Published in final edited form as:

Nat Phys. 2017 September ; 13(9): 859–863. doi:10.1038/nphys4156.

Spectroscopic evidence of a new energy scale for superconductivity in H₃S

F. Capitani¹, B. Langerome¹, J.-B. Brubach¹, P. Roy^{1,*}, A. Drozdov², M.I. Erements², E. J. Nicol³, J. P. Carbotte^{4,5}, and T. Timusk^{4,5,†}

¹Synchrotron SOLEIL, AILES Beamline, Saint-Aubin, 91190, France

²Biogeochemistry Department, Max Planck Institute for Chemistry, PO Box 3060, 55020 Mainz, Germany

³Department of Physics, University of Guelph, Guelph, ON N1G 2W1, Canada

⁴Department of Physics and Astronomy, McMaster University, Hamilton, ON L8S 4M1, Canada

⁵The Canadian Institute for Advanced Research, Toronto, ON M5G 1Z8, Canada

Abstract

The discovery of a superconducting phase in sulfur hydride under high pressure with a critical temperature above 200 K has provided fresh impetus to the search for superconductors at ever higher temperatures. Although this system displays all the hallmarks of superconductivity, the mechanism through which it arises remains to be determined. Here we provide a first optical spectroscopy study of this superconductor. Experimental results for the optical reflectivity of H₃S, under hydrostatic pressure of 150 GPa, for several temperatures and over the range 60 to 600 meV of photon energies, are compared with theoretical calculations based on Eliashberg theory. Two significant features stand out: some remarkably strong infrared active phonons at around 160 meV, and a band with a depressed reflectance in the superconducting state in the region from 450 meV to 600 meV. In this energy range H₃S becomes more reflecting with increasing temperature, a change that is traced to superconductivity originating from the electron-phonon interaction. The shape, magnitude, and energy dependence of this band at 150 K agrees with our calculations. This provides strong evidence of a conventional mechanism. However, the unusually strong optical phonon suggests a contribution of electronic degrees of freedom.

Keywords

superconductivity; H₃S; optical data; the electron-boson spectral density

* pascale.roy@synchrotron-soleil.fr. † timusk@mcmaster.ca.

Author contributions

This project has been initiated and supervised by T.T., M.I.E. and P.R. Samples have been synthesized and characterized by A.D. and M.I.E. Infrared measurements and data treatment were carried by B.L., F.C., J.B.B., P.R. and T.T. The calculations were performed by E.J.N. and J.P.C. All authors contributed to the writing of the paper.

Competing financial interests

The authors declare no competing financial interests.

PACS numbers: 74.25.Gz, 74.20.Mn, 74.25.Jb

High temperature superconductivity in dense phases containing hydrogen was predicted by Ashcroft^{1–3} and more specifically in H₂S by Li *et al.*⁴. The verification of these predictions was the discovery of a new superconductor with a transition temperature T_c of 203 K by Drozdov *et al.*⁵. Hydrogen sulfide, confined under the high pressure of 155 GPa in a diamond anvil cell (DAC), becomes superconducting, showing both zero electrical resistivity below T_c and a Meissner effect. Furthermore, the superconducting phase has been found to be H₃S by x-ray diffraction⁶. Calculations based on density functional theory (DFT) suggest that superconductivity in H₃S is caused by the electron-phonon interaction, enhanced by a combination of the light mass of hydrogen and very strong coupling to high energy modes^{7–11}. What is lacking is an experimental verification of this mechanism. A step in that direction would be the identification of the spectrum of bosons that couple to the charge carriers to form the glue that leads to superconducting pairing.

The mechanism whereby conventional metals become superconductors is well established and involves the electron-phonon interaction^{12,13}. The current-voltage characteristics of tunneling junctions¹² and optical spectroscopy^{14–17} have yielded detailed information on the electron-phonon spectral density $\alpha^2F(\Omega)$ as a function of phonon energy $\hbar\Omega$. These phonon spectra were further verified by neutron scattering¹⁸.

It is an experimental challenge to extend these methods to the recently discovered hydrogen sulfide under pressure of 150 GPa for several reasons. The sample size $\approx 50 \mu\text{m}$ clearly excludes neutron studies, while the DAC environment does not allow photoemission measurements. Optical studies through infrared transmission are difficult as they require thin films of the order of tens of nanometers, or less, which are difficult to make in current state-of-the-art of DACs⁵.

Reflectance measurements seem to be the best alternative in such a high pressure environment¹⁹. Nevertheless, several problems remain to be resolved, which result from the minute size of the sample, and the presence of diamond in the optical path. To overcome these difficulties, we adopted the method of measuring reflectivity at various temperatures and then evaluated the temperature ratio between the superconducting state to the normal state. These temperature ratios were then compared to theoretical ratios from DFT and Eliashberg theory. Alternatively, for normal reflectance measurements, we used the reflectivity from either surface of the diamond (or an NaCl insulating layer) as a reference.

Through these methods, we provided the evidence for the superconducting transition in H₃S under pressure of 150 GPa and demonstrated the high energy scale involved.

Fig. 1(a) shows the calculated reflectivity R_n in the normal metallic state at 200 K of H₃S, as the dashed red curve, and in the superconducting state, R_s as the solid blue curve. The details of these calculations are given in the Supplementary Information (SI). As shown in Fig. 1(a), a superconductor with an isotropic gap is a perfect reflector of electromagnetic radiation, *i.e.* $R_s = 1$, up to a photon energy $\hbar\omega = 2\Delta$. Above this energy, the reflectance drops to approximately the normal metallic state value.

Fig. 1(b) shows the calculated reflectance ratio, $R_s(T)/R_n$ for two values of the elastic scattering rate γ_n , one sample is near the clean limit while the other one is closer to the dirty

limit (see the following section and the SI). The gap () gives rise to a step at $2\Delta = 73$ meV in the calculated reflectivity²⁰. This drop is larger if the sample is closer to the dirty limit, *i.e.* if the scattering rate is larger than the gap: $\gamma_r \gg 2\Delta$. Such effect is directly translated into the reflectivity ratio, as illustrated in Fig. 1(b), where a $\sim 3\%$ drop of $R_s(T)/R_n$ is expected at 73 meV in the dirty limit whereas it is reduced to $\sim 1\%$ in the clean limit.

In the following, we will focus our investigation on a sample in the dirty limit measured over three regions: the gap region, 65 to 100 meV, the range of direct absorption by optically active phonons, 100 to 200 meV, and the boson region, 450 to 600 meV, where the reflectance ratio is depressed by some 3.5 % at 450 meV and rises between 450 and 800 meV as the energy increases. This depression of reflectance is due to the strong scattering from bosonic excitations with $\hbar\Omega \approx 200$ meV.

The energy gap

Fig. 2(a) shows the theoretical $R_s(T)/R_n(200\text{K})$ for a sample in the dirty limit ($\gamma_r = 135$ meV as determined below) at two different temperatures: $R_s(150\text{ K})/R_n$ and $R_s(50\text{ K})/R_n$. These two temperatures correspond respectively to a superconducting sample close to T_c (150 K) and one in a well-established superconducting state (50 K). Here, the drop in reflectance ratio is larger when the temperature is lowered and the onset of this structure shifts from 50 meV for $T = 150$ K to 73 meV at 50 K.

Fig. 2(b) shows our measured $R_s(T)/R_n$ for a sample of H_3S determined to be in the dirty limit at two temperatures compared with the corresponding theory curves. R_n was measured at 200 K. Data are limited to the energy region where the superconducting gap is expected (as highlighted in Fig. 2(a)).

For this sample, the DC resistivity was used to determine T_c and the elastic scattering rate γ_r . The temperature dependence of the resistivity is shown in the inset of Fig. 2(b), where an abrupt drop indicates a superconducting critical temperature $T_c \approx 200$ K. Note that the measured resistivity is not quite linear in temperature above 200 K but rather increases by an additional 20 %. This provides a first indication that the bosons involved in the inelastic scattering have high energies since a deviation from a linear T law is seen only at low temperatures in ordinary metals. The resistivity above T_c is well described by the dashed curve (shown in orange in the inset of Fig. 2(b)) obtained with $\gamma_r = 135$ meV, thus confirming the dirty limit nature of this sample (see SI for further details).

As shown in Fig. 2(b), we observe a clear feature at 76 meV that is present in the superconducting state only. The measurement at 50 K shows a 3% increase at 76 meV while the measurement at 150 K, closer to T_c , shows a modest increase slightly above the limit of our experimental sensitivity of about 1%. The intensity of this feature and its temperature dependence are in good agreement with the theoretical behavior of the superconducting gap (see dashed curves).

Notice, however, that there are a few discrepancies between our observed gap signature and the predicted one: (i) - the theory predicts a step-like feature while our experimental curve is peak-like; (ii) - according to theory, as the temperature is increased, the gap is expected to

close, while the gap feature gets weaker but does not shift significantly. We suggest that these effects may be caused by a temperature dependent absorption by the TO-LO reststrahlen band of NaCl, shifted to higher frequencies by pressure (NaCl is used as an insulating layer in the DAC). The narrowing of this band as the temperature is lowered could explain the strong reduction of the signal at a lower temperature in the 60 to 70 meV region. A run with a larger spot showed an increase in the amplitude of these features (further details can be found in the SI). Finally, we note that while our theoretical model predicted a gap at 73 meV, our data fits a somewhat higher value of 76 meV.

Structure from bosons

The straightforward technique to extract the boson spectrum of a new superconductor is through an analysis of the absolute reflectance in the energy region $\hbar\omega \approx 2 - \hbar\Omega_{log}$, where Ω_{log} is the superconducting gap and Ω_{log} is a characteristic boson energy. Such a measurement is difficult to realize in a high pressure system. As we have done for the gap structure measurements, we adopt the method of measuring reflectance ratios using the normal state reflectance as a reference and comparing these ratios with calculations from DFT and Eliashberg theory.

Fig. 3(a) shows that the main feature in the ratio is the strong 3.5 % and 2.5 % drop at 50 and 150 K, respectively, just above the 250 meV range followed by a region of positive slope above 400 meV. Unfortunately, the drop occurs in the region of strong phonon absorption in the diamond anvil and cannot be accessed for accurate measurements. In what follows, we focus instead on the the slope of $R_s(T)/R_n$ in the somewhat broader region 450 to 600 meV, as highlighted in white in Fig. 3(a). The theory gives a slope of $1.05 \times 10^{-4} \text{ meV}^{-1}$ at 200 GPa. We have also digitized the 157 GPa $\alpha^2F(\omega)$ spectrum shown in the supplemental information of Ref. 23, have redone our calculations and have found a slope of $1.5 \times 10^{-4} \text{ meV}^{-1}$. Our experimental value for this slope is $0.95 \pm 0.1 \times 10^{-4} \text{ meV}^{-1}$ at 150 GPa, in reasonable agreement with the calculations although the higher pressure theory agrees somewhat better with our experiments. We obtained this value by averaging three runs on two separate samples. If we include a fourth run done with a third sample (shown in detail in Fig. 3b), we obtain an average slope of 0.78.

The measured reflectance ratio $R_s(T)/R_n$ at selected temperatures (solid lines) are shown in Fig. 3(b), together with theoretical calculations in Fig. 3(c). As the temperature increases, the slope of the feature decreases and the measured reflectance ratio approaches unity in good agreement with the corresponding theoretical curves.

This behaviour indicates that superconducting H₃S becomes a *better* reflector in the multi-boson region as the temperature is *increased*, in agreement with Eliashberg calculations (see SI, Fig. 2S). This effect and the good agreement between theory and experiment for the slope of $R_s(T)/R_n$ in the region 450 to 600 meV demonstrates that H₃S is an Eliashberg superconductor, driven by the electron-phonon interaction with strong coupling to high phonons of order of 200 meV.

Optically active phonons

In order to estimate the absolute reflectance of H_3S , we exploited the NaCl insulating layer surrounding the sample as a reference, as illustrated in the inset of Fig. 4(a). Although its reflectance level is low, it has the advantage of having a constant reflectance for energies above its TO-LO phonon band. The TO-LO phonon energy of NaCl at ambient pressure is below our region of interest. However this band moves to higher frequencies as the pressure increases²². It may therefore reach the investigated region but there are no optical constant data in the literature in this high pressure range.

The ratio of the signal from the sample in normal state to that from the NaCl is shown in Fig. 4(a) (solid red curve). For comparison, a ratio for a sample with an ideal unit reflectance for the whole energy range is shown as a dashed black curve. It is difficult to estimate the absolute value of the NaCl signal in our experiment for two reasons. First, the index of refraction of NaCl at this pressure is not known. Secondly, there is the effect of the beam spot spilling over the sample or the metal electrodes which, with their high reflectance, increase artificially the measured signal from NaCl (see the schematics of the spot size and the cell in Fig. 5). This enhancement of the NaCl reflected signal is expected over the whole energy range.

Despite these effects, several spectroscopic features stand out in Fig. 4. The most striking is a strong absorption band at 150 meV. We attribute this feature to a group of optically active phonons in H_3S , predicted to occur in this energy range by Errea *et al.*²³. Our models show that they are expected to cause a decrease in reflectance of H_3S . No other spectroscopic signatures in the 100 to 600 meV range are observed, except a broad band from 350 to 550 meV, perhaps caused by a structure in the H_3S density of states near the Fermi level or by interband transitions. Finally, one can see a rapid drop in the reflectance ratio below 100 meV which might come from the TO-LO band of NaCl, which as shifted to higher energies due to the high pressure. Notice that the diamond phonons absorption is cancelled out since both the sample and reference beams travel through the same thickness of diamond.

Using the diamond front surface as reference, we also derived the parameters of the phonons at ~ 150 meV and compared them with theoretical predictions in terms of energy and intensity. The calculated and measured phonon absorptions are presented in Fig. 4(b). Here, I_n is the signal from the beam focused on the sample and I_d from the beam on the front surface of the diamond (see inset). Just as with the NaCl reference, a strong asymmetric depression of reflectance with a minimum at 153 meV is apparent. This feature is temperature independent and persists up to room temperature. As for the evaluation using NaCl reference, this ratio is not an exact measure of the sample reflectance due to possible spillover. However we can estimate the relative value of the drop due to phonon structure to be 0.11 ± 0.02 (see SI for details). The measured reflectance of H_3S in this frequency region can be nicely reproduced (drop of 0.14) by a model conductivity that includes two components, a Drude peak with a plasma frequency of 14 eV and a damping calculated from the DFT bosonic spectral function (see SI for details), and a Lorentz oscillator with a center energy of 160 meV, a plasma energy of 2500 meV and a damping of 1.0 meV. Fig. 4(b) also presents the expected reflectance from this model along with another model with a plasma

energy of only 400 meV. This lower plasma frequency would be consistent with what is expected for TO phonons in H₃S. It is obvious that this latter phonon model does not fit the data. These comparisons suggest that phonons in H₃S are coupled to electronic degrees of freedom, causing a remarkable increase in their strength.

Conclusions

This optical study, combined with DFT and Eliashberg theory, provides evidence for the conventional superconducting mechanism in H₃S under pressure and demonstrate the high energy scale involved.

An unexpected result of our work is the observation of optically active phonons at 160 meV and their dramatically enhanced oscillator strength. This quasi electronic strength enhancement may be related to the anharmonic potential found by Errea *et al.*⁸. Such “charged phonons” where lattice vibrations acquire electronic oscillator strength have been reported in organic conductors and C₆₀^{24,25} and more recently in bilayer graphene²⁶. The details of the mechanism vary from system to system but generally involve a Fano type interaction between a discrete phonon state and a continuous electronic background.

We observed a feature at 76 meV in good agreement with the theoretical gap structure. We also showed evidence for the predicted boson depression of reflectance in the 450 to 600 meV region in the superconducting state. This high energy scale is in accord with the model where the pairing glue comes from a phonon with a characteristic energy of the order of 200 meV.

Therefore, we have presented spectroscopic evidence that the superconductivity mechanism in H₃S is the electron-phonon interaction with a bosonic spectral function $\alpha^2F(\Omega)$ as calculated from DFT and Eliashberg theory.

Methods

The samples were synthesized in the high pressure laboratory in Mainz (Max Planck Institute for Chemistry, Mainz). H₂S was first confined into diamond anvil cells and annealed at 300 K to generate the H₃S phase with a superconducting T_c of ~ 200 K⁵. The pressure was determined using Raman spectroscopy of the diamond anvil following the method described by Eremets *et al.*²⁷. This measurement was done prior to all of the spectroscopic runs. Fig. 5 shows a schematic view of the cross section and a camera picture of a typical DAC used. Four electrodes were used to measure the DC resistivity and to establish the superconducting transition temperature⁵. Four samples, approximately 50 to 80 μm in diameter were investigated. a layer of NaCl was used as an insulator.

The reflectance measurements were carried out at the AILES beam line at the SOLEIL synchrotron²⁸, using a setup specially designed for measurements of samples at high pressure and low temperature²⁹. The DAC was in thermal contact with the cold tip of a helium flow cryostat and could be moved along the three directions by piezoelectric drivers. A camera was used to view the radiation beam spot on the sample and to maintain optimal alignment. The reproducibility of signal from one measurement to another was $\lesssim 1\%$. The

IR radiation was focused on the sample and further collected with a 15x Cassegrain objective. A Bruker IFS125HR Michelson interferometer was used with various beamsplitters and detectors to cover the energy range from 50 to 800 meV. In particular, the range 60 to 600 meV was optimally measured using a custom made He cooled MCT detector³⁰.

In order to measure the absolute reflectance of H₃S, we focused the IR on the NaCl layer and collected a reference spectrum from it. The front surface of the diamond anvil was also used as a reference. However, when using this latter reference, the intense phonon absorption of the diamond does not cancel out. A further difficulty was the presence of a thin layer of ice on the surface of the diamond anvil. While this layer has little effect on the spectra taken with the NaCl reference, it does affect the temperature ratio since the sublimation temperature of water is about 160 K. Therefore, the ice is absent in the normal state spectra but is clearly present in the superconducting spectra. We corrected for this effect by means of a procedure outlined in the Supplementary Information.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank Phil Allen, Dave Embury, Ion Errea, Francesco Mauri, Warren Pickett, Antonio Sanna and Dave Tanner for helpful discussions. We also thank Maxime Deutsch, Laurent Manceron and MBaye Faye for useful discussions and for technical guidance. JPC, EJN and TT were supported by the Natural Science and Engineering Research Council of Canada (NSERC). JPC and TT received additional support from the Canadian Institute for Advanced Research (CIFAR). M.I.E. received financial support from the European Research Council 2010-Advanced Grant 267777. BL and FC received financial support from SOLEIL synchrotron. The high pressure low temperature set-up was developed through a grant from Region Centre.

References

1. Ashcroft NW. Metallic hydrogen: A high-temperature superconductor? *Phys Rev Lett.* 1968; 21:1748–1749.
2. Richardson CF, Ashcroft NW. High temperature superconductivity in metallic hydrogen: Electron-electron enhancements. *Phys Rev Lett.* 1997; 78:118–121.
3. Ashcroft NW. Hydrogen dominant metallic alloys: High temperature superconductors? *Phys Rev Lett.* 2004; 92:187002. [PubMed: 15169525]
4. Li Y, Hao J, Liu H, Li Y, Ma Y. The metallization and superconductivity of dense hydrogen sulfide. *The Journal of Chemical Physics.* 2014; 140:174712. [PubMed: 24811660]
5. Drozdov A, Eremets M, Troyan I, Ksenofontov V, Shylin S. Conventional superconductivity at 203 Kelvin at high pressures in the sulfur hydride system. *Nature.* 2015; 525:73–76. [PubMed: 26280333]
6. Einaga M, et al. Crystal structure of the superconducting phase of sulfur hydride. *Nat Phys.* 2016; 12:835–838. [PubMed: 28553364]
7. Duan D, et al. Pressure-induced metallization of dense (H₂S) 2H₂ with high-*tc* superconductivity. *Sci Rep.* 2014; 4:6968. [PubMed: 25382349]
8. Errea I, et al. High-pressure hydrogen sulfide from first principles: a strongly anharmonic phonon-mediated superconductor. *Phys Rev Lett.* 2015; 114:157004. [PubMed: 25933334]
9. Bernstein N, Hellberg CS, Johannes M, Mazin I, Mehl M. What superconducts in sulfur hydrides under pressure and why. *Phys Rev B.* 2015; 91:060511.

10. Papaconstantopoulos D, Klein B, Mehl M, Pickett W. Cubic H₃S around 200 GPa: An atomic hydrogen superconductor stabilized by sulfur. *Phys Rev B*. 2015; 91:184511.
11. Flores-Livas JA, Sanna A, Gross E. High temperature superconductivity in sulfur and selenium hydrides at high pressure. *Eur Phys J B*. 2016; 89:1–6.
12. McMillan W, Rowell J. Lead phonon spectrum calculated from superconducting density of states. *Phys Rev Lett*. 1965; 14:108.
13. Carbotte J. Properties of boson-exchange superconductors. *Rev Mod Phys*. 1990; 62:1027.
14. Joyce R, Richards P. Phonon contribution to the far-infrared absorptivity of superconducting and normal lead. *Phys Rev Lett*. 1970; 24:1007.
15. Farnworth B, Timusk T. Phonon density of states of superconducting lead. *Phys Rev B*. 1976; 14:5119.
16. Hwang J, Carbotte J. Deriving the electron–phonon spectral density of MgB₂ from optical data, using maximum entropy techniques. *J Phys: Condens Matter*. 2014; 26:165702. [PubMed: 24695073]
17. Carbotte J, Timusk T, Hwang J. Bosons in high-temperature superconductors: an experimental survey. *Rep Prog Phys*. 2011; 74:066501.
18. Stedman R, Almqvist L, Nilsson G. Phonon-frequency distributions and heat capacities of aluminum and lead. *Phys Rev*. 1967; 162:549.
19. Perucchi A, Baldassarre L, Postorino P, Lupi S. Optical properties across the insulator to metal transitions in vanadium oxide compounds. *J Phys: Condens Matter*. 2009; 21:323202. [PubMed: 21693963]
20. Nicol E, Carbotte J. Comparison of pressurized sulfur hydride with conventional superconductors. *Phys Rev B*. 2015; 91:220507.
21. Kamarás K, et al. In a clean high-*T_c* superconductor you do not see the gap. *Phys Rev Lett*. 1990; 64:84. [PubMed: 10041279]
22. Hofmeister A. Ir spectroscopy of alkali halides at very high pressures: Calculation of equations of state and of the response of bulk moduli to the *b*₁-*b*₂ phase transition. *Phys Rev B*. 1997; 56:5835.
23. Errea I, et al. Quantum hydrogen-bond symmetrization in the superconducting hydrogen sulfide system. *Nature*. 2016; 532:81–84. [PubMed: 27018657]
24. Rice M. Organic linear conductors as systems for the study of electron-phonon interactions in the organic solid state. *Phys Rev Lett*. 1976; 37:36.
25. Rice M, Choi H-Y. Charged-phonon absorption in doped C₆₀. *Phys Rev B*. 1992; 45:10173.
26. Kuzmenko AB, et al. Gate tunable infrared phonon anomalies in bilayer graphene. *Phys Rev Lett*. 2009; 103:116804. [PubMed: 19792392]
27. Eremets MI. Megabar high-pressure cells for raman measurements. *J Raman Spectrosc*. 2003; 34:515–518.
28. Roy P, Rouzières M, Qi Z, Chubar O. The AILES infrared beamline on the third generation synchrotron radiation facility SOLEIL. *Infrared Phys Techn*. 2006; 49:139–146.
29. Voute A, et al. New high-pressure/low-temperature setup available at the AILES beamline. *Vib Spectrosc*. 2016; 86:17–23.
30. Faye M, et al. Improved mid infrared detector for high spectral or spatial resolution and synchrotron radiation use. *Rev Sci Instrum*. 2016; 87

Fig. 1. Theoretical reflectivity of H₃S.

(a) Calculated absolute reflectivity in the normal metallic state at 200 K (dashed red line) and in the superconducting state at $T = 20$ K (solid blue line) of H₃S for $\gamma_r = 135$ meV. (b) Ratio of the reflectivity in the superconducting state divided by the normal state value for a sample in the dirty limit (solid blue line), *i.e.* elastic scattering rate $\gamma_r = 135$ meV, and the same ratio for a sample in the clean limit (dashed blue line), $\gamma_r = 28$ meV. Note the three regions where the reflectivity in the superconducting state differs from the metallic: (i) The superconducting gap is predicted to give rise to a sharp step of 3.6 % at 73 meV in the dirtier

sample and a weaker step for the clean sample; (ii) in the 100-200 meV region, direct absorption by phonons can give rise to absorbing features, as indicated by $\hbar\Omega$; (iii) in the 300-500 meV region, a strong depression at energies between $2\hbar\Omega$ and $2\hbar\Omega + 2\hbar\Omega$ is due to scattering from bosonic excitations, with a recovery at larger energy values.

Fig. 2. The superconducting gap of H₃S.

(a) The curves show the theoretical reflectivity ratio in the superconducting state at 50 K (dashed blue line) and at 150 K (dotted red line) divided by value in the normal state at 200 K, $R_s(T)/R_n$ for a sample in the dirty limit. The white area highlights the energy region where the measurements presented in panel (b) were performed. (b) The blue and red solid curves indicate the measured $R_s(T)/R_n$ for $T = 50$ K and 150 K, respectively with R_n measured at 200 K. The drop of the signal below 70 meV is due to instrumental artifacts. The corresponding calculated reflectivity ratios are shown as dashed curves. The inset

presents the DC resistivity (black curve) of the same H_3S sample. Data have been normalized to unity at 200 K. The sudden drop of resistivity at 200 K indicates the critical superconducting temperature T_c . Data between 200 and 300 K are well reproduced by a curve obtained with a residual elastic scattering rate $\gamma_r = 135$ meV, thus indicating that this sample is in the dirty limit.

Fig. 3. The bosonic signature of H_3S .

(a) The curves show the calculated $R_s(T)/R_n$ for a superconducting sample in the dirty limit at 50 K (dashed blue line) and at 150 K (dotted red line) divided by value in the normal state at 200 K. The light blue line corresponds to a measured $R_s(T)/R_n$ at 150 K averaged over three runs. The white area highlights the energy region where the measurements presented in the lower panel were performed. (b) The red, light blue and dark blue lines show $R_s(T)/R_n$ at selected temperatures for a single run. Note the decrease of the slope as the temperature approaches T_c . The error bars $\pm 0.15\%$ at 470 meV are the RMS variations based on three

runs on two samples. All curves have been normalized at 600 meV. (c) The calculated values of $R_s(T)/R_n$ at temperatures corresponding to panel b. The pressure of the calculations is 200 GPa while the measured curves are at 150 GPa.

Fig. 4. Phonon structures in the reflectance of H₃S.

(a) The measured reflectance of H₃S in the normal state, evaluated using the NaCl layer as the reference (R_n/R_{NaCl}), is presented over a large energy range. The white area highlights an energy region where a strong phonon absorption is observed, indicated by an arrow. The red pale portion of the spectrum around 250 meV corresponds to the diamond absorption range where measurements are not possible. The drop of the reflectance ratio to 1.5 at low frequency is due to the restrahlen band of NaCl. The dashed black curve is the calculated reflectance of a perfect reflector divided by the NaCl reference at ambient pressure. A

constant correction factor was applied to this curve to compensate for the smaller sample (size $\sim 50 \mu\text{m}$), while for NaCl, the light is reflected from the complete spot size ($\sim 70 \mu\text{m}$). (b) The measured reflectance of H_3S in the normal state at 300 K, evaluated using the front surface of diamond as reference (black curve), is shown in the phonon region. The vertical marks represent the predicted energies of H_3S phonons according to Errea *et al.*²³. The calculated reflectance of H_3S with an optically active phonon centered at 160 meV and a plasma energy $\omega_p = 400$ meV is shown as a grey dotted curve, while the red dashed curve is obtained with an enhanced plasma energy of 2500 meV.

Fig. 5. Diamond Anvil Cell

(a)-(b): Schematic view of the used diamond anvil cell (DAC) showing the diamond anvils, the insulating NaCl layer (orange), the sample (red), a stainless steel gasket (blue) and the four electrodes for the resistivity measurements. (c) Camera picture of the visible synchrotron radiation focused on and reflected from the sample (orange spot in the center). The dashed circles correspond approximately to the spot size in the mid infrared, which is larger than the sample causing the reflected light to include some extra contribution from NaCl or from the electrodes. The same is true when measuring the reflectivity of the NaCl layer (used as a reference), which includes extra contributions from the H_3S sample. A yellow light passing through the NaCl allows the visualization of the cell in transmission. (d) Photo of the sample inside the DAC seen through an optical microscope. The four electrodes (darker outer zones) around the sample can be also observed.