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Sigma Bonded Radical Cation Complexes: A Theoretical Study

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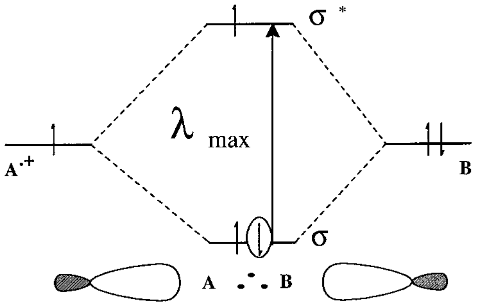
A theoretical study on the nature of bonding in several weakly bound radical cation complexes from second and third row hydrides is presented. It is shown that characterization of a two-center three-electron or 2c−3e bond based on its bond distance and binding energy may be misleading in many cases. It is also observed that the ab inito quantum chemical bond order index cannot be taken as a definite signature of a 2c−3e bond. Instead, it is suggested that appropriate localized molecular orbital need be used to test the presence of a 2c−3e bond. Localization of relevant molecular orbital in the 2c−3e bonded systems also suggests that the newly formed bond is of sigma character. Normal-mode analysis is performed to identify the stretching mode in the 2c−3e bonded radical cation complexes. Geometry optimizations are carried out at MP2 and restricted open shell Becke's half-and-half (BHH) nonlocal exchange and Lee−Yang−Parr (LYP) nonlocal correlation functionals (BHHLYP) with 6-31++G(d,p) basis set. Hessian calculations are done at the BHHLYP level. Excited-state calculations are performed following the configuration interaction with single electron excitation (CIS) method, and the lowest optical transition wavelengths (λ_{max}) in the 2c−3e bonded complexes are reported. BHHLYP functionals have been found to describe the 2c−3e bonded systems well within the restricted open shell formalism.

Introduction

In gas-phase ion−molecule reactions of the type $A^{\bullet+} + B$, first the ion ($A^{\bullet+}$) approaches the molecule (B) as a result of long-range ion−dipole moment interactions until the repulsive charge distributions of the electrons of both the ion and molecule prevent a closer distance (r_{AB}). The generated radical cation complex ($A{\cdot\cdot}B^{\bullet+}$) can subsequently undergo rearrangement of the atoms or groups of atoms to form another complex followed by dissociation into different products. In this scenario, if a molecular radical cation ($A^{\bullet+}$) reacts with its parent (A), then the reaction proceeds through the formation of a dimer radical cation ($A_2^{\bullet+}$). An important question lies in the nature of the binding of these dimer radical cations or in general the radical cation complexes. Is there any chemical bond between the two approaching heteroatoms? If a bond forms, what is the nature of such a bond and how do we test the existence of such a bond? Such information is very essential to understand gas-phase ion−molecule reactions which are constituents of a variety of environmental changes. Such knowledge can be used to understand free radical induced biological reactions in condensed media.

There are many reports in the literature stating that a radical cation with an unpaired electron in p orbital of a heteroatom gets stabilized by coordination with a free p-electron pair from another unoxidized heteroatom, thus making a new two-center three-electron (or 2c−3e) bond[1−14] which was first described by Linus Pauling.[15] A simple molecular orbital representation of this form of bonding can be described by the potential energy diagram in Scheme 1. The MO diagram suggests that the 2c−3e bond energy should be approximately half that of a normal two-center two-electron bond (2c−2e), and the corresponding bond should be much longer than a 2c−2e bond as the anti bonding orbital is occupied by a single electron. The bond order of such a bond should be 0.5, and this type of chemical bond between two atoms, A and B, is traditionally shown as $A\therefore B$ and also known as hemi bond.

SCHEME 1



Bond strength of a 2c−3e bond is expected to depend on the extent of p-orbital interactions. However, Baird pointed out that the strength of a 2c−3e bond does not vary linearly with orbital overlap.[16] In the valence bond (VB) formalism, this interaction is depicted as a resonance between two VB structures: $A{:}\ {}^{\bullet}B^{+} \leftrightarrow {}^{+}A^{\bullet}\ {:}B$. The energy of a 2c−3e bond increases with the resonance energy, and the resonance energy is large if the two VB structures are close in energy.[17] Clark reported that the strongest 2c−3e bond is expected between the systems with the same ionization potential values; that is, the strongest 2c−3e bonds are observed in dimer radical cations of the type $(A\therefore A)^{\bullet+}$.[18−21] This is explainable as the energy difference between the VB structures may be approximated as the difference between the ionization potentials of two counterparts.[17] Radom and co-workers have provided additional insights toward the understanding of 2c−3e bonding behavior based on their systematic ab initio MO studies on many 2c−3e bonded systems.[22,23] McKee and co-workers have offered more knowledge toward the understanding of 2c−3e bonding based on their combined theory and experimental results on many sulfur and

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halogen systems.[24−31] Of late, a few additional ab initio studies have been reported[32,33] including a report on a 2c−3e bonded complex involving an organic unsaturated system.[34] However, the analysis of such bonding has been restricted to either through the knowledge of bond length or by binding energy. On many occasions this may lead to a misjudged 2c−3e bonded complex. Bond order calculated following semiempirical quantum chemical methods has been found to be a good indicator for the presence of such a bond.[9,10] However, there is no report in the literature on the validity of ab initio quantum chemical bond order between the two heteroatoms in such complexes to be used as the signature of a 2c−3e bond. To the best of our knowledge, no theoretical calculation is reported to provide a clear picture on a 2c−3e bond showing that it is originated by the head on overlapping of two p-orbitals and the newly formed bond is of sigma character. This can be done by localization of appropriate molecular orbitals following one of the standard schemes of orbital localizaion.

The experimental characterization of 2c−3e bonding has often been indirect, and the transient optical absorption maximum ($\lambda_{\max}$) is used as an indicator for such bonding. Sulfur-, nitrogen-, and halogen-centered 2c−3e bonded radical cation complexes are formed in solution and give rise to an extremely broad and structureless UV/visible absorption band from which indirect information on the nature of 2c−3e bonds are obtained.[1−14] Low-temperature matrix isolation and time-resolved pulse radiolysis coupled to an optical detection technique have often been used to measure the absorption maximum ($\lambda_{\max}$) in the UV/visible region which corresponds to the energy gap between the doubly occupied σ bonding orbital and the singly occupied σ^* antibonding orbital. This σ/σ^* energy gap has often been correlated to the strength of a 2c−3e bond. A low $\lambda_{\max}$ value indicates a large separation between the doubly occupied σ and singly occupied σ^* orbitals because of a strong interaction of the corresponding p orbitals resulting in a strong 2c−3e bond. A direct measurement of the 2c−3e bond strength has been made following mass spectroscopic studies of gas-phase ion−molecule association equilibrium to measure the bond enthalpy in intermolecular 2c−3e bonded sulfur- and halogen-centered dimer radical cations.[28−31,35−41] However, these studies have been restricted only to a very few systems because of the inherent experimental limits. Moreover, the question remains to be answered whether the complexes studied in those experiments were bound by a 2c−3e bond or not. Electron spin resonance (ESR) has played an important role in elucidating the nature of bonding in such systems by probing the degree of localization of the unpaired electron.[42−44] This method has been successful in indicating that the unpaired electron density is distributed equally on two sulfur atoms in the case of sulfur-centered 2c−3e bonded radical cation complexes. Very recently, a real time probing of 2c−3e bonded complex has also been performed following femtosecond laser spectroscopy.[45]

In the present study, we have focused our attention to the fundamental aspects of bonding in these complexes from valence parameters as well as localized orbital based analysis. In what follows, we will see that on many occasions the analysis of three electron bonded species based on bond length or binding energy consideration does not give the correct identification. We intend to find out the parameters which definitely indicate the presence of a 2c−3e bond in a radical cation complex and can be used as the signature of such a bond. The bonding nature in a few radical cation complexes from the hydrides of second and third row elements will be presented on the basis of the results from a systematic ab initio molecular electronic structure calculation and provide an in-depth analysis of 2c−3e bonding.

Theoretical Approach

Previous reports have shown the importance of electron correlation for the correct description of such open shell systems.[18,23] The calculation of electron correlation by means of Möller−Plesset perturbation at the second order (MP2) has been examined to be adequate.[23] We have applied the MP2 level of theory to optimize the geometry of the most stable conformer of these radical cation complexes with the 6-31++G(d,p) basis set. Dissociated unoxidized parts and radical cations are also optimized at the MP2/6-31++G(d,p) level of theory. A complete search has been performed to find out the geometries of the most stable conformer of different radical cation complexes without any symmetry restrictions following the Gaussian 94 program system.[46] Single-point energies for all of the open shell systems are recalculated at the same level of theory with MP2/6-31++G(d,p) geometry under restricted open shell (ROHF) formalism to avoid any error in energy because of the spin contaminated wave function. Becke's half-and-half (BHH) nonlocal exchange and the Lee−Yang−Parr (LYP) nonlocal correlation functionals (BHHLYP) have also been applied with the 6-31++G(d,p) basis set for determining the most stable equilibrium structure under the ROHF method as implemented in the GAMESS suit of program.[47] The BHHLYP functional includes 50% Hartree−Fock exchange, 50% Slater exchange, and the additional correlation effects of the LYP functional, and this was found to provide accurate geometries for radical cation systems.[48] The bond order between two atoms has been calculated by following the definition of Mayer.[49,50] According to this definition, the generalized bond order (B_{XY}) between a pair of atoms (X and Y) is given by

$$B_{\mathrm{XY}} = \sum_{\mu\in \mathrm{X}}\sum_{\nu\in \mathrm{Y}}(\mathrm{DS})_{\mu\nu}(\mathrm{DS})_{\nu\mu} + \sum_{\mu\in \mathrm{X}}\sum_{\nu\in \mathrm{Y}}(\mathrm{D^sS})_{\mu\nu}(\mathrm{D^sS})_{\nu\mu}$$

where the one-electron density matrix (ρ) in AO basis has been partitioned into D and $\mathrm{D^s}$; D is the part of the one electron density because of the core or the doubly occupied orbitals, $\mathrm{D^s}$ represents that because of singly occupied orbitals, and S refers to the overlap matrix between two orbitals. Hessian calculations are also done at the BHHLYP level of theory with BHHLYP/6-31++G(d,p) optimized geometry to check the nature of stationary geometries. The localized molecular orbitals play a significant role in understanding chemical concepts such as bonds, nonbonding electron pairs, core orbitals, and valency in terms of quantum chemical description of molecules. The population-based procedure of orbital localization[51] has been followed at present, and the localized molecular orbitals of interest are viewed as contour plots in different planes following the graphics utility of GAMESS. CIS (configuration interaction with single electron excitation) calculations are done to find out the excitation wavelength to excite an electron from the highest doubly occupied bonding orbital to the lowest singly occupied anti bonding orbital ($\sigma \rightarrow \sigma^*$) of 2c−3e bonded complexes with the BHHLYP/6-31++G(d,p) optimized geometry under ROHF formalism adopting GAMESS.

Results and Discussion

The geometry of the symmetrical ($\mathrm{A{\cdots}A}|^{\bullet+}$) and a few unsymmetrical ($\mathrm{A{\cdots}B}|^{\bullet+}$) radical cation complexes from NH_3, H_2O, HF, PH_3, H_2S, HCl, CH_3F, and CH_3Cl have been fully optimized without any symmetry restriction at the MP2 and

TABLE 1: Calculated Bond Distances and Other Molecular Properties of Radical Cation Complexes at Their Most Stable Equilibrium Geometry

	MP2/6-31++G(d,p)					BHHLYP/6-31++G(d,p)^c		previous report	
			total atomic spin density over atoms						
species (A··B)	r_{AB}(Å)	$D_{AB}{}^a$ (kcal/mol)^b	A	B	bond order (B_{AB})	r_{AB}(Å)	$D_{AB}{}^a$ (kcal/mol)	r_{AB}(Å)	$D_{AB}{}^a$ (kcal/mol)
$(H_3N{\cdot\cdot}NH_3)^{\bullet+}$	2.17	37.7	0.61	0.61	0.36	2.19	36.6	2.16	37.9^d
$(H_2O{\cdot\cdot}OH_2)^{\bullet+}$	2.04	43.3	0.55	0.55	0.50	2.04	39.9	2.04	43.1^d
$(HF{\cdot\cdot}FH)^{\bullet+}$	1.86	43.2	0.52	0.52	0.52	1.86	41.0	1.88	37.4^d
$(H_3P{\cdot\cdot}PH_3)^{\bullet+}$	2.92	26.1	0.51	0.51	0.38	2.94	29.1	2.69	29.4^d
$(H_2S{\cdot\cdot}SH_2)^{\bullet+}$	2.84	29.8	0.56	0.56	0.55	2.85	32.8	2.82	31.3^d
$(HCl{\cdot\cdot}ClH)^{\bullet+}$	2.65	29.0	0.52	0.52	0.50	2.68	32.8	2.65	31.3^d
$(H_3CF{\cdot\cdot}FCH_3)^{\bullet+}$	1.91	13.6	0.49	0.49	0.34	1.96	17.5		25.1^e
$(H_3CCl{\cdot\cdot}ClCH_3)^{\bullet+}$	2.63	30.4	0.51	0.51	0.45	2.66	31.0		32.0^e
$(H_3N{\cdot\cdot}PH_3)^{\bullet+}$	2.25	32.5	0.21	0.81	0.43	2.28	34.2	2.30	36.6^f
$(H_2O{\cdot\cdot}SH_2)^{\bullet+}$	2.46	21.7	0.05	1.05	0.16	2.42	23.7		23.8^f
$(HCl{\cdot\cdot}FH)^{\bullet+}$	2.45	15.4	1.01	0.02	0.14	2.34	17.7		
$(H_3N{\cdot\cdot}OH_2)^{\bullet+}$	2.41	19.1	1.18	0.02	0.07	2.34	20.4		
$(H_3N{\cdot\cdot}SH_2)^{\bullet+}$	2.44	37.5	0.37	0.77	0.44	2.46	31.4	2.44	33.3^f
$(H_3N{\cdot\cdot}FH)^{\bullet+}$	2.47	12.0	1.20	−0.01	0.0	2.42	12.7		
$(H_3P{\cdot\cdot}OH_2)^{\bullet+}$	2.58	16.8	1.02	0.01	0.07	2.44	18.4	2.51	22.2^f
$(H_3P{\cdot\cdot}SH_2)^{\bullet+}$	2.81	21.6	0.64	0.41	0.48	2.84	24.0		20.8^f
$(H_3P{\cdot\cdot}FH)^{\bullet+}$	2.83	9.7	1.04	−0.01	0.0	2.74	10.1	2.72	13.4^f
$(H_3CCl{\cdot\cdot}ClH)^{\bullet+}$	2.62	16.0	0.74	0.28	0.42	2.71	18.2		

[a] D_{AB} refers to the calculated energy for $A{\cdot\cdot}B^{\bullet+} \rightarrow A^{\bullet+} + B$ where A has lower electron population at the equilibrium structure of the complex. [b] Restricted open shell MP2 energy calculated with MP2 optimized geometry. [c] Restricted open shell results. [d] MP4 energy from ref 23. [e] B3LYP energy from ref 28. [f] MP2 energy from ref 18.

BHHLYP levels of theory adopting the 6-31++G(d,p) basis set, and a few important calculated parameters are displayed in Table 1 for their most stable conformers. The hydrogen bonded complexes and the complexes leading to hydrogen atom transfer are excluded because the main objective of this study is to address the nature and characterization of 2c−3e bonding. All of the calculated parameters are shown in order, first for symmetrical systems and then for unsymmetrical ones. The most important geometrical parameter in these radical cation complexes is the distance between the two heteroatoms. These are calculated at ab initio and less expensive density functional theory and are displayed in Table 1. The corresponding structures with the heteroatom bond distances are depicted in Figure 1a−r. The present calculated results on bond distance indicate that, for the symmetrical systems, BHHLYP and MP2 results are fairly close, and the largest difference is 0.05 Å in the case of $[H_3CF{\cdot\cdot}FCH_3]^{\bullet+}$. In all of these cases, the distances calculated at the BHHLYP level are larger than that of the MP2 results. However, for the unsymmetrical systems, the calculated BHHLYP distances are shorter than calculated MP2 distances for most of the systems with a maximum difference of 0.14 Å for $[H_3P{\cdot\cdot}OH_2]^{\bullet+}$ and larger than that of MP2 distances for few systems with a maximum difference of 0.14 Å for $[H_3CCl{\cdot\cdot}ClH]^{\bullet+}$. The previous reported MP2/6-311G(d,p) optimized bond distances are close to the present BHHLYP or MP2 data except for the $[H_3P{\cdot\cdot}PH_3]^{\bullet+}$ system where the reported distance between two P atoms is too short. The earlier calculated MP2/6-31G(d) bond distance between P and F in the $[H_3P{\cdot\cdot}FH]^{\bullet+}$ system is close to the present BHHLYP value and shorter than the present MP2/6-31++G(d,p) distance. For the $[H_3P{\cdot\cdot}OH_2]^{\bullet+}$ system, the earlier reported bond distance between P and O at the MP2/6−31D(d) level lies between the present MP2 and BHHLYP level results.[18] It is to be noted that for all of the symmetrical systems of the type $(A{\cdots}A|^{\bullet+})$ a nonsymmetrical solution for geometry has been tried by making the geometry in one unit of the two A units slightly different from the other. However, the geometry has been converged to the symmetric structure.

The calculated binding energy for the radical cation systems at the BHHLYP level of theory is always higher than that at the MP2 level except for the studied second row symmetric radical cation complexes and $[H_3N{\cdot\cdot}SH_2]^{\bullet+}$. An earlier report showed the presence of spin contamination for most of the radical cation complexes optimized at the MP2 level of theory.[21] Thus, the present binding energies are calculated at the restricted open shell MP2 level with the MP2 optimized geometries to avoid error because of spin contamination for open shell systems. For the sake of comparison, the previously reported binding energies of the studied systems at the best level of theory are also displayed in Table 1. The binding energies are calculated from the difference in energy of the complex and the two fragments (one fragment is oxidized). For the unsymmetrical radical cation complexes, the fragment with the heteroatom, which has a lower population density in the complexed form, is considered for the oxidized fragment in the binding energy calculation. We have failed to isolate any complex other than the H atom transfer from [CH3F··FH]$^{\bullet+}$; hence, the calculated parameters for this system are not reported.

Now the important question is on the nature of bonding between the two heteroatoms in these radical cation complexes. The calculated bond distances between the two heteroatoms are larger than the distances for respective single bonds, and their binding energies are also lower than the respective single bond energies in all of the cases. These are the two parameters normally being used to support the presence of a 2c−3e bond. How good are they to describe such bond? Let us reexamine the bonding features in these complexes. The calculated total atomic spin densities over the two heteroatoms are tabulated in Table 1. In all of the symmetrical radical cation complexes, the spin density is calculated to be equally distributed over the two atoms. However, in the case of unsymmetrical radical cation complexes $(A{\cdots}B|^{\bullet+})$, there is a wide range of difference in atomic spin density distribution over the two atoms. It is seen that the binding energy is more for the complexes where the difference in spin density distribution is less. However, this parameter fails to provide a definite picture of 2c−3e bonding and hence cannot be used as an indicator for a 2c−3e bond. Spin density distributions were used to provide some idea about the nature of bonding in 2c−3e bonded complexes earlier

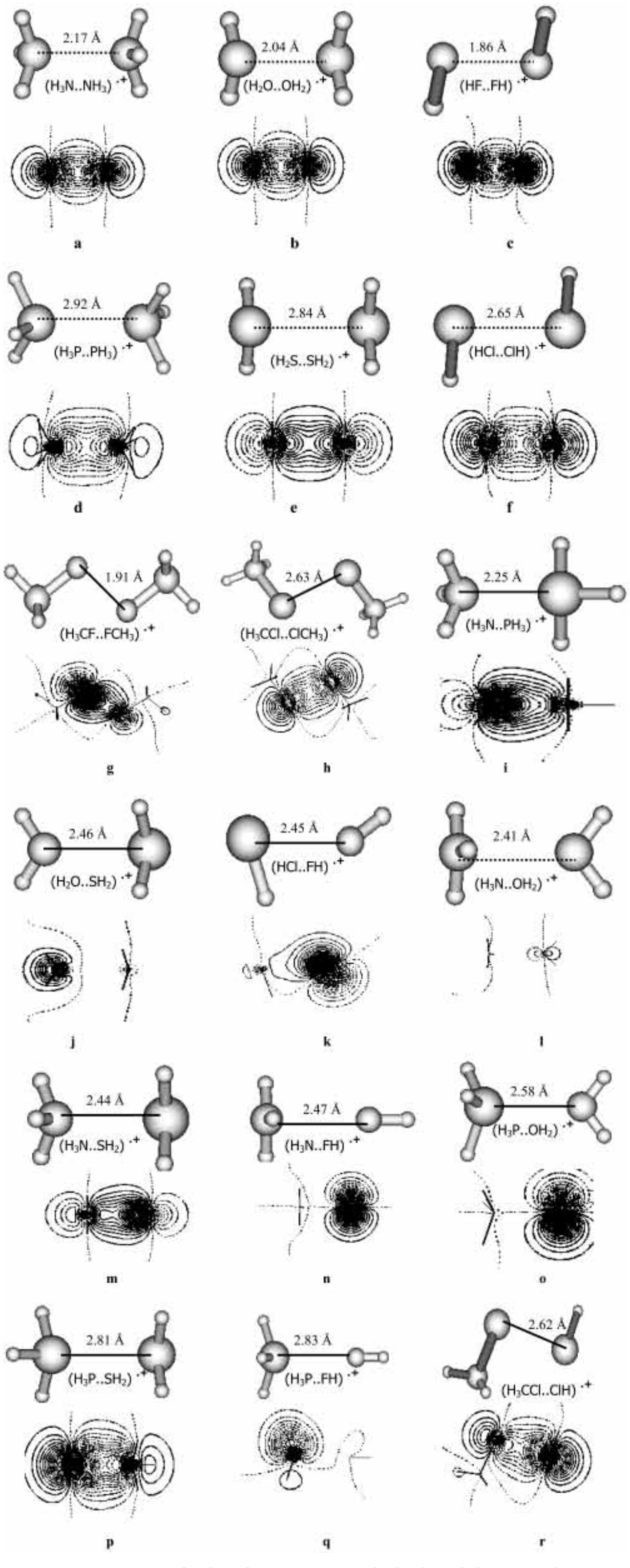

Figure 1. (a−r). Calculated structures with the bond distances between the two heteroatoms of the most stable conformer of different radical cation complexes (H atom transfer complexes are excluded) at the MP2/6-31++G (d,p) level of theory (upper part). Contour plots of the highest doubly occupied orbitals with the MP2/6-31++G (d,p) level optimized geometries (lower part). The interval between two successive contours is 0.05 Bohr$^{-3/2}$.

though.[26] Bond order is a powerful parameter that has intuitive support to the chemist's way of visualization of a chemical bond. This parameter has been successfully used for years to indicate a bond either of single or multiple nature. As it is described in the previous section, the formal bond order should be close to 0.5 in the case of a 2c−3e bond. The equation proposed by Mayer to calculate quantum chemical bond order has been successfully applied for normal bonds.[52] The same definition has been applied for the present systems to calculate the bond order between the two heteroatoms at the equilibrium geometries of the radical cation complexes, and they are displayed in Table 1. The results show that in a few systems the calculated bond order is close to 0.5 and in the rest of the cases they are either 0 or close to 0. The systems for which the bond order between the two heteroatoms is computed to be 0.5 or close to 0.5 definitely suggest the presence of a 2c−3e bond. Bond orders between two N, P, and F atoms in the case of $[H_3N{\cdot\cdot}NH_3]^{\bullet+}$, $[H_3P{\cdot\cdot}PH_3]^{\bullet+}$, and $[H_3CF{\cdot\cdot}FCH_3]^{\bullet+}$ are less than the value intuitively predicted to be 0.5, which may be due to the limitation in the definition of bond order index adopted. In the case of $[H_3N{\cdot\cdot}OH_2]^{\bullet+}$, $[H_3N{\cdot\cdot}FH]^{\bullet+}$, $[H_3P{\cdot\cdot}OH_2]^{\bullet+}$, and $[H_3P{\cdot\cdot}FH]^{\bullet+}$, the computed bond order between N and O/F or P and O/F are 0.0, and this definitely indicates the absence of any 2c−3e bond in these complexes. However, assignment based on bond length or binding energy (the criteria normally used in the previous reports to describe such bond) fails to give the correct picture in these systems. We now take up a few specific systems for the analysis.

The calculated F−Cl bond length in $[HCl{\cdot\cdot}FH]^{\bullet+}$ is 2.45 Å which is ∼150% of the normal F−Cl bond length (1.63 Å), and the calculated binding energy is 15.4 kcal/mol which is ∼25% of the normal F−Cl bond. In the case of $[H_3P{\cdot\cdot}OH_2]^{\bullet+}$, the calculated P−O bond length is ∼157% of a normal P−O bond, and the calculated binding energy is ∼12% of a normal P−O bond. The similar features can also be found in the case of $[H_3P{\cdot\cdot}FH]^{\bullet+}$. This analysis based on bond length and binding energy apparently suggests the presence of a 2c−3e bond between two heteroatoms in these radical cation complexes as was done in a previous report,[18] and the present analysis definitely predicts the absence of such a bond. So, we find that computed bond order index can be applied to trace the nature of bonding in these cases of weakly bound systems. However, the computed bond order index also fails to provide a clear picture on the nature of bonding for the complexes $[H_2O{\cdot\cdot}SH_2]^{\bullet+}$ and $[HCl{\cdot\cdot}FH]^{\bullet+}$ as the computed bond orders between the two heteroatoms are ∼0.15, which cannot speak definitely on the presence or absence of a 2c−3e bond. This may be due to an inaccurate definition of quantum chemical bond order index adopted at present. In a continuing effort to understand the nature of 2c−3e bonding better, we now turn to other molecular properties calculated for these complexes.

The highest doubly occupied molecular orbitals of the most stable radical cation complexes are localized following a population-based localization procedure and, the localized orbitals are viewed as contour plots. These plots are shown in Figure 1a−r. In the case of the symmetric radical cation complexes, the contour plots clearly show the head-on mixing of p orbitals of the heteroatoms. This clearly tells that these weak complexes are bound by a 2c−3e hemi bond, and the newly formed bond is of σ character. Though the calculated bond order indexes are lower than the formal values expected for symmetrical 2c−3e bonded radical cation complexes from NH_3, PH_3, and CH_3F, the localized orbitals provide a definite picture on the presence of such a bond. When we move to the relevant figures for unsymmetrical $(A{\cdots}B|^{\bullet+})$ radical cation complexes, the important features are in the same direction with what we find from calculated bond order indexes. There is no

TABLE 2: Calculated Vibrational Frequency for the Stretching Mode of the 2c−3e Bond and the Lowest Optical Transition Wave Length in the Most Stable Equilibrium Geometry of the 2c−3e Bonded Complexes

	BHHLYP/6-31++G(d,p)	CIS/6-31++G(d,p)//BHHLYP/6-31++G(d,p)
species A∴B	A∴B stretching vibrational frequency (cm^{-1})	λ_{max}(nm)[a]
$(H_3N\therefore NH_3)^{\bullet+}$	420	250
$(H_2O\therefore OH_2)^{\bullet+}$	465	345
$(HF\therefore FH)^{\bullet+}$	512	690
$(H_3P\therefore PH_3)^{\bullet+}$	210	280
$(H_2S\therefore SH_2)^{\bullet+}$	215	355 (370)[b]
$(HCl\therefore ClH)^{\bullet+}$	240	730
$(H_3CF\therefore FCH_3)^{\bullet+}$	390	1005
$(H_3CCl\therefore ClCH_3)^{\bullet+}$	247	695
$(H_3N\therefore PH_3)^{\bullet+}$	251	222
$(H_2O\therefore SH_2)^{\bullet+}$	270	306
$(H_3N\therefore SH_2)^{\bullet+}$	313	275
$(H_3P\therefore SH_2)^{\bullet+}$	270	297
$(H_3CCl\therefore ClH)^{\bullet+}$	221	1140

[a] Optical transition wavelength from the highest doubly occupied σ bonding orbital to lowest singly occupied σ^* orbital. [b] Solution phase experimental value from ref 3.

orbital overlapping in the case of $[H_3N{\cdot\cdot}OH_2]^{\bullet+}$, $[H_3N{\cdot\cdot}FH]^{\bullet+}$, $[H_3P{\cdot\cdot}OH_2]^{\bullet+}$, and $[H_3P{\cdot\cdot}FH]^{\bullet+}$ complexes. Moreover, the relevant localized molecular orbitals for $[H_2O{\cdot\cdot}SH_2]^{\bullet+}$ and $[HCl{\cdot\cdot}FH]^{\bullet+}$ provide definite evidence on the absence of 2c−3e bonding between the two heteroatoms. As seen from Figure 1 parts h and i, there are no orbital overlapping, thus there is no question of any 2c−3e bonding in the radical cation complexes of $[H_2O{\cdot\cdot}SH_2]^{\bullet+}$ and $[HCl{\cdot\cdot}FH]^{\bullet+}$. The computed bond order of ∼0.15 between O−S and Cl−F may be due to inherent limitation in the definition of bond order suggest by Mayer. Thus, a more general and accurate definition on quantum chemical bond order is warranted to test the reliability of the analysis based on bond order index.[53]

Hessian calculations are performed at the BHHLYP/6-31++G(d,p) level of theory to find out the frequencies for the complexes that are bound by a 2c−3e bond as described above. The normal-mode analysis is done, and the mode for the stretching vibration between the two heteroatoms in the 2c−3e bonded complexes is isolated. The calculated frequencies for the stretching vibration mode of the 2c−3e bonds are displayed in Table 2. The calculated results show that the 2c−3e bonded stretching frequency is the highest for the $[HF\therefore FH]^{\bullet+}$ complex. The stretching frequency for the symmetrical radical cation systems is predicted to increase from left to right in a row and to decrease from the second row to third row complexes in a group among the studied systems. The calculated stretching frequencies do not directly reflect the bond strengths, and this is understood as the frequencies also depend on the atomic masses. However, the calculated force constants are also seen to follow the same pattern as the frequencies and fail to provide any correlation with the bond strengths.

Configuration interaction calculations with single electron excitation are done to gather knowledge on the low lying optical transitions with the same set of basis functions. In each case, the lowest transition corresponded to an excitation from the highest doubly occupied bonding σ orbital to the lowest singly occupied antibonding σ^* orbital ($\sigma \rightarrow \sigma^*$). The transition wavelengths (λ_{max}) for the lowest transition in all of the 2c−3e bonded complexes are calculated and listed in Table 2. The present calculated gas phase λ_{max} for $[H_2S\therefore SH_2]^{\bullet+}$ is 25 nm less than the reported solution phase experimental value of 370 nm.[3] Because the magnitude of splitting between the σ and σ^* orbitals is related to the degree of interaction between the orbitals from the two heteroatoms forming the 2c−3e bond, experimental λ_{max} is often taken to correlate the 2c−3e bond strengths. The present calculated values on λ_{max} for NH_3 containing 2c−3e bonded complexes ($[H_3N\therefore NH_3]^{\bullet+}$, ($[H_3N\therefore PH_3]^{\bullet+}$, and ($[H_3N\therefore SH_2]^{\bullet+}$) do not follow the same trend as suggested by their calculated 2c−3e bond strengths. PH_3 containing 2c−3e bonded complexes also does not suggest any such correlation between calculated λ_{max} and bond strengths. However, such correlations have often been traced with the experimental results on λ_{max} with the respective 2c−3e bond strengths.

Conclusions

The nature of bonding between the two heteroatoms in several weakly bound radical cation complexes from second and third row hydrides are studied. We found that the earlier characterization of a 2c−3e bond based on bond distance and binding energy may be misleading in many cases. It is observed that in most of the cases the calculated bond order between the two heteroatoms in the complexes which are bound by a 2c−3e bond is close to 0.5. However, this index has limitations and cannot be used as a definite indicator to test the presence of a 2c−3e bond. Localized molecular orbital provides a clear indication in the presence or absence of a 2c−3e bond in all of the radical cation complexes studied. Localization of relevant molecular orbitals in the equilibrium geometries of 2c−3e bonded systems also suggest that the p orbitals are mixed head-on resulting sigma character of the newly formed bond. The frequencies for the stretching mode of the 2c−3e bond in such complexes are reported. The lowest optical transition wavelengths (λ_{max}) in the 2c−3e bonded complexes are also calculated, but these results failed to give any correlation to the calculated 2c−3e bond strengths. The calculated gas phase λ_{max} value for the lowest transition in $[H_2S\therefore SH_2]^{\bullet+}$ is lower than the experimental solution phase value by ∼25 nm. Becke's half-and-half (BHH) nonlocal exchange and Lee−Yang−Parr's (LYP) nonlocal correlation functionals (BHHLYP) have been found to describe 2c−3e bonded systems well under restricted open shell formalism. It may be revealing to see the effectiveness of BHHLYP density functional method to elucidate the nature of bonding, producing geometrical parameters, binding energies, and correlating the solution phase experimental results available on many S-centered radical cation systems supposed to be bonded by a 2c−3e or hemi bond and of biological interest. Such results with better insights will be presented in a future paper including excited-state studies on the lowest optical transition wavelengths.

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(53) To check the validity of the calculated bond orders, the AIM method by Bader was also applied following the suggestion made by one of the reviewers. The calculated AIM bond orders are close to 0.6 in all of those systems where the localized orbitals suggest the presence of a 2c−3e bond. However, the AIM bond orders for $[HCl{\cdot\cdot}FH]^{\bullet+}$, $[H_2O{\cdot\cdot}SH_2]^{\bullet+}$, and $[H_3P{\cdot\cdot}OH_2]^{\bullet+}$ are calculated to be 0.33, 0.41, and 0.34, respectively. For the rest of the systems studied, the AIM bond orders are close to 0. The same sets of basis functions were chosen for AIM calculations as was done with Mayer bond order. It appears that the Mayer definition for bond order works better for the present systems, and the search for an accurate and more general definition of bond order remains alive.