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InOH: A Quantum Chemical Study

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The structure and energetics of the InOH molecule were thoroughly studied using higher level ab initio and density functional theories for the first time. The bond angle, θ(InOH), and harmonic vibrational frequency, ν_2 (bending), calculated using a 6-311++G(2d,2p) basis set were in good agreement with recent experimentally determined values. The use of triple-ζ plus double polarization with diffusion function basis set was required to reproduce the experimental values. The bent structure of the InOH molecule is energetically more stable than the linear structure. Because the energy difference between the two structures is very small, 0.22 and 0.20 kcal/mol using the QCISD(T) and CCSD(T) levels, respectively, the shape of the molecule might best be characterized as quasilinear. This finding is consistent with the potential energy curve being flat when the relative energy is plotted as a function of θ. The linear structure has one imaginary frequency corresponding to its bending mode. The bond dissociation energies, D_o(In−OH), of 4.33 and 4.32 eV obtained using the QCISD(T) and CCSD(T) levels, respectively, are greater than that for many alkali and alkaline-earth hydroxides. The predicted HInO isomer is less stable than the InOH molecule by 59.2 kcal/mol, at the QCISD level.

1. Introduction

The InOH molecule has been studied experimentally[1−4] and its importance in semiconductor-surface technology has been discussed in recent years.[3] It plays a key role in the H-induced removal of In_2O_3 from the surface-oxide layer of InP-semiconductor substrates.[3] It has also been previously studied in flames[5] and in low-temperature matrixes.[6,7]

The gas-phase study of Lakin et al.[1] revealed that the InOH molecule has a bent structure with θ(In−O−H) of 132°, and there is a strong indication of quasilinearity in its ground electronic state, which complicates the interpretation somewhat for the value determined for ν_2 (bending). They measured 378 cm^{-1} for ν_2 (bending), compared with 422 cm^{-1} from a previous report.[6]

Because the structure and other important properties of the transient InOH molecule are not clear and no theoretical study has yet been done, we investigated both the linear and bent structures of InOH. The present investigation includes (i) the equilibrium geometry, (ii) the relative energy, (iii) a potential energy curve, (iv) a vibrational frequency analysis, (v) the bond energy, and (vi) the existence of the HInO isomer.

2. Computational Details

The structure and harmonic vibrational frequencies were calculated using MP2, MP3, and MP4(SDQ) levels in ab initio theory and the following three hybrid density functionals, B3LYP, B3P86, and B3PW91, in density functional theory. These three hybrid density functional methods are a combination of Becke's three-parameter exchange functional (B3)[8] with three different correlation functionals: LYP,[9] P86,[10] and PW91.[11] These combinations make the B3LYP, B3P86, and B3PW91 hybrid DFT methods. Both QCISD[12] and CCD[13] higher levels of theories have also been used to obtain the accurate structure and vibrational frequencies. The frequencies were calculated by taking analytical second derivatives using MP2 theory and through single numerical differentiation of the first analytical derivatives in the other theoretical approaches. In all the calculations we used valence triple-ζ plus polarization (TZ+P) with a relativistic effective core potential (RECP) for the In atom while the following basis sets, Dunning Huzinaga[14] standard DZ+P, 6-311++G(d,p), 6-311++G(2d,2p), and 6-311++G(3d,2p), were used for O and H atoms. The valence basis set of the RECP of Wadt and Hay[15] with the outer ns^2np^1 explicitly treated with the recommended triple-ζ was used.[16,17] The polarization function was obtained from Huzinaga's data.[18]

We obtained the relative energy, ΔE ($E_{\mathrm{linear}} - E_{\mathrm{bent}}$), with a zero-point energy (ZPE) correction in all the above-said levels. In addition, CCSD//CCD,[19−22] CCSD(T)//CCD,[12] and QCISD(T)//QCISD[12] levels of theory were used to obtain accurate ΔE values. To analyze the bending nature of the InOH molecule, we draw the potential-energy curve (PEC), where the relative energy is plotted as a function of θ(In−O−H), using the MP2 level of theory with 6-311++G(2d,2p) basis sets for the O and H atoms. The dissociation energy, D_o(In−OH), was calculated using the QCISD(T)//QCISD, CCSD(T)//CCD, B3LYP, B3P86, and B3PW91 levels with the ZPE correction. Because InOH exists at elevated temperatures where isomers may also be present, we considered the HInO structure. In the above ab initio theories, all electrons (except the In inner shell electrons) were included in the correlation effect. For this purpose we used FULL key word. All calculations were performed using Gaussian 94[23] on an NEC SX-4 supercomputer.

3. Results and Discussions

(i) Geometry. The study of Vacek et al.[24] shows that the structure of metal monohydroxides is highly dependent on the basis sets and the ab initio approaches used. In the present

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TABLE 1: Bond Angle, θ(InOH) in Degrees[a]

theory	DZ+P	6-311++G-(d,p)	6-311++G-(2d,2p)	6-311++G-(3d,2p)
MP2	148.4	152.4	135.1	141.4
MP3	150.6	153.2	137.4	144.1
MP4(SDQ)	150.6	153.3	135.0	140.7
CCD	148.8	152.1	136.5	141.9
QCISD	149.2	151.1	135.0	141.0
B3LYP	161.2	180.0	140.7	140.0
B3P86	152.2	180.0	138.6	138.3
B3PW91	150.7	180.0	137.4	138.2

[a] Basis sets indicated are for O and H atoms. For In, ECP with the TZ+P basis set was used. [b] The experimentally determined bond angle is 132°.[1]

TABLE 2: Bond Length, *R* in Angstroms, Angle, θ in Degrees, for Linear and Bent Structures of the InOH Molecule[a]

	linear		bent		
theory	*R*(In−O)	*R*(O−H)	*R*(In−O)	*R*(O−H)	θ(InOH)
MP2	1.920	0.951	1.951	0.955	135.1
MP3	1.905	0.943	1.933	0.947	137.4
MP4(SDQ)	1.916	0.948	1.947	0.953	135.0
CCD	1.911	0.945	1.938	0.949	136.5
QCISD	1.914	0.947	1.945	0.952	135.0
B3LYP	1.918	0.953	1.942	0.956	140.7
B3P86	1.913	0.952	1.940	0.955	138.6
B3PW91	1.915	0.952	1.944	0.955	137.4

[a] Basis sets are ECP with TZ+P for the In atom and 6-311++G(2d,2p) for the O and H atoms.

investigation we incorporated a variety of basis sets and a number of level of theories in order to obtain the most reliable structure. Calculated θ(InOH) values are summarized in Table 1.

From Table 1 it is clear that θ is more dependent on the basis sets than on the level of theories in ab initio. With the DZ+P basis set, nearly all the theories predict a θ(InOH) value around 150°, while the experimentally determined value is 132°.[1] With the 6-311++G(d,p) basis set, the θ value increased by about 2−4°. The use of an additional d function on oxygen and p function on hydrogen improved the agreement with experiment, yielding a θ(InOH) of 135° with both the MP4 and the QCISD levels. A further extension of the basis set, however, increased the bond angle. Due to the more flexibility and higher electronegativity of oxygen, the use of a basis set of triple-ζ quality with double polarization and diffusion functions was required to obtain a realistic structure for the metal hydroxides. One should be very careful, however, when using additional d functions on oxygen because this increases the flexibility by expanding the polarization space around oxygen, thereby yielding erroneous results, especially for molecules with flat potential-energy surfaces. It should be emphasized that there is no bent structure indicated for InOH when density functional calculations are carried out using a 6-311++G(d,p) basis set.

Table 2 shows the geometrical parameters of both structures for the InOH molecule, calculated at different levels of theory using a 6-311++G(2d,2p) basis set for oxygen and hydrogen. The values calculated using the MP2, MP4(SDQ), and QCISD levels are similar, whereas the values obtained using the MP3 and CCD levels differ from the former three. The θ(InOH) value calculated from MP3 differs from that determined using QCISD by 2.4°. Among the results determined from the three hybrid density functional approaches, the θ(InOH) calculated from the B3PW91 functional agrees with that from ab initio methods. Finally, the structure obtained using the QCISD level is *R*(In−O) = 1.945 Å, *R*(O−H) = 0.952 Å, and θ(In−O−H) = 135°.

TABLE 3: Energy Difference, ΔE in kcal/mol, between the Linear and Bent Structures of InOH Calculated at Various Levels of Theory[a]

	DZ+P		6-311++G(2d,2p)	
theory	before ZPE	after ZPE	before ZPE	after ZPE
MP2	0.12	−0.14	0.45	0.11
MP3	0.09	−0.15	0.40	0.05
MP4(SDQ)	0.11	−0.12	0.50	0.14
CCD	0.12	−0.14	0.46	0.09
CCSD	0.12	−0.14	0.50	0.14
QCISD	0.11	−0.15	0.51	0.15
CCSD(T)	0.13	−0.13	0.57	0.20
QCISD(T)	0.12	−0.14	0.59	0.22
B3LYP	0.03	−0.12	0.28	−0.06
B3P86	0.06	−0.19	0.34	−0.01
B3PW91	0.08	−0.17	0.38	0.02

[a] Basis sets used are ECP with TZ+P for the In atom and DZ+P and 6-311++G(2d,2p) for the O and H atoms.

(ii) Relative Energy. The calculated energy differences (ΔE) between the linear and bent structures are presented in Table 3. The ΔE values are very small. The calculations using the DZ+P basis set reveal that the bent structure is more stable than the linear one when the ZPE correction is not made. However, with the ZPE correction the linear structure is the more stable of the two by approximately 0.15 kcal/mol, regardless of which theoretical approach is used. On the other hand, the experimentally determined results indicate that the InOH has a bent structure. This discrepancy is attributable to the lack of reliability of the harmonic ZPE correction when used with small basis sets. This finding indicates that the ZPE correction should be applied to the total electronic energy with extreme caution in instances where the PEC is flat.[25] As noted earlier, the DZ+P basis set does not permit an adequate description of the structure of the InOH molecule.

The calculation using a 6-311++G(2d,2p) basis set, on the other hand, yields a more reliable θ; the ΔE values favor a bent structure. Even with the ZPE correction, the bent structure is the more stable, in agreement with the experimentally determined result. The addition of another d function to the oxygen atom decreases ΔE; therefore, some levels predict a more stable linear structure when the ZPE correction is used. As a point of interest, because the density functionals are independent of the size of the basis set, calculations using the two larger basis sets produce similar ΔE values.

As anticipated,[12] the inclusion of triples with QCISD and CCSD levels increases the ΔE value. The barrier to linearity is 0.22 and 0.20 kcal/mol using the QCISD(T) and CCSD(T) levels, respectively, with a 6-311++G(2d,2p) basis set. Among the three DFT functionals, the B3PW91 is the only one that predicts a more stable bent structure.

(iii) Potential Energy Curve. To understand the nature of the bending in InOH, we plotted the potential energy curve of InOH (see Figure 1). The curve is almost flat in the region between 110° and 180° where the energies are almost the same. As a result, the structure of the InOH molecule can move freely between linear and bent. The energy difference between the linear and bent structures is also very low, as in the AlOH molecule.[24,26] Thus, there is compelling evidence that InOH exists as a quasilinear molecule despite its bent equilibrium structure. This is consistent with the suggestion of Vacek et al.[24] that if the electronegativity of an atom is between 1 and 2.2 (that of In is 1.78), it may form quasilinear hydroxides, as happens with AlOH[27] and MgOH.[28]

(iv) Vibrational Frequencies. The calculated vibrational frequencies for the bent InOH structure are summarized in Table

TABLE 4: Harmonic Vibrational Frequencies, ν, of the InOH Molecule[a]

	MP2		QCISD		B3PW91		
mode	DZ+P	6-311++G(2d,2p)	DZ+P	6-311++G(2d,2p)	DZ+P	6-311++G(2d,2p)	expt
ν_2 bending	216	301	218	332	198	305	378[b] 422[c]
ν_3(In-O) (str)	560	522	557	527	555	523	542[b] 523[c]
ν_1(O−H) (str)	4015	3943	4034	3978	3985	3941	

[a] Basis sets used are ECP with TZ+P for the In and DZ+P and 6-311++G(2d,2p) for the O and H atoms. [b] Values taken from ref 1. [c] Values taken from ref 5.

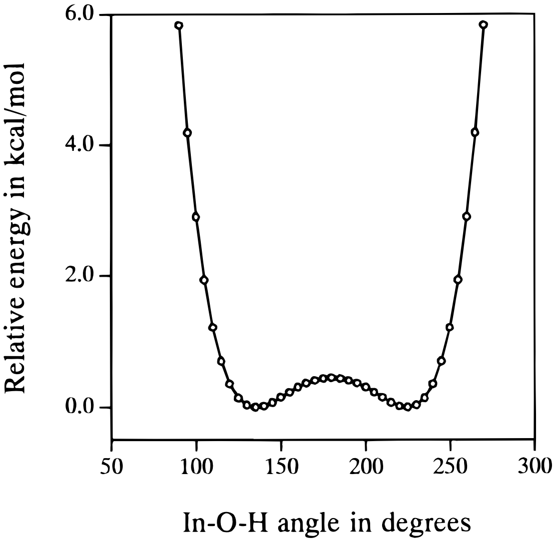

Figure 1. Potential energy curve with respect to In−O−H angle at MP2.

4. The bending mode obtained with a 6-311++G(2d,2p) basis set is relevant to the experimental value. The values for ν_3, the In−O stretching mode, obtained using all of the calculational methods, are close to the recent experimentally determined value of Lakin et al.[1] The O−H stretching frequency, not available in the experimental study because of its weak intensity, is listed in Table 4. In most of the calculations, an imaginary frequency (examples of which are 197i and 202i calculated using the MP2 and QCISD methods, respectively, with a 6-311++G(2d,2p) basis set) was found for the linear structure. The transition-state vectors indicate a bent mode.

(v) Bond Energy. The bond energy, D_o, and bonding behavior for InOH were studied. The bond energies calculated by five levels of theory, each including the ZPE correction and using a 6-311++G(2d,2p) basis set, are 4.33 (QCISD(T)), 4.32 (CCSD(T)), 4.44 (B3LYP), 4.49 (B3P86), and 4.34 eV (B3PW91). These values agree with the dissociation energy of LiOH (4.64) and are greater than those of the following metal hydroxides: NaOH (3.51), KOH (3.61), RbOH (3.58), CsOH (3.78), and MgOH (3.31), all in electronvolts.[29]

To characterize the nature of the bonding between the metal atom and the OH group in metallic hydroxides, we calculated the atomic charges (q_c) using a natural population analysis scheme.[30] For comparison, q_c values were calculated for BOH, BeOH, AlOH, LiOH, and NaOH, along with InOH, using the QCISD/6-311++G(2d,2p) level (Figure 2). The calculated atomic-charge distributions are in the order $(B)^{0.561}(OH)^{-0.561} < (Al)^{0.868}(OH)^{-0.868} < (In)^{0.892}(OH)^{-0.892} < (Be)^{0.942}(OH)^{-0.942} < (Li)^{0.979}(OH)^{-0.979} < (Na)^{0.993}(OH)^{-0.993}$. Linearity increases with ionic bonding in the same sequence. These values indicate that the bonding between the metal atom and the hydroxide group is partially covalent in AlOH, InOH, and BeOH. It is evident from Figure 2 that the smaller the bond angle, the more covalent the bond; the larger the bond angle, the more ionic the bond. Therefore, one may conclude that although the AlOH and InOH molecules have strong ionic bonds between the metal and the OH group, there is some covalent character present, thus accounting for their quasilinearity.

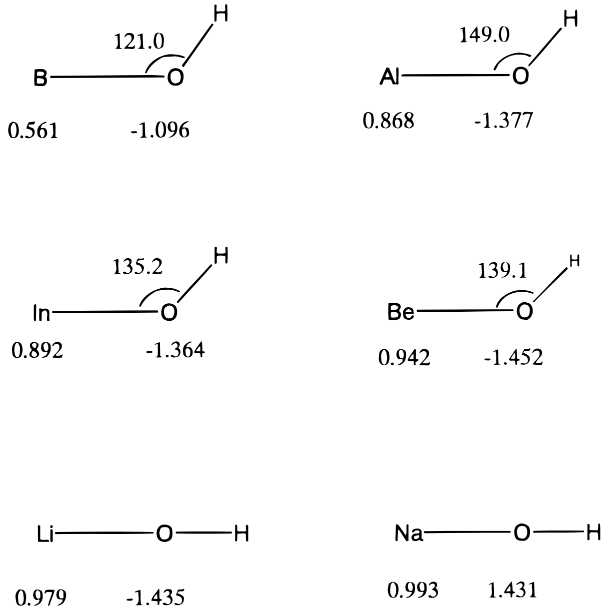

Figure 2. Bond angles in degrees and NPA charges in atomic units calculated using the QCISD/6-311++G(2d,2p) level of theory.

(vi) HInO Isomer. HInO, which is a structural isomer of the InOH molecule, may exist at high temperatures. In the HInO isomer, the In 5s electron would likely be involved in bonding, and the electronic transition (hybridization) should, therefore, occur at much higher energies. Vacek et al.[24] concluded that HAlO should be observable because of its kinetic stability with respect to isomerization. For this reason, we considered the likelihood of HInO's existence using the various levels of theory with a 6-311++G(2d,2p) basis set. The energy differences calculated between the bent InOH and HInO structures are 52.5 (MP2), 59.2 (QCISD), 56.6 (B3LYP), 58.7 (B3P86), and 58.9 (B3PW91) kcal/mol, a small enough difference to permit the existence of HInO. The calculated bond lengths for HInO are $R(\mathrm{In-H}) = 1.691$ Å and $R(\mathrm{In-O}) = 1.794$ Å at the QCISD level. In the case of AlOH, the HAlO isomer is less stable than the AlOH isomer by about 40.5 kcal/mol.[24] Thus, in many respects, one would expect the InOH and AlOH systems to exhibit similar behaviors.

4. Conclusions

The structure and energetics of the InOH molecule were studied using advanced ab initio and hybrid density functional theories along with reliable basis sets. The results obtained using a 6-311++G(2d,2p) basis set are in good agreement with recent experimental studies. The minimum energy structure of the InOH molecule is bent (135°), and the energy barrier between the more stable bent structure and the linear structure is very small, around 0.2 kcal/mol. The use of triple-ζ plus double polarization and diffusion function quality basis sets was essential in obtaining the structure of the metal hydroxide whose PEC is flat. Because of the small energy difference and flat PEC, it is very likely that the molecule is quasilinear and thus is more flexible. The linear structure has one imaginary frequency corresponding to bent-mode vectors, making it a transition state. Our results suggest some covalent character in the ionic bond between the In atom and the OH radical. The HInO structure may coexist with the InOH structure.

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