Infrared Peak Splitting from Phonon Localization in Solid Hydrogen

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We show that the isotope effect leads to a completely different spectroscopic signal in hydrogen-deuterium mixtures, compared to pure elements that have the same crystal structure. This is particularly true for molecular vibrations, which are the main source of information about the structure of high-pressure hydrogen. Mass disorder breaks translational symmetry, meaning that vibrations are localized almost to single molecules, and are not zone-center phonons. In mixtures, each observable infrared (IR) peak corresponds to a collection of many such molecular vibrations, which have a distribution of frequencies depending on local environment. Furthermore discrete groups of environments cause the peaks to split. We illustrate this issue by considering the IR spectrum of the high-pressure phase III structure of hydrogen, recently interpreted as showing novel phases in isotopic mixtures. We calculate the IR spectrum of hydrogen-deuterium mixtures in the $C2/c$ and $Cmca$-12 structures, showing that isotopic disorder gives rise to mode localization of the high-frequency vibrons. The local coordination of the molecules leads to discrete IR peaks. The spread of frequencies is strongly enhanced with pressure, such that more peaks become resolvable at higher pressures, in agreement with the recent measurements.

The phase diagram of hydrogen is of intense interest at present as the search for crystalline metallic hydrogen heats up [1–5]. Critically, metallic hydrogen must not only be made [6], but an unambiguous experimental signal to prove its existence is needed. It is therefore central to the endeavor that the expected spectroscopic signature is properly understood.

Because of the poor x-ray scattering and small sample sizes, precision crystallography of high-pressure hydrogen has proved impossible and most information is gleaned from Raman and infrared (IR) spectroscopy. This measures the vibrational frequencies within the crystal, and cannot determine crystal structure. However, it often provides enough information to distinguish between theoretically produced candidate structures. For this combined calculation-experiment solution of crystal structure to work, it is essential that the calculated spectra are well understood.

Because of the mass difference between the isotopes, the spectroscopic signal in hydrogen and deuterium is different. For harmonic phonons, at the same atomic volume this gives a simple frequency rescaling of $\sqrt{2}$. Variations from this give information about anharmonic behavior, which is normally larger for the lighter isotope. But there are practical difficulties in "equal volume" comparisons. For a given volume, the calculated pressure and free energy depend on zero-point effects, which can be different in D_2 and H_2 by up to 10 GPa [7–9]. Volume is extremely difficult to measure experimentally, while the "diamond edge" pressure scale has been twice recalibrated by up to 20 GPa in the last ten years [10].

Although the H_2 and D_2 spectra are related by a simple scaling, the spectrum of hydrogen deuteride (HD) can be far more complicated. This is mainly because, once the reaction $2HD \Leftrightarrow H_2 + D_2$ reaches equilibrium, the solid

contains three molecular types. Molecular modes such as vibrons and rotons then split into three, while lattice modes such as layer vibration adopt an average frequency. Furthermore, because of mass disorder, Bloch's theorem no longer applies and the difference in masses can drive mode localization, provided the frequency is high enough [11,12]. These features mean that the spectroscopic signal from hydrogen-deuterium mixtures, whether Raman or IR, can look very different from the single element even if the underlying structure is identical. The importance of high frequency in allowing localization means that it is the vibron spectra where this is most pronounced [4,12].

Phase III of elemental H_2 and D_2 has a particularly strong and simple IR signature [13–18], so it was surprising when very complex spectra were found in recent experiments starting with HD at low temperatures [1]. At low pressures only the HD infrared peak was observed, corresponding to phase II. Upon entering phase III, an H_2 peak was observed, but no D_2. Subsequently two new phases were reported, based on the infrared spectra. The first transition to a new phase IV* happened at 200 GPa where both the HD and H_2 peak split in two and two new D_2 vibron peaks appeared. The second transition around 250 GPa to a so-called HD-PRE phase was identified by further splitting in the HD vibron.

Different phase behavior in isotopic mixtures from pure elements is extremely difficult to understand with equilibrium thermodynamics. The electronic structure in the Born-Oppenheimer approximation is the same in each case, so isotopic differences are due to vibrational effects, notably zero-point energy, which depends on mass. (We disregard the possibility that all previous experiments on H/D were somehow trapped in a para- or orthoground state, and that
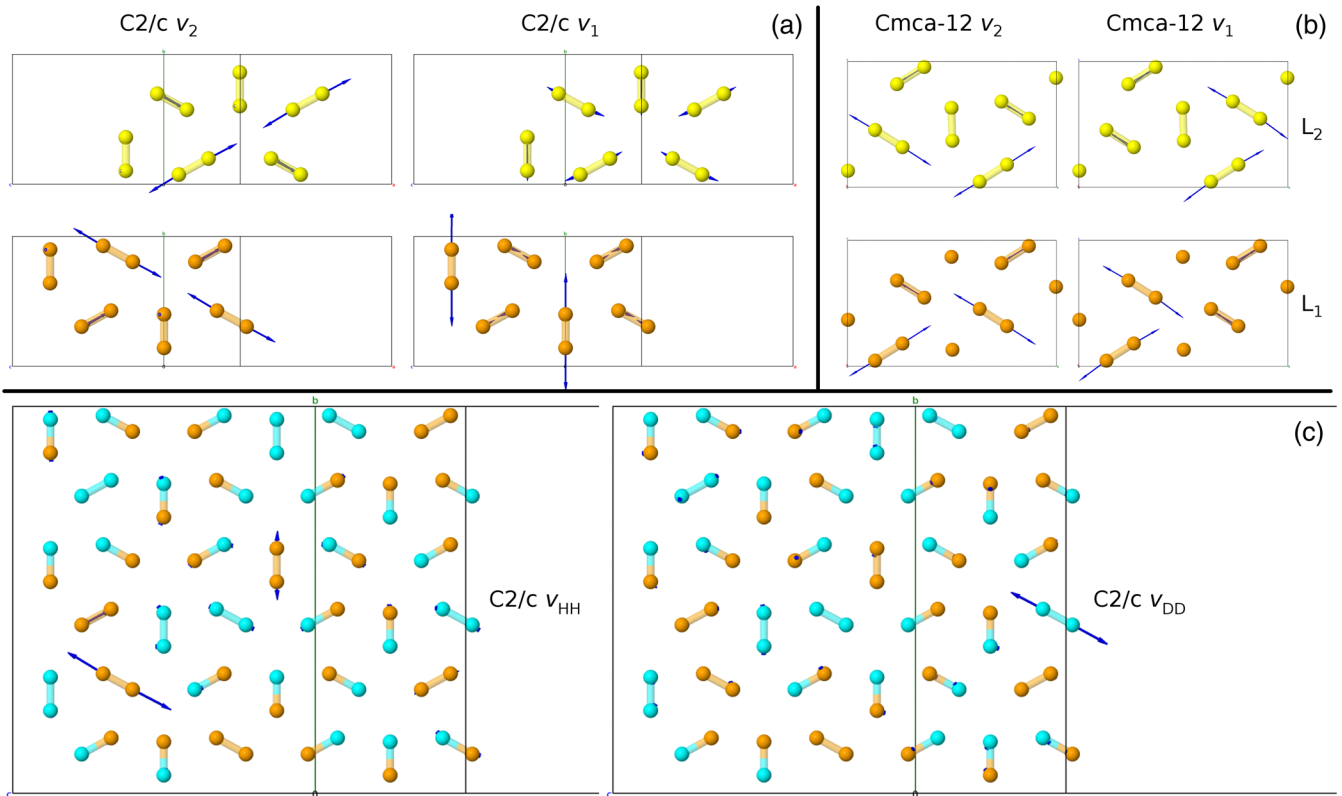
FIG. 1.   Upper panels show the two most intense IR-active vibron modes at 250 GPa in pure hydrogen, assuming (a) $C2/c$ and (b) $Cmca$-12 structures (24 atoms). The unit cells comprise two layers, shown separately for clarity (L_1, orange, and L_2, yellow). (c) Displacements corresponding to IR-active vibrons from the $C2/c$ cell (288 atoms) of disordered mixture at 250 GPa: orange, H; cyan, D. Isotopic symmetry breaking means that all modes obtain some IR activity. The highly localized vibron modes shown are representative examples for the spectrum generated by mixtures.

those different nuclear states somehow lead to the same energetics that are, in turn, different from the energetics of HD that has no ortho or para states.) Hydrogen and deuterium exhibit the same phase sequence, so different HD phases would require that, as mean molecular mass increases from 1 to 1.5 to 2, the structure is first destabilized then restabilized by increasing mass. This observation is sufficiently unexpected as to merit further explanation.

Density functional theory (DFT) calculations using the PBE functional [19] have produced a range of possible candidate structures for hydrogen under these conditions, with good agreement for Raman and IR spectra of phases III and IV in pure isotopes [19–25]. In calculations with static ions, DFT exhibits no isotope effects: these enter only through the vibrational behavior, mainly zero-point effects. Spectroscopy probes this vibrational behavior, so isotopic differences can be studied using lattice dynamics. Here we calculate the expected IR spectroscopic signature from candidate structures above 150 GPa and below room temperature.

We calculated the pressure evolution of the infrared spectra for 50:50 hydrogen-deuterium mixtures at the equilibrium concentrations of 25% H_2, D_2 and 50% HD. According to now-routine calculations the energetically favored crystal is one of a number of similar structures such as $C2/c$ or $P6_122$ that can be viewed as atomic layers [22,25], or as

close-packed molecules [26]. We choose to represent these phases with $C2/c$ and for contrast, we also consider the $Cmca$-12 structure, predicted to be stable at higher pressures (Fig. 1). We calculated the full Raman spectra, but we concentrate on the vibron modes because they can be directly compared with experiment (Fig. 2) and because the low-frequency modes do not show localization effects [12].

$C2/c$ has two strongly IR-active vibron modes for pure hydrogen, which reduce in frequency with increased pressure. This unusual softening can be traced to the weakening of the covalent bond, which lengthens and loses charge as pressure increases. A cursory inspection of the full pressure dependence for $C2/c$ (Fig. 2) shows two peaks at the onset of phase III (150 GPa), a single peak in the range 170–230 GPa, and two peaks above 250 GPa. Based only on these results, it would be easy to draw a mistaken conclusion that this peak "splitting" signified a phase transition: but since all calculations are in the same phase this can be ruled out—it is simply the effect of different pressure dependencies of the mode frequencies. To avoid this type of confusion, in this Letter we draw a distinction between peaks, the spectroscopic observables, and modes, their calculated cause.

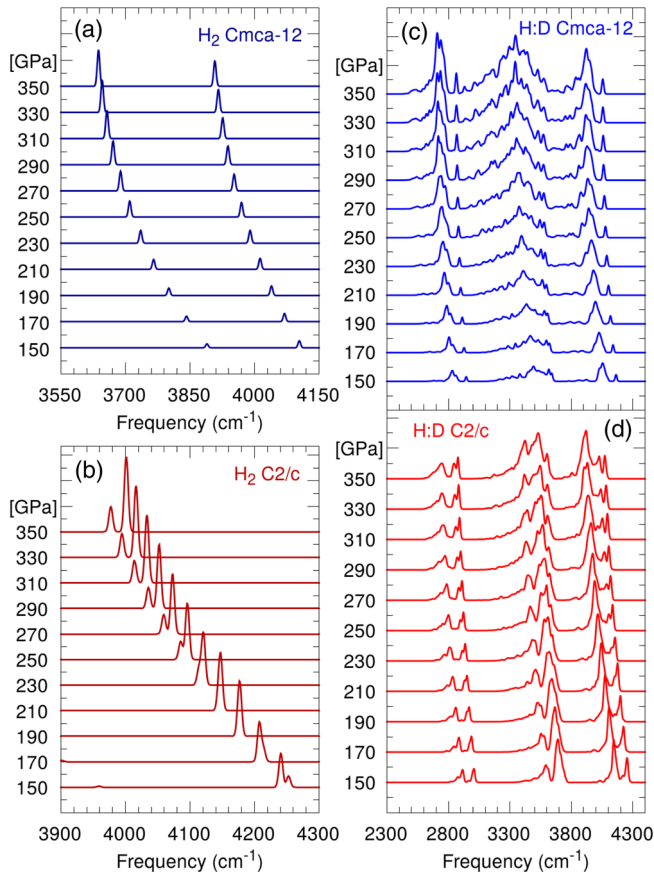Lattice dynamics in mixtures is considerably more involved than in pure elements, and we have developed

FIG. 2.   Stacked plot of simulated vibronic infrared signal at different pressures (shown on the y axis) for the two candidate structures $C2/c$ and $Cmca$-12. Intensities are calculated so spectra at different pressure points are comparable. On the left is pure hydrogen as (a) $Cmca$-12 and (b) $C2/c$. Normal-mode linewidths narrower than experimental resolution [17] are chosen to emphasize the impossibility of resolving the two $C2/c$ modes below 230 GPa. On the right we show the data for 50:50 hydrogen-deuterium mixtures (c) $Cmca$-12 and (d) $C2/c$. Comparison in Fig. 4 (and Supplemental Material) shows that $C2/c$ is a better candidate than $Cmca$-12. At low pressures $C2/c$ has six distinct peaks, two for each molecular type (H_2, HD, and D_2). The two peaks per molecule type here are not connected to the distinct peaks in the pure hydrogen spectra, but rather a signature of local molecular environments. This splitting is an indirect indication of mode localization, which confers some IR activity to all modes [28].
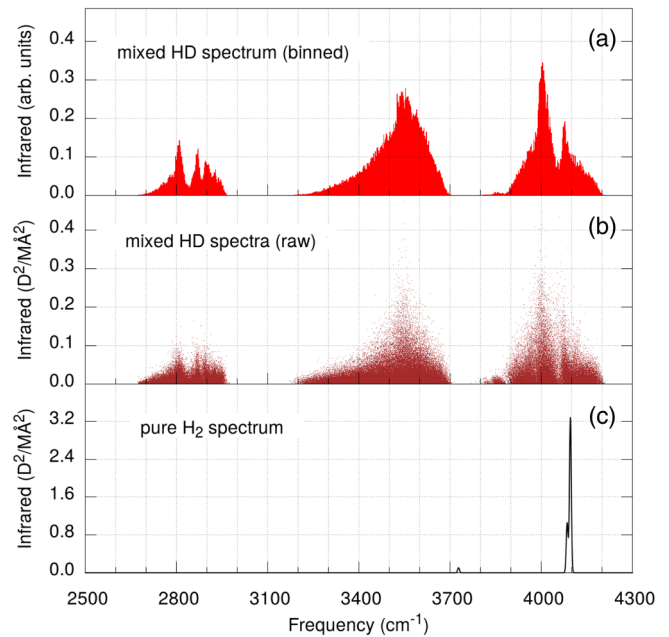

FIG. 3.   Method used to calculate spectra in mixtures at 250 GPa from 288 atom calculations, explained in detail in Supplemental Material [27]. (a) mixture data binned up in a histogram for comparison with experiment. (b) dot for the intensity of each of 144000 localized modes generated from 1000 random samples of hydrogen-deuterium mixtures. (c) IR spectrum of pure hydrogen $C2/c$.

sophisticated methods to tackle the problem using extended supercells (see Fig. 3 [4,27]). The difficulty arises because the disorder breaks translational symmetry so that crystal momentum, k, is no longer a good quantum number and the Γ-point selection rule $k = 0$ becomes meaningless. The twofold D/H mass difference is sufficient to cause the vibron modes to become localized. This broken symmetry confers IR activity on all modes. Comparing Figs. 3(b) and 3(c) shows that the IR activity of any individual mode in the mixture is much lower than for the Γ-point phonon in H_2. So whereas the pure H_2 spectrum has peaks corresponding to a few unique normal modes, the peaks in the mixtures correspond to many different localized modes (cf., Fig. 1). The localized modes

form three groups based on H_2, HD, and D_2 vibrations, with each group split further due to different local environments.

Coupling between molecules causes dispersion in vibron energies. Typically, the antisymmetric IR-active modes are shifted to higher frequencies and the symmetric Raman modes to lower frequencies. In HD mixtures, the coupling is weaker than in pure hydrogen because H_2, HD, and D_2 have different resonant frequencies. So at an equivalent pressure the dispersionlike effects are smaller. Consequently strongly IR-active H_2-type modes can be expected to have lower frequencies than in pure H_2, while Raman frequencies for the equivalent modes in mixtures tend to be higher. Because all modes have some IR activity, the peaks are skew with a low-frequency tail.

The H_2 IR vibron frequency is sometimes used experimentally to measure pressure. The different dispersion between H_2-like peaks in mixtures and pure elements makes this approach unreliable.

In our isotopic mixture calculations, at low pressures, we find that the modes cluster to produce six clear distinct vibron peaks in $C2/c$, two for each molecular species H_2, HD, and D_2. These modes are typically localized on one molecular type (Fig. 1). At higher pressures (above 230 GPa), we find the remarkable result that all the peaks split further, but most notably the HD signal splits into three peaks. The qualitative difference from the pure elements arises from the existence of a finite number of well-defined environments in which the molecule can find itself. This type of splitting is also observed in the $Cmca$-12 structure.
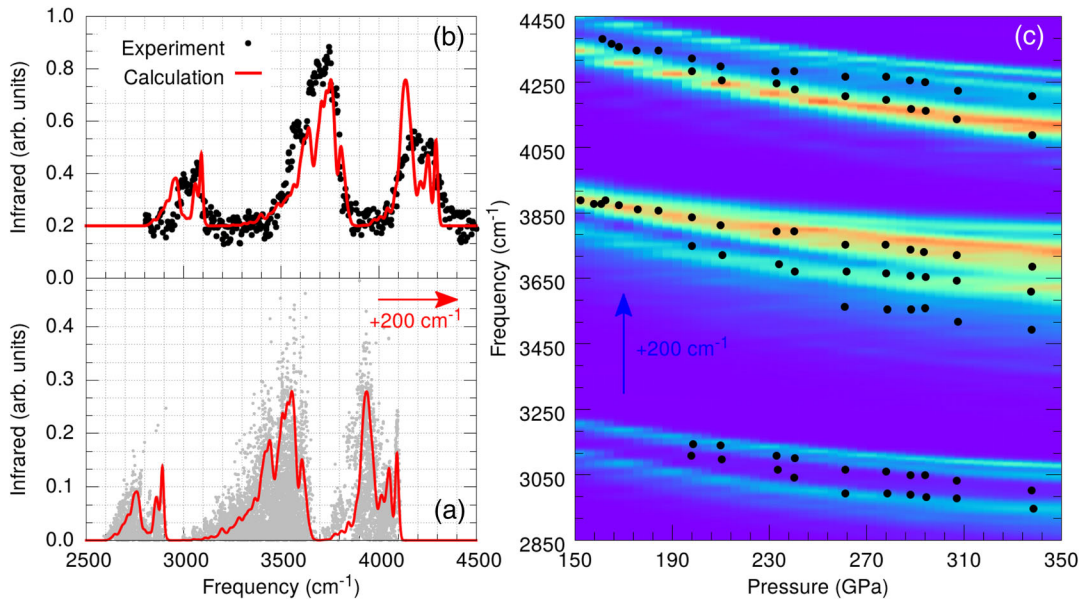
FIG. 4.   Comparison of calculated IR in $C2/c$ mixtures (see also Fig. 2) to the recent raw experimental data [1]. We have removed the Gaussian fits made to the data by Dias *et al.* since this approach is invalid to describe localized modes. Theoretically calculated spectra are systematically some 200 cm^{-1} softer than experimental spectra, due to a combination of errors including neglect of temperature, zero-point effects in calculated pressure, calibration of the experimental pressure, and choice of exchange-correlation functional [7,10,28]. (a) $C2/c$ spectra at 300 GPa from 3000 randomized samples: gray dots are individual modes, and the red line is a histogram. (b) Comparison of the calculations to the digitized experimental data at 307 GPa [1,31]. (c) Color map showing the calculated pressure dependence of the IR intensity compared to the equivalent experimental data [1].

The central result from the calculations is that the different appearance of the IR spectra in isotopic mixtures compared to pure elements is a consequence of mode localization rather the different crystal structures.

We now compare our results to the recent experiments reported by Dias *et al.* For convenience the main data from that paper are reproduced in Supplemental Material. Consistent with previous studies of pure H_2 and D_2 and free-energy calculation assuming the $C2/c$ structure, they report the onset of phase III around 150 GPa. The observed IR spectrum (see Supplemental Material [1,27]) is consistent with our lattice dynamics [Fig. 1(c)] assuming mass scaling appropriate for HD molecules.

At around 200 GPa, Dias *et al.* report a change in the IR spectra with new peaks appearing at frequencies consistent with phase III of H_2 and D_2. Each of these peaks is further split, so they label this phase HD-IV*, while noting that its phase lines are very different to the previously named phase IV and IV'.

We presume that this change is associated with the conversion of $2HD \Leftrightarrow H_2 + D_2$. The equilibrium state has H and D distributed randomly between molecules, consistent with calculations showing negligible dependence of binding energy on isotope ordering [4]. After the transition from II to III, the HD dissociation might occur by lattice rebonding. Previous molecular dynamics calculations in similar layers of phase IV have shown that the isotope-disordered equilibrium can be reached by solid-state molecular rebonding effects on the picosecond time scale, albeit at higher temperatures [29,30], and that the

dissociation rate increases exponentially with pressure as the bond weakens.

To compare our calculated results with experiment, we calculated phonon frequencies and IR intensities at a range of pressures from 3000 isotopically disordered samples based on the $C2/c$ structure. In Fig. 4 we compare experimental data points [1] and calculations without making any assumption about the number of peaks in either case. Our calculations of mixtures in the $C2/c$ phase produce peak splitting in excellent agreement with this data: $Cmca$-12 is significantly worse. Similar analysis has been done across a range of pressures, and by tracing the evolution it is possible to pick out persistent features. Unlike the phonons of pure hydrogen, these peaks all have similar pressure dependence. This surprising result can be traced back to the localization of the modes, and the splitting being due to the nearby environment rather than the long range symmetry. As pressure increases stronger coupling between molecules both broadens the splitting and equalizes the IR activity of the modes, making it possible to resolve the distinct local environments as seen in the HD-PRE phase. The important point is that the improved ability of resolve multiple peaks with increasing pressure does not correspond to a breaking of symmetry or to a structural phase transition.

Thus we propose that observed phases III, IV*, and HD-PRE, all have the same crystal structure, probably $C2/c$ [22] or a closely related structure [25]. The observed changes in the IR spectrum are due to isotopic effects rather than structural change. Free-energy calculations imply that III-IV* involves an isostructural $2HD \Leftrightarrow H_2 + D_2$

equilibration reaction and that only the structure with disordered H and D atoms should appear on the equilibrium phase diagram.

As the thermodynamic equilibrium phase IV* is approached, D_2 molecules form and a peak corresponding to D_2 vibrons is observed. (We note that the experimental sample had a slight excess of hydrogen over deuterium.) The splitting of the IR vibron peaks in IV* is due to different modes and local environments in isotope-disordered $C2/c$, as opposed to the two-layer structure in phase IV, IV', and V.

We have shown that due to mode localization the Raman and infrared spectra of hydrogen-deuterium mixtures are a lot more complex than those of pure isotopes, even for the same crystal structures. Moreover, under pressure the dispersion of phonon bands increases, such that vibron frequencies move further apart. So our main message is that the observation of different numbers of well-resolved peaks does not necessarily indicate a different crystal structure. This applies both to a single system under pressure, where modes have different pressure dependencies (Fig. 2) and when comparing spectra of disordered mixtures to those with a single molecular type.

These effects are sufficient to explain the multiple peaks observed in recent IR data without recourse to new crystal structures [1]. There is no reason to suppose that the equilibrium phase diagram for hydrogen-deuterium mixtures contains any phases other than those observed in pure hydrogen.

Thanks to the richness of the spectra, spectroscopic measurement with the resolution reported by Dias *et al.* on mixtures provides important data that cannot be obtained from pure H_2 or D_2. Although spectroscopy does not provide a conclusive crystal structure determination, in combination with calculation $Cmca$-12 can be ruled out and a layered structure such as with molecules arranged close to hcp such as $C2/c$ remains a favored candidate for phase III [26].

Very recent work reporting cold metallic hydrogen remains controversial [6]; there is no indication about the crystal structure, or even whether the sample is crystalline. This can be addressed with spectroscopy, but as yet no data are available. When it comes, the resolution is likely to be poor and interpretation difficult, and to relate it to candidate crystal structures it will be essential that it is analyzed correctly as we have described. Our work here shows that studies of isotopic mixtures will provide additional information not available from pure hydrogen or deuterium, which will be crucial in finally deciphering how the long-sought Wigner-Huntingdon transition occurs.

Open data and codes for this letter is available at Ref. [32].

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