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# Blue- and Red-Shifting CH $\cdots$ O Hydrogen Bonded Complexes between Haloforms and Ethers: Correlation of Donor $\nu_{\text{C-H}}$ Spectral Shifts with C–O–C Angular Strain of the Acceptors

Anamika Mukhopadhyay, Prasenjit Pandey, and Tapas Chakraborty\*

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

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In 1:1 CH $\cdots$ O hydrogen bonded complexes between haloforms and ethers, a correlation of the spectral shifts of  $\nu_{\text{C-H}}$  bands ( $\Delta\nu_{\text{C-H}}$ ) of the donors (haloforms) with C–O–C angular strain of the acceptors (ethers) is investigated by the electronic structure theory method at the MP2/6-311++G\*\* level. The calculation predicts that the three-member cyclic ether (oxirane) that has the smallest C–O–C angle induces a much larger blue shifting effect on  $\nu_{\text{C-H}}$  transition of fluoroform compared with that by the open chain analogue, dimethyl ether. The natural bond orbital (NBO) analysis reveals that the effect originates because of higher “s” character in the hybrid lone electron pair orbital of the oxygen atom of the former, which is responsible for a smaller contribution to  $n(\text{O}) \rightarrow \sigma^*(\text{C-H})$  hyperconjugation interaction energy between the donor–acceptor molecules. The optimized structures of the two complexes are largely different with respect to the intermolecular orientational parameters at the hydrogen bonding sites, and similar behavior is also predicted for the two chloroform complexes. Partial optimizations on a series of structures show that the total binding energy of the complexes are insensitive with respect to those geometric parameters. However, the  $\Delta\nu_{\text{C-H}}$ , hyperconjugation interaction energies and hybridization of the carbon-centric bonding orbital of the C–H bond are sensitive with respect to those parameters. The predicted  $\Delta\nu_{\text{C-H}}$  of each complex is analyzed with respect to the IR spectral shift measured by van der Veken and coworkers in cryosolutions of inert gases.<sup>27,31,32</sup> The disagreement found between the measured and calculated IR shifts is interpreted to be the outcome of deformation of the complex geometries along shallow binding potential energy surfaces owing to solvation in the liquefied inert gases.

## 1. Introduction

Structure and spectroscopic properties of the molecular complexes stabilized by CH $\cdots$ O hydrogen bonds (HBs), where weakly acidic C–H groups are HB donors and electronegative oxygen atoms of various functional groups are HB acceptors, have been extensively discussed in recent literature.<sup>1–15</sup> Energetically although such HBs are much weaker compared with their classical X–H $\cdots$ Y counterparts, where both X and Y are electronegative elements, collectively, the former types are found to be important in determining the structure of biological macromolecules as well as synthetic supramolecular assemblies.<sup>16–22</sup> To understand the properties of such noncovalent weak bonds, a number of dimeric model complexes have been investigated by different vibrational spectroscopy as well as electronic structure theory methods.<sup>1–15,23–39</sup> An intriguing spectroscopic feature of these weak H-bonded complexes, reported in many cases in recent years, is the blue-shifting of the donor C–H stretching ( $\nu_{\text{C-H}}$ ) fundamentals with concomitant lowering of the transition intensities.<sup>23,27,31,32,37</sup> Enhancement of the transition intensities with blue-shifting are also reported in a few cases,<sup>39</sup> and these features contrast the well-known generic properties of the H-bonded complexes where red-shifting of X–H (donor) stretching frequency occurs with enhancement in infrared ( $\nu_{\text{X-H}}$  transition) intensity.<sup>40</sup> Although no direct relationship has been established, so far correlating the extent

of  $\nu_{\text{C-H}}$  blue-shifting with the binding energies of C–H $\cdots$ O complexes, electronic structure calculation predicts a correlation of the shifts with shortening of the C–H covalent bond length,<sup>6,8,9,27,31,32,34</sup> and in this sense, the behavior appears to be opposite to what happens in the case of classical X–H $\cdots$ Y-type HBs, where complex formation leads to elongation of X–H covalent bonds with enhancement of transition intensities.<sup>40</sup>

In a recent paper, we reported identification of 1:1 C–H $\cdots$ O HB complexes of chloroform (HB donor) with several small cyclic ketones (HB acceptor) in CCl<sub>4</sub> solution at room temperature.<sup>39</sup> The complex formation was probed by measuring the spectral blue shifting of  $\nu_{\text{C-H}}$  band of chloroform using infrared spectroscopy. It was observed that the shifts depend systematically on ring size of the cyclic ketones. The extent of shift decreases with the increase in size of the cyclic ketone rings. Electronic structure calculations performed both at density functional theory (DFT) as well as MP2 levels also predict that the proton affinity of the cyclic ketones bears a correlation with the ring size, and it increases monotonically from cyclobutanone to cyclohexanone, that is, with release of the angular strain at the carbonyl functional group. The goal of the present article is to show that if ethers are used as HB acceptors, the spectral shifts of the haloform  $\nu_{\text{C-H}}$  transitions in 1:1 complexes also depend on the C–O–C angular strain of the ethers. We also show that the values of  $\Delta\nu_{\text{C-H}}$  depend very sensitively on relative orientation between two complexing molecular partners at the HB site on very flat binding potential energy surfaces.

\* To whom correspondences should be addressed. Tel: +91 33 2473 4971 ext. 470. Fax: +91 33 2473 2805. E-mail: pctc@iacs.res.in.

**TABLE 1: Comparison between the Observed and Predicted Spectral Shifts of the Two Haloform C–H Stretching Fundamentals ( $\Delta\nu_{\text{C-H}}$ ) for Complexation with Oxirane ( $\text{C}_2\text{H}_4\text{O}$ ) and DME ( $\text{C}_2\text{H}_6\text{O}$ )**

complex		measured	theoretically predicted			
HB acceptor	HB donor	$\Delta\nu_{\text{C-H}}$ ( $\text{cm}^{-1}$ )	MP2/6-311++G(d,p) ( $\text{cm}^{-1}$ )	MP2/6-31+G(d,p) ( $\text{cm}^{-1}$ )	MP2/6-31+G(d) ( $\text{cm}^{-1}$ )	MP2/6-31G(d) ( $\text{cm}^{-1}$ )
$\text{C}_2\text{H}_4\text{O}\cdots\text{H}-\text{CF}_3^a$		+24.1	+50.8	+46.5	+47.2	+62.3
$\text{C}_2\text{H}_6\text{O}\cdots\text{H}-\text{CF}_3^c$		+17.7	+27.5	+17.5	+22.4	+42.4
$\text{C}_2\text{H}_4\text{O}\cdots\text{H}-\text{CCl}_3^a$		+1.3	+24.9	+4.0	+8.4	-14.6
$\text{C}_2\text{H}_6\text{O}\cdots\text{H}-\text{CCl}_3^b$		-8.3	-1.0	-13.3	+1.1	-23.0

<sup>a</sup> Ref 32. <sup>b</sup> Ref 31. <sup>c</sup> Ref 27.

A number of mechanisms have been proposed to explain the blue-shifting of the  $\nu_{\text{C-H}}$  transitions and shortening of C–H covalent lengths in C–H...O HB complexes.<sup>2–10,12–14</sup> At the beginning, Hobza and coworkers proposed a two-step mechanism,<sup>6,8,27</sup> wherein the electron density is transferred first from the electron-rich site of a HB acceptor to a remote part of the donor, followed by charge reorganization within the latter molecule, and this eventually leads to shortening of C–H bond lengths. The mechanism proposed by Alabugin et al.<sup>9</sup> is essentially an interplay of the repolarization/rehybridization of the carbon centric orbital of the donor C–H bond by the electric field of the acceptor oxygen and  $n(\text{O}) \rightarrow \sigma^*(\text{C-H})$  hyperconjugative charge transfer from the lone electron pair orbitals on O to the antibonding orbital of the C–H covalent bond. In the long range, the said repolarization/rehybridization enhances the “s” character of carbon-centric bonding orbital of the donor C–H covalent bonds resulting in shortening of the C–H bond lengths. In the case of cyclic ketone...chloroform complexes, we showed that the mechanism is very effective in interpreting the observed spectral shifts of the chloroform  $\nu_{\text{C-H}}$  transition.

To address the issues of the present study, dimethyl ether (DME) and ethylene oxide (oxirane) are selected as the HB acceptors. These two molecules are the smallest members of the linear and cyclic ether families, and with respect to the  $\angle\text{C-O-C}$  angular strain, the differences between these two molecules is largest. Fluoroform and chloroform are selected as the two HB donor molecules. Precise values of infrared spectral shifts of the  $\nu_{\text{C-H}}$  bands of these two haloforms in the 1:1 complexes with the two said ethers are available from the IR spectra measured by van der Veken and coworkers in the cryosolutions of inert gases.<sup>27,31,32</sup> The results of our studies are presented in this article in the following sequence. First, on the basis of the physical properties of the two ethers, an intuitive correlation of the  $\nu_{\text{C-H}}$  shifts of the two haloforms is attempted. In the second step, the detailed predictions of the structure and infrared spectra of the complexes, obtained from electronic structure calculations at MP2/6-311++g(d,p) level of theory are presented. Finally, we show that the predicted spectral shift ( $\Delta\nu_{\text{C-H}}$ ) in each complex is very sensitive on relative orientation of two complexing partners on a flat binding potential energy surface. We have discussed the implication of such prediction for the purpose of correlating the results of gas-phase calculation with those observed in IR spectroscopy studies performed in cryosolutions of large inert gas atoms.

## 2. Theoretical Methods

The geometries of the four monomer species (chloroform, fluoroform, DME, and oxirane) and four 1:1 complexes were optimized by the MP2/6-311++G(d,p) theoretical method.<sup>41</sup> Basis set superposition error (BSSE) corrections on the calculated binding energies were performed by the counterpoise method.<sup>42</sup> Normal mode vibrational frequencies corresponding

to these optimized structures were also calculated at the same level of theory (MP2/6-311++G(d,p)). Relaxed scans with respect to the C–H...O bond angle were carried out, where the geometrical parameters of a complex for fixed values of  $\angle\text{C-H}\cdots\text{O}$  were allowed to be optimized. To calculate the natural charges at the donor–acceptor sites, hybridization characteristics of various bonding orbitals, and hyperconjugation interaction between the nonbonded lone-pair orbitals on carbonyl oxygen ( $n(\text{O})$ ) and  $\sigma^*(\text{C-H})$  orbital of chloroform, we performed NBO analysis. The effects for the use of different basis sets on optimized geometry, spectral shift, and the energetic and geometric parameters obtained from natural bond orbitals of the complexes were tested using 6-31 g(d), 6-31+G(d), 6-31+G(d,p), and 6-311++G(d,p) basis sets. The G03 program package was used to perform the calculations for the present study.<sup>43</sup>

## 3. Review of the Observed $\nu_{\text{C-H}}$ Shifts of Haloforms in 1:1 Complexes with Oxirane and DME

Table 1 shows the measured  $\nu_{\text{C-H}}$  shifts of  $\text{CHF}_3$  and  $\text{CHCl}_3$  for complexations with oxirane and DME, as reported by van der Veken and coworkers for IR spectral studies in cryosolutions of inert gases.<sup>27,31,32</sup> The  $\nu_{\text{C-H}}$  fluoroform undergoes blue shifting on complexations both with oxirane and DME. However, the same of chloroform experiences red shifting in the 1:1 complex with DME and a tiny blue shifting ( $1.3 \text{ cm}^{-1}$ ) with oxirane. Furthermore, a scrutiny of the (1, 2) and (3, 4) complex pairs reveals that oxirane can induce more blue shifting effect on  $\nu_{\text{C-H}}$  of a haloform than DME. Second, the  $\nu_{\text{C-H}}$  of fluoroform shows a larger tendency to display the blue-shifting effect than that of chloroform. We rationalize these observations in the following sections.

## 4. Results and Discussion

### 4.1. Physical Attributes of the Ethers and Haloforms.

Some relevant geometric and electronic structure parameters of the two ethers and two haloform molecules predicted by ab initio calculation at MP2/6-311++G(d,p) level are presented in Table 2. In the optimized structures, the  $\angle\text{C-O-C}$  angles of oxirane and DME are  $\sim 62^\circ$  and  $\sim 111^\circ$ , respectively. Because of such large difference in angular strain, the hybridization of the carbon-centric orbitals of the C–O  $\sigma$  bonds of the two ether molecules (NBO analysis) is predicted to be very different, and this is also reflected in hybridization of the lone-electron pair orbitals on O atoms of the ethers, where the “s” character of the oxirane orbital is much larger ( $s = 65\%$ ) compared with DME ( $s = 42.5\%$ ). The natural charge on the oxygen atom of DME ( $-0.649$ ) is also predicted somewhat larger compared with that of oxirane ( $-0.608$ ). These two electronic structure parameters indicate that the oxygen atom of DME is expected to be more polarizable compared to oxirane, and these differ-

**TABLE 2: Few Relevant Geometric and Electronic Structure Parameters of the Ethers and Haloforms**

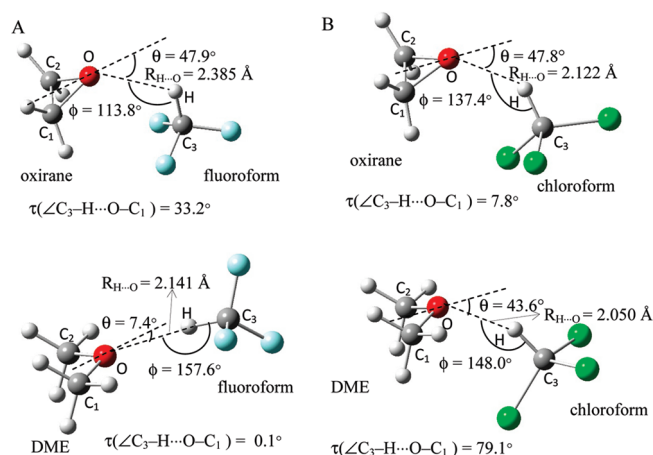
monomer parameters	MP2/6-311++G(d,p)	
	oxirane	DME
$\angle \text{C}-\text{O}-\text{C}$ (deg)	61.6	110.8
dipole moment (Debye)	2.44	1.65
proton affinity (kcal/mol)	190.0	197.2
hybridization of the lp(1) on O atom	sp <sup>0.54</sup>	sp <sup>1.35</sup>
hybridization of the lp(2) on O atom	sp <sup>1.00</sup>	sp <sup>1.00</sup>
% s of lp(1) of O atom	64.91	42.52
% s of lp(2) of O atom	0.00	0.00
$q(\text{O})$	-0.608	-0.649
$q(\text{H})$	0.194	0.096
$q(\text{C})$	-0.251	1.086
$q(\text{Cl/F})$	0.019	-0.394
dipole moment (Debye) (calculated)	1.32	1.99

ences are reflected in proton affinity values of the two molecules, which are 197 and 190 kcal/mol, respectively. These parameters also imply that the HB acceptor ability of DME oxygen is possibly larger compared with oxirane.

The net binding energy of a complex would of course depend on detailed structural features of the complexes, which determine the interactions among various groups of the two molecules. For example, although the natural charge on oxirane oxygen is little smaller compared with DME, the dipole moment of the former (2.44 D) is much larger than that of the latter molecule (1.65 D) because of the larger difference in angular orientations of the two C–O bond dipoles in the two ether molecules. Second, the dipole moments of  $\text{CHCl}_3$  and  $\text{CHF}_3$  are 1.32 and 1.99 D, respectively, and apparently, this difference originates because of the larger electronegativity of F compared with Cl. The data presented in Table 2 show that the distribution of the natural charges on H, C, and halogen atoms in the two haloform molecules are very different. Because of such differences, the gas-phase geometries and binding energies of the  $\text{CHCl}_3$  and  $\text{CHF}_3$  complexes could be significantly different. We review these points after presenting the results of the electronic structure calculation.

**4.2. Intuitive Predictions for Donor  $\nu_{\text{C-H}}$  Shifts in the Four Complexes.** In a typical  $\text{X}-\text{H}\cdots\text{Y}$  type HB complex, the red-shifting effect of the HB donor group originates primarily because of two factors: (1) lengthening of the  $\text{X}-\text{H}$  bond due to Coulombic attraction of the partially charged  $\text{H}^{\delta+}$  atom of the polar  $\text{X}-\text{H}$  bond by the oppositely charged  $\text{Y}^{\delta-}$  atom of the acceptor and (2) hyperconjugative charge transfer from a lone electron pair orbital on Y to the antibonding orbital of the  $\text{X}-\text{H}$  bond [ $\text{Y}(n) \rightarrow \sigma^*(\text{X}-\text{H})$ ]. As shown in Table 2, the natural +ve charge on chloroform H atom being nearly twice compared with that of fluoroform, the former would experience larger Coulombic attraction by the electronegative oxygen atom of any of the two ether molecules resulting in larger bond length elongation. The carbon atom of  $\text{CHF}_3$  has a large positive natural charge (+1.09), but the same of chloroform is weakly negatively charged (-0.25). Consequently, a direct Coulombic attraction between the carbon atom of  $\text{CHF}_3$  and negatively charged ether oxygen along the  $\text{C}-\text{H}\cdots\text{O}$  bond direction would lead to shortening of the  $\text{C}-\text{H}$  bond and spectral blue-shifting of  $\nu_{\text{C-H}}$ , but the same would be unfavorable in the case of chloroform. Therefore, with respect to these two factors, chloroform is likely to have a tendency to display larger red-shifting effect compared with fluoroform.

The  $\text{Y}(n) \rightarrow \sigma^*(\text{X}-\text{H})$  hyperconjugation interaction energy of a haloform with the two ethers depends on hybridization of

**Figure 1.** Fully optimized structures along with some important geometrical parameters of the four complexes calculated by ab initio theoretical method at MP2/6-311++G(d,p) level.

the lone electron pair orbitals involved in the charge transfer process and excess charge on oxygen atom. The NBO analysis shows that of the two lone electron pair orbitals of the oxygen atom, one is pure p type, and the other is a hybrid orbital. The hybrid orbital of oxirane has more “s” character (65%) compared with DME (42.5%). Consequently, the lone pair electrons of oxirane are more tightly bound to the nucleus and have lesser tendency to be involved in hyperconjugative charge transfer process. Second, the natural charge on DME oxygen is a little larger compared with oxirane. Therefore, with respect to both the factors, the hyperconjugation interaction of DME with haloforms is expected to be more effective than with oxirane. Therefore, the  $\nu_{\text{C-H}}$  of a haloform molecule would experience more red-shifting effect on complexation with DME than with oxirane.

Another important factor that contributes to blue-shifting effect is repolarization of the donor C–H bond by the electric field of the electronegative ether oxygen.<sup>9</sup> A repolarization with increased positive charge on donor H atom makes it more electropositive, and according to Bent’s rule, this would cause rehybridization of the carbon-centric orbital of C–H bond resulting in more “s” character.<sup>44</sup> The natural charges on various atoms of the two isolated haloform molecules obtained from NBO analysis (Table 2) indicate that the partial charge on H atom of the fluoroform C–H bond is somewhat smaller compared with that of chloroform. Therefore, there is more room for repolarization of the fluoroform C–H bond compared with that of chloroform. Below, we analyze these possibilities in light of detailed predictions of the electronic structure parameters by quantum chemistry calculation.

#### 4.3. Theoretically Predicted Structures and Spectral Shifts.

The optimized structures of the four complexes, calculated by MP2/6-311++g(d,p) theoretical method, are presented in Figure 1, and some important geometrical parameters are also displayed with these structures. It is apparent that in all four cases, the orientation of the donor molecules with respect to acceptors is distinctly different, and in no structure does the C–H group of the haloform approach the acceptor site (O atom) collinearly; that is, the  $\angle \text{C}-\text{H}\cdots\text{O}$  angle, labeled here by  $\phi$ , is always  $<180^\circ$ . Second, the orientation of the C–H group with respect to the bisector of  $\angle \text{C}-\text{O}-\text{C}$  angle (denoted by  $\theta$ ) and also the dihedral angle  $\angle \text{C}-\text{O}\cdots\text{H}-\text{C}$  (denoted by  $\tau$ ) are different in the four complexes. These differences indicate that in addition to the interactions immediately at the H-bonding sites, interac-



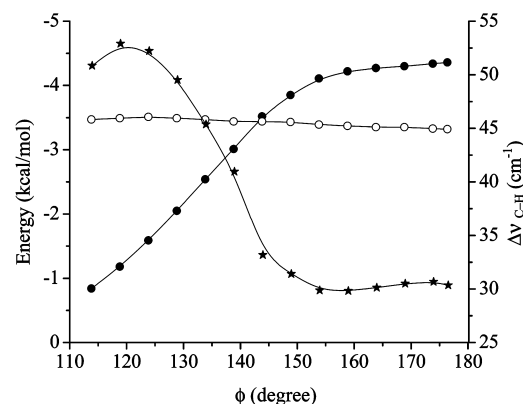
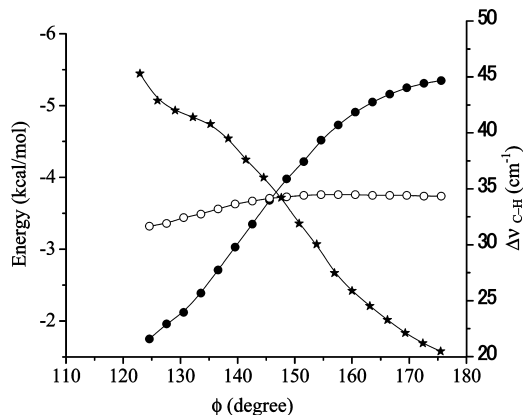
tions among other atoms of the two molecules are important to determine the resultant gas-phase geometries of these binary complexes.

Interestingly, the energetic data of the complexes (details in Supporting Information) show that the binding energies of chloroform with the two ethers are predicted to be same (3.92 kcal/mol), although the electronic structure parameters, such as dipole moment and natural charge distributions on various atoms of the two ethers, are very different. Likewise, the binding energies of the fluoroform with the ethers are also very similar, 3.42 and 3.76 kcal/mol, respectively. In contrast, the contributions of the hyperconjugation interaction energies of a haloform with the two ethers are distinctly different in the optimized structures of the complexes. Therefore, in oxirane $\cdots$ fluoroform and DME $\cdots$ fluoroform complexes, the contributions of this energy corresponding to the optimized structures are 0.84 and 4.73 kcal/mol, respectively. Similarly, in the case of two chloroform complexes, the hyperconjugation energies are also significantly different. An apparent reason for these differences is due to different values of HB distance ( $R_{H\cdots O}$ ) in the optimized structures; for example, in oxirane $\cdots$ fluoroform and DME $\cdots$ fluoroform complexes, the values of  $R_{H\cdots O}$  are 2.385 and 2.141 Å, respectively. This could have a significantly different effect in the short-range intermolecular interactions, like hyperconjugation, because the interaction depends on the overlap between the donor–acceptor orbitals. Below, we also show that a second factor that affects the hyperconjugation interaction of these systems is orientation of the  $\sigma^*(C-H)$  orbital of the haloform with respect to the lone electron pair orbitals of the donor atoms and also the hybridization characteristics of these orbitals.

In Table 1, we have presented the calculated (MP2/6-311++G\*\*) spectral shifts ( $\Delta\nu_{C-H}$ ) of the haloform C–H groups corresponding to the fully optimized structures of the four complexes. A comparison with the measured spectral shifts (Table 1) shows that the sequence of the predicted  $\Delta\nu_{C-H}$  in the four complexes is consistent with the observed sequence. However, in terms of the actual values of the shifts, the predictions are quite off from the observations. Because the net spectral shift in a complex is a compromise between the red- and blue-shifting effects, the data presented in Table 1 indicate that in each case the red-shifting effect is underestimated by the calculation. We show below that the origin for this discrepancy is due to smaller hyperconjugation interactions in the optimized gas-phase structures, and these structures could easily be distorted by weak solvent perturbations. Also shown in detail is how predicted shifts ( $\Delta\nu_{C-H}$ ) are easily altered as a result of changes in structural parameters of the complexes on very shallow binding potential energy surfaces.

**A. Oxirane $\cdots$ CHF $_3$  and DME $\cdots$ CHF $_3$ .** It has been pointed out before that despite having similar binding energies, the geometries of these two complexes, in terms of the three orientational parameters ( $\theta$ ,  $\phi$ , and  $\tau$ ), are very different (Figure 1). Therefore, the values of these parameters in the case of the oxirane $\cdots$ CHF $_3$  complex are 47.9, 113.8, and 33.2°, respectively, and the corresponding values for DME $\cdots$ CHF $_3$  complex are 7.4, 157.6, and 0.1°. We show here that in addition to different hybridization characteristics of the lone electron pair orbitals of the two ethers, these orientational parameters are indeed responsible for smaller  $n(O) \rightarrow \sigma^*(C-H)$  hyperconjugation energy of the former complex (0.84 kcal/mol) compared with the latter (4.73 kcal/mol).

For the oxirane $\cdots$ CHF $_3$  complex, the structure and  $\Delta\nu_{C-H}$  were calculated earlier by Hobza and Havlas using MP2 method,

A. oxirane $\cdots$ fluoroformB. DME $\cdots$ fluoroform

**Figure 2.** Predicted changes of the total binding energy (—○—), contribution of the hyperconjugation energy (—●—), and spectral shifts ( $\Delta\nu_{C-H}$ ) of C–H stretching fundamentals (—★—) of fluoroform in partially optimized structures of (A) oxirane $\cdots$ fluoroform and (B) DME $\cdots$ fluoroform complexes on scanning the  $\phi$  geometric parameter by MP2/6-311++G(d,p) theoretical method.

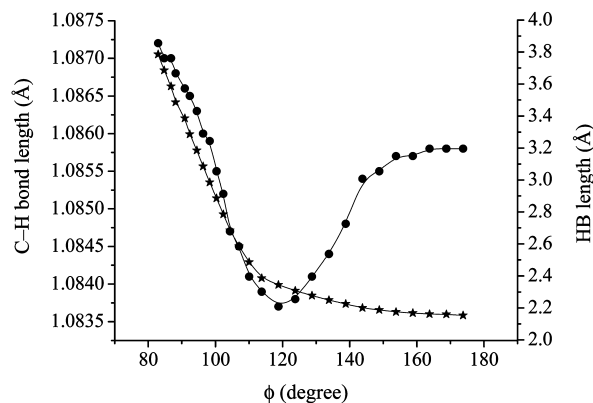
and the results for use of a series basis sets were compared.<sup>45</sup> A nonplanar structure, similar to the one shown in Figure 1A, was suggested to be favored over the planar structure. In the latter case, the C–H bond of the fluoroform molecule was put to point toward the O atom of oxirane along the bisector of  $\angle C-O-C$ , and this corresponds to  $\phi = 180^\circ$  and  $\theta$  and  $\tau = 0$ . For the first case (nonplanar structure), the values of  $\Delta\nu_{C-H}$  calculated for use of 6-31G(d), 6-31++G(d,p), and 6-31++G(2d,p) basis sets are 62, 28, and 43  $\text{cm}^{-1}$ , respectively, and obviously, the changes with improvements of the basis sets are not systematic. For the planar structure of the complex, the calculated spectral shifts for use of the three said basis sets were 45, 33, and 29  $\text{cm}^{-1}$ , that is, on increasing the level of calculation, the predicted shifts approach the observed shifts. However, the Hessian corresponding to the planar geometry showed two negative eigenvalues, which indicated that the planar geometry ( $\phi = 180^\circ$  and  $\tau = 0^\circ$ ) does not correspond to an energy minimum conformation.

To look into how the energy and spectral shifts ( $\Delta\nu_{C-H}$ ) of this complex are affected as a result of changes of the three said orientational parameters, we performed a scan with respect to  $\phi$  (step size  $5^\circ$ ) starting from the respective optimized structures by the MP2/6-311++G\*\* method. At each point (partially optimized structure), the vibrational frequencies were calculated, and the hyperconjugation energies were evaluated by NBO analysis. In Figure 2, we have shown the changes in total binding energy, the contribution of the hyperconjugation

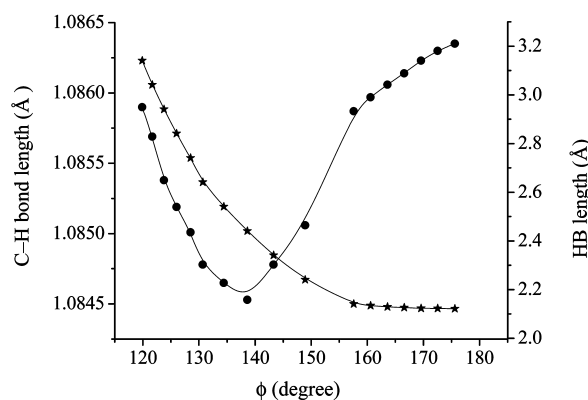
energy, and  $\Delta\nu_{\text{C-H}}$  as a function of  $\phi$  for oxirane...CHF<sub>3</sub> and DME...CHF<sub>3</sub> complexes. Therefore, as the donor C-H group approaches the acceptor site collinearly, that is,  $\phi \rightarrow 180^\circ$ , the hyperconjugation energies sharply increase and blue shifting of  $\nu_{\text{C-H}}$  is reduced, however, the total binding energy of each complex remains almost same, that is, the binding potential energy curves of both complexes with respect to  $\phi$  are very flat. This also implies that the increased contribution of hyperconjugation energy must be compensated by lowering of the contributions of other intermolecular interaction energies as the values of  $\phi$  is increased. A scrutiny of the optimized structures reveals that two F atoms of CHF<sub>3</sub>, bearing large natural negative charge (−0.394) are aligned eclipsed with respect to the two H atoms linked with the two adjacent carbon atoms of oxirane, and in the case of the DME complex, only one H atom of the methyl group is eclipsed with one of the F atoms of CHF<sub>3</sub>. As  $\phi$  is scanned, the eclipsed orientations are altered, as evidenced with the associated changes of the values of other two orientational parameters,  $\theta$  and  $\tau$ . The best match between the measured and predicted values of  $\Delta\nu_{\text{C-H}}$ , in the case of the oxirane...CHF<sub>3</sub> complex, occurs for a structure where  $\phi = 176^\circ$ , and the values of  $\theta$  and  $\tau$  are 34 and 15°, respectively (Figure 2A). It is worth mentioning that a negative frequency is predicted for each partially optimized structure corresponding to  $\phi$  between 148 and 163°. However, for structures corresponding to  $\phi > 165^\circ$ , all frequencies are predicted to be positive. For DME...CHF<sub>3</sub> complex, the predicted value of  $\Delta\nu_{\text{C-H}}$  corresponding to its fully optimized structure ( $\phi = 157^\circ$ ) is 27.5 cm<sup>−1</sup>. However, the best match with the experimental value of  $\Delta\nu_{\text{C-H}}$  (20.5 cm<sup>−1</sup>) occurs for a structure corresponding to  $\phi = 175^\circ$ . It is notable that the hyperconjugation energy at the optimized structure of this complex is much larger compared with the previous complex, mainly because of larger optimized value of  $\phi$ . At the best matching condition, although the values of  $\phi$  of the two complexes are practically same, the hyperconjugation energy of the latter complex is relatively larger compared with the former, and it reveals that the HB acceptor abilities of the two ether oxygen atoms are different.

It is noted that as the geometries of the two complexes are partially optimized by scanning with respect to  $\phi$ , the HB distance ( $R_{\text{H}\cdots\text{O}}$ ) and C-H bond length of fluoroform are concurrently altered and the changes are displayed in Figure 3. The HB distance attains the shortest value when the donor group is directed almost linearly ( $\phi = 176^\circ$ ) toward the O atom of oxirane. Second, for values of  $\phi$  within the range of 110–180°, the HB distance ( $R_{\text{H}\cdots\text{O}}$ ) shows a slow variation, but below 110° this shows a sharp increase. The C-H bond length of CHF<sub>3</sub> displays a steady decrease and attains the lowest value for  $\phi \approx 120^\circ$ , but it increases again for  $\phi > 120^\circ$  and settles to a value of  $\sim 1.086$  Å when  $\phi = 176^\circ$ , and at this position, the value of  $R_{\text{H}\cdots\text{O}}$  is smallest. The shape of the C-H bond length variation indicates that two opposing factors responsible for the changes. At shorter values of  $R_{\text{H}\cdots\text{O}}$ , the population of the  $\sigma^*(\text{C-H})$  orbital increases significantly (not shown here) because of the  $n(\text{O}) \rightarrow \sigma^*(\text{C-H})$  hyperconjugation interaction, and this causes weakening and elongation of the bond. Nearly similar changes are manifested in the case of the DME...fluoroform complex. For  $\phi > 165^\circ$ , the C-H bond length shows a little elongation, and the change is consistent with a small increase in the hyperconjugation energy. However, for  $\phi$  in 140–160° range, C-H bond length shows a sharp decrease, and the smallest value is attained for  $\phi = 138^\circ$ . The concomitant increase in the HB

## A. oxirane...fluoroform



## B. DME...fluoroform

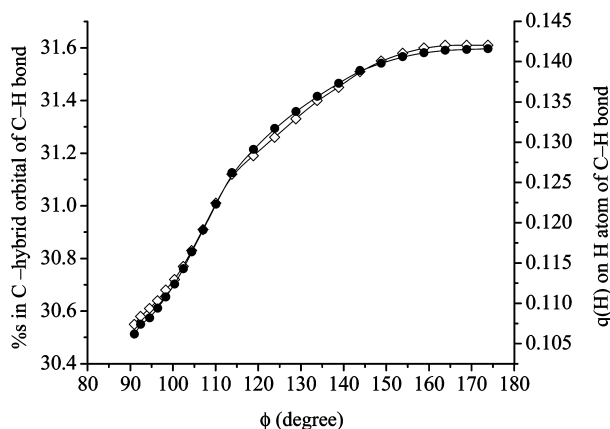
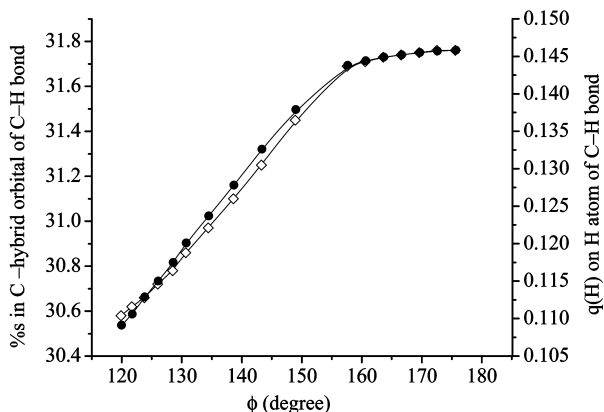


**Figure 3.** Changes of the C-H bond length of fluoroform moiety (—●—) and HB length (—★—) in the partially optimized structures of (A) oxirane...fluoroform and (B) DME...fluoroform complexes predicted on scanning  $\phi$  by MP2/6-311++G(d,p) theoretical method.

distance implies that this change is due to lowering of the hyperconjugation energy.

Figure 4 shows the changes of hybridization of the carbon-centric bonding orbital of the C-H covalent bond of CHF<sub>3</sub> and natural charge on H atom with  $\phi$ . Comparison with Figure 3 indicates that these changes are consistent with the lowering of  $R_{\text{H}\cdots\text{O}}$  and follows Bent's rule of structure organic chemistry.<sup>44</sup> The repolarization/rehybridization strengthens the C-H bond as the donor group approaches the acceptor site and results in shortening of the bond, as depicted in Figure 3, and this happens because of the increase in "s" character in the carbon-centric hybrid orbital of the bond. Therefore, the interplay between the repolarization/rehybridization and hyperconjugation explains the shape of the curve for the C-H bond length with changes of  $\phi$  orientation angle.

In addition to spectral shifting of the  $\nu_{\text{C-H}}$  transition, the frequencies of a few other vibrational modes of the HB donor molecule are also noticeably affected upon complexation. Therefore, the C-H bending mode, which is degenerate in isolated CHF<sub>3</sub> ( $\delta_{\text{C-H}} = 1426$  cm<sup>−1</sup>) splits into 1399 and 1438 cm<sup>−1</sup> in the optimized structure of the asymmetric-shaped oxirane...CHF<sub>3</sub> complex. This frequency gap is gradually reduced in the partially optimized structures with the increase in  $\phi$ . Similarly, the degeneracy of the antisymmetric C-F stretching mode is also lost in the complex, and the frequency of the symmetric C-F stretching shows a large shift. Quite similar behavior is also predicted for the DME...CHF<sub>3</sub> complex, and the primary reasons for these changes are due to repolar-

A. oxirane $\cdots$ fluoroformB. DME $\cdots$ fluoroform

**Figure 4.** Changes of the “s” character (%) in the carbon centric bonding orbital of the C–H bond (—●—) and development of natural positive charge ( $q$ ) on the H atom (—◇—) of fluoroform obtained by performing NBO analysis on the partially optimized structures of (A) oxirane $\cdots$ fluoroform and (B) DME $\cdots$ fluoroform complexes predicted by scanning  $\phi$  by MP2/6-311++G(d,p) theoretical method.

ization/rehybridization effect of various bonding orbitals of the donor molecule. These changes are consistent also with the two-step mechanism for charge transfer/reorganization suggested by Hobza.

The results presented here reveal an interesting correlation between the structures of the two complexes and the respective spectral shift ( $\Delta\nu_{\text{C-H}}$ ). Although their fully optimized structures (in terms of  $\phi$ ,  $\theta$ , and  $\tau$ ) are significantly different, the structures deduced by scanning with respect to  $\phi$  and for which the predicted values of  $\Delta\nu_{\text{C-H}}$  match the respective measured values in cryosolutions appear to be surprisingly very similar. We provide the following interpretation of this correlation incorporating solvation of the polar molecular moieties by the polarizable inert gas atoms. Because the polarizability of the heavy inert gases is significantly high, they would be easily polarized by the molecules with large dipole moments and with large natural charges on atoms. The molecular parameters presented in Table 2 indicate that fluoroform as well as two of its polar HB complexes can make such effects on Xe atoms in the liquid phase (dipole-induced dipole, ion-induced dipole interactions, etc.) and are expected to be extensively solvated. However, the shape of the fully optimized gas-phase structure of oxirane $\cdots$ CHF $_3$  complex being folded, solvation can be hindered because of lesser extent of exposed surface area, and this structure could be unfavorable in liquid xenon. The solvation occurs to a maximum extent for the unfolded geometry of the

complex corresponding to  $\phi \approx 180^\circ$  and  $\theta \approx 0^\circ$ . As shown in Figure 2, the gas-phase binding energy of this unfolded structure is nearly the same as that of the fully optimized folded structure. Therefore, under the influence of solvation, the former is expected to be favored in the inert gas liquids, and the same argument should also be valid in the case of DME $\cdots$ CHF $_3$  complex. Under such similar geometric orientation, the spectral shift of  $\nu_{\text{C-H}}$  transition of fluoroform would be determined by the local interaction at the HB donor–acceptor sites of the two ether molecules. The data presented in Figure 2 indicate that for similar extended geometries, the hyperconjugation energy of DME $\cdots$ CHF $_3$  complex is nearly 1 kcal/mol larger compared with the oxirane $\cdots$ CHF $_3$  complex, and this would be responsible for relatively less blue-shifting of the former complex compared with the latter.

**B. Oxirane $\cdots$ Chloroform and DME $\cdots$ Chloroform.** The optimized geometries of these two complexes, presented in part B of Figure 1, show again that despite having the same binding energies, their predicted structures are somewhat different with respect to the three orientational parameters. Therefore, in the oxirane $\cdots$ chloroform complex, the value of  $\phi$  ( $137.4^\circ$ ) is smaller compared with that of DME $\cdots$ chloroform ( $148^\circ$ ), and this results in a somewhat longer value of the HB distance of the former complex compared with the latter and also  $\sim 2$  kcal/mol smaller value of hyperconjugation energy (Supporting Information). The comparison between the measured and calculated values of  $\Delta\nu_{\text{C-H}}$  reveals again that the contribution of the intermolecular interactions that induced red-shifting effects, that is, hyperconjugation, is underestimated in both of the optimized structures, and this behavior is similar to the case of the two CHF $_3$  discussed in above section.

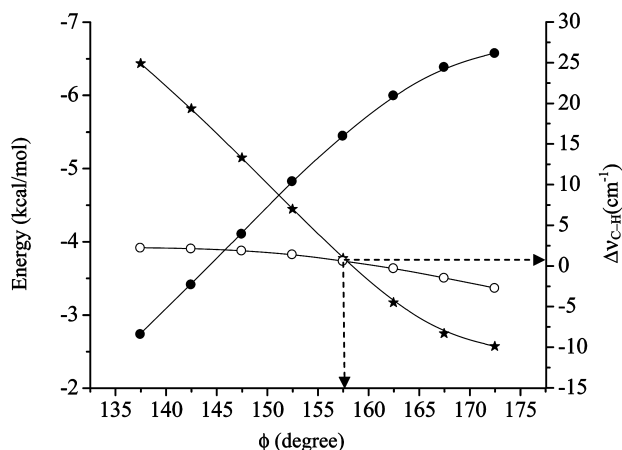
The effect of gradual increase in  $\phi$  on binding energy, spectral shift, and contribution of hyperconjugation energy of the two complexes is displayed in Figure 5. The hyperconjugation energy sharply increases in both cases with concomitant lowering of the value of  $\Delta\nu_{\text{C-H}}$ , that is, from blue to red. The dotted arrows indicate that the predicted spectral shift matches with the respective measured shift for a value of  $\phi \approx 157^\circ$  for both complexes. Therefore, it appears that similar to the case of the two fluoroform complexes (discussed above), the best matching of  $\Delta\nu_{\text{C-H}}$  between prediction and experiment occurs for nearly the same value of  $\phi$  in the two chloroform complexes. The total binding energy curves also appear flat with respect to change of  $\phi$ . Under the best matching geometric condition, the hyperconjugation energy of DME $\cdots$ chloroform complex is  $\sim 1$  kcal/mol larger compared with the oxirane $\cdots$ chloroform complex, and this is the likely origin for relatively larger red shifting for the chloroform  $\nu_{\text{C-H}}$  transition in the former.

The changes in chloroform C–H bond length and HB distance of the two complexes with  $\phi$  are compared in Figure 6, and the nature of the changes is similar to the case of the two CHF $_3$  complexes discussed above. These changes can again be explained in terms of the same electronic factors, that is, an interplay between repolarization/rehybridization and  $n(\text{O}) \rightarrow \sigma^*(\text{C-H})$  hyperconjugation interaction. The corresponding changes of the carbon-centric hybrid orbital of the C–H bond and natural charges on the H atom in the two complexes are displayed in Figure 7. The shortest values of C–H bond length are predicted for  $\phi$  in the range of  $120$ – $130^\circ$ . For these orientations, the HB distance is nearly  $0.3$  Å larger compared with the optimized values, and consequently, the values of hyperconjugation energies are much smaller.

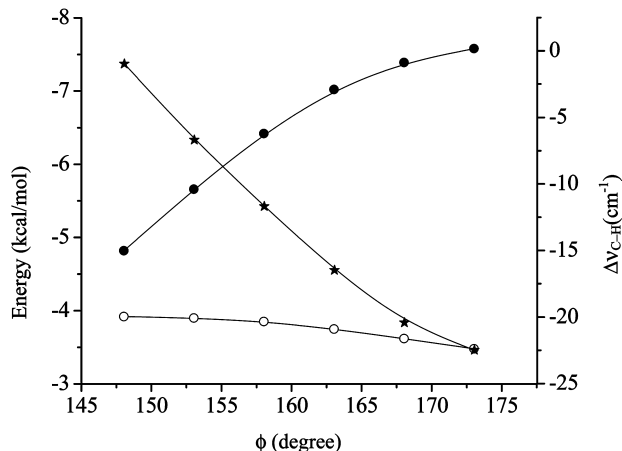
A comparison between the features depicted in Figures 2 and 5 indicates that the best match of  $\Delta\nu_{\text{C-H}}$  between experiment



## A. oxirane...chloroform



## B. DME...chloroform

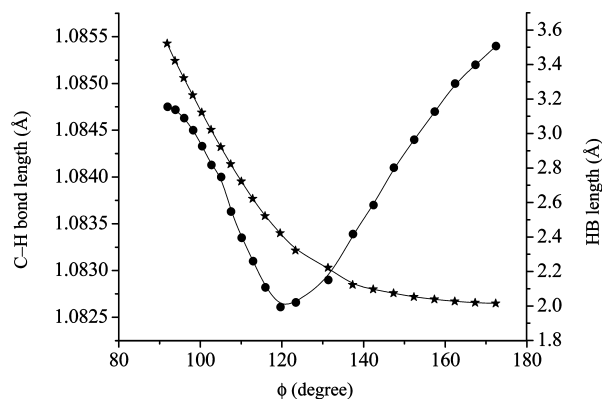


**Figure 5.** Changes of the total binding energy (—○—), contribution of the hyperconjugation energy (—●—), and spectral shifts ( $\Delta\nu_{C-H}$ ) of C—H stretching fundamentals (—★—) of chloroform in partially optimized structures of (A) oxirane...chloroform and (B) DME...chloroform complexes predicted in partially optimized structures obtained by scanning the  $\phi$  geometric parameter using MP2/6-311++G(d,p) theoretical method.

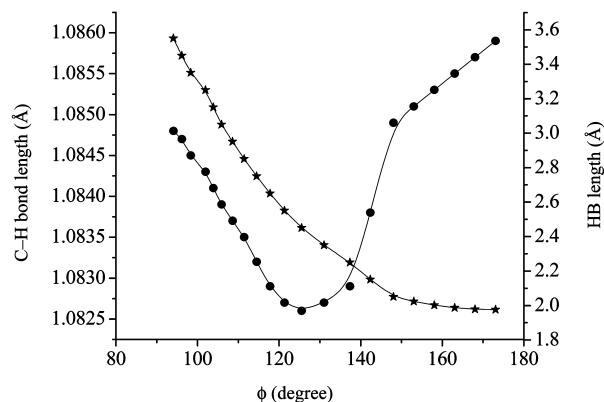
and prediction occurs for a relatively smaller value of  $\phi$  in the case of the two chloroform complexes. This can again be rationalized by taking into consideration the subtle role of solvation by a heavier inert gas liquid on the geometry of the complexes. The data presented in Table 2 indicate that the dipole moment of  $\text{CHCl}_3$  is smaller compared with that of  $\text{CHF}_3$ , and natural charges on various atoms of the former molecule are also much smaller compared with those of the latter molecule. In consequence, the role of solvation by the inert gas liquid should be less significant in the case of the two chloroform complex, and the solvation process would exert little influence to deviate the gas-phase geometry. In addition, Figures 2 and 5 also reveal that for the best matching geometries, the hyperconjugation energies of the chloroform complexes are larger compared with the fluoroform complexes, and this also explains the origin of larger blue shifting of the  $\nu_{C-H}$  bands for the latter two complexes.

**4.4. Effect of Basis Set on Spectral Shifts and Binding Energies.** We briefly mention here the effects observed for use of basis sets of different sizes in electronic structure calculation on predicted values of  $\Delta\nu_{C-H}$ , binding energies, and geometric shapes of the four complexes studied here. The relevant predictions are summarized in Table 1 and the Supporting

## A. oxirane...chloroform



## B. DME...chloroform

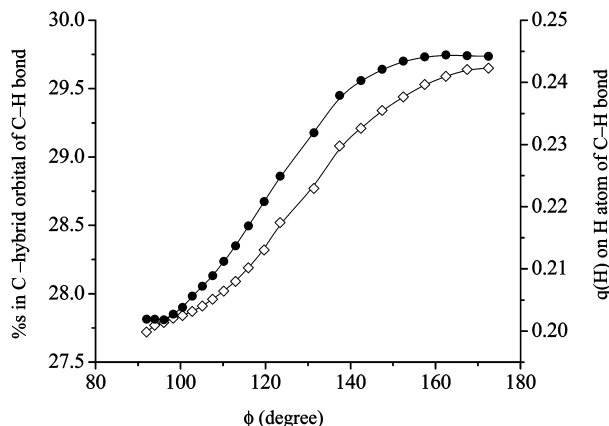


**Figure 6.** Variation of the C—H bond length of fluoroform moiety (—●—) and HB length (—★—) in the partially optimized structures of (A) oxirane...chloroform and (B) DME...chloroform complexes predicted on scanning  $\phi$  by MP2/6-311++G(d,p) theoretical method.

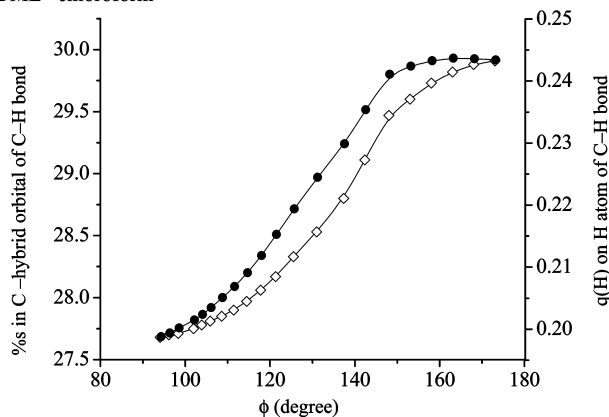
Information. Use of basis sets of inadequate size is often considered to be the origin for disagreement between the measured and predicted frequencies in quantum chemistry studies. However, for the present systems, the effects are not manifested systematically. Therefore, for the oxirane... $\text{CHF}_3$  complex, the predicted value of  $\Delta\nu_{C-H}$  appears to be similar for the use of 6-311++G(d,p), 6-31+G(d,p), and 6-31+G(d) basis sets. Consistent with this, the binding energies predicted for the use of these basis sets are also same (Supporting Information). Smaller hyperconjugation predicted for the use of the 6-311++G(d,p) basis in NBO analysis is consistent with more folded orientation of the HB donor group (i.e., smaller  $\phi$ ) toward the acceptor site. Likewise, in the case of the DME... $\text{CHF}_3$  complex, the predicted binding energies for use of the first three basis sets are similar. A relatively smaller spectral shift ( $\Delta\nu_{C-H}$ ) is predicted for use of the 6-31+G(d,p) basis set is again consistent with the predicted contribution of hyperconjugation energy (Supporting Information). For the two chloroform complexes, the binding energies are also not sensitive to the nature of the basis set used. Therefore, we conclude this section with the inference that the disagreements noted between the measured IR shifts of haloform  $\nu_{C-H}$  transitions of the four complexes (Table 1) and the predictions by ab initio electronic structure calculations are not due to limitations of the basis sets. The relative orientations between the HB donor—acceptor molecules, which sensitively affect the contribution of hyperconjugation interaction, are important, but those can be easily deformed by solvation of the polarizable inert gas atoms in the liquid phase. Therefore, incorrect



## A. oxirane...chloroform



## B. DME...chloroform



**Figure 7.** Changes of the “s” character (%) in the carbon centric bonding orbital of the C–H bond (—●—) and development of natural positive charge ( $q$ ) on the H atom (—◇—) of chloroform obtained by performing NBO analysis on the partially optimized structures of (A) oxirane...chloroform and (B) DME...chloroform complexes predicted by scanning  $\phi$  by MP2/6-311++G(d,p) theoretical method.

prediction of the complex geometries in the inert gas liquids by the gas-phase electronic structure calculation is inferred to be the primary source of the said disagreement.

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**Supporting Information Available:** Binding energy and hyperconjugation energy of complexes at different levels of theory. Important geometric parameters of complexes at different levels of theory. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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