Article

An *Ab Initio* MP2 Study of HCN-HX Hydrogen Bonded Complexes

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Um estudo *ab initio* MP2/6-311++G** foi realizado para obter geometrias, energias de establização e propriedades vibracionais dos complexos de hidrogênio HCN-HX com X = F, Cl, NC, CN e CCH. Os resultados obtidos revelaram que: (i) os valores calculados dos comprimentos das ligações de hidrogênio estão em excelente concordância com seus valores exeperimentais; (ii) a força da ligação-H está associada com a transferência de carga intermolecular e segue a ordem: HCN-HNC ≈ HCN-HF > HCN-HCl ≈ HCN-HCN > HCN-HCCH; (iii) correção BSSE introduz uma redução média de 2.4 kJ/mol na energia de estabilização MP2/6-311++G**; (iv) as energias do ponto-zero calculadas reduzem a estabilidade destes complexos e estão em boa concordância com os valores experimentais disponíveis; (v) a frequência de estiramento da molécula livre H-X sofre, como esperado, um deslocamento para baixo no espectro após a formação da ligação de hidrogênio e quanto mais curta a distância da ligação-H menor será este deslocamento; (vi) a intensidade no infravermelho deste estiramento H-X sofre a mudança mais pronunciada após a complexação, verificando-se um aumento substancial devido ao termo de fluxo de carga; (vii) as frequências de estiramento intermolecular destes complexos HCN-HX mostram uma concordância muito boa com os seus valores experimentais; e, finalmente, (viii) Os resultados obtidos para HCN-HX seguem o mesmo perfil daqueles observados para os complexos do tipo acetileno-HX. Entretanto, nestes últimos, as mudanças nas propriedades moleculares de suas moléculas livres, após a complexação, são menos pronunciadas do que aquelas observadas para os complexos HCN-HX.

An *ab initio* MP2/6-311++G** study has been performed to obtain geometries, binding energies and vibrational properties of HCN-HX H-bonded complexes with X = F, Cl, NC, CN and CCH. These MP2/6-311++G** results have revealed that: (i) the calculated H-bond lengths are in very good agreement with the experimental ones; (ii) the H-bond strength is associated with the intermolecular charge transfer and follows the order: HCN-HNC ≈ HCN-HF > HCN-HCl ≈ HCN-HCN > HCN-HCCH; (iii) BSSE correction introduces an average reduction of 2.4 kJ/mol on the MP2/6-311++G** binding energies, *i.e.* 11% of the uncorrected binding energy; (iv) the calculated zero-point energies reduce the stability of these complexes and show a good agreement with the available experimental values; (v) the H-X stretching frequency is shifted downward upon H-bond formation. This displacement is associated with the H-bond length; (vi) The more pronounced effect on the infrared intensities occurs with the H-X stretching intensity. It is much enhanced after complexation due to the charge-flux term; (vii) the calculated intermolecular stretching frequencies are in very good agreement with the experimental ones; and, finally, (viii) the results obtained for the HCN-HX complexes follow the same profile as those found for the acetylene-HX series but, in the latter case, the effects on the properties of the free molecules due to complexation are less pronounced than those in HCN-HX.

Introduction

Recently, we have performed a systematic *ab initio* study[1,2] using different basis sets at the Hartree-Fock (HF) and Möller-Plesset 2 (MP2) levels of theory[3] in order to arrive at a better understanding of the nature of hydrogen bonding in T-type molecular complexes involving acetylene as proton acceptor and monoprotic linear acids as proton donors. That study revealed that larger charge-transfer values are associated with stronger hydrogen bonds and larger H-X stretching frequency downward displacements, in agreement with the experimental data for these complexes[4].

In another work[5], we analyzed, by means of principal component[6] and factorial design[7] models, how *ab initio* wave function modifications affect the H-bond energies of acetylene-HX complexes. We have also analyzed the HCN-HX linear complexes, which have been the target of many theoretical[8] and experimental[9] studies, and concluded that at least MP2/6-311++G** calculations are needed to correctly predict the H-bond energies of the HCN-HX complexes with X = F, Cl and CN. Del Bene *et al.*[8(a),8(b)] have also shown that intermolecular distances and vibrational shifts of H-bonded complexes are well described with the second-order many-body Möller-Plesset level of theory using a split-valence basis set with polarization and diffuse functions. Indeed, our calculations[1,2] with the larger 6-311++G** basis set at the MP2 level have correctly predicted the binding energy, the H-bond distance and the shift of the H-X stretching frequency of the acetylene-HX complexes with X =F, Cl, CN, NC, CCH. This level of calculation was found to be essential for an ade-

quate description of nonspherical atomic densities and polarizability effects[10].

In this work, we present a comparative study of the molecular properties of both HCN-HX and HCCH-HX complexes in the series defined by X = F, Cl, CN, NC and CCH. Our interest is to analyse how the change of proton acceptor affects the structural, electronic, and vibrational properties of the monoprotic linear acids, as well as their binding energies. The 6-311++G** basis set at the MP2 level is used for all species. The calculations were performed on a VAX 6620 computer using the GAUSSIAN 92 program[11].

Results and Discussion

Structural properties

The molecular geometries of the HCN-HX complexes and of the separated molecules were fully optimized at the MP2/6-311++G** level of calculation. The results are shown in Table 1. The following conclusions can be drawn: (i) The HC and HX bond lengths increase upon H-bond formation. The most significant change is found in the HX bond length which is directly involved in the H-bonding. The lengthening (δr_{HX}) in the HCN-HX complex is larger by approximately 0.004 Å than that found for the corresponding acetylene-HX T-complex. For instance, δr_{HF} is 0.011 Å in HCN-HF whereas it is only 0.007 Å in acetylene-HF. (ii) This lengthening is mainly due to charge transfer from the nitrogen lone-pair in HCN to the σ^* antibonding orbital in HX, considering that the minimum energy electrostatic potential is along the molecular axis. (iii) The MP2/6-311++G** H-bond lengths ($r_{N\cdots H}$) are in very good agreement with the corresponding experimental

Table 1. MP2/6-311++G** optimized structural parameters for the HCN-HX complexes with X = F, NC, Cl, CN and CCH. Experimental values in parentheses.

Structural parameter(Å)	HCN-HX complex				
	X = F	X = NC	X = Cl	X = CN	X = CCH
r_{HC}	1.069	1.069	1.069	1.069	1.068
δr_{HC}	0.001	0.001	0.001	0.001	0.000
r_{CN}	1.168	1.169	1.170	1.170	1.171
δr_{CN}	-0.003	-0.003	-0.002	-0.001	-0.001
r_{HX}	0.927	1.013	1.282	1.074	1.069
δr_{HX}	0.011	0.012	0.008 (0.011)[b]	0.006	0.004
r_{NH}	1.888	1.983	2.106	2.264	2.417
$r_{N\cdots X}$	2.815 (2.805)[a]	2.996	3.388 (3.405)[b]	3.338 (3.331)[a]	3.486 (3.480)[a]

[a]From Ref. [9(h)]; [b]From Ref. [9(e)].

values. For instance, the calculated value for $r_{N...F}$ in HCN-HF is 2.815 Å, very close to the experimental value of 2.805 Å. The MP2/6-311++G** calculations have also yielded excellent results for the acetylene-HX T-complexes. (iv) The C≡N bond lengths in HCN decrease upon H-bond formation, in contrast to what is found for the HC and HX distances.

Electronic properties

Table 2 shows values of uncorrected (ΔE) and corrected ($\Delta E'$) binding energies, binding energies corrected by zero-point energies (ZPE), dipole moments (μ), polarity enhancements ($\Delta\mu$) and intermolecular charge transfers (ΔQ^{corr}) of the HCN-HX linear complexes. ΔE was determined by subtracting the total energy of each hydrogen complex from the sum of the total energies of its isolated molecules. Since the binding energies include a basis set superposition error (BSSE)[12] due to the supermolecule approach, the full counterpoise method of Boys and Bernardi[13] was employed to estimate the BSSE, resulting in the corrected $\Delta E'$ values. The polarity enhancement ($\Delta\mu$) was calculated as the difference between the complex dipole moment and the sum of the dipoles of the isolated molecules. ΔQ^{corr}, which represents the amount of charge transferred from the proton acceptor (HCN) to the proton donor molecule after complexation, was calculated using the standard Mulliken atomic charges corrected by a specific overlap tensor element of the charge-charge flux-overlap (CCFO) model[14] for infrared intensities.

From Table 2 we see that the ΔE values can be ordered as HCN-HNC ≈ HCN-HF > HCN-HCl ≈ HCN-HCN > HCN-HCCH considering the accuracy for ΔE at this level of calculation. The same order is verified for both the dipole enhancement and the intermolecular charge transfer. ΔE shows a good correlation with ΔQ^{corr} (R = 0.96 and n = 5), analogously to what was found for the acetylene-HX series. It is interesting to note that ΔQ^{corr} values are almost identical to those found for the acetylene-HX species (see Fig. 1). The ΔQ^{corr} values therefore do not reflect the change from acetylene to hydrogen cyanide, despite the binding energies in HCN-HX being systematically larger than those in acetylene-HX. For a given HX proton donor, the binding energy is invariantly stronger in HCN-HX than in acetylene-HX by ≈ 40%. For instance, in HCN-HNC the value of ΔE is 30.9 kJ/mol as compared to 18.4 kJ/mol in acetylene-HNC.

The $\Delta\mu$ dipole enhancement, in turn, correctly reflects the proton acceptor change. For proton donors, ΔE shows a good correlation with $\Delta\mu$ (R = 0.94 and n = 10), which of course means that larger ΔE values are associated to larger $\Delta\mu$ values.

The calculated ΔE values are in good agreement with the corresponding experimental binding energies. For instance, ΔE is 20.8 kJ/mol for HCN-HCl using the MP2/6-311++G** calculation, whereas experimental value is 23.0 kJ/mol[9(j)]. For ease of comparison, we used "experimental electronic binding energies" derived from Del Bene et al.[8(b)] using the experimental binding enthalpies. Thus, the value of the equilibrium dissociation energy for HCN-HF is 28.77 kJ/mol using high resolution FTIR spectroscopy[9(d)], whereas its "modified" value is 29.7 kJ/mol. This MP2/6-311++G** value is 30.4 kJ/mol.

The BSSE correction introduces an average reduction of 2.45 kJ/mol to the MP2/6-311++G** results (11% of the

**Table 2.** MP2/6-311++G** values of the uncorrected (ΔE) and corrected ($\Delta E'$) binding energies, binding energies including zero-point contributions (ΔE^{zpe}), dipole moments (μ), polarity enhancements ($\Delta\mu$) and intermolecular charge transfers (ΔQ^{corr}) for HCN-HX complexes with X = F, NC, Cl, CN and CCH. Experimental values are given in parentheses.

Parameter	Complex				
	HCN-HF	HCN-HNC	HCN-HCl	HCN-HCN	HCN-HCCH
ΔE (kJ mol^{-1})	30.4 (29.7)[a]	30.9	20.8 (23.0)[b]	19.5 (18.8)[c]	10.9
$\Delta E'$ (kJ mol^{-1})	27.6	28.6	17.0	17.7	9.3
ΔE^{zpe} (kJ mol^{-1})	22.5 (21.7)[f]	25.4	16.3	15.8 (15.9)[e]	8.2
μ (Debye)	5.86 (5.61)[d]	7.44	5.20	6.73	3.53
$\Delta\mu$ (Debye)	0.89 (0.80)[d]	1.13	0.82	0.73	0.53
ΔQ^{corr} (e)	0.060	0.059	0.048	0.032	0.022

[a]From Ref. [9(d)]; [b]From Ref. [9(j)]; [c]From Ref. [9(l)]; [d]From Ref. [9(a)]; [e]From Ref. [9(o)]; [e]From Ref. [9(p)].
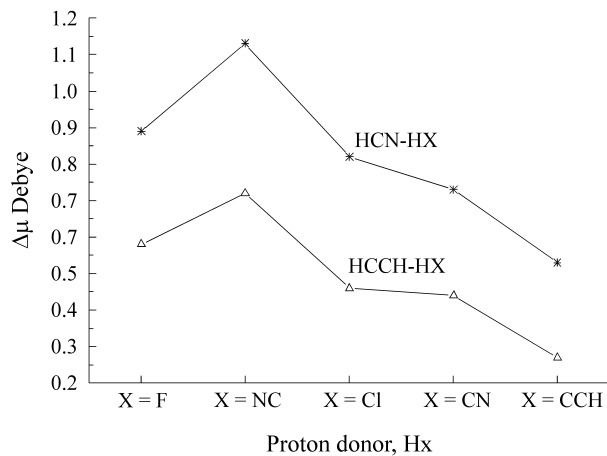
(a)
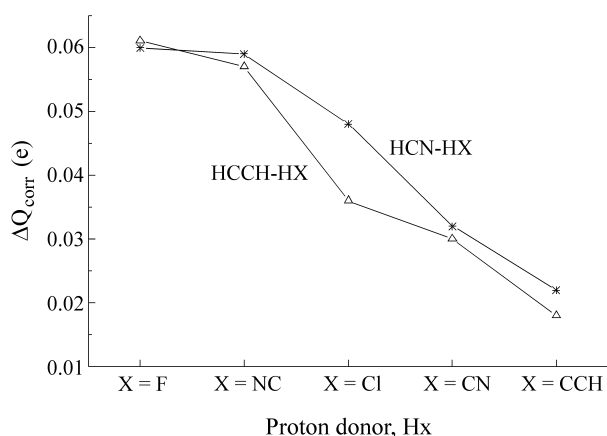
(b)

Figure 1. Calculated profiles of the dipole enhancements ($\Delta\mu$) in (a) and the intermolecular charge transfers (ΔQ^{corr}) in (b) for the HCN-HX and acetylene-HX complexes.

uncorrected ΔE). This value is much lower than that found for the acetylene-HX complexes (33%)[2]. It is also interesting to note that the BSSE correction for HCN-HF obtained from Del Bene[9(a)] is 2.5 kJ/mol using a MP4/cc-pVTZ+ calculation, which is in excellent agreement with our value of 2.8 kJ/mol. Furthermore, the uncorrected ΔE values for HCN-HF using both the MP4/cc-pVTZ+ and MP2/6-311++G** calculations are also in very good agreement, *i.e.*, 31.3 kJ/mol and 30.4 kJ/mol, respectively. The BSSE corrections do not alter the order of the values of the binding energies: HCN-HNC $\approx$ HCN-HF > HCN-HCl $\approx$ HCN-HCN > HCN-HCCH.

Since zero-point vibrational energy contributions have a non negligible effect on the stabilities of hydrogen-bonded complexes, we have evaluated these contributions using the MP2/6-311++G** level of theory for the HCN-

HX complexes. The zero-point contributions given in Table 2 vary from 7.9 kJ/mol for HCN-HF to 2.7 kJ/mol for HCN-HCCH. The initial order of the binding energies of the HCN-HX complexes are not altered by correction of the zero-point vibrational energies. The MP2/6-311++G** corrected values (ΔE^{zpe}) are in very good agreement with the corresponding available experimental values. For instance, the calculated value for ΔE^{zpe} in HCN-HF is 22.5 kJ/mol, very close to the experimental value of 21.7 kJ/mol.

Vibrational properties

HX stretching frequencies and infrared intensities

The calculated harmonic frequencies of the HX molecules are overestimated by 5-7% with respect to the experimental frequency values, whereas the calculated infrared intensities are 20 to 30% larger than the experimental values, except for HCl, when the overestimation is only by 9%. These differences are due to lack of anharmonicity correction, basis set truncation, and incomplete treatment of electron correlation.

Upon H-bond formation the HX stretching frequency is shifted downward. For instance, the calculated displacement is 242 cm^{-1} for HF after complexation, in excellent agreement with the experimental value of 245 cm^{-1}. Larger shifts are associated with stronger H-bond strengths, analogously to what was found for the acetylene-HX complexes. This implies that, since the H-bonds are stronger in the HCN complexes, the $\Delta\nu_{HX}$ shifts in HCN-HX must be larger than the corresponding shifts in the acetylene-HX series. In Table 3 values of $\Delta\nu_{HX}$ for acetylene-HX are given in brackets. For HCN-HF, for instance, $\Delta\nu_{HX}$ is -242 cm^{-1}, whereas it is only -157 cm^{-1} in acetylene-HF. Therefore, the weakness of the HF bond after complexation in HCN-HF is larger by about 100 cm^{-1} than what was found in acetylene-HF.

Del Bene *et al.*[8(a)] have also obtained similar results for the HCN-HX and CH$_3$CN-HX complexes, with X = F or Cl, using MP2 and B3LYP calculations with a 6-31+G(d,p) basis set. The CH$_3$CN-HX complexes are more strongly bound than the HCN-HX ones since the substitution of methyl for hydrogen in HCN increases both the electron density on the nitrogen and the polarizability of the proton-acceptor molecule. Therefore, their HX stretching frequency shifts are larger than those in the HCN-HX species.

As can be seen from Table 3, the HX stretching intensities of the proton donor molecule are much enhanced upon H-bond formation. The calculated ratio, $A_{HX}C/A_{HX}$is, varies from 12.5 in HCN-HCl to 2.5 in HCN-HCCH. It is now well established that this increase is due to the charge-flux term[1,2], which is strongly affected by complexation, in contrast to what happens with the hydrogen charge. The latter is always positive, whereas the charge-flux is slightly

negative in the free molecule and becomes quite positive after complexation. In the complex, the hydrogen charge and the charge-flux have the same algebraic sign, then, since the HX stretching intensity is proportional to the square sum of these terms, it is enormously increased upon complexation. Table 4 shows the MP2/6-311++G** values of HX stretching intensities, hydrogen corrected charges and charge-fluxes of HX before and after complexation. For instance, the charge-flux term goes from -0.074e in the free HF molecule to 0.532e after complexation, whereas q^o_H remains around 0.4e. The more pronounced effect on the HX stretching is found for chlorine, where the ratio is 12.5. The intensity ratios in the series are in the order Cl > F > NC > CN > CCH, analogously to what was found for the acetylene-HX complexes[2].

Other vibrational modes

The C≡N stretching of the HCN proton acceptor molecule is little affected by complexation, the C≡N frequency being only slightly shifted upward. The most pronounced effect is found for fluorine, that exhibits a displacement of 31 cm^{-1}, which is in very good agreement with the experimental value of 24 cm^{-1}, while the smaller, 7 cm^{-1} occurs when X = CCH. The C≡N stretching intensity either before and after complexation is very weak, about 1 Km/mol.

The doubly degenerate bending frequencies of HX with X = CN, NC and CCH are shifted upward upon H-bond formation, as in the acetylene-HX complexes. The shifts are 257 cm^{-1} for X = NC, 101 cm^{-1} for X = CN and 45 cm^{-1} for X = CCH, respectively, corresponding to bending frequencies in the free molecule of 506 cm^{-1}, 729 cm^{-1} and 765 cm^{-1}, respectively. The bending intensities are slightly increased by ≈ 1.2 after complexation. For instance, the bending intensity of HNC goes from 157 Km/mol in the free molecule to 188 Km/mol upon H-bond formation.

It is interesting to note that the bending intensities can be estimated from hydrogen corrected charge in HX by means of the following equation[15]:

$$A^{HX\ bend} \cong K\,(q^0_H)^2 \qquad (1)$$

where K = 975 for intensity values in Km/mol. It is important to point out that the charge-flux term is zero for bending modes in linear molecules[16,17]. Thus, for instance, using the value given in Table 4 for the hydrogen charge in acetylene in the HCN-HCCH complex, q^o_H = 0.22e, one obtain a predicted intensity of 47 Km/mol, in good agreement with the MP2/6-311++G** calculated values, *i.e.*, 52 Km/mol.
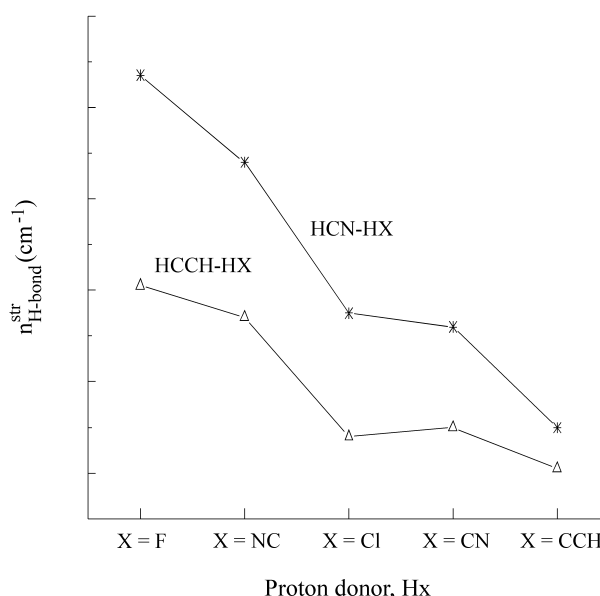
Figure 2. The MP2/6-311++G** intermolecular stretching frequencies for HCN-HX and acetylene-HX with X = F, NC, Cl, CN and CCH.

Table 3. MP2/6-311++G** values of the harmonic frequencies, frequency shifts, infrared intensities and intensity ratios after complexation of the HX stretching. Experimental values are given in parentheses, whereas the corresponding MP2/6-311++G** values for acetylene-HX are given in brackets.

Mode	HCN-HX	ν_{HX}^{is} (cm^{-1})	$(\nu_{HX}^C - \nu_{HX}^{is})$ (cm^{-1})	A_{HX}^{is} (Km/mol)	A_{HX}^C/A_{HX}^{is}
HX stretch	X = F	4199 (3961)[d]	-242 [-157] (-245)[a]	142 (77)[e]	6.1 [4.2]
	X = NC	3838	-218 [-139]	266	4.2 [3.1]
	X = Cl	3085 (2888)[g]	-111 [-69] (-79)[b]	35 (32)[e]	12.5 [7.2]
	X = CN	3484 (3311)[d]	-76 [-43] (-70)[c]	77 (59)[e]	4.3 [2.9]
	X = CCH	3458 (3282)[f]	-27 [-13]	95 (70)[f]	2.5 [1.9]

[a]From Refs. [9(d)]; [b]From Ref. [9(k)]; [c]From Ref. [9(g)]; [d]From Ref. [9(q)]; [e]From Ref. [9(m)]; [f]From Ref. [9(n)]; [g]From Ref. [9(e)].

Table 4. MP2/6-311++G** values of H-X stretching intensities and their intensity parameters before and after complexation.

Complexes	A^{strHX} (Km/mol)	q^o_H (e)	$(\partial q_H/\partial R_{HX})R_{HX}$ (e)
HF	142	0.447	-0.074
HCN-HF	864	0.403	0.532
HCl	35	0.225	-0.038
HCN-HCl	452	0.207	0.471
HCN	77	0.269	-0.013
HCN-HCN	333	0.262	0.301
HNC	266	0.443	0.006
HCN-HNC	1116	0.401	0.620
HCCH	95	0.224	-0.011
HCN-HCCH	237	0.215	0.222

Table 5. Harmonic frequencies and IR intensities of the new low-frequency vibrational modes. Experimental data in parentheses.

Complex	Vibrational properties	New vibrational modes		
		stretch-H	bend(HCN)	bend(HX)
HCN-HF	v_i (cm^{-1}) A_i (Km/mol)	167 (168) [a] 4	80 11	598 177
HCN-HNC	v_i (cm^{-1}) A_i (Km/mol)	148 5	63 5	159 28
HCN-HCl	v_i (cm^{-1}) A_i (Km/mol)	115 (111) [b] 3	53 15	311 56
HCN-HCN	v_i (cm^{-1}) A_i (Km/mol)	112 (119) [c] 1	47 7	137 45
HCN-HCCH	v_i (cm^{-1}) A_i (Km/mol)	90 1	27 27	106 3

[a]From Ref. [9(r)]; [b]From Ref. [9(e)]; [c]From Ref. 9[(g)].

New vibrational modes

The formation of HCN-HX complexes gives rise to new vibrational modes, which are given in Table 5. The values of the harmonic frequencies and IR intensities of these new modes exhibit several features: (i) The MP2/6-311++G** intermolecular stretching frequencies (stretch-H or v_{Hb}) are in very good agreement with the available experimental values, analogously to what was found for the acetylene-HX complexes. In the latter case, the values of the intermolecular stretching frequencies are lower than the corresponding values in HCN-HX (see Fig. 2), in agreement with their binding energies. Experimental values also confirm the larger intermolecular stretching frequencies in HCN-HX relative to the corresponding values in acetylene-HX. For instance, the H-stretch experimental value in HCN-HCN is 119 cm^{-1}, whereas the corresponding value in acetylene-HX is only 82 cm^{-1}. Values of v_{Hb} in both the HCN-HX and acetylene-HX complexes follow the order F > NC > Cl ≈ CN > CCH, in agreement with the corresponding H-bond lengths. On the other hand, their intensities are very weak. (ii) The new bending frequencies of HX arising after complexation are larger than those in the HCN proton acceptor molecule. Furthermore, the IR bending intensities of HX are more intense than those of HCN, except for X = CCH. For instance, the HX bending intensity is 45 Km/mol in HCN-HCN whereas its value in the HCN proton acceptor molecule is only 7 Km/mol. The corresponding frequencies are 137 cm^{-1} and 47 cm^{-1}, respectively. (iii) Finally, it is interesting to point out that the new bending mode of HX for X = F or Cl, which corresponds to a pure rotation in the free HX molecule, becomes infrared-active after complexation. Besides, it has a fairly large intensity, especially in HF (177 Km/mol), determined for the most part by the hydrogen corrected charge. For instance, the calculated intensity in HCN-HCl is 56 Km/mol, whereas the value estimated by Eq. 1 is 42 Km/mol.

Conclusions

Our MP2/6-311++G** calculations show that the structural, electrical and vibrational changes that take place in the free HCN and HX molecules after complexation follow the same behaviour as those found in the acetylene-HX complexes. In the latter ones, however, the effects are less pronounced than in HCN-HX, which are more strongly bound. The binding energies in these complexes show a good linear correlation with their dipole enhancements.

The intramolecular vibrational modes exhibit the usual effects of H-bonding formation, which are: (i) The HX stretching frequency is shifted downward whereas its IR intensity is much enhanced after complexation due to the charge-flux, (ii) The HCN proton acceptor spectrum is little affected by complexation and (iii) The new vibrational modes show several interesting features, especially the intermolecular stretching frequency and the bend modes of HF and HCl in HCN-HX, which are pure rotations in the free molecule.

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