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Electronic bonding and optical properties of the H₂-H₂O phase at high pressure

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The electronic structure and the optical properties of the cubic hydrate H₂-H₂O at high pressure are elucidated by means of first-principles local-density calculations. The results are compared with the *Ic* phase of ice. It is shown that the encapsulated H₂ molecules interact weakly with the H₂O network. The valence-band structure is only slightly modified while the conduction band becomes very different. A number of important physical properties including the bulk modulus, optical-absorption spectrum, refractive index, pressure dependence of the gap, etc., are predicted for H₂-H₂O.

Recently, a crystalline phase in the system H₂-H₂O was discovered at a pressure above 2.3 GPa at room temperature by Vos *et al.* using a single-crystal diamond-anvil cell and a combination of Raman scattering and x-ray-diffraction techniques.¹ This clathrate hydrate crystallizes in a cubic phase ($a=6.434$ Å, space group *Fd3m*) closely related to the metastable cubic ice *Ic* ($a=6.35$ Å). The water molecules form a diamond lattice with the H₂ molecules occupying the voids in a 1:1 stoichiometric ratio. The electronic structure and bonding of such a mixture are of great fundamental interest to materials physics and chemistry. It also has profound astrophysical implications, since many such compounds may exist in planetary and interstellar matters at pressure substantially higher than earth's atmospheric pressure.² The behavior of hydrogen at high pressure is highly complicated, and has been a subject of intense research in recent years.³ Ice itself has a very rich phase diagram with more than ten different phases existing under different thermodynamic conditions.⁴ Although much experimental and theoretical work has been done on ice in the past 50 years, surprisingly few band-structure calculations exist. Part of the reason is the presence of proton disorder inherent to many of the ice phases. For ice *Ic*, there are few band calculations using empirical methods.^{5,6} More recently, Lee *et al.* studied the energetics of the high-pressure phase ice *X* with symmetric H bonding via an *ab initio* molecular-dynamics simulation,⁷ and obtained a transition pressure of 49 GPa, rather close to experimental observations.^{8,9} We have recently initiated a study of the band structure and optical properties for *all* ice phases with ordered structures using a first-principles approach.^{10,11}

In this paper, we report a detailed study of the electronic structure and optical properties of the H₂-H₂O phase by means of first-principles local-density calculations within the density-functional theory (DFT).¹² In recent years, the DFT in the local approximation has been quite successful in predicting the ground-state properties of many solids, although

the band gap of an insulator calculated from the bare Kohn-Sham eigenvalues is known to be too small.¹³⁻¹⁵ This is because the DFT is essentially a theory for the ground state. A single exchange-correlation potential is inadequate for an insulating system where it ought to be discontinuous across the band gap.^{14,15} However, quasiparticle calculations¹⁶ indicate that the wave functions for the unoccupied conduction bands (CB's), after including the self-energy correction for the many-particle interaction, differ very little from the local-density-approximation (LDA) result. Thus, meaningful results on the optical properties can still be obtained from the LDA calculation and compared with experimental observations.¹⁷ In the present paper, we compare the result for H₂-H₂O with a parallel calculation on ice *Ic*. We find that the encapsulated H₂ molecules interact weakly with the water sublattice. However, the CB is drastically modified. As a result, the optical-absorption spectra of H₂-H₂O and ice *Ic* are quite different.

We used the self-consistent orthogonalized linear-combination-of-atomic-orbitals (OLCAO) method¹⁷ to calculate the electronic structure. This method is especially suitable for complex systems such as fullerene,¹⁸ alkali-metal-doped fullerenes,¹⁹ as well as complex oxides.¹⁹ The OLCAO method is an all-electron method in which the basis set is expanded in terms of atomic orbitals that are formed by Gaussian-type orbitals (GTO's). To achieve a greater variational freedom in the basis set, we included the excited atomic-state orbitals of H 2*s*, H 2*p*, O 3*s*, and O 3*p* in the basis expansion. The use of an extended basis set is extremely important in obtaining accurate optical results. The Kohn-Sham equation is solved self-consistently. A correlation effect is included via the Wigner interpolation formula.²⁰ The total one-electron potential and the crystal charge density are expressed as sums of atom-centered functionals which are also expressed as combinations of GTO's with coefficients determined numerically. This facilitates the evaluation of multicenter integrals.¹⁷ In the H₂-H₂O calcula-

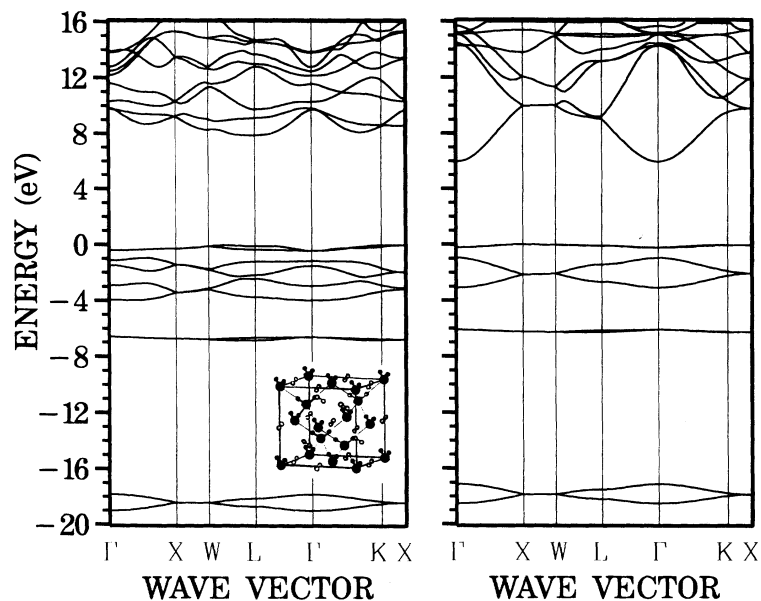


FIG. 1. Band structure of $\text{H}_2\text{-H}_2\text{O}$ hydrate (left panel) and Ic phase of ice (right panel). Inset: sketch of the crystal structure from Ref. 1.

tion, it is necessary to distinguish two types of H in the system, H(1) associated with the water molecule, and H(2), associated with the H_2 molecules in the void space. The orientation of the H_2 molecule in the crystal is probably random but with its center of mass localized in a diamond sublattice interpenetrating with the tetrahedrally bonded H_2O sublattice.¹ We used the structure suggested by Vos *et al.*¹ depicted in the inset of Fig. 1, which turns out to have lower energy than other configurations. The crystal potential and the charge-density distribution are iterated to full self-consistency using eight special \mathbf{k} points in the irreducible portion of the Brillouin zone (BZ). For the density-of-states (DOS) and optical calculations, 89 \mathbf{k} points were used for the BZ sum. The optical-properties calculation includes the full evaluation of all relevant transition-matrix elements between Bloch states at each \mathbf{k} point.

It is necessary to investigate the possible orientations of the H_2 molecules inside the H_2O cage by means of total-energy calculations. We assume three different orientations of the two H_2 molecules in the unit cell. (a) The two H_2 molecules are each along the tetrahedral bonding directions of the O host lattice, so the angle between the two H_2 molecules is 109.5° . (b) The second H_2 molecule is rotated to be parallel to the c axis of the cubic lattice. (c) The second molecule is further rotated to be parallel to the first H_2 molecule. We found configuration (a) has the lowest, and (b) has the highest energy. However, the differences in energy are very small, of the order of 0.02–0.05 eV per molecule. The subsequent band-structure and optical-properties calculations were therefore based on configuration (a) for the H_2 molecular orientations in the unit cell.

Figure 1 shows the calculated bare Kohn-Sham band structures of $\text{H}_2\text{-H}_2\text{O}$ and ice Ic (Ref. 11). $\text{H}_2\text{-H}_2\text{O}$ has an indirect LDA gap of 7.9 eV with the top of the valence band (VB) at a point along the $L\text{-}\Gamma$ direction. The bottom of the CB is at L . The minimum direct gap at L is almost the same as the indirect gap. As noted, the true gap may be somewhat larger. The calculated DOS for $\text{H}_2\text{-H}_2\text{O}$ and its partial com-

ponents are shown in Fig. 2. In the VB region, the molecular-bonding states of H_2 are confined to the -1 - to -4 -eV region. The CB is rather flat and has a mixed character with orbital origin from both the H_2O and H_2 molecules. We shall compare the band structure of $\text{H}_2\text{-H}_2\text{O}$ with that of the Ic phase of ice. Ic has a direct LDA gap of 6.0 eV at Γ . The bottom of the CB is at Γ with a fairly small effective mass. The top of the VB consists of a very flat, doubly degenerate localized band from the nonbonding orbital of O. The same band exists in $\text{H}_2\text{-H}_2\text{O}$ with the degeneracy removed along certain symmetry directions because of weak interaction with the H_2 molecules. The next set of VB's with a width of about 2 eV corresponds to the intramolecular-bonding states between O $2p$ and H(1). The other peaks are the strong O-H(1) bonding levels within the water molecule. Thus the VB structure of Ic is very similar to that of $\text{H}_2\text{-H}_2\text{O}$ while the CB structure is very different. The main effects of inserting H_2 molecules into the tetrahedrally bonded H_2O network can be summarized as follows: (1) introduction of intramolecular levels in the VB region from -1 to -4 eV, (2) complete modification of the lower CB resulting in an enlarged band

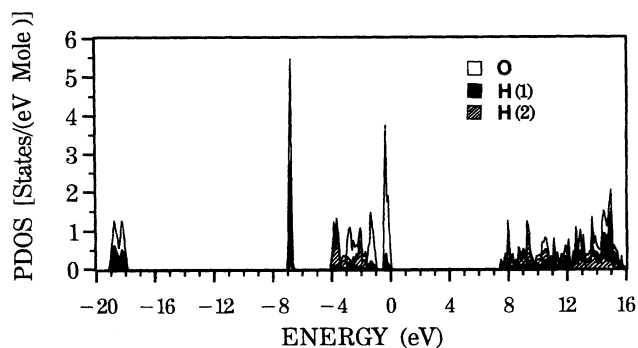


FIG. 2. Total DOS of $\text{H}_2\text{-H}_2\text{O}$. Partial components from H(1), H(2), and O are as indicated.

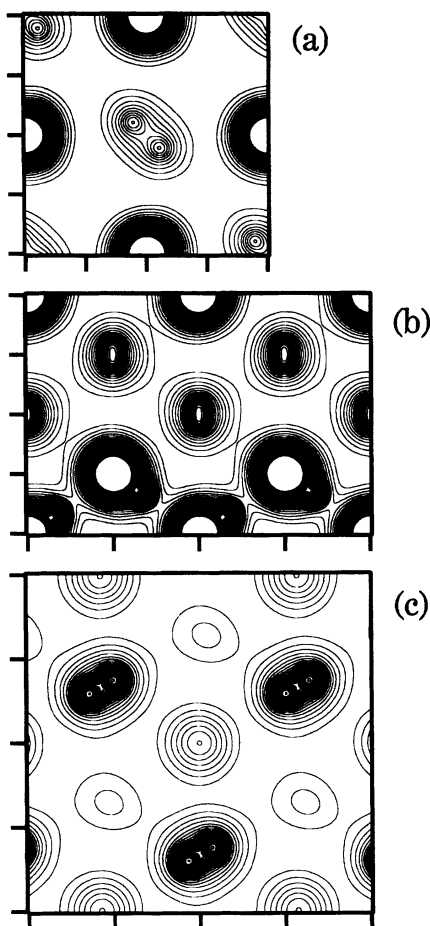


FIG. 3. Charge-density distribution in $\text{H}_2\text{-H}_2\text{O}$ hydrate on (a) [100] plane; (b) [110] plane; (c) [111] plane. Contour lines are from 0.01 to 0.5 by 0.01 in units of electrons/(a.u.)³.

gap and a much reduced electron effective mass, and (3) slight lowering of the intramolecular-bonding levels of O 2*p* and O 2*s* with H(1) in H_2O .

The charge-density distributions of the $\text{H}_2\text{-H}_2\text{O}$ crystal in the [100], [110], and [111] planes are shown in Fig. 3. The [100] plane contains one of the H_2 molecules while the [110] plane contains one of the protons in the H_2O molecule. It is quite clear that the charge density of the H_2 molecule has little overlap with that of O in the H_2O molecule, indicating very weak interaction between the two. The proton in the H_2O molecule only distorts the O charge distribution in the direction of the O-H...O bond. The network type of linkage of the water molecules is evident. The H_2 molecules fill the open spaces and total-energy calculations show only small energy differences for different molecular orientations. This confirms the conjecture¹ that the space filling of the charge density from H_2 molecules is responsible for stabilizing the cubic-crystal structure.

The substantial difference in the CB structures of $\text{H}_2\text{-H}_2\text{O}$ and ice *Ic* should also be manifested in its optical properties. Figure 4 shows the calculated frequency-dependent real and imaginary parts of the dielectric function of $\text{H}_2\text{-H}_2\text{O}$ up to 40 eV. The $\epsilon_2(\omega)$ curve is characterized by a very sharp absorption edge at 7.9 eV with many sharp peaks up to

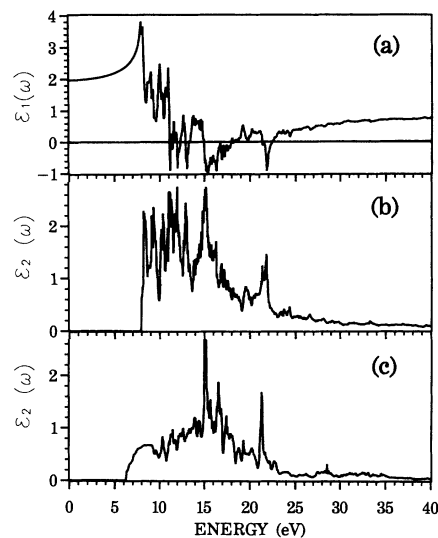


FIG. 4. Calculated real [$\epsilon_1(\omega)$] (a) and imaginary [$\epsilon_2(\omega)$] (b) parts of the dielectric function of the $\text{H}_2\text{-H}_2\text{O}$ hydrate. (c) Calculated $\epsilon_2(\omega)$ of ice *Ic*.

20 eV, and another prominent peak at 21.8 eV. These structures can be easily assigned to band-to-band transitions using Fig. 1. The fact that substantial absorption exists above 20 eV underscores the importance of having accurate high CB states, which can only be obtained if the basis set is sufficiently large. The $\epsilon_2(\omega)$ curve for ice *Ic* is shown in Fig. 3(c) for comparison.¹¹ This spectrum, with its major structure near 15 eV, is qualitatively different from that of $\text{H}_2\text{-H}_2\text{O}$. In fact, the calculated $\epsilon_2(\omega)$ for *Ic* is in good agreement with the experimental data of Kobayashi for ice *Ih*.²¹ *Ih*, or the

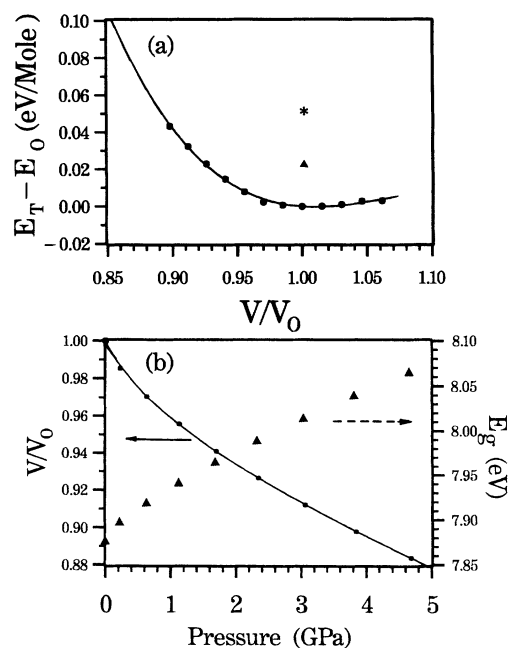


FIG. 5. (a) Total energy vs unit-cell volume of $\text{H}_2\text{-H}_2\text{O}$. The two data points are the calculated total energy at equilibrium volume for the other two configurations of molecular orientations. (b) Change of volume and band gap at *L* with increase in pressure.

ordinary ice, is a proton-disordered phase but with a local bonding structure almost identical to that of *Ic*. However, the optical absorption for *Ih* near the threshold is complicated by the presence of an excitonic level.²¹ Exciton formation in H₂-H₂O is not expected because both the CB and the VB edges are very flat. The calculated static-electronic dielectric constant at zero frequency $\epsilon(0)$ is 1.99 for H₂-H₂O and 1.73 for *Ic*. The calculated refractive index for the two crystals is thus close to 1.41 and 1.32, respectively. The difference in the refractive index between the two crystals is significant since it implies that the presence of the H₂-H₂O phase may be detected by optical means. We have also investigated the dependence of the optical properties of H₂-H₂O on the molecular orientation of H₂. Calculations were repeated for the other two cases of orientations. We found virtually no difference in the $\epsilon(\omega)$ curves, and the difference in the refractive index is less than 0.004. Apparently, the insertion of H₂ molecules into the ice cage changes the CB significantly. But once they are inserted, the orientation of the H₂ molecule has little effect on the CB.

We have also investigated the bulk properties of the H₂-H₂O phase under increased pressure. The total energy of the crystal is calculated as a function of crystal volume *V* under the assumption that the geometry of the H₂O and H₂ molecules remains intact. Any effect of quantum correction is neglected since the crystal is formed at room temperature. Figure 5(a) shows the calculated total energy vs *V*. Also shown are the two calculated data points corresponding to the other two molecular orientations of H₂. We obtained an equilibrium volume V_0 of 262.37 Å³, which is only 1.5% smaller than the experimental value obtained at a pressure of 3.1 GPa.¹ We consider this level of agreement to be excellent, considering the uncertainty in the pressure measurement to be at least 0.2 GPa. By fitting the calculated *E* vs *V*/ V_0 curve to the Murnaghan equation of state,²² we predict a bulk modulus *B* of 24.7 GPa for H₂-H₂O. At this date, there is no

reported experimental value for H₂-H₂O crystal. For ice VII at a high pressure, the reported values for *B* are 23.7±0.9 GPa,²³ only slightly smaller than the predicted values for H₂-H₂O. Figure 5(b) shows the *P*-*V* relationship obtained from Fig. 4(a). Also shown is the pressure dependence of the band gap at *L* in H₂-H₂O. Our calculation predicts that as *P* is increased, the gap value increases nonlinearly. By fitting the data to a quadratic form of $E_g(P) - E_g(0) = \alpha P + \beta P^2$, we have obtained the parameters α and β to be 0.054 eV/GPa and -0.003 eV/GPa², respectively. It is therefore unlikely H₂-H₂O will become metallic at ultrahigh pressure. Hemley *et al.* had shown that for ice VII at ultrahigh pressure of 128 GPa, the band gap remains above the absorption edge of the diamond windows (3.0 eV).²³ However, at such a high pressure, there could be significant rearrangement in both the H₂O and the H₂ molecules that may result in different molecular arrangements, bond lengths, and bond angles, and a concomitant change in the electronic structure.

In conclusion, we have investigated the electronic and optical properties of H₂-H₂O formed at high pressure by means of first-principles local-density calculations. We found that the VB structure closely resembles that of ice *Ic*, but the CB structure is qualitatively different, resulting in different optical properties. The interaction of the H₂ molecule with the water cage is found to be weak. We have also predicted a number of fundamental physical properties of the H₂-H₂O crystal including bulk modulus, refractive index, fundamental gap and its pressure dependence, etc., which may be of crucial importance in the detection of this compound in planetary matters.

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- ¹W. L. Vos, L. W. Finger, R. J. Hemley, and H.-K. Mao, *Phys. Rev. Lett.* **71**, 3150 (1993).
- ²A. H. Delsemme and P. Swings, *Ann. Astrophys.* **15**, 1 (1952); S. L. Miller, *Proc. Natl. Acad. Sci. U.S.A.* **47**, 1798 (1961); J. I. Lunine and D. J. Stevenson, *Astrophys. J. Suppl. Ser.* **58**, 493 (1985).
- ³Ho-Kwang Mao and R. J. Hemley, *Am. Sci.* **80**, 234 (1992).
- ⁴See, for example, N. H. Fletcher, *The Chemical Physics of Ices* (Cambridge University Press, London, 1970); also, *Physics and Chemistry of Ice*, edited by E. Whalley, S. I. Jones, and L. W. Gold (Royal Society of Canada, Ottawa, 1973).
- ⁵G. P. Parravicini and L. Resca, *Phys. Rev. B* **8**, 3009 (1973); L. Resca and R. Resta, *Phys. Status Solidi B* **81**, 129 (1977).
- ⁶M. Zaider, D. E. Orr, and J. L. Fry, *Nucl. Tracks Radiat. Meas.* **16**, 159 (1989).
- ⁷C. Lee, D. Vanderbilt, K. Laasonen, R. Car, and M. Parrinello, *Phys. Rev. Lett.* **69**, 462 (1992); *Phys. Rev. B* **47**, 4863 (1993).
- ⁸K. R. Hirsch and W. B. Holzapfel, *J. Chem. Phys.* **84**, 2771 (1984).
- ⁹A. Polian and G. Grimsditch, *Phys. Rev. Lett.* **52**, 1312 (1984).
- ¹⁰Lichi Liu and W. Y. Ching, *Bull. Am. Phys. Soc.* **47**, 576 (1993).
- ¹¹W. Y. Ching, Lichi Liu, and Y.-N. Xu, *Ferroelectrics* **153**, 25 (1994).
- ¹²W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965); L. J. Sham and W. Kohn, *ibid.* **145**, 561 (1966).
- ¹³S. B. Trickey, F. R. Green, and F. W. Averill, *Phys. Rev. B* **8**, 4822 (1973).
- ¹⁴J. P. Perdew and M. Levy, *Phys. Rev. Lett.* **51**, 1884 (1983).
- ¹⁵L. J. Sham and M. Schlüter, *Phys. Rev. Lett.* **51**, 1888 (1988).
- ¹⁶M. S. Hybertsen and S. G. Louie, *Phys. Rev. B* **34**, 5390 (1986).
- ¹⁷See, for example, W. Y. Ching, *J. Am. Ceram. Soc.* **73**, 3135 (1990).
- ¹⁸W. Y. Ching, M.-Z. Huang, Y.-N. Xu, W. G. Harter, and F. T. Chan, *Phys. Rev. Lett.* **67**, 2045 (1991); W. Y. Ching, M.-Z. Huang, Y.-N. Xu, and F. Gan, *Mod. Phys. Lett. B* **6**, 309 (1992); Y.-N. Xu, M.-Z. Huang, and W. Y. Ching, *Phys. Rev. B* **46**, 223 (1992).
- ¹⁹M.-Z. Huang, Y.-N. Xu, and W. Y. Ching, *J. Chem. Phys.* **96**, 1648 (1992); Y.-N. Xu, M.-Z. Huang, and W. Y. Ching, *Phys. Rev. B* **44**, 13 171 (1991); **46**, 6572 (1992); **47**, 8249 (1993).
- ²⁰E. P. Wigner, *Phys. Rev.* **46**, 1002 (1934).
- ²¹K. Kobayashi, *J. Phys. Chem.* **87**, 4317 (1983).
- ²²F. D. Murnaghan, *Proc. Natl. Acad. Sci. U.S.A.* **30**, 244 (1944).
- ²³R. J. Hemley, A. P. Jephcoat, H. K. Mao, C. S. Zha, L. W. Finger, and D. E. Cox, *Nature* **330**, 737 (1987).

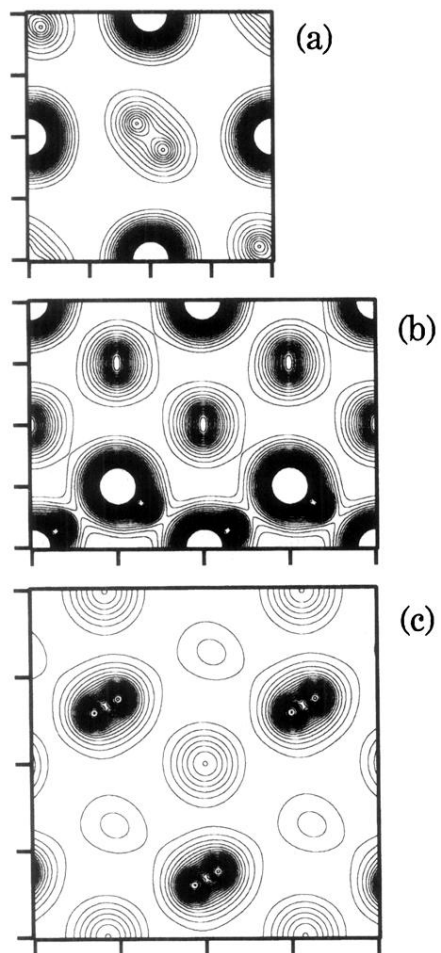


FIG. 3. Charge-density distribution in H₂-H₂O hydrate on (a) [100] plane; (b) [110] plane; (c) [111] plane. Contour lines are from 0.01 to 0.5 by 0.01 in units of electrons/(a.u.)³.