Iodine molecule modifications with high pressure

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(Dated: May 6, 2020)

Metallization and dissociation are key transformations in diatomic molecules at high densities particularly significant for modeling giant planets. Using X-ray absorption spectroscopy and atomistic modeling, we demonstrate that in halogens, the formation of a connected molecular structure takes place at pressures well below metallization. Here we show that the iodine diatomic molecule first elongates of 0.02 Å up to a critical pressure of \(P_c \approx 7\) GPa developing bonds between molecules. Then its length continuously decreases with pressure up to 20 GPa. Universal trends in halogens are shown and allow to predict for chlorine a \(P_c \approx 47 \pm 5\) GPa for molecular bond-length reversal. Our findings tackle the molecule invariability paradigm in molecular phases at high pressures and may be generalized to other abundant diatomic molecules in the universe, including hydrogen.

Diatomic molecules play a fundamental role in life on Earth and have also a prominent presence in other planetary systems. In fact, for solar Jovian planets, as well as for exoplanets,¹ a key ingredient for the description of their interior is how the structure of diatomic molecules like \(\text{H}_2\) or \(\text{N}_2\) evolves with pressure. From a more fundamental point of view, the study of diatomic molecular systems under high pressure contributes to our global understanding of how chemical bonds are modified with increasing atomic density.² One of the most studied problems concerns the metallization of these molecular solids, which is supposed to occur under sufficiently high pressure. Naturally, the most researched system, and also the most difficult to study, is hydrogen, whose metallization remains the Grail of this field.²quirrel. In solid iodine, similar studies up to 6 GPa were addressed in \(\text{Br}_2\) ¹⁵a,c which showed at 25 GPa a cusp-type evolution of the intramolecular distance with pressure. In solid iodine, similar studies up to 6 GPₐ\(^1⁶\) showed that the intramolecular distance increases with pressure, but no cusp-type evolution was observed. For liquid iodine, the intramolecular distance was observed to increase faster with pressure and finally a dissociation around 1000 K and 4.5 GPa was detected.²²In the present work, we combine XAS experiments and density-functional theory calculations to explore the iodine evolution at higher pressures and ambient temperature. We show that the two heavier halogenes present a similar transitions providing an excellent benchmark to explore particular features in the evolution of diatomic molecules under increasing density.

In particular, halogens constitute the ideal diatomic molecules to answer questions which have not been satisfactorily addressed to date: How do diatomic molecules evolve before dissociation? Are diatomic molecules invariable during their compression in the molecular phases?

So far few studies of molecular systems have addressed this question. Molecules as \(\text{C}_{60}\) fullerenes were shown to slightly deform during compression²⁰ and iodine molecules evolve to different polyanion arrangements when iodine filled carbon nanotubes are submitted to high pressures.²¹ In deuterated water, the D-O bond was shown to increase at a rate of \(4 \times 10^{-4} \) Å GPa⁻¹ during the compression of ice VIII over the range from 2 to 10 GPa.²⁸ With the use of X-ray absorption spectroscopy (XAS) the question of the evolution of the intramolecular bonding with increasing density in a diatomic molecule was addressed in \(\text{Br}_2\) ¹⁵ which showed at 25 GPa a cusp-type evolution of the intramolecular distance with pressure. In solid iodine, similar studies up to 6 GPa ¹⁶ showed that the intramolecular distance increases with pressure, but no cusp-type evolution was observed. For liquid iodine, the intramolecular distance was observed to increase faster with pressure and finally a dissociation around 1000 K and 4.5 GPa was detected.²²In the present work, we combine XAS experiments and density-functional theory calculations to explore the iodine evolution at higher pressures and ambient temperature. We show that the two heavier halogenes present a similar

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FIG. 1. Evolution with pressure of the iodine-iodine distances for the first 12 neighbors through different phases from X-ray diffraction data (filled symbols) and from EXAFS data (hollow symbols). The proposed distance distribution in the modulated incommensurate phase V, as proposed by Ref. 11, is shown by a bar at ∼25 GPa. Numbers in boxes are the coordination numbers. The inset shows the low-pressure Cmca structure of halogens. The light colored atoms are in the second layer. The symbols \( r \), \( r_1 \) and \( r_2 \) represent the intramolecular bond-length, first-neighbor and second-neighbor intermolecular distances, respectively, and \( \theta_1 \), ..., \( \theta_4 \) the angles shown in the figure.

scheme of intramolecular bond evolution with pressure allowing to predict the high pressure behavior of chlorine.

Iodine, bromine and chlorine crystallize at low pressures within the phase I, Cmca structure as shown in the inset of Fig. 1. This is a lamellar structure where each layer is composed of zig-zag chains of diatomic molecules. We denote the intra-chain distance between molecules \( r_1 \) and inter-chain distance as \( r_2 \) as shown in inset of Fig. 1. In halogen crystals, X-ray diffraction studies do not detect any evolution of the intramolecular distance. The latter is found to remain constant (2.7 Å for iodine) up to the emergence of phase V, which is an incommensurate modulated phase. On the other hand, XAS data show a steady increase of the iodine molecular distance, but not cusp-type evolution as observed in bromine. Dissociation of iodine, which is considered as associated to phase II, is preceded by metallization. In fact, the lamellar structure of iodine leads to an anisotropic change of regime in the electrical conduction observed at 13 and 18 GPa, perpendicularly and parallel to layers respectively. High pressure X-ray diffraction and XAS data for iodine can be gathered to provide the evolution with pressure of the different interatomic distances up to the 12th neighbor as shown in Fig. 1.

Bromine follows an analogous scheme of phase transformations as iodine, but taking place at higher pressures. In particular the transition from phase I to phase V is observed at 84 GPa and to the monoatomic phase II at 115 GPa. As mentioned, accurate XAS experiments have shown, in the case of bromine, a cusp-type evolution of the Br–Br intramolecular distance. It is experimentally observed that the intramolecular distance first increases with pressure up to 25±5 GPa at a rate of 2.5 \( \times \) 10\(^{-3} \) Å GPa\(^{-1} \) decreasing then at a slightly lower rate until the phase I instability. Bromine metallization is proposed at about 60 GPa from electrical conductivity experiments. In the following, using also high pressure X-ray absorption experiments, we show that iodine follows a similar cusp-type evolution of its intramolecular distance. We performed 3 different high pressure experiments: a K-edge (\( \sim \)33.1 keV) XAS study using a diamond anvil cell (DAC) pressure apparatus (we will refer to “K-DAC” experiment), a K-edge XAS study using a Paris-Edinburgh press (“K-PE”) and a L\(_I\)-edge (\( \sim \)5.2 keV) using a DAC (“L-DAC”). In addition we performed DFT modeling, which pointed to a similar change of behavior as the one observed experimentally. Details of the experiments, data analysis as well as calculation methodologies.
are provided in the supporting information.

Figures 2(a) and (b) show the XANES part of the iodine spectra as a function of pressure in experiments done at the iodine L_{1} and K-edges for the K-DAC experiment. These two edges allow us to explore the allowed dipolar s–p transitions and to put into evidence the so-called “pre-edge peak”, a prominent peak appearing below the X-ray absorption edge due to the electronic transition from the 1s electrons to unfilled 3p states associated with the σ-antibonding molecular orbitals (σ^{*}). In the following we will refer to that peak as the 1s → 3σ^{*} transition. The width of the pre-edge peak increases with pressure up to ~7-10 GPa decreasing then within the Cmca phase (see supplemental material). A change of the pre-edge peak pressure evolution was also observed in bromine at 25±5 GPa. Because of dipolar selection rules, the structures at the beginning of the iodine K-edge XAS are the projection of the p-density of free states modified by the presence of the 1s core-hole. This pre-edge peak appears well detached from the L_{1} spectra, but due to the shorter core-hole lifetime in K-edge, the pre-edge peak appears in that case embedded in the pre-edge region. The XANES region shows a progressive evolution with pressure of its different resonances pointing out to a progressive phase transition with phase mixture when evolving from phase I to V at ~20 GPa [Fig. 1(b)]. Only the K-edge spectrum taken in phase II (labeled “> 30 GPa”, as the pressure probe was lost at that pressure) shows a very distinct XANES pattern.

High pressure EXAFS data were acquired in the two different K-edge experiments. Figure 2(c) shows the EXAFS oscillations as a function of pressure for the K-DAC experiment and panel (d) plots the pseudo-radial distribution function (PRDF) obtained from the Fourier transform of that same data. The lowest distance peak in the PRDF corresponds to the intramolecular distance. Other interatomic distances are difficult to appreciate in the PRDF at the lower pressures due to the limited photoelectron mean free path, but they can be progressively observed with increasing pressure. Only the spectrum taken in phase II (labeled “> 30 GPa”) shows the disappearance of the initial molecular distance, corroborating the XANES observation of phase mixture between 20 and 30 GPa with presence of phase I.

The EXAFS analysis could only be done on the pure phase, i.e., below 20 GPa for the K-DAC experiment. In the K-PE experiment the maximum pressure reached was of 12.3 GPa and all the data could be analyzed. Different EXAFS fitting protocols were tested. Best fits were obtained when fixing all structural parameters to the ones provided by X-ray diffraction experiments and leaving the intramolecular distance evolution as the only free parameter. Examples of EXAFS data fits are included in the supplemental material. The obtained evolution with pressure of the intramolecular distance showed to be very robust with respect to details of the fitting procedure. The obtained distance evolution for experiments K-DAC and K-PE is shown in Fig. 3(a). We have also included the evolution of the I–I distance of solid iodine from the EXAFS experiments of Ref. 10. All the three experiments agree to show that the iodine molecule first expands by ~0.02 Å up to a pressure of about ~7 GPa. Our data shows that at higher pressure the intramolecular distance contracts and returns to its ambient conditions value at ~20 GPa. The maximum amplitude variation of the intramolecular distance is then of ~1%.

FIG. 3. (a) Evolution with high pressure of the iodine intramolecular distance as obtained by EXAFS. Full circles and squares are from our two distinct experiments. Empty circles are from Ref. 10. (b) Intramolecular distance as a function of the relative volume calculated with DFT. The symbol V_{0} denotes the equilibrium volume of the crystalline cell at ambient pressure.

To obtain more insight on the observed evolution of the molecular distance evolution with pressure, we performed DFT simulations. We calculated the lattice parameters and volume of the iodine Cmca structure with different exchange-correlation and van-der-Waals functionals as shown in Tab. S1. By comparing these results with experiments, we chose the most reliable exchange functional for our calculations (see methods section for more details). The lattice parameters that we calculated at ambient pressure (a = 7.244 Å, b = 4.547 Å and c = 9.745 Å) are in very good agreement with the experimental values of a = 7.103 Å, b = 4.632 Å and c = 9.789 Å giving a calculated volume of 321.02 Å^{3} (322.12 Å^{3} in experiments). The density of the calculated structure is slightly larger than the experimental one and therefore the theoretical pressures were underestimated. In other words, a smaller calculated ambient volume can be rationalized as the theoretical structure was already pre-compressed. A similar effect was also observed for bromine.

For bromine, EXAFS experiment revealed that there was a reversal of the evolution of the intramolecular bond length under pressure at 25±5 GPa. Theoretical simulations observed a similar effect at about 7 GPa. In iodine, our experiments show a similar cusp-type behavior at ~7 GPa. To take into account the strong underestimation of this effect by calculations, we performed simulations of iodine in a pressure range from -2 GPa to 20 GPa. Here negative pressures means that the atomic volume
FIG. 4. (a) Comparison of intramolecular distance as a function of pressure for iodine (filled symbols) and bromine (empty symbols) as obtained from EXAFS experiments. The bromine data are from Refs. 3 and 10. (b) Variation of the intramolecular distance with respect to the corrected scaled volume. The gray bar indicates the location of the critical value, $\tilde{V}_c$. (c) Variation of the corrected scaled volume as function of pressure for iodine, bromine and chlorine. For chlorine The equation of state (EOS) function which presented in Ref. 15 was used to predict the variation of the intramolecular distance (more detailed information can be found in the supplemental material Ref. 26). Vertical lines correspond to pressures for the cusp transition, $V_{cusp}^\text{I} = 1.53$ and to the metallization transition, $V_{cusp}^\text{metal} = 1.37$. (d) The charge density difference plots of Cmca phase of iodine at selected pressures with respected to values of -1 GPa.

is expanded with respect to the volume at atmospheric pressure, $V_0$. The obtained evolution of the atomic volume agrees perfectly with X-ray diffraction data, with all calculated intermolecular distances decreasing with pressure. Figure 3(b) shows the intramolecular bond length as a function of the relative volume $V/V_0$. We observe an anomalous evolution of this quantity which also shows a cusp-type profile, but with a lower amplitude when compared with experiments. The peak of the intramolecular bond length is found at around -0.5 GPa which corresponds to $V/V_0 \sim 1.03$.

In Fig. 4(a) we compare our experimental result for the evolution of the iodine intramolecular distance with pressure with the one for bromine. We observe that both iodine and bromine follow a similar pattern. The pressure slopes are comparable for the two halogens but change sign at $P_c \sim 7$ GPa for iodine instead of 25 GPa for bromine. In both cases, the intramolecular distances increase with pressure at a rate of 3.0 (0.5) $10^{-3}$ Å/GPa$^{-1}$ up to $P_c$ and then decreases at a lower rate of 1.5-2.0 $10^{-3}$ Å/GPa. We show in Fig. 4(b) the variation of the atomic volume $V$ for bromine and iodine in the Cmca phase with respect to the scaled volume $\tilde{V}$. The scaled volume is defined as $\tilde{V} = V/(r^3)$, following Ref. 13 where $r$ is the intramolecular length. In our case, we have corrected the scaled volume to take into account the measured pressure dependence of iodine and bromine intramolecular bond-lengths. As shown in Fig. 4(b), when plotting the intramolecular distance variation in iodine and bromine against the corrected scaled volume, we observe that they peak at the same value, which we estimate graphically at $\tilde{V}_{cusp} = 1.53 \pm 0.05$. We use this value to make an estimation of $P_c$ for chlorine. We have then included in Fig. 4(c) the evolution of the chlorine $\tilde{V}$ calculated from the atomic volume of Ref. 15. We estimated chlorine $\tilde{V}$ by finding out the change of the molecular bond-length which allows for a common scaled critical volume at metallization, $V_{cusp}^\text{metal}$, for the three halogens matching experimental values (see S.I. for details). This leads on one side to an estimate of the corresponding intramolecular cusp pressures in I$_2$, Br$_2$ and Cl$_2$ of respectively 7 GPa (fixed from our results), 27.5 GPa and 47±5 GPa for $V_{cusp}^\text{I} = 1.53 \pm 0.05$ and to respective metallization pressures of 14 GPa, 57 GPa and 200 GPa (this last fixed from Ref. 15 corresponding to $V_{cusp}^\text{metal} = 1.37 \pm 0.02$). We obtain for Chlorine a pressure rate of change of the intramolecular bond up to the cusp pressure of 2.0(0.5) $10^{-3}$ Å/GPa. This value is lower than the pressure rate of change for iodine and bromine (3.0(0.5) $10^{-3}$ Å/GPa) consistently with the lower intramolecular distance of Cl$_2$ (1.99 Å) as compared with Br$_2$ (2.27 Å) and I$_2$ (2.715 Å). We note that our measured and predicted values of cusp critical pressure correspond to the crossing pressures of the Raman scattering $A_g$(S) and $B_{3g}$(S) zone-center phonon modes which provides robustness to our observations and our prediction for chlorine. In Fig. 5(d) we plot the calculated differential electronic charge density (ECD) in the (100) plane of the Cmca structure, taking as reference the corresponding ECD at -1 GPa. We observe that with increasing pressure the electronic density in the region between the parallel molecules, which corresponds to $r_2$ in Fig. 1, becomes progressively more important. This change is particularly important for the first calculated pressures and is concomitant to weak changes in the valence band electronic density of states (see S.I.), supporting the idea that the pressure-induced dilatation of the I$_2$ molecule may be attributed to a redistribution of the ECD to create intermolecular bonds between parallel molecules and then a connected molecular structure. Similar conclusions were
In conclusion we have shown that the length of the iodine molecule is modified with pressure. With increasing density, the iodine molecule elongates up to a critical pressure of $\sim 7$ GPa within the $Cmca$ phase. From this pressure, the molecule length starts to decrease. The evolution of the scaled volume of I$_2$ and Br$_2$ allows to predict a similar bond-length reversal in the $Cmca$ Cl$_2$ crystal at $47 \pm 5$ GPa. Our atomistic modeling shows that the observed behavior may be attributed to an electron charge redistribution to stabilize in-plane intermolecular bonds leading to a connected molecular structure. This structure appears at pressures well below metallization. The possibility that this observed behavior could be extended to other diatomic molecules including hydrogen, constitutes an open question which may contribute to a better understanding of high density matter in the universe.

ACKNOWLEDGMENTS

J.S. acknowledges the Project Funded by the National Natural Science Foundation of China under Grant No. 11804129 and financial support from the China Scholarship Council. Computational resources were provide by x2016096017 Project of Curie. A.S.M acknowledges support from the PLECE platform of the University of Lyon.

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