \text{ cm}^{-1} \text{ K}^{-1}$ . We note that, even though at 250 GPa the isothermal pressure-induced vibron softening  $(d\nu/dP)_T$  is much larger than that at 150 GPa (ref. 6), the behaviour of the vibron frequency is still mostly driven by thermal effects. In addition to the apparent change of sign of the slopes in the solid, the behaviour of the vibrational mode in the presumed liquid state just above phase I at pressures greater than 200 GPa is different from those at lower compressions (Fig. 2). Figure 2a–d shows that the width and position of the vibrational mode are temperature independent in this state. The absence of a discontinuous jump implies similar molar volumes (densities) on both sides of the transformation line (or melting curve), which in turn would imply a flattening of the melting curve. Interestingly, Fig. 2 shows that the negative slope of the vibron FWHM with temperature is larger than that at lower pressures, leading to an FWHM decrease in phase I by a factor of two to three within 50–75 K.

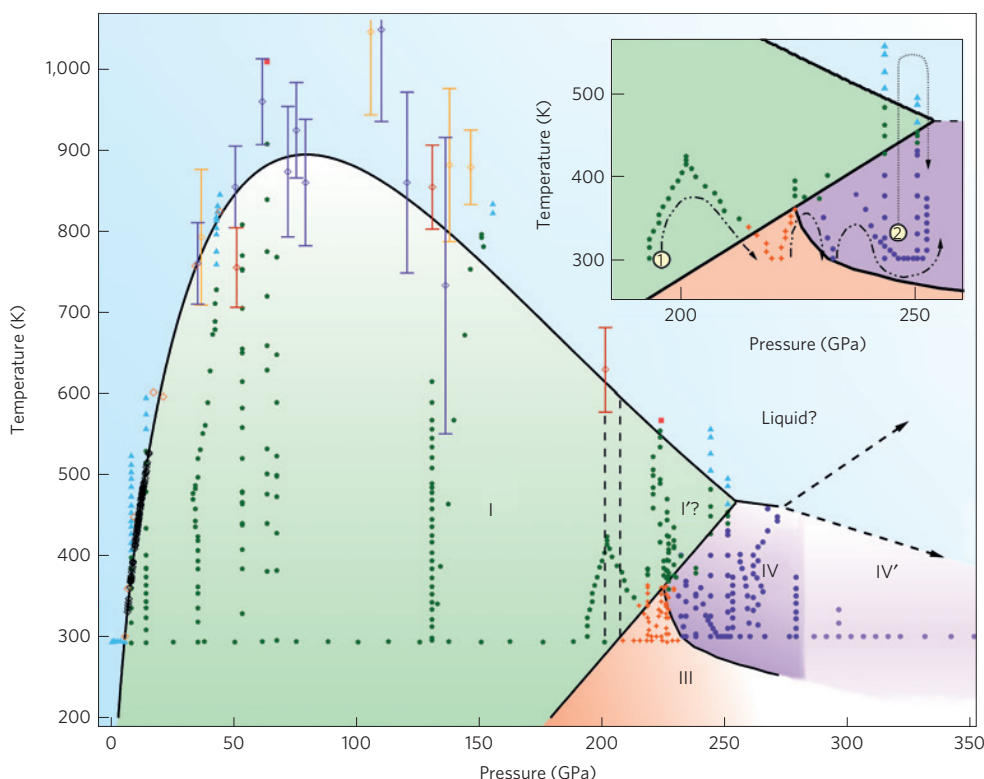
Two phase transitions are clearly detectable when hydrogen is heated above 200 GPa, III  $\leftrightarrow$  I  $\leftrightarrow$  new phase (or liquid), and above 230 GPa the phase sequence is IV  $\leftrightarrow$  I  $\leftrightarrow$  new phase (or liquid) (Figs 2a and 3a–d). At these pressures the transformations are characterized by noticeable modifications of the Raman spectra with temperature, such as disappearance of the librational modes,

change of slope of the vibrational band, two- to threefold decrease of the FWHM and the disappearance of the second vibrational band  $\nu_2$  (IV  $\leftrightarrow$  I). The combined high-temperature runs (Fig. 3) show that the phase line separating phases I and III does not change its slope at the I–III–IV triple point and continues as the I–IV phase line. Phase IV seems to be stable in a surprisingly narrow range of temperatures above ambient and is superseded by phase I, which occupies a significant portion of the phase diagram up to and above 200 GPa. We traced the I–IV line to 255 GPa and 480 K, where it intersects the extrapolated melting curve forming a triple point, only the third known triple point on the hydrogen phase diagram and what could be the first on its melting curve. The sequence of phases versus temperature at pressures between 225 and 250 GPa is quite instructive. It starts in phase III, and although its structure is unknown it is likely to have some ordering when compared with phase I, for example layered structures with non-rotating molecules<sup>16</sup>. As temperature is increased, phase III transforms to phase IV, more disordered than III, with a big discontinuity in the frequency of the  $\nu_1$  vibron and the appearance of  $\nu_2$  (ref. 14). If phase IV is heated further, it transforms to phase I, even more orientationally disordered, without any discontinuity in the position of  $\nu_1$  (Fig. 2); in fact, the phase transformation is obvious only because of the (dis)appearance of the free-like molecular vibron  $\nu_2$ . Phase I in this  $P$ – $T$  range seems to be quite different from that at lower pressures and temperatures; it is possible that the sign reversal of the position and FWHM slopes described above could be driven by the continuous transformation to a different solid phase that is structurally very similar to phase I, for example, phase I' (Fig. 3). In turn, phase I(I') either melts or transforms to a solid state with complete orientational disorder (no observable lattice modes).

If the described changes in Raman spectra are indeed caused by melting, then the  $P$ – $T$  paths, as shown in Fig. 3, provide further experimental limits on the phase diagram and pose some



**Figure 2 | Representative Raman spectra of hydrogen on heating at different pressures.** **a**, Raman spectra on heating in phases IV and I and HPHT phase at 245 GPa. The observed DE frequency is indicated on room and highest temperature spectra. **b–e**, Positions (**b,d**) and FWHMs (**c,e**) of the vibrational modes  $\nu_1$  and  $\nu_2$  at 245 (**b,c**) and 250 GPa (**d,e**) in phase IV. Note that the positions and FWHMs at 250 GPa were measured with temperature decreasing. The error bars are from the fits to the data. The vertical dashed lines indicate the IV  $\leftrightarrow$  I  $\leftrightarrow$  HPHT phase transitions.



**Figure 3 | Proposed phase diagram of hydrogen up to 325 GPa.** The inset shows the  $P$ - $T$  paths (1 and 2) taken during temperature cycles. The melting curve is a Kechin fit<sup>5</sup> to the data points obtained here and in our previous study. Previous data are overlaid with different colour hollow diamonds: purple, ref. 8; yellow, ref. 7; orange, ref. 6; red, ref. 9; black, ref. 4. The phase lines between phases I, III and IV and the new phase (liquid) are from this study and refs 13,14. The red squares show where the  $H_2$  rapidly diffused from the sample chamber. The vertical dashed lines at around 190 GPa indicate the pressure region in which  $(d\nu/dT)_p$  in phase I changes sign. The dashed lines ending with arrows are possible continuations of the transformation line (or melting curve). The lines between the phases have an error bar of about  $\pm 10$  GPa but are consistent with our other studies<sup>13,14</sup>.

interesting questions about a possible melting minimum and the proposed liquid ground state<sup>1,2</sup>. The  $P$ - $T$  paths shown require the extrapolated melting curve to change slope after the I-IV-liquid triple point. The possible continuations of the melting curve (shown with the dashed lines in Fig. 3) effectively rule out the liquid state at temperatures below  $\sim 300$  K and pressures below 400 GPa. In fact, a very recent theoretical study found that the melting curve remains flat at around 300 K up to 500 GPa, where it regains a positive slope<sup>17</sup>, which is in very good qualitative and quantitative agreement with the current study. In principle, the liquid ground state could still exist at much higher pressures (for example, above 500 GPa) and its existence would be determined by such factors as the  $P$ - $T$  conditions at which the molecular disassociation of hydrogen occurs, by the zero-point energy terms of the atomic liquid and/or solid versus other energy terms contributing to the Gibbs free energy. The latest theoretical calculations, where some of these effects were taken into account, either do not find the liquid ground state up to 600 GPa (ref. 17) or place it above 900 GPa following the predicted atomic solid phase<sup>18</sup>.

It is important to stress the limitations of Raman spectroscopy as a method to detect melting, and therefore we need to consider other phenomena that could have led to the changes in the Raman spectra here and in previous melting studies. We can speculate that the drastic changes observed in the Raman spectra on increasing temperature could be due to a solid-solid phase transformation. The amalgamated data could probably rule out this speculation for the following reasons: the Raman spectra at the highest temperatures are very simple and characterized by a relatively narrow (at given pressures) single vibrational mode and absence of rotational/librational modes (Figs 1a and 2a). Therefore, the overall appearances of the Raman spectra are identical in the liquid state over a broad pressure range (Figs 1a and 2a, 130 and 245 GPa, with Supplementary Fig. 4, 14 GPa). The above assumption would also imply that there is a new solid molecular phase of hydrogen located somewhere between 130 and 270 GPa with very high melting temperatures. The presence of such a new high-temperature solid phase (instead of a liquid state) would be an interesting observation in itself and pose several questions that would require a profound revision of our current theoretical understanding of hydrogen in these conditions. If it were a new, structurally simple solid phase, then new models are clearly needed proposing such a structure and predicting melting temperatures that do not decrease above 120–140 GPa. Several theoretical papers<sup>9–11,17,18</sup> present results on melting, which are in reasonable qualitative agreement with our measurements. However, experimental advancements in methods that could directly determine melting of hydrogen at these conditions (for example, Brillouin spectroscopy, X-ray diffraction) would be highly beneficial. Nevertheless, our presented data further broaden our understanding of a system that was previously found to be highly elusive experimentally at these conditions and is still revealing fascinating physics.

## Methods

**Loading.** We have conducted a total of 50 independent experiments varying in pressures from 3 to 360 GPa. Pressure was generated in long high-temperature piston-cylinder diamond anvil cells of our own design equipped with diamonds of culet dimensions ranging from 250 to 20  $\mu\text{m}$ . The experimental runs mostly followed a procedure similar to the one previously described in ref. 6. However, owing to improved stability of pressures and temperatures in the cells and a refined experimental practice, we have managed to probe a much greater regime of  $P$ - $T$  space, for example, 555 K at 223 GPa (Supplementary Methods). Rhenium foils 200–250  $\mu\text{m}$  thick were used as gasket material to form the sample chamber. The hydrogen gas was clamped at  $\sim 0.175$ – $0.200$  GPa at 300 K and compressed to the target pressure (see 'Pressure and temperature measurements').

**Optical measurements.** We have used 514.15 and 647.1 nm excitation wavelengths to collect the spectra. Owing to the quantum efficiency of the visible CCD (charge coupled device) used, the high-energy modes, for example

hydrogen vibrons above  $3,500\text{ cm}^{-1}$ , are much weaker than the low-energy lattice modes if probed with 647.1 nm wavelength (compare the spectra shown in Figs 1a and 2a measured with 514.15 nm and Fig. 2 in ref. 13 measured with 647.1 nm). However, in most of the cases when 514.15 nm excitation is used, the pressure-induced fluorescence from the stressed diamonds obscures the Raman signal, leaving 647.1 nm excitation as the only available source.

**Pressure and temperature measurements.** After clamping hydrogen gas at 0.2 GPa, pressure was increased at 300 K until it reached its required value. The pressures were determined using both the frequency of the diamond edge (DE) with the calibration proposed in refs 19,20 and the vibrational mode of the hydrogen sample<sup>21</sup>, to be consistent with our previous work<sup>13,14</sup>. When the desired pressure according to the vibron frequency was reached, the frequency of the stressed DE was noted as a reference point (Supplementary Fig. 2); in most of the runs the agreement between the two was within 10–15 GPa, as shown in ref. 21. During the heating run the pressure was either adjusted by keeping the frequency of the DE constant or determined later on the assumption that the frequency of the DE is temperature independent. In cases when the sample was brought back to room temperature, the frequency of the hydrogen vibron provided further information on the pressure change during the heating-cooling cycle. Typical examples are provided in Supplementary Methods; for example, Supplementary Fig. 2 shows that a net pressure increase of  $\sim 30$  GPa was observed when pressure was not adjusted during the experiment. However, when pressure was adjusted, a quasi-isobar could be reliably tracked to within  $\pm 5$  GPa on heating.

For heating we used two custom built resistive heaters placed around the diamonds and body of the cell. Temperature was determined using one or two thermocouples attached to one of the diamonds and/or gasket.

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### Author contributions

R.T.H. and P.D-S. carried out the experiments, analysed the data and wrote the paper. E.G. conceived and designed the project, carried out the experiments, analysed the data and wrote the paper.

### Additional information

Supplementary information is available in the [online version of the paper](#). Reprints and permissions information is available online at [www.nature.com/reprints](http://www.nature.com/reprints). Correspondence and requests for materials should be addressed to E.G.

### Competing financial interests

The authors declare no competing financial interests.