J. Phys. Chem. A **2009,** *113,* 5217–5223

On the Intramolecular Origin of the Blue Shift of A−H Stretching Frequencies: Triatomic Hydrides HAX

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Received: January 20, 2009; Revised Manuscript Received: March 2, 2009

A series of intermolecular complexes formed between the triatomic hydrides HAX and various interaction partners are investigated computationally aiming (1) to demonstrate that either an appearance or nonappearance of a blue shift of the A−H stretching frequency is directly related to the sign of the intramolecular coupling that exists between the two degrees of freedom, the A−H and A−X bond lengths, and (2) to offer the following conjecture: the theoretical protonation of a triatomic neutral molecule HAX at the site X is a simple and rather efficient probe of a red or blue shift that the stretching frequency ν(A−H) undergoes upon complex formation regardless of whether this bond is directly involved in hydrogen bonding or not. In other words, to predict whether this A−H bond is capable to display a blue or red shift of ν(A−H), it suffices to compare the equilibrium structures and vibrational spectra of a given molecule with its protonated counterpart. The two above goals are achieved invoking a series of 11 triatomic molecules: HNO, HSN, HPO, and HPS characterized by a negative intramolecular coupling; HON and HNS as intermediate cases; and HOF, HOCl, HCN, HNC, and HCP with a positive intramolecular coupling. For these purposes, the latter molecules are investigated at the MP2/6-311++G(2p,2d) level in the neutral and protonated $HAXH^+$ forms as well as their complexes with H_2O and with the fluoromethanes H_3CF, H_2CF_2, and HCF_3.

1. Introduction

The blue shift of the C−H stretching frequency that appears in the complexes containing a hydrogen bond C−H···Y continues to be an actively investigated phenomenon (for recent extensive discussions and reviews see refs 1−16). To explain the origin of this blue shift that definitely contrasts to the conventional red shift traditionally associated with the attractive hydrogen-bonding interaction,[17−22] several theoretical models[1,6,9−13,15,22−32] have been proposed.

The blue- and red-shifted A−H···B hydrogen-bonding interactions have common as well as distinctly different features. A typical example of a common, nondiscriminative facet is that there is no essential difference in electron density rearrangements.[2,4,8,22] On the other hand, their distinction is closely related to the interplay of hyperconjugation and rehybridization that can be traced by analyzing the natural bond orbitals.[12,22] The repulsive or Pauli steric interactions have also been named as the cause.[9] Many models emphasize the importance of the molecular response to external electric fields[1,6,10,11,13] and also the negative sign of the dipole moment derivative, $\partial\mu/\partial R$(A−H), that is in contrast to the positive sign in conventional hydrogen bond donors. Most groups active in the field would probably agree that the standard theory of molecular interactions suffices to explain the phenomenon of the blue-shifted hydrogen bonding.

Recently, in a series of papers,[23−32] we have proposed a model that also explains the intramolecular origin of the blue shifts, however, from a somewhat different perspective. This model is based on the idea that the structural response of a molecule to an external perturbation is intimately connected to the intrinsic topology of the intramolecular potential energy surface (PES). Let us consider the PES of a triatomic molecule HAX in which the A−H group can act as a hydrogen bond donor or in which the A−X bond can act as a hydrogen bond acceptor. Treating only the stretching degrees of freedom R(A−H) and R(A−X), two modes of intramolecular coupling (IC) are conceivable: Stretching of the A−H (A−X) bond causes either a stretch of the A−X (A−H) bond (positive IC, negative $k_{\text{A-X,A-H}}$) or a contraction of the A−X (A−H) bond (negative IC, positive $k_{\text{A-X,A-H}}$). Which type of coupling is present is thus determined by the sign of the internal coupling (IC) which is just opposite to the sign of the off-diagonal harmonic force constant $k_{\text{A-X,A-H}}$. Interaction of HAX with a partner molecule M may now lead either to an elongation or to a contraction of the A−H bond and, consequently, to red or blue shifts of the A−H stretching frequency. This interaction can occur either via a hydrogen bond involving the A−H bond, A−H···M, or in a complex with an A−X···M bond without the participation of A−H in a hydrogen bond and, finally, also in cyclic complexes in which A−H and A−X act simultaneously as hydrogen bond donors and acceptors, respectively. Blue-shifted A−H stretching vibrations may be observed in the case of negative IC irrespective of whether HAX acts as hydrogen bond donor or acceptor, whereas for molecules with positive IC a hydrogen bond with a conventional red shift is expected.

The above model allows us to predict beforehand whether a given molecule can be treated as a candidate for a blue-shifted A−H stretching frequency in some intermolecular complex or in a series of complexes by analyzing only a selected section of the intramolecular PES. The blue-shift effect already appears at asymptotically large distances where a weak electric dipole

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10.1021/jp9005923 CCC: $40.75

field mimics the interacting partner M. We have termed the structural response of the A−H bond on the A−X bond as negative intramolecular response (NIR). The positive off-diagonal force constant $k_{\text{A-X,A-H}}$ that predetermines the NIR is obviously an intrinsic property of some class of polyatomic molecules themselves. Let us name these as the NIR-type molecules.The blue shift can appear if either only the A−H or the A−X bond is directly involved in complex formation with M or in cyclic complexes involving both the A−X and A−H bonds. In this sense, the blue-shifted hydrogen bonds can be considered as only a special case of the more general phenomenon of the NIR.

2. The Idea Behind The Present Work

In this work, we intend to further thoroughly illustrate the concept of the dominant role of the IC. To do so, we present the results of a systematic computational study of the blue-shifted A−H stretching frequencies of a large class of molecules, namely, the triatomic hydrides HAX, which allow us to conceptually simplify quite cumbersome calculations. Eleven triatomic hydrides have been selected, HNO, HON, HNS, HSN, HPO, HPS, HOF, HOCl, HCN, HNC, and HCP, to study their intermolecular complexes with $M = H_2O$ and with the fluoromethanes $M = H_3CF$, H_2CF_2, and HCF_3. Notice that some of these triatomic hydrides (HON, HSN, HPO, and HPS) have never been treated within the context of hydrogen bonding. All 11 triatomics are calculated as singlets. The electronic ground state of the HON molecule is actually a triplet.

The idea of the present work is to study a variety of possible manifestations of the blue shifts in the complexes HAX−M on the basis of the PESs of the selected triatomic hydrides. It is obvious that the interacting partner M, either a proton acceptor or a proton donor or both, has its own important role. If it acts as a proton acceptor, it depends, as mentioned above, on the interaction strength whether the blue shift survives or is suppressed by conventional hydrogen bonding. If it acts as a proton donor to the atom X of HAX, the blue shift definitely takes place.

The layout of the present work was chosen as follows. First, to clearly demonstrate that the blue shift phenomenon is indeed merely a consequence of the negative IC (positive $k_{\text{A-X,A-H}}$) that exists in a free HAX molecule, we investigate HAX by means of a one-dimensional scan of the A−X bond, thereby optimizing the remaining geometry parameters, and we also report the harmonic stretching force constants $k_{\text{A-X,A-H}}$. Second, we show that the structural response of the A−H bond to protonation of the HAX molecules at the site X is intimately connected to the type of IC and depends on the sign of $k_{\text{A-X,A-H}}$ in particular. In addition, we probe the structural response of HAX to a homogeneous electric dipole field applied in the direction of the A−H bond. Third, the above studies lead to a natural partitioning of the given 11 triatomics into three groups: (A) HNO, HSN, HPO, and HPS with negative IC; (B) HOF, HOCl, HCN, HNC, and HCP as conventional hydrogen bond donors with positive IC; and (C) HON and HNS as the intermediate group. Fourth, we discuss the proposed classification of the triatomic hydrides from the viewpoint of their intermolecular complexes with M.

3. Computational Methodology

All calculations of the studied monomers, HAX and M, and their HAX−M complexes were performed within the second-order perturbation Møller−Plesset frozen-core method (MP2)[33] in conjunction with the basis set 6-311++G(2d,2p) using the GAUSSIAN 03 suite of programs.[34] This computational level is certainly sufficient for our purposes. Because of the floppy nature of most of the studied complexes, all geometry optimizations were carried out with the TIGHT option. Only the calculated interaction energies, the A−H distances, and the harmonic A−H stretching frequencies are reported. The counterpoise corrections to the basis set superposition error (BSSE) were dispensed with since their explicit inclusion does not alter the trends discussed below.

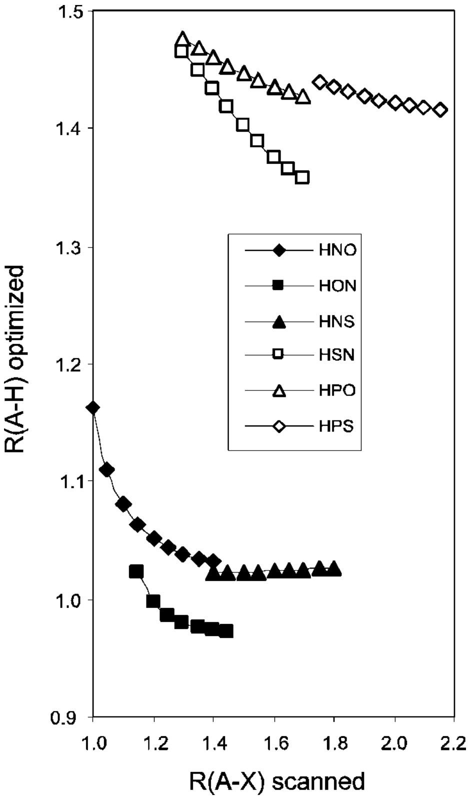

Figure 1. MP2/6-311++G(2d,2p) optimized A−H distances obtained upon scanning the A−X distance of the triatomic hydrides HNO, HON, HNS, HSN, HPO, and HPS. Both distances are given in Å.

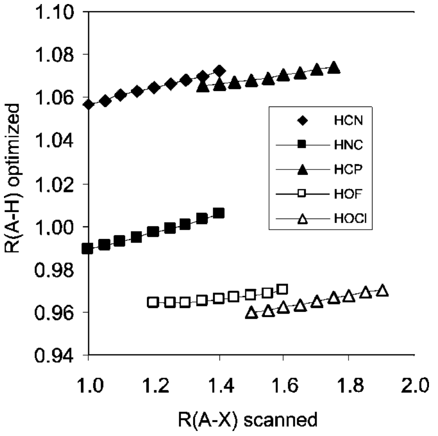

Figure 2. MP2/6-311++G(2d,2p) optimized A−H distances obtained upon scanning the A−X distance of the triatomic hydrides HCN, HNC, HCP, HOF, and HOCl. Distances are given in Å.

4. Computational Results

4.1. Intramolecular A−X Scans. Figures 1 and 2 plot the scans of the optimized A−H distances *R*(A−H) versus *R*(A−X) of the 11 triatomic hydrides HAX. The five triatomics HNO,

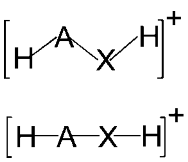

Figure 3. Sketch of the structures of nonlinear- and linear-protonated HAX.

TABLE 1: MP2/6-311++G(2d,2p) Calculated Off-Diagonal Force Constants $k_{A\text{-}X,A\text{-}H}$ (in mdyn Å^{-1}) of Triatomic Hydrides HAX

HAX	$k_{A\text{-}X,A\text{-}H}$
HNO	0.76
HSN	0.67
HPO	0.29
HPS	0.13
HON	0.87
HNS	−0.08
HOF	−0.17
HOCl	−0.19
HCN	−0.25
HNC	−0.31
HCP	−0.15

HON, HSN, HPO, and HPS, shown in Figure 1, feature the negative IC, that is, if R(A−X) increases, R(A−H) decreases and vice versa. HNS displays a rather weak, slightly positive IC. The five triatomics HOF, HOCl, HCN, HNC, and HCP (see Figure 2) clearly reveal the opposite behavior: if R(A−X) increases, R(A−H) increases as well, which is governed by the positive IC. The off-diagonal force constants $k_{A\text{-}X,A\text{-}H}$, as calculated at the equilibrium structures of HAX, are compiled in Table 1. They are correspondingly positive for molecules such as HNO, HON, HSN, HPO, and HPS that possess a negative IC, negative for molecules such as HOF, HOCl, HCN, HNC, and HCP that posses a positive IC, and almost vanish for HNS.

4.2. Protonation. Protonation is one of only a few fundamental phenomena that play a central role in physics, chemistry, and biology.[35−41] It is measured in terms of the proton affinity (PA). Protonation is closely related to the hydrogen-bonding interaction, and that is why the PA is a rather effective quantity to estimate the strength of the latter interaction which is often evaluated in terms of the red shift of the stretching frequency ν(A−H).[17−22,42−50] Bearing in mind that the conventional, red-shifted and blue-shifted hydrogen bonds have a common root, hydrogen bond, despite the different viewpoints on their very nature,[1−16,22−31] we demonstrate below that the structural consequences of selective protonation are rather significant for an understanding of the blue shifts. This selective protonation is in our case chosen as protonation at the site X of the triatomics HAX as sketched in Figure 3 for the nonlinear HAXH$^+$ with HAX = HNO, HON, HNS, HSN, HPO, HPS, HOF, and HOCl and for the linear ones HCN, HNC, and HCP.

For this purpose, we present in Table 2 the optimized distances R(A−H) and the stretching frequencies ν(A−H) of the equilibrium structures of HAX and their protonated species HAXH$^+$. We observe that for four of the studied molecules, HNO, HSN, HPO, and HPS, R(A−H) contracts when HAX is protonated at X and the concomitant stretching frequency ν(A−H) is strongly blue-shifted. Evidently, there is no hydrogen bond that is responsible for this blue shift. The maximum A−H bond length reduction of 53.0 mÅ and the largest blue shift of 475 cm^{-1} are realized for the HSN molecule.

The five conventional hydrogen bond donors, namely, HOF, HOCl, HCN, HNC, and HCP, display the opposite behavior, that is, upon protonation at X the A−H bond is stretched and ν(A−H) is red-shifted. Their maxima, ΔR_{max}(A−H) = 80.1 mÅ and $|\Delta\nu_{max}$(A−H)$|$ = 202 cm^{-1}, take place for HNC and HOF, respectively, and ΔR_{min}(A−H) = 9.1 mÅ and $|\Delta\nu_{min}$(A−H)$|$ = 66 cm^{-1} for HCP.

TABLE 2: MP2/6-311++G(2d,2p) Optimized A−H Bond Lengths (in Å) and Harmonic A−H Stretching Frequencies (in cm^{-1}) of Neutral HAX and Their Protonated Species HAXH$^+$ and Bond Length Changes (in mÅ) and Frequency Shifts in HAXH$^+$ Relative to Neutral HAX

	neutral		protonated			
HAX	R(A−H)	ν(A−H)	R(A−H)	ν(A−H)	ΔR(A−H)	$\Delta\nu$(A−H)
HNO	1.0468	3061	1.0377	3317	−9.1	256
HSN	1.4064	2102	1.3534	2577	−53.0	475
HPO	1.4469	2178	1.4184	2455	−28.5	277
HPS	1.4244	2314	1.4096	2457	−14.8	133
HON	0.9845	3395	0.9962	3411	11.7	16
HNS	1.0251	3379	1.0300	3405	4.9	26
HOF	0.9665	3797	0.9854	3595	18.9	−202
HOCl	0.9655	3804	0.9779	3654	12.4	−150
HCN	1.0633	3464	1.0759	3343	12.6	−121
HNC	0.9958	3825	1.0137	3630	17.9	−195
HCP	1.0692	3366	1.0783	3300	9.1	−66

The two triatomics, HON and HNS, are intermediate; the effect of protonation is small for them and is not absolutely definitive: although R(A−H) increases by 11.7 and 4.9 mÅ, respectively, for the protonated molecules HONH$^+$ and HNSH$^+$, ν(A−H) is blue-shifted weakly ca. 16−26 cm^{-1}.

4.3. Field Scans. For a deeper understanding of the response properties of the given triatomic hydrides, we apply a homogeneous electric dipole field in the direction of the A−H bond. The results are documented in Figures 4−6 which show the plots of the optimized R(A−H) distances of our triatomic hydrides as functions of the field strength. As seen first in Figures 4 and 5, the molecules HNO, HSN, HPO, and HPS behave as the typical blue-shifted ones. The A−H bond shrinks in weak attractive electric dipole fields. As we observe, there exists a critical threshold field strength that reverses the above trend and the A−H bond elongates again. That is why these plots have a parabola-type shape. In other words, the strength of the electric field alone suffices to change the structural response in the neighborhood of its threshold. This is actually a rather important conclusion regarding a homogeneous electric dipole field in the direction of the A−H bond. For stronger electric fields, that is, those above the threshold, which might be generated, for example, by the fluorine anion F$^-$, a significant elongation of the A−H bond is computationally predicted.

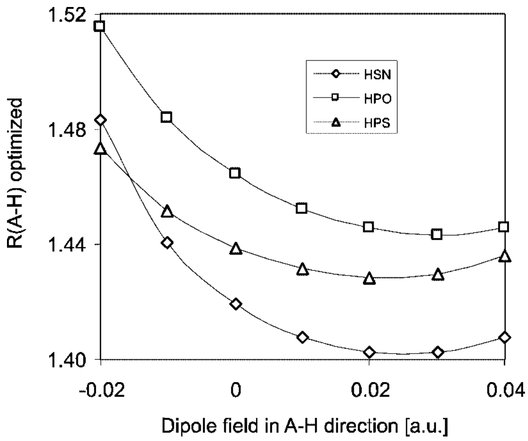

Figure 4. MP2/6-311++G(2d,2p) optimized A−H distances (in Å) of HSN, HPO, and HPS as a function of an electric dipole field in the direction of the A−H bond.

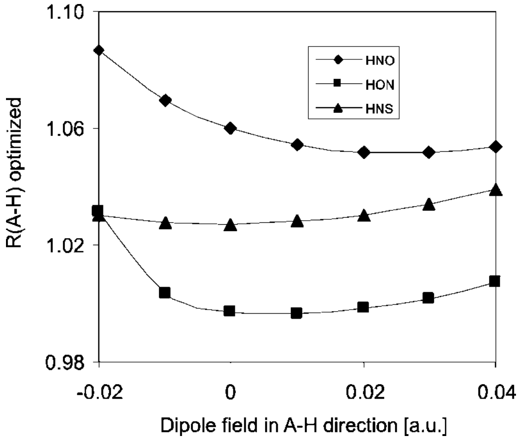

Figure 5. MP2/6-311++G(2d,2p) optimized A−H distances (in Å) of HNO, HON, and HNS as a function of an electric dipole field in the direction of the A−H bond.

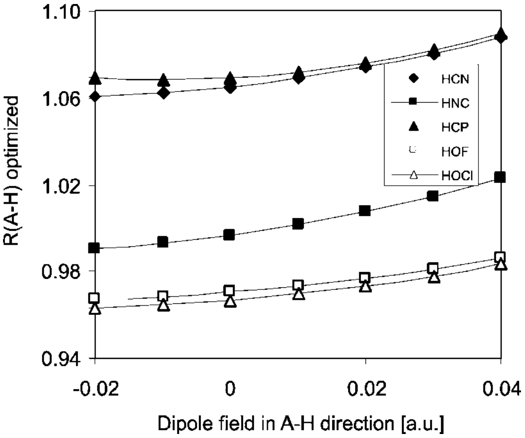

Figure 6. MP2/6-311++G(2d,2p) optimized A−H distances (in Å) of HOF, HOCl, HCN, HNC, and HCP as a function of an electric dipole field in the direction of the A−H bond.

In contrast, the five conventional hydrogen bond donors, HOF, HOCl, HCN, HNC, and HCP (see Figure 6), do not disclose any indication of bond contraction. The R(A−H) elongation takes place over the entire range of the field strength. Interestingly, as shown in Figure 5, the intermediate characters of HNS and HON are also manifested in these field scans. In the neighborhood of zero-field strength, the R(A−H) curves are pretty flat around their weakly expressed minima. As anticipated, the dipole moment derivatives, $\partial\mu/\partial R$(A−H), calculated at the equilibrium geometries, are either negative as for HNO, HSN, HPO, and HPS or positive as for HCN, HNC, HCP, HOF, and HOCl or close to zero as for HNS and HON.

Summarizing altogether the above results, we classify all our triatomic HAX molecules into three groups:

- Group A includes HNO, HSN, HPO, and HPS. They are possible candidates to reveal blue-shifted A−H stretches in intermolecular complexes.
- Group B consists of the five conventional hydrogen bond donors HCN, HNC, HCP, HOF, and HOCl.
- Group C contains HON and HNS for which the response is not quite certain.

4.4. Intermolecular Complexes of HAX with H_2O and Fluoromethanes. In this subsection, we intend to substantiate the conclusions that were drawn in the previous subsections 4.1−4.3 and to justify the classification of the HAX molecules, offered at the end of 4.3, especially from the viewpoint of molecular complexation. The hydrogen-bonding interaction and thus its red- or blue-shift manifestation is a matter of at least two interacting partners. For this purpose, the complexation of HAX with a few simple interaction partners M, M = H_2O, H_3CF, H_2CF_2, and HCF_3 is the objective of this subsection. In these complexes, HAX can act as proton donor, as proton acceptor, or as both.

4.4.1. M = H_2O. In Figure 7, the structures of the complexes of H_2O with nonlinear and linear HAX are sketched. HNO and HCN are taken as representatives. While interacting with H_2O, the nonlinear HAX admits at least two minimum energy structures: the cyclic structure $\mathbf{I}^{da}$ with two hydrogen bonds in which HAX plays the role of proton donor and proton acceptor simultaneously and the open structure $\mathbf{II}^{a}$ in which HAX is the proton acceptor. Only for HOF and HOCl, the $\mathbf{II}^{a}$'s are saddle points. For some of the HAX−H_2O complexes, there may be other minima as well, but consideration of these two types suffices for our purposes. In general, according to Table 3 that lists the stabilization energies of the complexes in Figures 7, the cyclic complexes $\mathbf{I}^{da}$ are more stable than the open $\mathbf{II}^{a}$ type structures.

The linear HAX may also form two structures with H_2O which, contrary to the previous case, are both open, namely, $\mathbf{III}^{d}$ where HAX is the proton donor and $\mathbf{IV}^{a}$ where HAX is the proton acceptor. The former is is more stable than the latter.

Bond length elongations ΔR(A−H) and frequency shifts $\Delta\nu$(A−H) of the above complexes are collected in Table 4. In accordance with the expectations based on the previous discussion, we obtain A−H bond length contractions and blue-shifted A−H stretching frequencies for group A of our triatomic HAX molecules. The calculated blue shifts are quite noticeable particularly for HNO at 85 cm^{-1} and for HSN at 136 cm^{-1}. They are larger for the cyclic structure $\mathbf{I}^{da}$ with two hydrogen bonds than for $\mathbf{II}^{a}$. It is, however, important to note that the blue shift is still present in structures $\mathbf{II}^{a}$ where the A−H bond does not participate in any hydrogen-bonding interaction.

In the complexes with H_2O, the group C molecules HON and HNS behave quite similarly to group B, comprising the conventional hydrogen bond donors for structures $\mathbf{I}^{da}$ and $\mathbf{III}^{d}$. There, ΔR(A−H) elongations and $\Delta\nu$(A−H) red shifts are calculated. For the structures $\mathbf{II}^{a}$ with HON and HNS, ΔR(A−H) is negligible, but in this case, blue shifts for ν(A−H) are present. The picture is also consistent for the $\mathbf{IV}^{a}$-type complexes with the linear HAX, although the red shifts are small.

4.4.2. Complexes with Fluoromethanes. Figure 8 presents the structures of the complexes of HAX with the three fluoromethanes. Again, HNO and HCN are chosen as representatives for bent and linear HAX. For bent HAX, the cyclic structures **V**, **VI**, and **VII** have been examined. These are not the only conceivable minima. In practically each case, alternative minima, in which the fluoromethanes are differently oriented or rotated, have also been found, however, with qualitatively the same characteristic red or blue shifts of ν(A−H). For the linear HAX, only the structures **VIII**, **IX**, and **X** have been calculated in which HAX plays the role of the proton donor. The computed stabilization energies are reported in Table 5, and ΔR(A−H) and $\Delta\nu$(A−H) are compiled in Table 6.

For the complexes of group A and group B molecules with fluoromethanes, the same pattern arises as for the complexes with H_2O. ΔR(A−H) is negative for group A and is positive for group B. These structure changes are accompanied by $\Delta\nu$(A−H) blue shifts for group A and by $\Delta\nu$(A−H) red shifts for group B. With HSN and HNO, the blue shifts are quite large. For the intermediate group C molecules HNS and HON, we

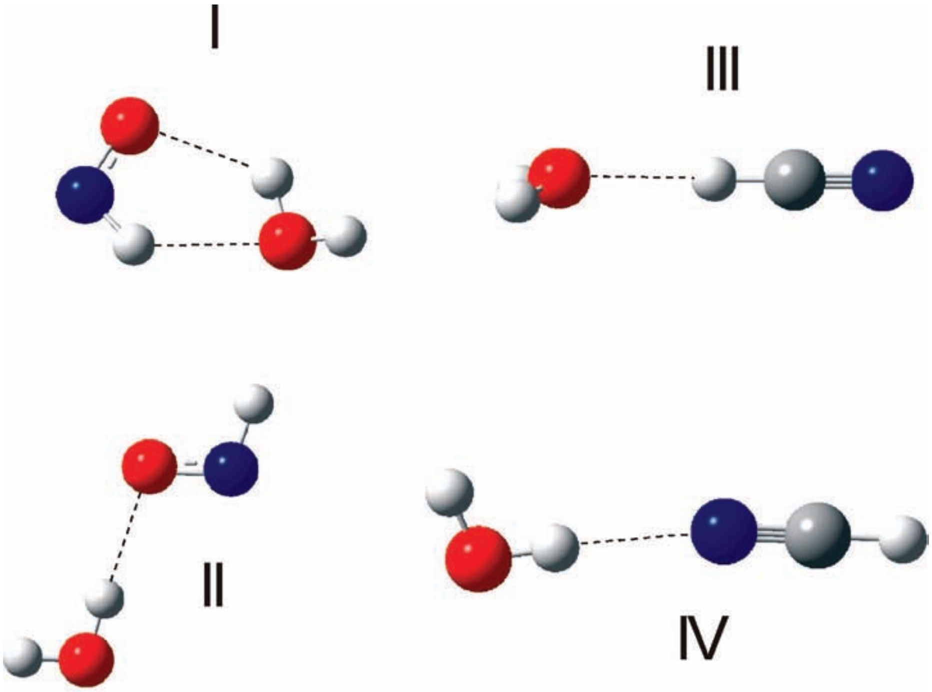

Figure 7. The structures of the HAX−H_2O complexes. For HNS, no minimum of this type was found. HNO and HCN are chosen as representatives for nonlinear and linear HAX molecules, respectively.

TABLE 3: MP2/6-311++G(2d,2p) Calculated Stabilization Energies Δ*E* (in kcal·mol^{-1}) of the Complexes of HAX with H_2O

bent HAX	**I**[da]	**II**[a]
HNO	−5.3	−3.0
HSN	−7.6	−5.9
HPO	−5.6	−4.9
HPS	−4.2	−3.4
HON	−12.2	−5.6
HNS	−5.2	no minimum
HOF	−8.3	saddle
HOCl	−8.0	saddle
linear HAX	**III**[d]	**IV**[a]
HCN	−5.4	−4.3
HNC	−8.7	−4.4
HCP	−3.0	−2.3

TABLE 4: MP2/6-311++G(2d,2p) Calculated Bond Length Changes Δ*R*(A−H) (in mÅ) and Shifts of the Harmonic A−H Stretching Frequencies Δ*ν*(A−H) (in cm^{-1}) in HAX−H_2O Complexes

	Δ*R*(A−H)		Δ*ν*(A−H)	
HAX	**I**[da]	**II**[a]	**I**[da]	**II**[a]
HNO	−3.5	−2.0	85	38
HSN	−15.0	−8.6	136	69
HPO	−7.4	−3.3	58	25
HPS	−4.4	−0.9	44	11
HON	17.4	0.0	−253	22
HNS	2.3	no minimum	−10	no minimum
HOF	11.6	saddle	−221	saddle
HOCl	12.0	saddle	−234	saddle
	III[d]	**IV**[a]	**III**[d]	**IV**[a]
HCN	7.8	0.4	−110	−2
HNC	17.4	0.8	−321	−8
HCP	4.5	1.0	−57	−9

predict quite significant blue shifts, again not consistent with the changes in *R*(A−H).

In all of the complexes with fluoromethanes considered, all of their C−H stretching modes are also blue-shifted, whether they take part in hydrogen bonds or not. The origin of these blue shifts is precisely the same kind of negative IC between C−H and C−F bonds as shown in Figure 5 of ref 24.

5. Summary and Conclusions

In the present work, we have performed a systematic computational investigation of the structure and vibrational spectra of complexes which are formed between triatomic hydrides HAX, on the one hand, and the H_2O molecule and fluoromethanes, on the other, as interacting partners. With the aid of several computational intramolecular tests, the tendency of the appearance or nonappearance of blue-shifted A−H stretches in the intermolecular complexes with and without involving the A−H group in hydrogen bonding could be predicted rather accurately. Those HAXs, which are characterized by a negative IC, respond with contraction of *R*(A−H) to protonation at the site X and to weak external dipole fields oriented along the A−H bond and have negative dipole moment derivatives. The HAXs with positive IC show the opposite intramolecular response. There also exist such molecules for which these tests do not provide a definitive answer. The subsequent calculations of the complexes have indeed proven that the predictions based solely on intramolecular tests were justified.

Protonation can be treated as a generally useful hallmark of a blue shift. In other words, the selective theoretical protonation of HAX at the site X can discriminate between HAX molecules that will show red-shifted hydrogen bonds and HAX molecules that can reveal nonconventional, blue-shifted hydrogen bonds. We have compared (this was done in Table 2) the A−H bond lengths and the harmonic *ν*(X−H) stretching frequencies of HAX and $HAXH^+$ and have observed a strikingly regular pattern: if a molecule is of the NIR type (group A: HNO, HSN, HPO, and HPS), its proton donor A−H bond contracts under

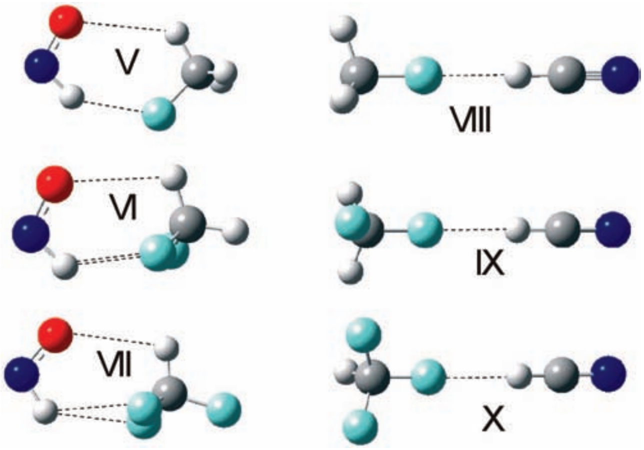

Figure 8. The structures of the complexes of HAX with fluoromethanes. Nonlinear and linear HAX representatives are correspondingly modeled by HNO and HCN.

TABLE 5: MP2/6-311++G(2d,2p) Calculated Stabilization Energies Δ*E* (in kcal·mol^{-1}) of the Complexes of HAX with Fluoromethanes

HAX	H_3CF	H_2CF_2	HCF_3
HNO	−3.6	−3.8	−3.5
HSN	−4.0	−5.1	−5.6
HPO	−2.7	−3.9	−4.6
HPS	−2.5	−3.2	−3.3
HON	−7.8	−6.7	−6.0
HNS	−3.7	−3.6	−3.1
HOF	−6.1	−4.7	−3.7
HOCl	−6.0	−4.6	−3.4
HCN	−4.0	−2.8	−3.6
HNC	−5.7	−4.6	−3.0
HCP	−2.3	−1.7	−1.3

TABLE 6: MP2/6-311++G(2d,2p) Calculated Bond Length Changes Δ*R*(A−H) (in mÅ) and Shifts of the Harmonic A−H Stretching Frequencies Δ*ν*(A−H) (in cm^{-1}) in the Complexes of HAX with Fluoromethanes

	Δ*R*(A−H)			Δ*ν*(A−H)		
HAX	H_3CF	H_2CF_2	HCF_3	H_3CF	H_2CF_2	HCF_3
HNO	−5.1	−3.1	−1.7	107	68	45
HSN	−13.0	−10.4	−7.4	120	98	73
HPO	−6.6	−6.7	−4.9	53	54	41
HPS	−3.1	−3.7	−3.1	37	34	36
HON	1.7	1.4	1.8	36	21	20
HNS	−0.1	−0.2	0.1	32	26	17
HOF	5.7	3.5	2.1	−92	−50	−23
HOCl	5.9	3.7	2.0	−101	−56	−24
HCN	2.9	1.6	1.1	−29	−13	−12
HNC	6.0	5.2	3.2	−95	−88	−53
HCP	1.8	0.9	0.5	−10	−2	−1

protonation and its concomitant stretching frequency is shifted to higher wavenumbers, and on the contrary, for the five molecules of group B (HOF, HOCl, HCN, HNC, and HCP) with a positive IC, the above trends are completely opposite. This seems to be obvious: to ease a strain caused by the protonation that simply fortifies the pattern seen from the scans of Figures 1 and 2, the adjacent bond A−H responds in its own way that is governed by the intramolecular coupling. We have also demonstrated that the above pattern is retained—albeit in a weaker fashion, as anticipated, since protonation is stronger than a hydrogen-bonding interaction—under complexation of the studied molecules either with a molecule of water or with one of the fluoromethanes. Since the latter pattern definitively bears a sign to distinguish whether the resultant complex is actually the conventional, red-shifted or the nonconventional, blue-shifted hydrogen-bonded one, we conclude that selective protonation of the studied molecule can be considered as a rather efficient probe for its red or blue shift under formation of a hydrogen-bonded complex with a proton acceptor or with a proton donor.

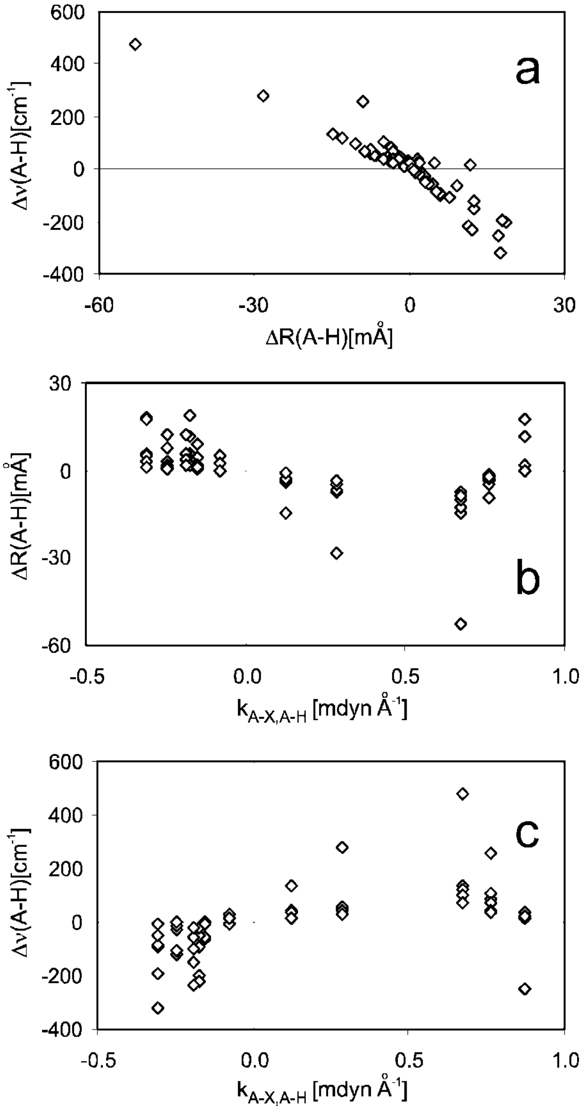

Figure 9. Intercorrelations between Δ*R*(A−H), Δ*ν* (A−H), and $k_{A\text{-}X,A\text{-}H}$: (a) Δ*R*(A−H) vs Δ*ν*(A−H), (b) Δ*R*(A−H) vs $k_{A\text{-}X,A\text{-}H}$, and (c) Δ*ν*(A−H) vs $k_{A\text{-}X,A\text{-}H}$ for all studied complexes and the protonated species $HAXH^+$.

Finally, we would also like to stress that our model draws the borderline between the conventional, red-shifted and nonconventional, blue-shifted hydrogen bonds by relying on the sign of the coupling constant $k_{A\text{-}X,A\text{-}H}$ of a given HAX. Hence, in this sense, it can only a provide a qualitative prediction of whether the blue shift of *ν*(A−H) may appear in complexes with HAX or not. Strictly taken, it excludes any quantitative prediction unless the stiffness of the A−H and A−X bonds, that is, the diagonal force constants, is examined in particular; notice that some explicit relations of this kind were derived within the harmonic approximation in ref 26. Not to talk of all the finer details of intermolecular interaction on the basis of the electrostatic properties of HAX and its interaction partner.

It is, nevertheless, tempting to investigate how the bond length changes and the frequency shifts depend on the value of $k_{\text{A-X,A-H}}$.

Therefore, on the basis of the global computational survey of all 51 complexes and 11 protonated species treated in the present work, we investigated the intercorrelations between ΔR(A−H), $\Delta\nu$(A−H), and $k_{\text{A-X,A-H}}$, and we display them in Figure 9. The correlation ΔR(A−H) against $\Delta\nu$(A−H) shown in Figure 9a is natural for conventional hydrogen bonding[51] particularly for O−H···O hydrogen bonds.[52] As clearly seen in this figure, this correlation extends to the blue-shift region rather well if one takes into account the large number of different types of A, X, and B atoms. Finally, Figure 9b and 9c shows the dependences of ΔR(A−H) and $\Delta\nu$(A−H), respectively, on $k_{\text{A-X,A-H}}$ which reveal rather regular patterns in the region of positive $k_{\text{A-X,A-H}}$, that is, the group A molecules.

Acknowledgment. The calculations reported in the present work were performed on the Linux-cluster Schrödinger III at the University of Vienna. The authors are grateful for ample supply of computer time on these installations. We thank the reviewers for useful suggestions and comments. One of the authors, E. S. K., also gratefully thanks Profs. Camille Sandorfy, Austin Barnes, and George V. Yukhnevich for encouraging discussions and useful suggestions.

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JP9005923